Acid Deposition Monitoring Network
in East Asia (EANET)

Report of the Inter-laboratory Comparison Project 2022

25th Inter-laboratory Comparison Project on Wet Deposition

18th Inter-laboratory Comparison Project on Dry Deposition

24th Inter-laboratory Comparison Project on Soil

23rd Inter-laboratory Comparison Project on Inland Aquatic Environment

December 2023
Network Center for EANET

Contents

1. INTRODUCTION

The Inter-laboratory Comparison Project was conducted among the analytical laboratories in participating countries of the Acid Deposition Monitoring Network in East Asia (EANET), based on the quality assurance / quality control (QA/QC) programs of EANET.

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

(i) to recognize the analytical precision and accuracy of the measurement in each participating laboratory;

(ii) to give further opportunities to improve the quality of the analysis on wet deposition, dry deposition (filter pack method), soil and inland aquatic monitoring of EANET;

(iii) to improve reliability of analytical data through the assessment of suitable analytical methods and techniques.

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

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

This report presented the results of the 25th Inter-laboratory Comparison Project on wet deposition, 18th Inter-laboratory Comparison Project on dry deposition, 24th Inter-laboratory Comparison Project on soil, and 23rd 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.

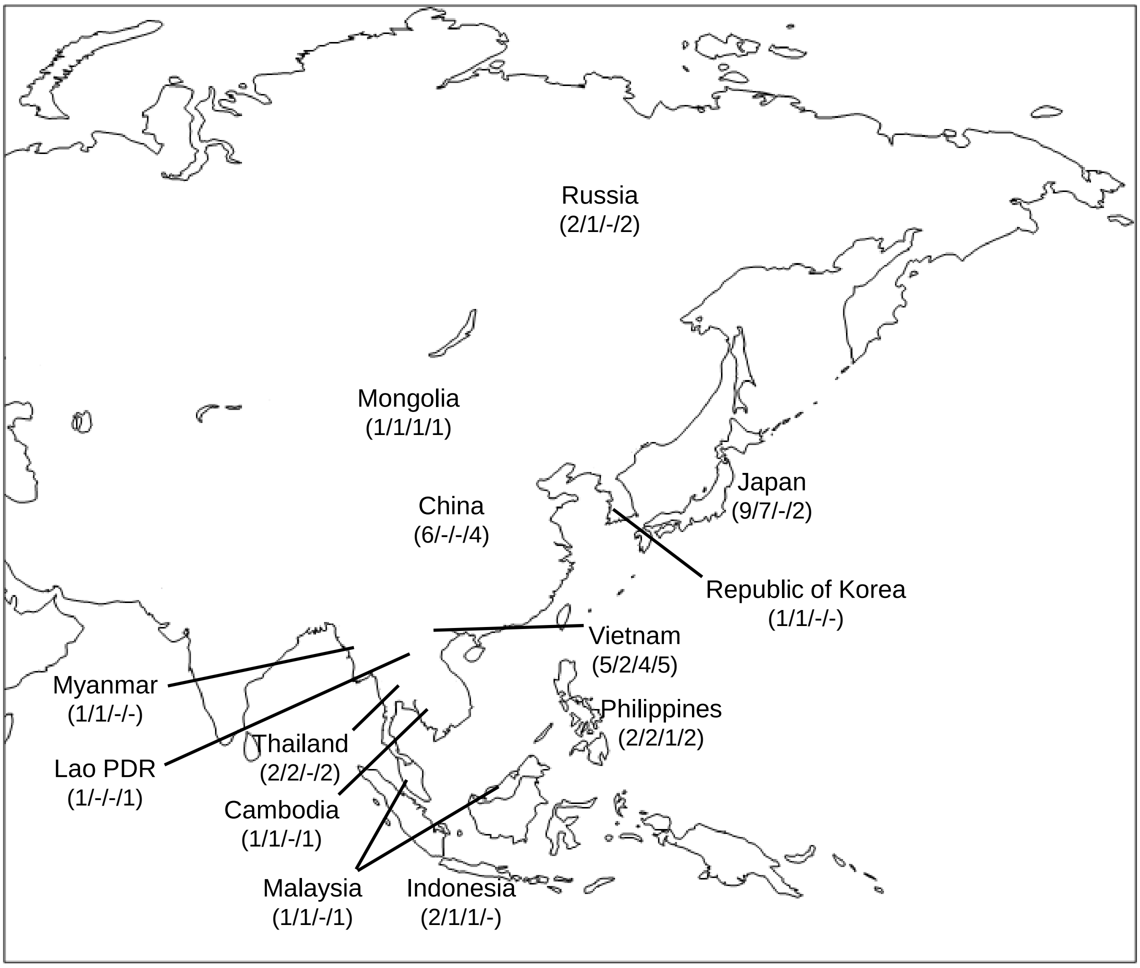


Figure 1.1 Number of participating laboratories in 2022

* The values in parentheses show the number of participating laboratories in each country.

(wet/dry/soil/inland aquatic environment)

Table 1.1 Participating laboratories and data submission status

Participating laboratories	Code	Data submission			
		Wet	Dry	Soil	IAE
Cambodia					
General Directorate of Environmental Protection (GDEP), Ministry of Environment	KH01				
China					
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	✔			
Indonesia					
Environmental Management Center (EMC), Ministry of Environment and Forestry	ID01				
Climatology,Meteorological and Geophysical Agency (BMKG)	ID02	✔			
Research Organization of Aeronautics and Space - National Research and Innovation Agency (LAPAN-BRIN)	ID03	✔	✔		
Indonesian Soil Research Institute (ISRI)	ID04			✔	
Research Center for Water Resources (RCWR), Agency for Research and Development, Ministry of Public Works	ID05				
Japan					
Institute of Environmental Sciences, Hokkaido Research Organization	JP01	✔	✔		
Niigata Prefectural Institute of Public Health and Environmental Sciences	JP02	✔	✔		
Nagano Environmental Conservation Research Institute	JP03	✔	✔		✔
Gifu Prefectural Research Institute for Health and Environmental Sciences	JP04	✔	✔		✔
Kochi Prefectural Institute of Health and Environment	JP07	✔			
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	✔			
Lao PDR					
Environmental Laboratory (EL), Natural Resource and Environment and Statistic Research Institute (NRESRI)	LA01	✔			✔
Malaysia					
Environmental Quality Division, Department of Chemistry Malaysia (DOC)	MY01	✔	✔		✔
Mongolia					
Central Laboratory of Environment and Metrology (CLEM)	MN01	✔	✔	✔	✔
Myanmar					
Department of Meteorology and Hydrology (DMH)	MM01	✔	✔		
Philippines					
Environmental Management Bureau - Central Office (EMB-CO)	PH01	✔	✔	✔	✔
Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR)	PH02	✔	✔		✔
Republic of Korea					
Aerosol research Lab. in National Institute of Environment Research	KR01	✔	✔		
Russia					
Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB)	RU01	✔	✔		✔
Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	RU02	✔			✔
Thailand					
Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MONRE)	TH01	✔	✔		✔
Environmental Research and Training Center (ERTC), Department of Environmental Quality Promotion	TH02	✔	✔		✔
Vietnam					
Environmental Laboratory - Center for Environmental Research - Vietnam Institute of Meteorology, Hydrology and Environment (IMHEN)- MoNRE	VN01	✔	✔	✔	✔
Mid- Central Regional Hydro Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	VN02	✔		✔	✔
Sub-Institute of HydroMeteorology and 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 :		**33**	**19**	**7**	**20**

Table 1.2 Laboratories in charge of the analysis of each monitoring site in EANET (2022)

Country	Site for deposition monitoring	Code	Plot for soil and vegetation monitoring	Code	Site for monitoring on inland aquatic environment	Code	Laboratory code			
							Wet	Dry (FP*)	Soil	IAE
Cambodia	Phnom Penh	*KHA001*					KH01	KH01		
					Sras Srang Lake	*KHI002*				KH01
China	Chingqing - Haifu	*CNA003*					CN04			
	- Jinyunshan	*CNA004*	Jinyunshan	*CNS004*	Jinyunshan Lake	*CNI004*	CN04		CN04	CN04
	Xi'an - Shizhan	*CNA005*					CN03			
	- Jiwozi	*CNA007*	Dabagou	*CNS007*	Jiwozi River	*CNI007*	CN03		CN03	CN03
	Xiamen - Hogwen	*CNA008*					CN02	CN02		
	- Xiaoping	*CNA009*	Xiaoping	*CNS009*	Xiaoping Dam	*CNI209*	CN02		CN02	CN02
	Zhuhai - Xiang Zhou	*CNA010*					CN01			
	- Zhuxiandong	*CNA011*	Zhuxiandong	*CNS011*	Zhuxiandong Stream	*CNI111*	CN01		CN01	CN01
	- Haibin-Park	*CNA012*								
	Wuzhishan	*CNA013*					CN05			
	Lijiang	*CNA014*					CN06			
Indonesia	Jakarta	*IDA001*					ID02	ID02		
	Serpong	*IDA002*	Bogor Research Forest	*IDS002*			ID01	ID01	ID01	
	Kototabang	*IDA003*					ID02			
	Bandung	*IDA004*			Patengang Lake	*IDI004*	ID03	ID03		ID01
	Maros	*IDA005*					ID02			
					Gunung Lake	*IDI006*				ID01
	Jembrana	*IDA006*					ID02			
	Lombok	*IDA007*					ID02			
Japan	Rishiri	*JPA001*					JP01	JP01		
	Ochiishi	*JPA002*					JP09	JP09		
	Sado-seki	*JPA004*					JP09	JP02		
	Happo	*JPA005*	Sekido-san	*JPS005*	Futago-ike Lake	*IPI005*	JP03	JP03	JP13	JP03
			Horyu-zan	*JPS105*					JP13	
	Ijira	*JPA006*	Ijira	*JPS006*	Ijira Lake	*JPI006*	JP04	JP04	JP04	JP04
			Yamato	*JPS106*					JP04	
	Oki	*JPA007*					JP09	JP09		
	Yusuhara	*JPA009*					JP07	JP09		
	Hedo	*JPA010*					JP08	JP08		
	Ogasawara	*JPA011*					JP10	JP10		
	Tokyo	*JPA012*					JP10	JP10		
	Niigata-maki	*JPA013*					JP02			
	Tsushima	*JPA014*					JP14	JP09		
Lao PDR	Vientiane	*LAA001*			Nam Houm Lake	*LAI001*	LA01	LA01		LA01
Malaysia	Petaling Jaya	*MYA001*	Pasoh Reserve Forest 1 / 2	*MYS001/ MYS101*			MY01	MY01		
	Tanah Rata	*MYA002*						MY01		
	Danum Valley	*MYA003*			Baru River	*MYI103*	MY01	MY01		MY01
	Kuching	*MYA004*					MY01			
	Gunung Brinchang	*MYA005*					MY01			
			UPMKB Rehabilitated Forest Planted in 1991 / 2008	*MYS005/ MYS105*						
					Kuala Tahan	*MYI006*				MY01
Mongolia	Ulaanbaatar	*MNA001*	Bogdkhan Mountain	*MNS001*			MN01	MN01	MN01	
	Terelj	*MNA002*	Terelj Mountain	*MNS002*	Terelj River	*MNI002*	MN01	MN01	MN01	MN01
Myanmar	Yangon	*MMA001*					MM01	MM01		
	Mandalay	*MMA002*								
Philippines	Metro Manila	*PHA001*	La Mesa Watershed	*PHS001*			PH01	PH01		
	Los Baños	*PHA002*	Mt. Makiling	*PHS002*	Pandin Lake	*PHI102*	PH01	PH01		PH01
			UP Quezon, Land Grant	*PHS102*						
	Mt. Sto. Tomas	*PHA003*	Boneco Long Term Ecological Research Site	*PHS003*	Ambulalakaw River	*PHI003*	PH02	PH02		PH02
Republic of Korea	Kanghwa						KR01	KR01		
	Cheju (Kosan)						KR01	KR01		
	Imsil	*KRA003*	Mt. Naejang	*KRS003*			KR01	KR01	KR01	
Russia	Mondy	*RUA001*	Ilchir Lake	*RUS001*			RU01	RU01	RU01	
			Okinskoe Lake	*RUS101*					RU01	
			Solar Observatory	*RUS201*					RU01	
	Listvyanka	*RUA002*	Bolshie Koty	*RUS002*	Pereemnaya River	*RUI102*	RU01	RU01	RU01	RU01
			Pereemnaya river Catchment	*RUS102*					RU01	
	Irkutsk	*RUA003*	Irkutsk	*RUS003*			RU01	RU01	RU01	
	Primorskaya	*RUA004*	Primorskaya	*RUS004*	Komarovka River	*RUI004*	RU02	RU01	RU01	RU02
Thailand	Bangkok	*THA001*					TH01	TH01		
	Samutprakarn	*THA002*					TH01			
	Pathumthani	*THA003*					TH02	TH02		
	Khanchanaburi	*THA004*	Vachiralongkorn Dam	*THS004*	Vachiralongkorn Dam	*THI004*	TH01	TH01		TH01
			Vachiralongkorn Puye	*THS104*						
Vietnam	Hanoi	*VNA001*					VN01	VN01		
	Hoa Binh	*VNA002*	Cave of Heaven	*VNS002*	Hoa Binh Reservoir	*VNI002*	VN01	VN01	VN01	VN01
			Thang Ranh	*VNS102*					VN01	
	Cuc Phuong	*VNA003*					VN04			
	Da Nang	*VNA004*					VN02			
	Can Tho	*VNA005*					VN03	VN03		
	Ho Chi Minh	*VNA006*					VN03	VN03		
	Yen Bai	*VNA007*					VN01	VN01		

* FP: Filter pack method

2. 25th INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

2.1 Introduction

In the 25th 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 middle of October 2022. Their analytical results were required to be submitted to the NC by 28 February 2023.

2.2 Procedures

2.2.1 Participating laboratories

The NC distributed the artificial rainwater samples to 34 laboratories in charge of chemical analysis in 13 countries of EANET. 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.

2.2.2 Description of samples

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

Table 2.1 Description of artificial rainwater samples

Artificial rain-water sample	Quantity of sample	Container	Number of samples	Note
No. 221w No. 222w	100 mL each	Polypropylene bottle 100 mL	One bottle each	- Fixed quantity of reagents are dissolved in pure water (EC < 0.15 mS m^{-1}) - Ions other than shown in Table 2.2 are not added

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

Table 2.2 Prepared values/concentrations of analytical parameters*

	pH -	EC 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}
No. 221w	4.70	2.98	45.3	32.1	52.8	30.3	42.8	4.9	30.2	8.6
No. 222w	5.15	1.13	14.5	13.1	25.5	15.1	20.5	2.5	7.0	4.3

* For 100 times diluted samples.

2.2.3 Analytical methods and data checking procedures

Before the measurement, the samples must be diluted 100 times accurately with pure water (EC < 0.15 mS m^{-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 SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}.

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

Table 2.3 Analytical methods recommended in the Technical Manual

Parameter	Analytical method
pH	Glass Electrode Method (preferably with the Electrode of non-leak inner cell)
EC	Conductivity Cell Method
SO_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 (R_1) and total electric conductivity agreement (R_2).

Calculation of ion balance (R_1)

(1) Total anion equivalent concentration (**A** [μeq L^{-1}]) was calculated by summing the concentrations of all anions (c [μmol L^{-1}]).

$$\mathbf{A}\ [\mu eq\ L^{-1}] = \sum n\, c_{Ai}\ [\mu mol\ L^{-1}] = 2c\,(SO_4^{2-}) + c\,(NO_3^-) + c\,(Cl^-)$$

n, c_{Ai} : electric charge and concentration [μmol L^{-1}] of anion “i”.

(2) Total cation equivalent concentration (**C** [μeq L^{-1}]) was calculated by summing the concentrations of all cations (c [μmol L^{-1}]).

$$\mathbf{C}\ [\mu eq\ L^{-1}] = \sum n\, c_{Ci}\ [\mu mol\ L^{-1}] = 10^{(6\text{-}pH)} + c\,(NH_4^+) + c\,(Na^+) + c\,(K^+) + 2c\,(Ca^{2+}) + 2c\,(Mg^{2+})$$

n, c_{Ci} : electric charge and concentration [μmol L^{-1}] of cation “i”.

(3) Calculation of ion balance (R_1)

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

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

Table 2.4 Allowable ranges for R_1 in different concentration ranges

C+**A** [μeq L^{-1}]	R_1 [%]
< 50	± 30
50 – 100	± 15
> 100	± 8

Comparison between calculated and measured values of electrical conductivity (R_2)

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

$$\Lambda \text{ calc } [\text{mS m}^{-1}] = \{349.7 \times 10^{(6-\text{pH})} + 80.0 \times 2c\,(SO_4^{2-}) + 71.4 \times c\,(NO_3^{-})$$
$$+ 76.3 \times c\,(Cl^{-}) + 73.5 \times c\,(NH_4^{+}) + 50.1 \times c\,(Na^{+}) + 73.5 \times c\,(K^{+})$$
$$+ 59.5 \times 2c\,(Ca^{2+}) + 53.0 \times 2c\,(Mg^{2+})\} / 10000$$

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

(2) Electrical conductivity comparison (R_2) 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) R_2 calculated by the above equation was compared with allowable ranges specified in the Technical Manual which are shown in Table 2.5. If R_2 was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

Table 2.5 Allowable ranges for R_2 in different ranges of EC

Λ meas [mS m^{-1}]	R_2 [%]
< 0.5	± 20
0.5 – 3	± 13
> 3	± 9

2.3 Results

The NC received the analytical results from 32 laboratories in the participating countries of EANET.

Basic statistics of submitted data summarized in Table 2.6 was calculated for each parameter of the artificial rainwater samples such as: average (Va), minimum (Min.), maximum (Max.), standard deviation (S.D.), and number of data (N). The outliers, exceeding three standard deviations, were excluded from the calculation. As shown in Table 2.6, the range of ΔV/Vp was between -4.3% to 1.8% for sample No. 221w, and -1.6% to 7.0% for sample No. 222w.

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

Sample No. 221w

Constituents		Prepared (Vp)	Average (Va)	ΔV/Vp[*1] %	S.D.	N	Min.	Max.
pH		4.70	4.79	1.8	0.10	31	4.56	5.02
EC	[mS m^{-1}]	2.98	2.85	-4.3	0.12	31	2.58	3.01
SO_4^{2-}	[μmol L^{-1}]	45.3	44.8	-1.1	1.15	31	42.2	46.3
NO_3^-	[μmol L^{-1}]	32.1	32.0	-0.4	2.03	31	28.1	39.3
Cl^-	[μmol L^{-1}]	52.8	52.6	-0.4	1.18	30	49.4	54.6
NH_4^+	[μmol L^{-1}]	30.3	29.0	-4.3	2.24	30	20.1	31.6
Na^+	[μmol L^{-1}]	42.8	42.3	-1.3	1.70	31	39.0	47.5
K^+	[μmol L^{-1}]	4.9	4.9	-0.4	0.40	31	3.7	5.6
Ca^{2+}	[μmol L^{-1}]	30.2	30.6	1.2	2.31	31	25.7	36.2
Mg^{2+}	[μmol L^{-1}]	8.6	8.5	-0.6	0.67	32	7.3	10.1

Sample No. 222w

Constituents		Prepared (Vp)	Average (Va)	ΔV/Vp[*1] %	S.D.	N	Min.	Max.
pH		5.15	5.16	0.2	0.21	31	4.53	5.50
EC	[mS m^{-1}]	1.13	1.12	-0.9	0.05	30	1.04	1.28
SO_4^{2-}	[μmol L^{-1}]	14.5	14.4	-0.9	0.67	31	12.3	15.5
NO_3^-	[μmol L^{-1}]	13.1	12.9	-1.5	0.72	30	11.1	15.5
Cl^-	[μmol L^{-1}]	25.5	25.5	0.0	1.29	30	23.3	29.8
NH_4^+	[μmol L^{-1}]	15.1	15.2	0.6	1.78	31	11.9	21.1
Na^+	[μmol L^{-1}]	20.5	20.5	0.0	1.46	32	17.5	23.7
K^+	[μmol L^{-1}]	2.5	2.7	7.0	0.77	32	0.6	4.3
Ca^{2+}	[μmol L^{-1}]	7.0	7.4	5.5	0.98	32	5.2	10.2
Mg^{2+}	[μmol L^{-1}]	4.3	4.2	-1.6	0.38	32	3.3	5.0

Note: *1, (Va-Vp)/Vp x 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 ±15% of deviation* from Vp. In this report, analytical data of the artificial rainwater samples were compared with Vp, and the data exceed DQO were marked with flags. The flag "E" indicates that the deviation from Vp exceeds ±15% but not ±30%, and the flag "X" indicates that the deviation from Vp exceeds ±30%.

*According to *Technical Manual for Wet Deposition Monitoring in East Asia -2010*, deviation is calculated using the following formula:
Deviation = [(analytical values) - Vp] x 100 / Vp

A set of data for each sample was evaluated by the data checking procedures described in section 2.2.3. The flag "I" and the flag "C" were put to the data sets with poor ion balance and poor conductivity agreement, respectively.

The results were evaluated by the following three aspects:

i) Comparison of concentration dependence on level of their concentration
– sample No. 221w and No. 222w,
ii) Comparison of individual parameters,
iii) Comparison of circumstances of chemical analysis in each participating laboratory.

Evaluation of analytical data on both sample No. 221w and No. 222w is presented in 2.3.1 Evaluation of laboratories' performance (by sample), evaluation of analytical data for each constituent is presented in 2.3.2 Evaluation of laboratories' performance (by analytical parameter), and evaluation of analytical data by the circumstances of chemical analysis such as analytical method used, experience of personnel in charge, and other analytical condition are presented in 2.3.4 Information on laboratories.

2.3.1 Evaluation of laboratories' performance (by sample)

1) Sample No. 221w

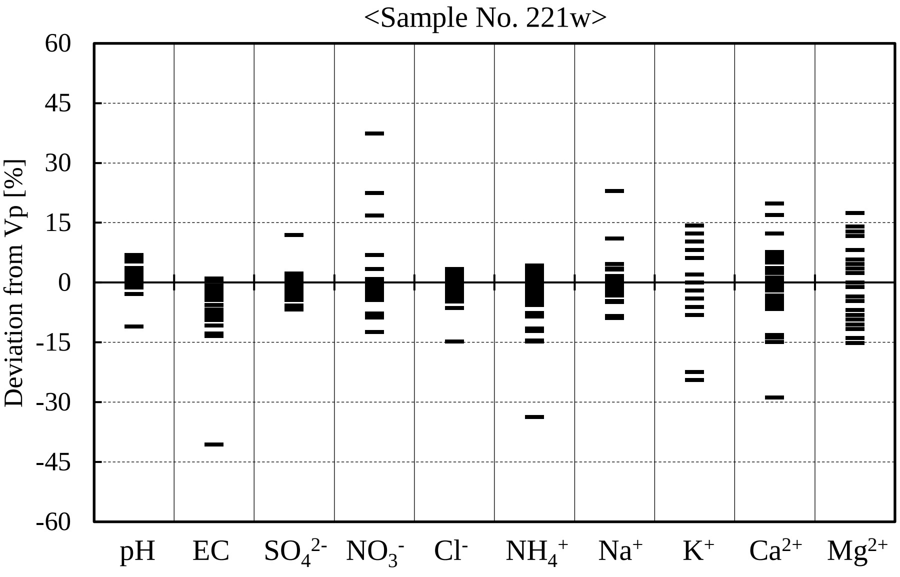
The number and percentage of the flagged data for sample No. 221w are shown in Table 2.7.
10 analytical data out of 319 were flagged by "E". And 6 analytical data out of 319 were flagged by "X". Data flagged by "E" and "X" shared 5.0 percent of all the submitted data for sample No. 221w.
The data normalized by prepared value in each parameter are shown in Figure 2.1.

Table 2.7 Number of flagged data for the Sample No. 221w

Charactarization of data	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Total
Data within DQO	32	31	32	29	31	29	31	29	29	30	303
Data with flag E[*1]	0	0	0	2	0	0	1	2	3	2	10
Data with flag X[*2]	0	1	0	1	0	3	0	1	0	0	6
Flagged data [%]	0.0	3.1	0.0	9.4	0.0	9.4	3.1	9.4	9.4	6.3	5.0

(Total data = 319)

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



Three plots are out of scale; NH_4^+:69.3% and 61.3%, K^+: -65.3%.

Figure 2.1 Distribution of the data normalized by prepared value in each parameter for sample No. 221w

The parameters which had the most flags were NO_3^-, NH_4^+, K^+ and Ca^{2+}. The analytical data submitted by the participating laboratories are shown in Table 2.8 with flags.

Table 2.8 Analytical Results of Sample No. 221w

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	4.72	3.01	45.9	31.9	53.4	30.9	44.3	4.9	31.7	8.5	0.7	-0.4
CN02	4.74	3.00	45.9	32.1	54.1	29.4	42.8	4.9	32.0	8.5	-0.5	-0.8
CN03	4.78	2.99	45.5	31.0	53.5	30.0	41.7	4.9	32.2	8.8	-0.1	-1.9
CN04	4.74	3.00	45.3	30.8	52.8	29.0	42.3	4.8	32.0	8.6	0.4	-1.4
CN06	4.78	2.89	45.7	31.8	54.6	30.3	41.4	5.0	30.6	8.2	-2.0	-0.3
ID02	4.68	2.85	44.3	29.6	49.4	27.7	44.2	4.6	30.4	8.5	2.2	1.5
ID03	4.87	2.58	46.3	29.3	50.7	25.8	43.5	4.8	31.0	8.6	-1.7	2.5
JP01	4.70	2.96	45.2	32.2	52.4	29.5	41.8	5.0	28.7	8.3	-1.4	-0.3
JP02	4.76	2.85	45.6	32.2	54.0	31.6	44.8	5.2	26.0	8.9	-2.5	0.5
JP03	4.74	2.94	45.4	31.8	53.1	31.2	43.3	4.7	30.1	8.2	-0.5	-0.3
JP04	4.74	2.95	45.1	31.4	52.3	30.6	40.8	4.8	29.2	8.2	-1.4	-1.2
JP07	4.76	2.93	45.0	31.2	52.4	30.2	41.8	4.6	28.2	7.9	-2.2	-1.7
JP08	4.74	2.87	45.1	31.9	53.0	30.0	42.7	4.9	29.9	8.5	-0.7	0.6
JP09	4.81	2.88	45.1	31.8	52.8	30.0	43.1	4.8	31.3	8.5	-0.5	-0.9
JP10	4.73	2.96	45.7	32.3	53.3	29.7	43.2	4.8	31.7	9.1	0.3	0.1
JP14	4.82	2.91	46.1	32.2	52.3	30.3	43.1	4.8	30.5	8.0	-1.8	-1.6
LA01	4.73	2.81	45.5	33.2	53.8	20.1 X	52.6 E	3.8 E	30.5	7.7	-1.9	1.8
MY01	4.79	2.90	46.1	32.1	53.5	29.3	42.6	4.5	29.6	7.8	-3.0	-1.1
MN01	4.56	2.78	45.0	34.3	50.3	49.0 X	47.5	5.6	32.5	8.6	9.6 I	10.5
MM01	4.80	1.77 X	42.6	28.1	51.9	30.3	43.0	4.9	28.5	7.6	0.3	21.3 C
PH01	4.75	2.95	45.4	31.0	50.9	31.3	39.2	4.6	30.9	7.4	-0.9	-1.5
PH02	4.79	2.74	42.7	37.5 E	51.8	31.0	42.5	1.7 X	33.9	9.3	0.9	2.3
KR01	4.73	2.71	42.2	31.6	52.2	26.6	42.0	5.0	28.9	8.5	-0.4	2.1
RU01	4.64	2.92	43.3	30.8	53.4	29.5	42.0	5.0	25.7	8.2	-1.1	1.0
RU02	4.18	3.00	50.7	39.3 E	45.0	51.3 X	39.0	5.5	21.5 E	10.1 E	9.6 I	22.3 C
TH01	4.86	2.76	44.7	44.1 X	52.5	26.8	39.1	4.7	35.3 E	9.1	-3.6	1.7
TH02	4.85	2.87	45.8	31.7	54.2	25.9	41.6	3.7 E	26.2	7.3 E	-7.6	-3.4
VN01	4.97	2.66	43.4	32.1	52.5	28.9	40.7	5.3	30.4	9.7	-1.7	-0.8
VN02	4.95	2.60	43.8	32.4	53.2	29.0	40.8	5.3	30.5	9.6	-2.0	1.0
VN03	4.82	2.72	44.4	30.7	---	28.6	42.2	5.3	32.2	9.0	---	---
VN04	5.00	2.70	42.5	31.7	51.8	28.8	40.7	5.2	30.5	9.8	-1.0	-2.4
VN05	5.02	2.75	44.9	31.3	51.4	28.0	42.4	5.4	36.2 E	8.5	0.6	-1.9
Vp	4.70	2.98	45.3	32.1	52.8	30.3	42.8	4.9	30.2	8.6	0.0	0.0
N of data	32	32	32	32	31	32	32	32	32	32		
Within DQO	32	31	32	29	31	29	31	29	29	30		
Flag E	0	0	0	2	0	0	1	2	3	2		
Flag X	0	1	0	1	0	3	0	1	0	0		

Note: "E", 15%<| Deviation |≦30% ; "X", 30%<| Deviation |
"I", Poor ion balance (R_1); "C", Poor conductivity agreement (R_2); "---", 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. 222w

The number and percentage of the flagged data for sample No. 222w are shown in Table 2.9. 21 analytical data out of 319 were flagged by "E". 17 analytical data out of 319 were flagged by "X". Data marked with flags shared up to 11.9 percent of all the submitted data for sample No. 222w.

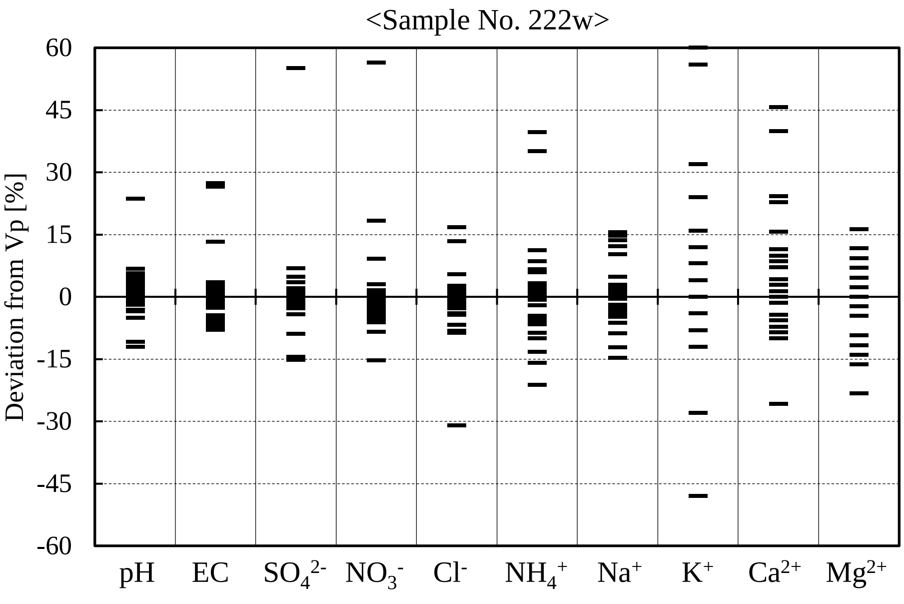
The normalized data by prepared value in each parameter are shown in Figure 2.2.

Table 2.9 Number of flagged data for the sample No. 222w

Charactarization of data	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Total
Data within DQO	31	30	30	28	29	27	31	21	25	29	281
Data with flag E*1	1	2	1	2	1	2	1	3	5	3	21
Data with flag X*2	0	0	1	2	1	3	0	8	2	0	17
Flagged data [%]	3.1	6.3	6.3	12.5	6.5	15.6	3.1	34.4	21.9	9.4	11.9

(Total data = 319)

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



Six plots are out of scale; NO_3^-: 60.3%, NH_4^+: -85.4%, K^+: 72.0%, 64.0%, 64.0%, -76.0%

Figure 2.2 Distribution of the data normalized by prepared value for each parameter for sample No. 222w

Analytical data of cations tended to be marked with more flags than those of anions. The analytical data submitted by the participating laboratories are shown in Table 2.10 with flags.

Table 2.10 Analytical Results of Sample No. 222w

Lab. ID[*1]	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	R_1	R_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}	%	%
CN01	5.15	1.13	14.5	12.7	25.5	16.4	21.5	2.5	7.5	4.4	2.9	0.8
CN02	5.15	1.15	14.8	12.9	26.2	15.0	20.8	2.5	7.5	4.4	0.3	-0.2
CN03	5.21	1.17	14.6	12.7	25.1	16.1	23.0	2.6	7.5	4.6	3.6	-2.1
CN04	5.20	1.17	14.7	12.6	25.2	15.2	20.0	2.7	7.3	4.5	0.5	-2.9
CN06	5.10	1.07	14.6	13.0	26.9	15.5	19.6	2.5	7.7	4.1	0.0	4.7
ID02	5.28	1.07	14.7	12.5	23.4	14.1	21.1	2.4	7.1	4.7	0.9	-1.0
ID03	5.24	1.05	12.3 E	12.0	23.3	13.1	20.9	2.5	7.8	4.4	5.3	-1.4
JP01	5.13	1.17	14.6	13.1	25.5	14.8	20.0	2.6	6.7	4.1	-1.0	-1.6
JP02	5.19	1.11	14.7	13.0	25.8	15.5	22.6	2.5	7.1	4.3	1.2	0.7
JP03	5.15	1.16	14.7	13.3	25.6	15.6	20.4	2.4	6.7	4.1	-0.9	-1.3
JP04	5.17	1.16	14.4	12.7	25.3	15.3	19.2	2.4	7.0	4.2	-0.6	-2.4
JP07	5.17	1.17	14.2	12.4	25.2	15.2	20.6	2.4	6.4	4.1	0.0	-3.2
JP08	5.15	1.10	14.4	12.7	24.8	15.0	20.4	2.4	7.3	4.3	1.3	0.9
JP09	5.31	1.10	14.4	12.9	25.5	15.4	20.5	2.4	7.0	4.2	-1.2	-2.3
JP10	5.13	1.17	14.8	13.0	26.1	15.0	20.7	2.4	7.6	4.6	0.9	-0.5
JP14	5.36	1.11	14.7	12.9	25.5	15.2	20.9	2.8	6.6	3.8	-2.8	-3.7
LA01	4.89	1.28	15.0	15.5 E	29.8 E	2.2 X	23.5	1.8 E	8.1 E	3.8	-8.0	1.2
MY01	5.24	1.14	15.5	12.7	25.6	15.0	20.1	2.2	6.3	3.7	-4.7	-2.9
MN01	4.97	1.12	14.1	14.3	23.8	20.4 X	23.7 E	3.1 E	8.6 E	4.5	11.8 I	8.4
MM01	4.53	1.43 E	13.2	11.1 E	24.4	13.6	18.7	2.3	7.1	3.6 E	16.0 I	12.6
PH01	4.99	1.13	14.4	13.1	24.5	16.0	20.6	2.8	8.7 E	3.7	5.7	5.2
PH02	5.38	1.10	14.1	13.5	28.9	16.8	19.6	0.6 X	8.7 E	5.0 E	-1.5	-1.3
KR01	5.19	1.07	12.4	12.4	25.0	11.9 E	19.7	2.9 E	6.4	4.6	0.6	-1.6
RU01	5.05	1.17	13.9	12.4	24.9	14.4	19.7	2.6	6.9	3.7	1.3	-0.5
RU02	4.59	1.44 E	22.5 X	20.5 X	17.6 X	21.1 X	18.0	3.3 X	6.5	3.9	3.4	14.5 C
TH01	6.37 E	1.11	14.4	21.0 X	25.9	13.8	19.7	2.3	10.2 X	4.8	-6.7	-6.1
TH02	5.22	1.12	14.1	12.3	25.5	12.7 E	17.5	1.3 X	5.2 E	3.3 E	-9.5 I	-5.4
VN01	5.44	1.06	14.5	13.3	25.3	14.2	19.5	4.0 X	7.1	4.3	-2.6	-2.5
VN02	5.40	1.05	14.6	13.3	25.8	14.3	19.8	4.1 X	7.2	4.5	-2.0	-0.8
VN03	5.23	1.04	14.8	12.8	---	15.1	23.3	4.3 X	9.8 X	4.4	---	---
VN04	5.50	1.07	14.3	13.2	24.8	14.2	19.2	3.9 X	7.0	4.2	-2.9	-4.4
VN05	5.33	1.08	15.2	12.8	25.6	15.1	21.5	4.1 X	7.7	4.6	0.8	0.1
Vp	5.15	1.13	14.5	13.1	25.5	15.1	20.5	2.5	7.0	4.3	0.1	-0.1
N of data	32	32	32	32	31	32	32	32	32	32		
Within DQO	31	30	30	28	29	27	31	21	25	29		
Flag E	1	2	1	2	1	2	1	3	5	3		
Flag X	0	0	1	2	1	3	0	8	2	0		

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

"I", Poor ion balance (R_1); "C", Poor conductivity agreement (R_2); "---", 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. 221w and 222w are shown in Figure 2.3. The percentage of the data within the DQO for sample No. 221w and 222w were 95.0% and 88.1%, respectively. The difference between both samples was 6.9%. In this project, the total number of flagged data was 54 (E: 31, X: 23) out of all the 638 data.

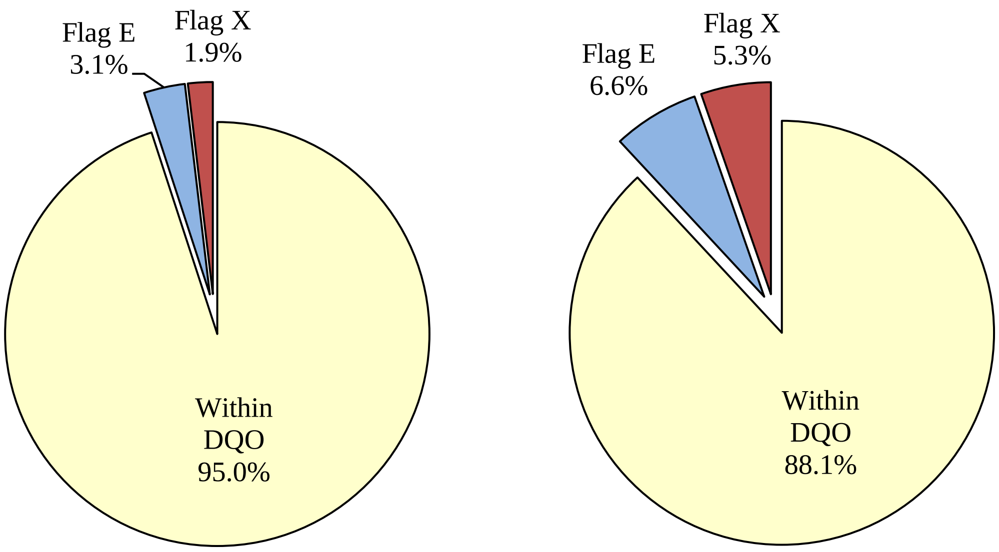


Figure 2.3 Percentage of flagged data for sample No. 221w and No. 222w (Left: No. 221w, Right: No. 222w)

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

The number of laboratories by number of flags is shown in Figure 2.4. The number of laboratories without flagged data was 17, which corresponds to 53.1% of all the participating laboratories.

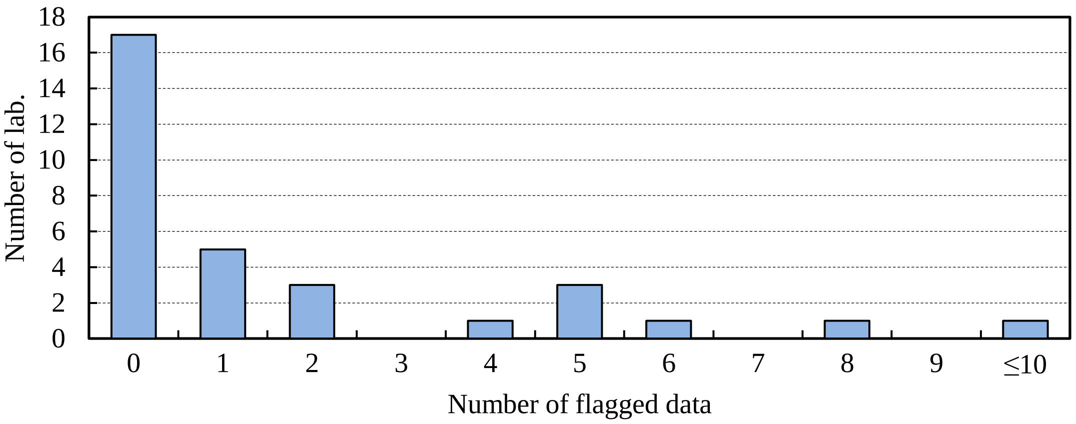


Figure 2.4 Distribution of the number of laboratory (by number of flags)

2.3.2 Evaluation of laboratories' performance (by analytical parameter)

The data normalized by Vp are shown in Figures 2.5 through 2.24 for each parameter. In scatter diagrams (lower figures), bold line means the prepared values of sample No. 221w and 222w, broken lines and dotted lines showed the values of Vp ± 15% and Vp ± 30%, respectively.

1) pH

All participating laboratories used pH meter with glass electrode method for the measurement of pH. The data of sample No.222w from TH01 was marked with flag "E".

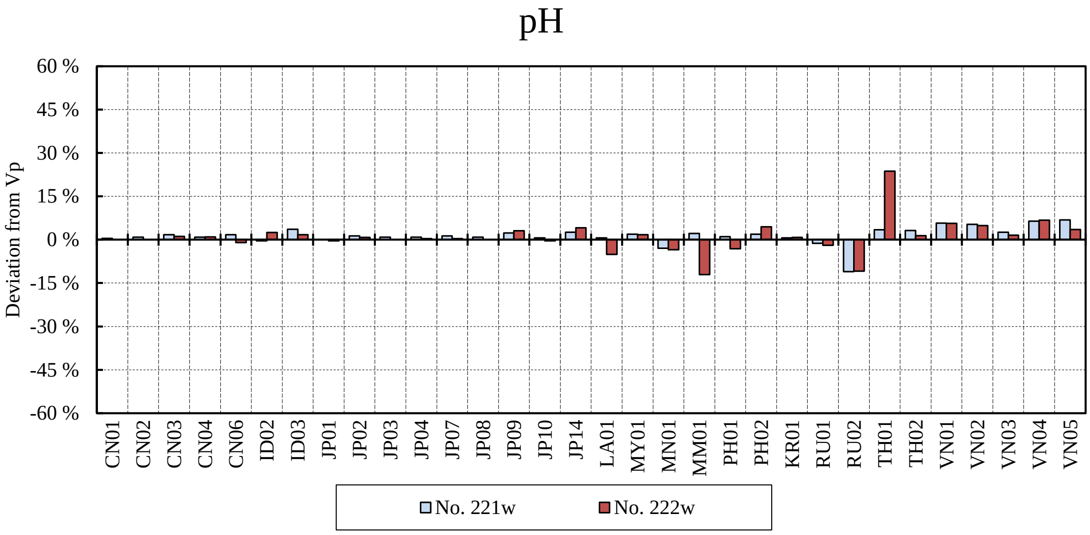


Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)

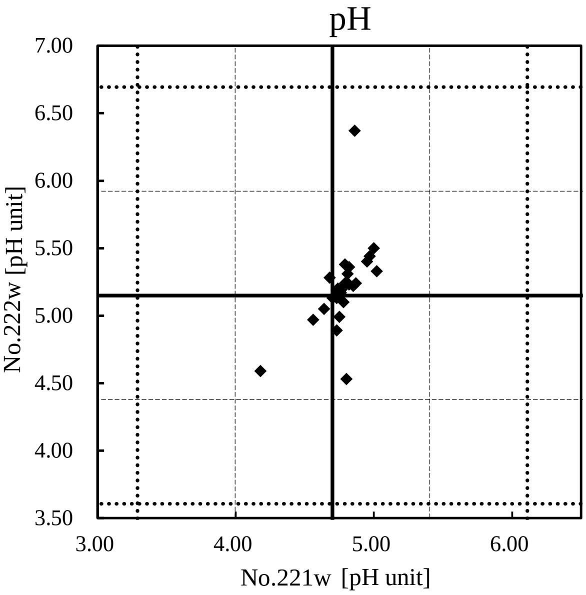


Figure 2.6 Scatter diagram for pH

2) EC

All participating laboratories used conductivity cell method for the measurement of EC. The data of sample No.222w from 2 laboratories (MM01 and RU02) were marked with flag "E". Additionally, sample No.221w from MM01 was marked with flag "X".

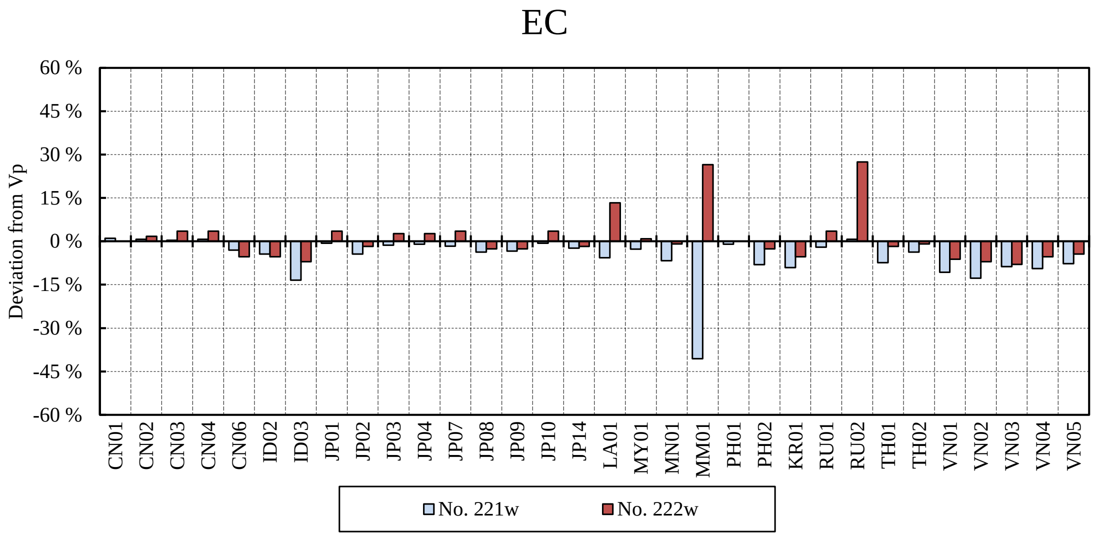


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)

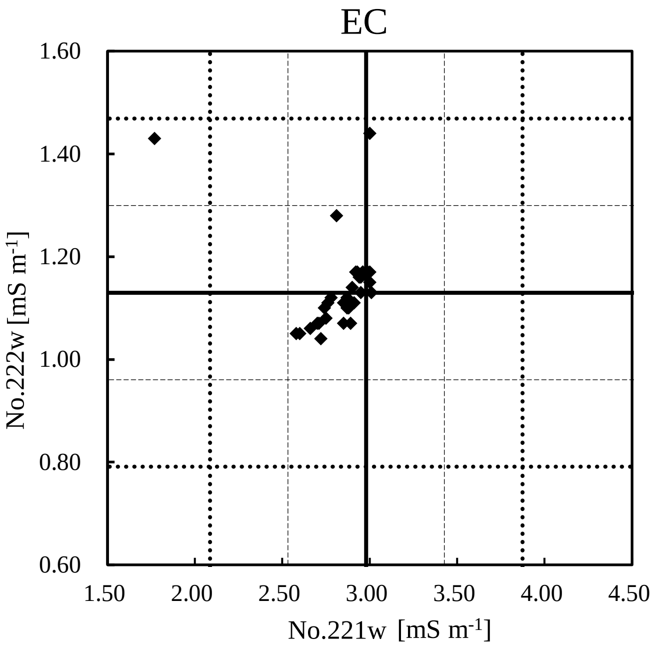


Figure 2.8 Scatter diagram for EC

3) SO_4^{2-}

The data of sample No.222w from ID03 was marked with flag “E”, and sample No.222w from RU02 was marked with flag “X”.

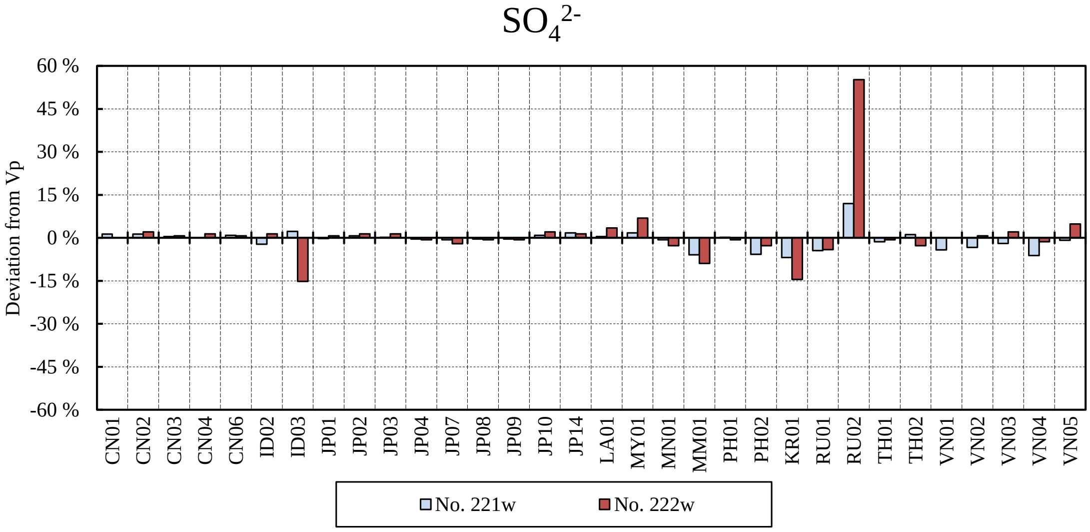


Figure 2.9 Deviation from prepared value for SO_4^{2-} (normalized by prepared value)

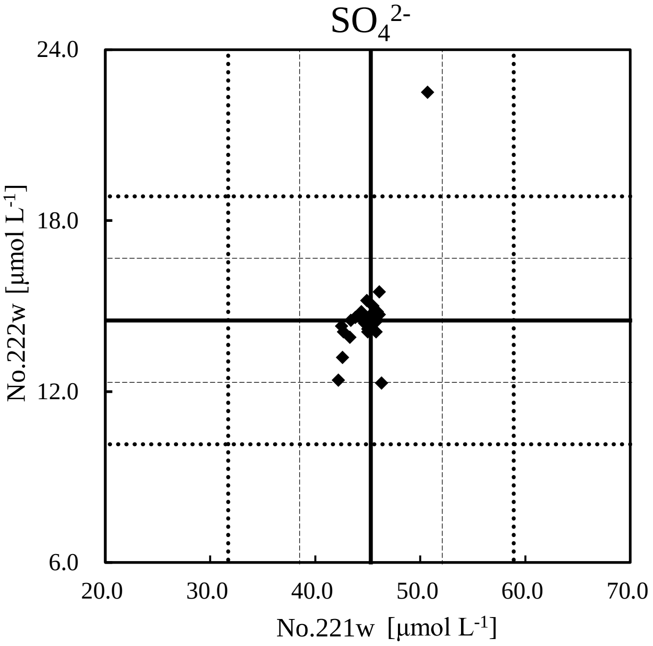


Figure 2.10 Scatter diagram for SO_4^{2-}

4) NO_3^-

The data of sample No. 221w from two laboratories (PH02 and RU02) and sample No.222w from 2 laboratories (LA01 and MM01) were marked with flag "E". Additionally, sample No. 221w from TH01 and sample No.222w from two laboratories (RU02 and TH01) were marked with flag "X".

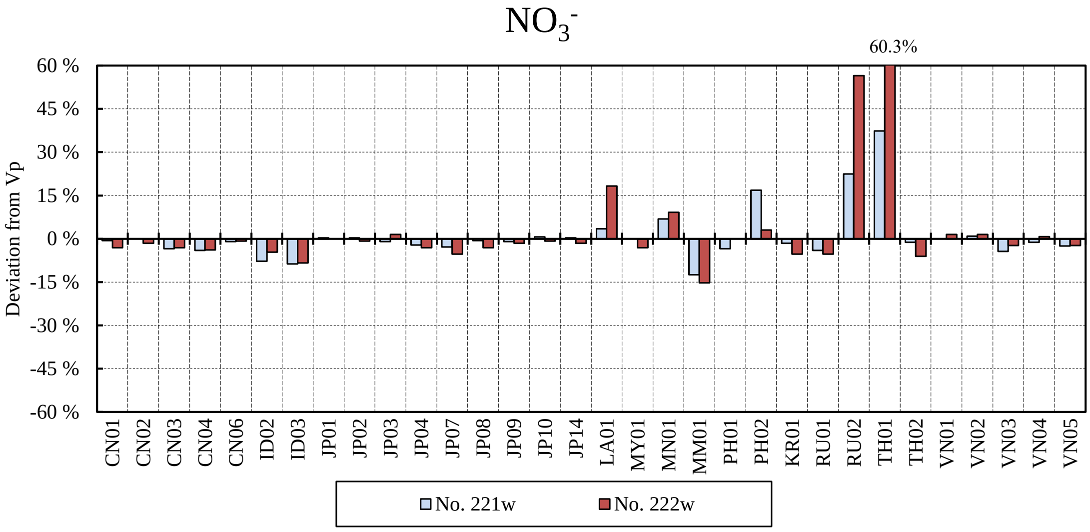


Figure 2.11 Deviation from prepared value for NO_3^- (normalized by prepared value)

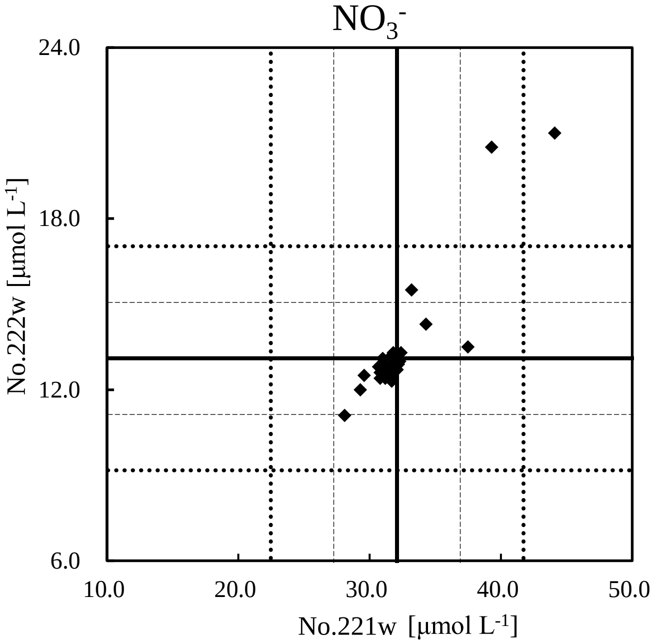


Figure 2.12 Scatter diagram for NO_3^-

5) Cl^-

The data of sample No.222w from LA01 was marked with flag “E”, and sample No. 222w from RU02 was marked with flag “X”.

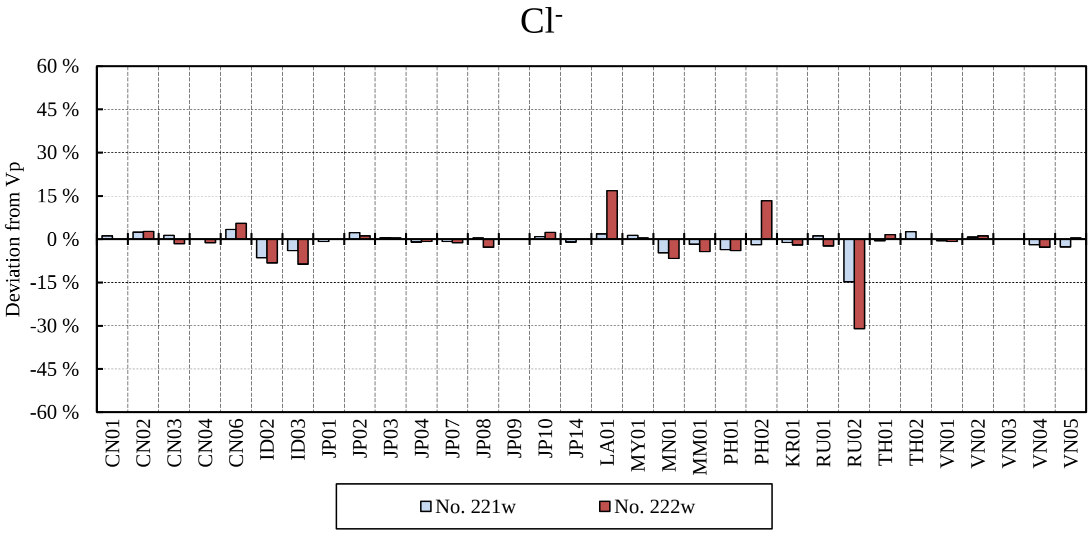


Figure 2.13 Deviation from prepared value for Cl^- (normalized by prepared value)

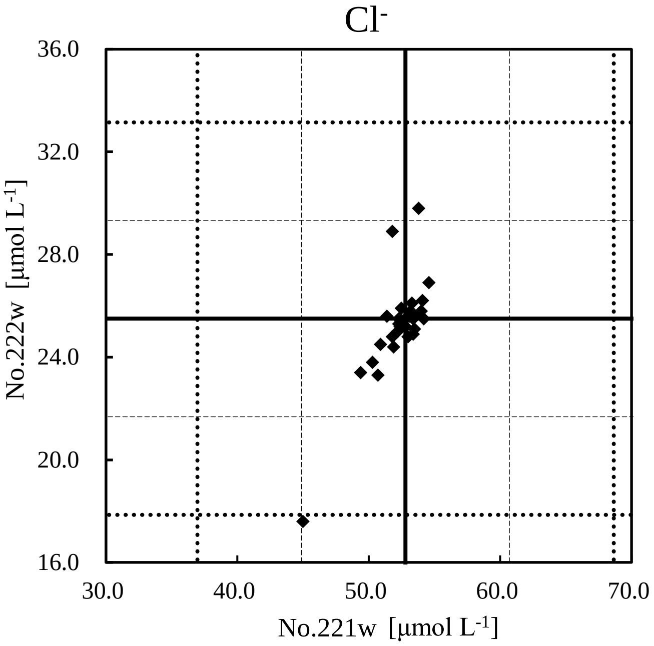


Figure 2.14 Scatter diagram for Cl^-

6) NH_4^+

The data of sample No.222w from 2 laboratories (KR01 and TH02) were marked with flag “E”. Additionally, the data of sample No.221w and No.222w from 3 laboratories (LA01, MN01 and RU02) were marked with flag “X”.

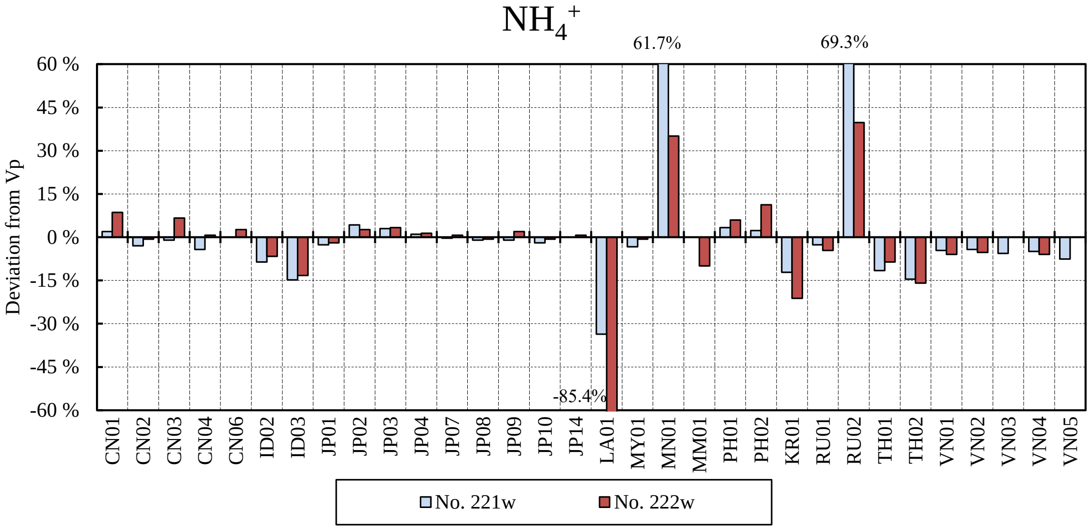


Figure 2.15 Deviation from prepared value for NH_4^+ (normalized by prepared value)

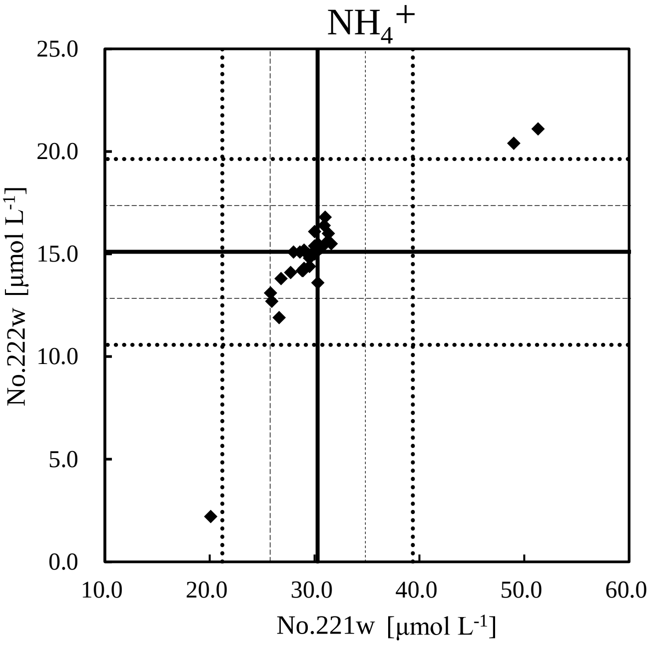


Figure 2.16 Scatter diagram for NH_4^+

7) Na^+

The data of sample No. 221w from LA01 and sample No.222w from MN01 were marked with flag “E”.

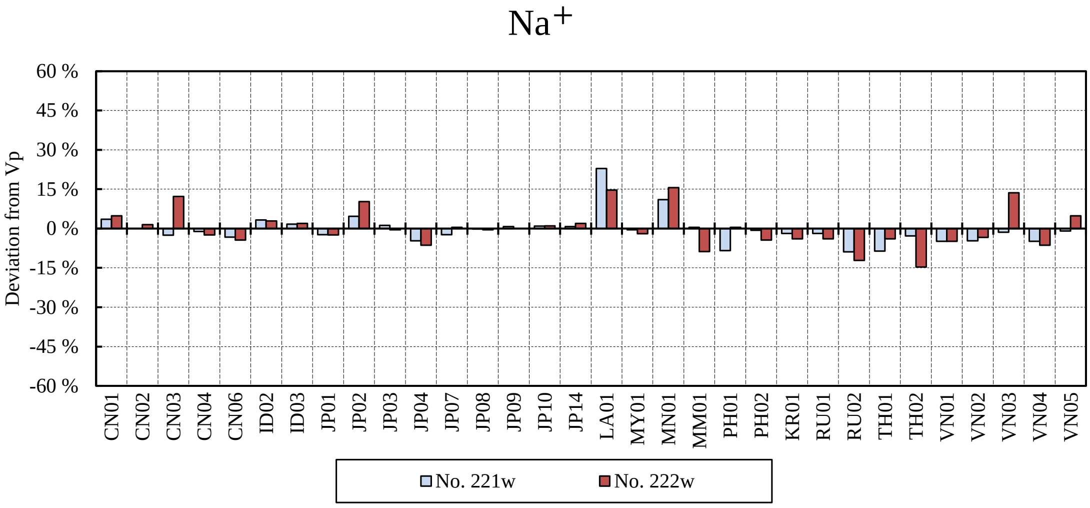


Figure 2.17 Deviation from prepared value for Na^+ (normalized by prepared value)

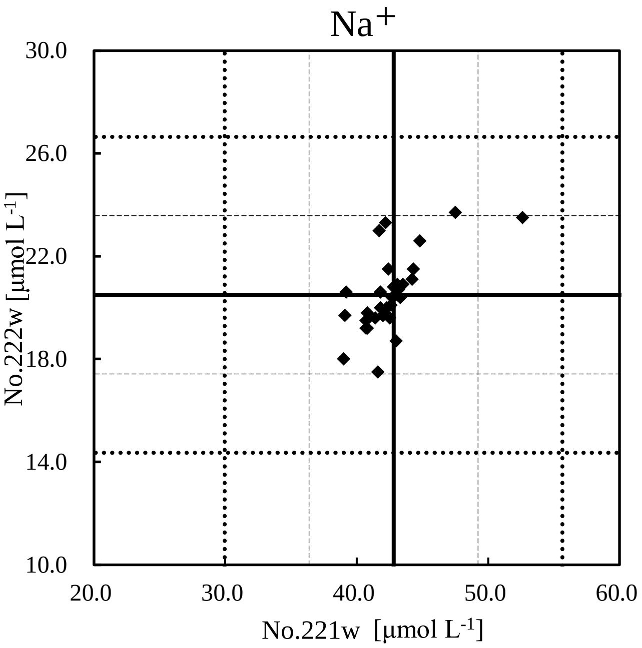


Figure 2.18 Scatter diagram for Na^+

8) K^+

The data of sample No. 221w from 2 laboratories (LA01 and TH02) and sample No.222w from 3 laboratories (LA01, MN01 and KR01) were marked with flag “E”. Additionally, the data of sample No.221w from PH02 and sample No. 222w from 8 laboratories (PH02, RU02, TH02, VN01, VN02, VN03, VN04 and VN05) were marked with flag “X”.

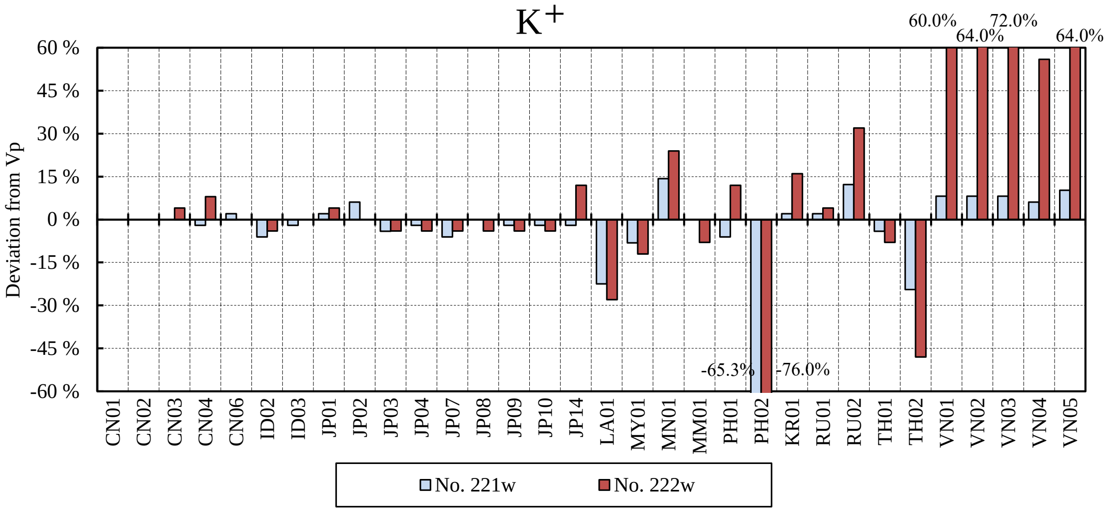


Figure 2.19 Deviation from prepared value for K^+ (normalized by prepared value)

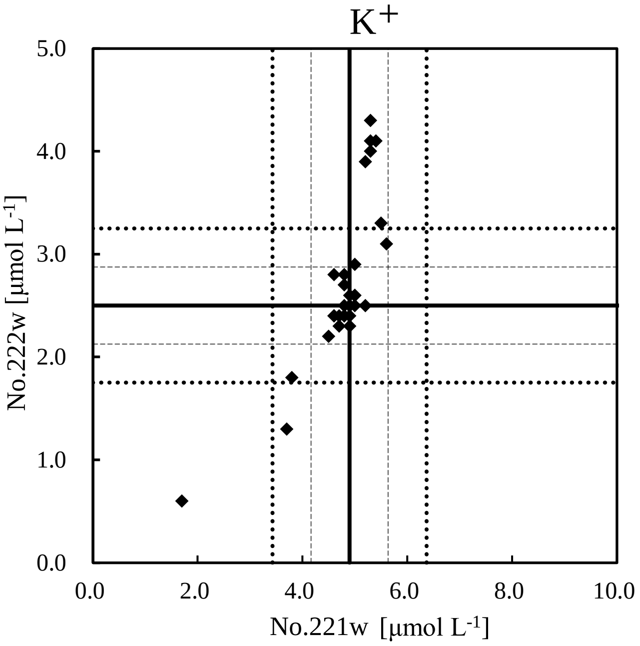


Figure 2.20 Scatter diagram for K^+

9) Ca^{2+}

The data of sample No. 221w from 3 laboratories (RU02, TH01 and VN05) and sample No. 222w from 5 laboratories (LA01, MN01, PH01, PH02 and TH02) were marked with flag "E". Additionally, the data of sample No.222w from 2 laboratories (TH01 and VN03) were marked with flag "X".

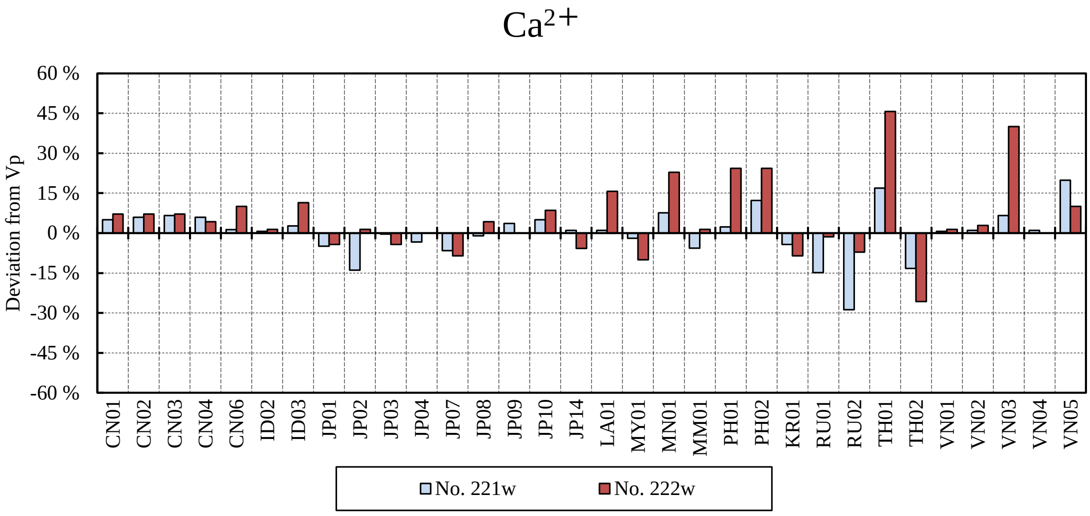


Figure 2.21 Deviation from prepared value for Ca^{2+} (normalized by prepared value)

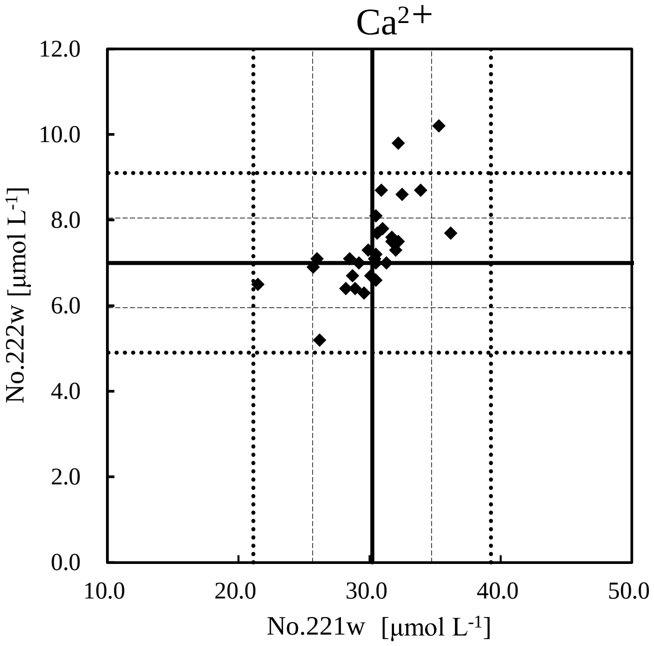


Figure 2.22 Scatter diagram for Ca^{2+}

10) Mg^{2+}

The data of sample No. 221w from 2 laboratories (RU02 and TH02) and sample No. 222w from 3 laboratories (MM01, PH02 and TH02) were marked with flag "E".

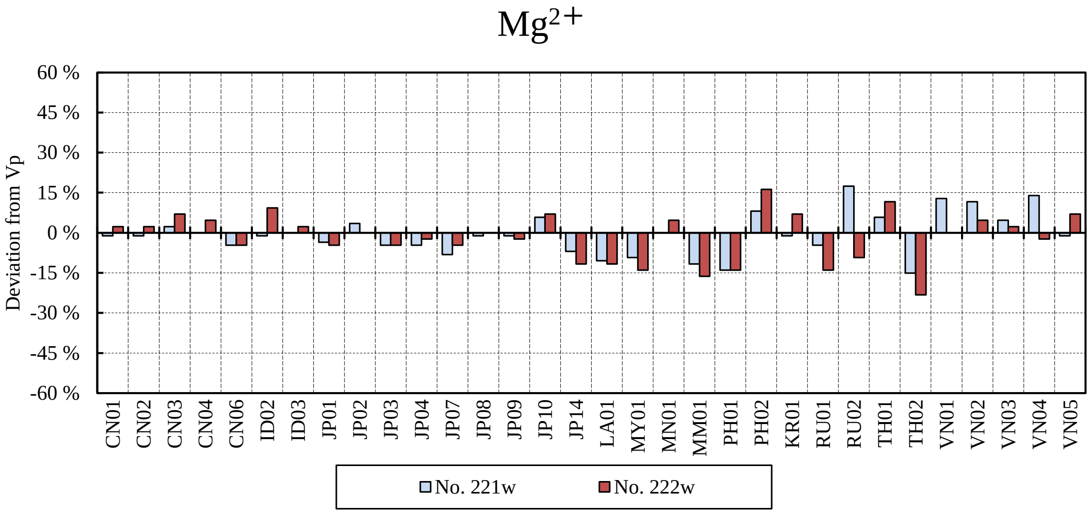


Figure 2.23 Deviation from prepared value for Mg^{2+} (normalized by prepared value)

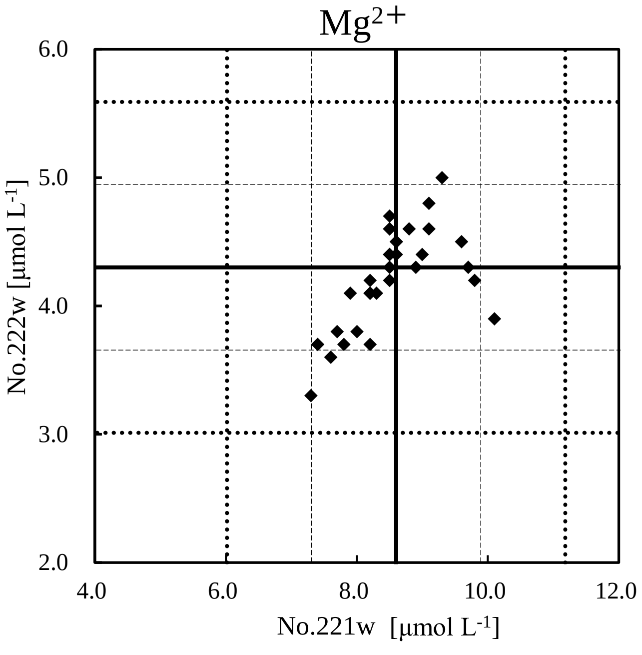


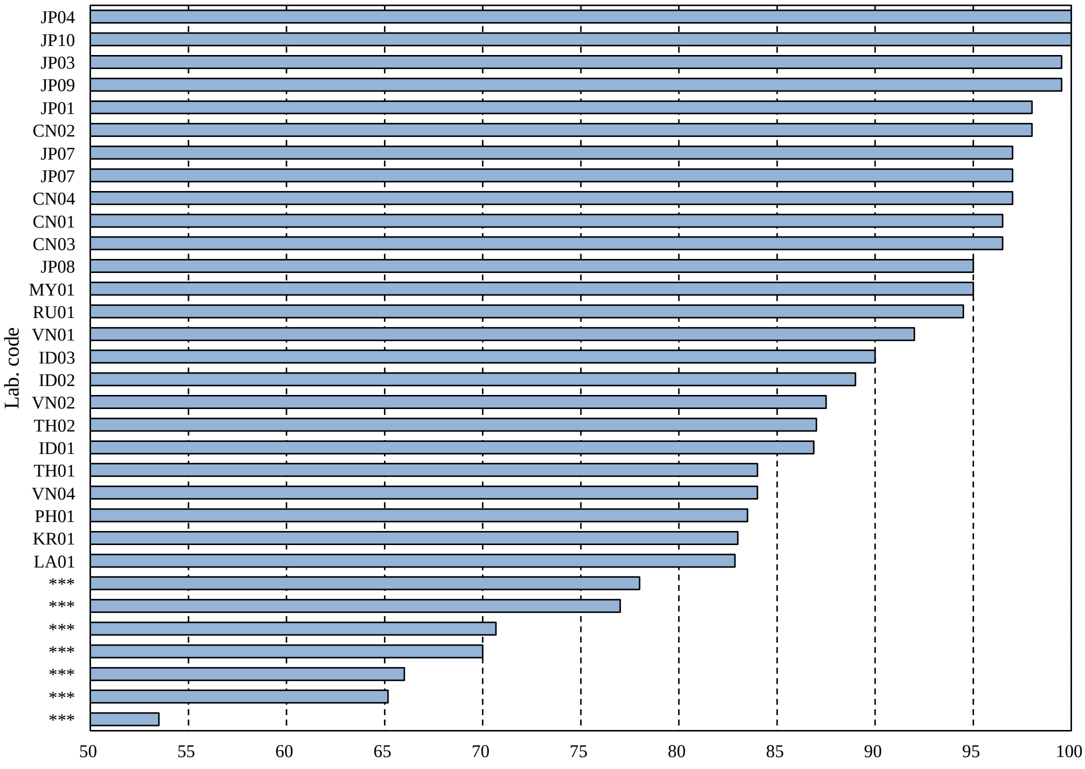
Figure 2.24 Scatter diagram for Mg^{2+}

11) Scatter diagrams

Most of constituents showed positive correlation between the submitted pairs of results of sample No. 221w and 222w. It suggested that systematic error could be the reason for the deviation of results in many of laboratories.

12) Percentage of the data within DQO

Figure 2.25 shows the percentage of the data within DQO for each participating laboratory from 2013 to 2022. All the analytical data of 2 laboratories (JP04 and JP10) met DQO, while the percentage of the data within DQO in 7 laboratories was below 80%.



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

Figure 2.25 Percentage of the data within DQO for each participating laboratory (2013-2022)

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. 221w were higher than those of No. 222w.

The relative standard deviations (R.S.D.) of each parameter for sample No. 221w and No. 222w are shown in the Figure 2.26. The R.S.D. values of sample No. 222w were higher than sample No.221w except for NO_3^-. K^+ had the largest R.S.D. value difference between sample No.221w and No. 222w. The R.S.D. of K^+ for sample No. 222w was the largest in this survey.

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

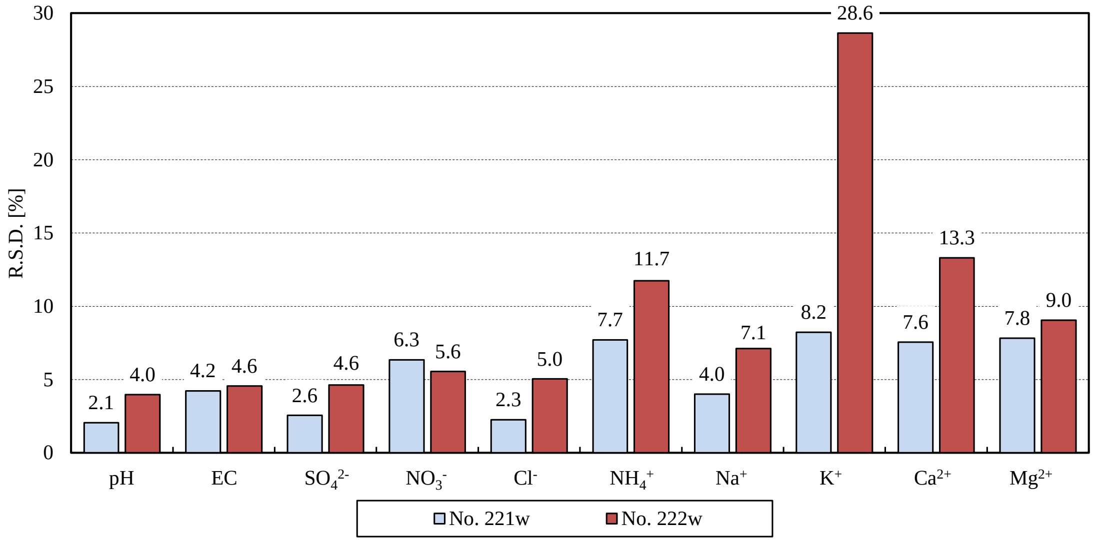


Figure 2.26 Relative standard deviations (R.S.D.) of each parameter

2.3.4 Information on laboratories

1) Number of analysts and their experience

Number of analysts and years of their experience are shown in Table 2.11 and Table 2.12, respectively. In Table 2.11, the letters of “A”, “B”, “C” and “D” refer to individual analysts in each laboratory who carried out analyses. In 17 laboratories, same analyst carried out the analyses for all parameters. No clear relationship between the number of analysts and flagged data was suggested.

Table 2.11 Number of analysts

Lab. ID	Total	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
CN01	1	A	A	A	A	A	A	A	A	A	A
CN02	2	A	A	B	B	B	B	B	B	B	B
CN03	2	A	A	B	B	B	B	B	B	B	B
CN04	1	A	A	A	A	A	A	A	A	A	A
CN06	3	A	B	C	C	C	C	C	C	C	C
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
JP02	1	A	A	A	A	A	A	A	A	A	A
JP03	1	A	A	A	A	A	A	A	A	A	A
JP04	2	A	A	B	B	B	B	B	B	B	B
JP07	1	A	A	A	A	A	A	A	A	A	A
JP08	1	A	A	A	A	A	A	A	A	A	A
JP09	1	A	A	A	A	A	A	A	A	A	A
JP10	1	A	A	A	A	A	A	A	A	A	A
JP14	1	A	A	A	A	A	A	A	A	A	A
LA01	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	4	A	A	B	B	B	A	C	D	D	D
PH02	1	A	A	A	A	A	A	A	A	A	A
KR01	1	A	A	A	A	A	A	A	A	A	A
RU01	3	A	A	B	B	B	A	C	C	C	C
RU02	3	A	A	B	B	B	B	C	C	C	C
TH01	1	A	A	A	A	A	A	A	A	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. 221w or No. 222w was marked with flag "E" or "X";
Dark mesh, Analytic data of both samples were marked with flag "E" or "X";
"---", Not measured

310 data out of all the submitted data (638), were analyzed by the analysts whose experience was less than 5 years, and they account for 48.6%. No clear relationship between the years of experience and flagged data was suggested.

Table 2.12 Years of experience

Lab. ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
CN01	7	7	7	7	7	7	7	7	7	7
CN02	4	4	4	4	4	4	4	4	4	4
CN03	10	10	1	1	1	1	1	1	1	1
CN04	14	14	14	14	14	14	14	14	14	14
CN06	5	2	5	5	5	5	5	5	5	5
ID02	8	2	15	15	15	15	15	15	15	15
ID03	18	18	18	18	18	18	18	18	18	18
JP01	19	19	19	19	19	19	19	19	19	19
JP02	1	1	1	1	1	1	1	1	1	1
JP03	1	1	1	1	1	1	1	1	1	1
JP04	3	3	3	3	3	3	3	3	3	3
JP07	1	1	1	1	1	1	1	1	1	1
JP08	1	1	1	1	1	1	1	1	1	1
JP09	3	3	3	3	3	3	3	3	3	3
JP10	3	3	3	3	3	3	3	3	3	3
JP14	1	1	1	1	1	1	1	1	1	1
LA01	3	3	3	3	3	3	3	3	3	3
MY01	10	10	10	10	10	1	1	1	1	1
MN01	15	15	19	19	19	19	19	19	19	19
MM01	1	1	1	1	1	1	1	1	1	1
PH01	1	3	3	3	3	1	1	1	1	1
PH02	5	5	5	5	5	5	5	5	5	5
KR01	17	17	17	17	17	17	17	17	17	17
RU01	24	24	9	9	9	24	23	23	23	23
RU02	2	2	2	2	2	2	1	1	1	1
TH01	1	1	1	1	1	1	1	1	1	1
TH02	24	24	24	24	24	24	24	24	24	24
VN01	6	6	9	9	9	9	9	9	9	9
VN02	13	13	9	9	9	9	9	9	9	9
VN03	8	8	11	8	---	8	11	11	11	11
VN04	18	18	18	18	18	18	18	18	18	18
VN05	10	10	15	15	15	15	15	15	15	15

Note: Light mesh, Analytic data of sample No. 221w or No. 222w was marked with flag "E" or "X";
Dark mesh, Analytic data of both samples were marked with flag "E" or "X";
"---", Not measured

2) Analytical instruments

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

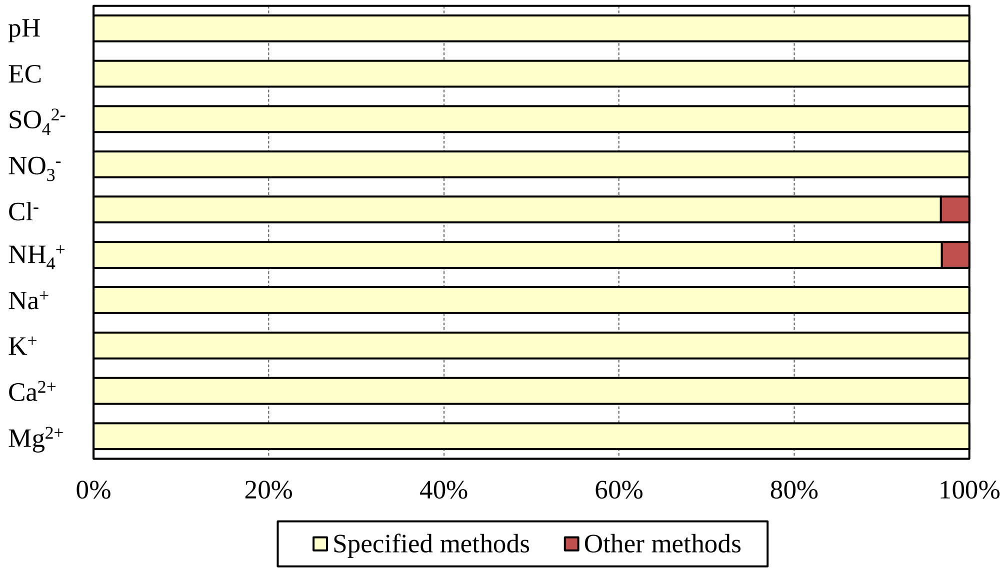


Figure 2.27 Percentage of laboratories that use the recommended methods

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

Lab. ID	SO_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
CN06	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
JP02	IC	IC	IC	IC	IC	IC	IC	IC
JP03	IC	IC	IC	IC	IC	IC	IC	IC
JP04	IC	IC	IC	IC	IC	IC	IC	IC
JP07	IC	IC	IC	IC	IC	IC	IC	IC
JP08	IC	IC	IC	IC	IC	IC	IC	IC
JP09	IC	IC	IC	IC	IC	IC	IC	IC
JP10	IC	IC	IC	IC	IC	IC	IC	IC
JP14	IC	IC	IC	IC	IC	IC	IC	IC
LA01	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	AAS	AAS	AES	AAS
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*	AAS	AES	AAS	AAS
TH01	IC	IC	IC	IC	IC	IC	IC	IC
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
AAS: Atomic Absorption Spectrometry
AES: Atomic Emission Spectrometry
SP: Spectrophotometry(Indophenol)
SP*: Spectrophotometry(Others)
TI: Titrimetry

3) Date of analysis

Figure 2.28 shows the distribution of "Start date" and "Finish date" of analysis at the participating laboratories. In total, 59% of all the submitted data was determined by the end of 2022, and 19% was determined later than the submission deadline of this project.

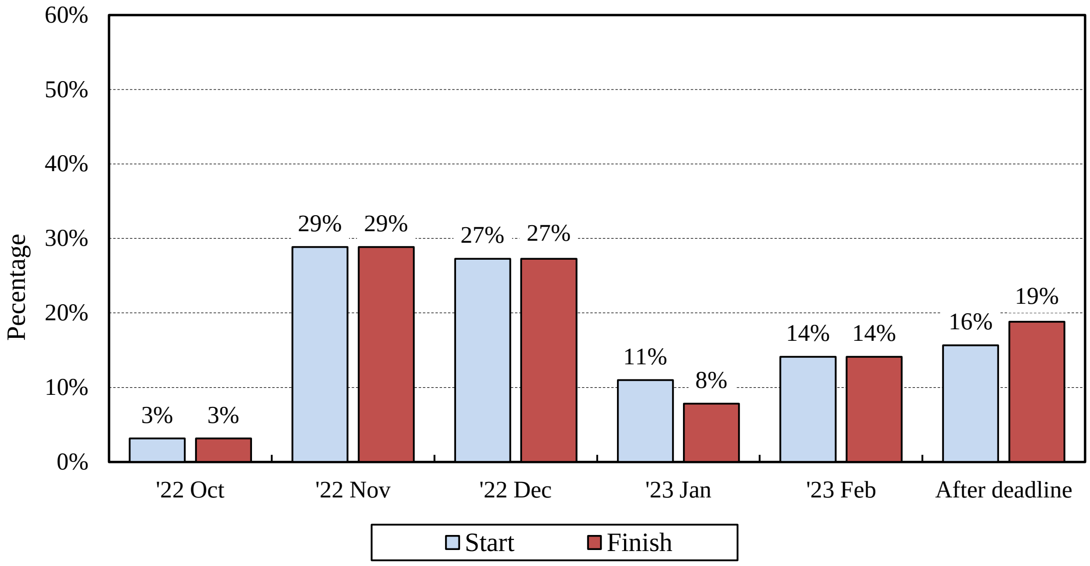


Figure 2.28 Distribution of start date and finish date of analysis

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

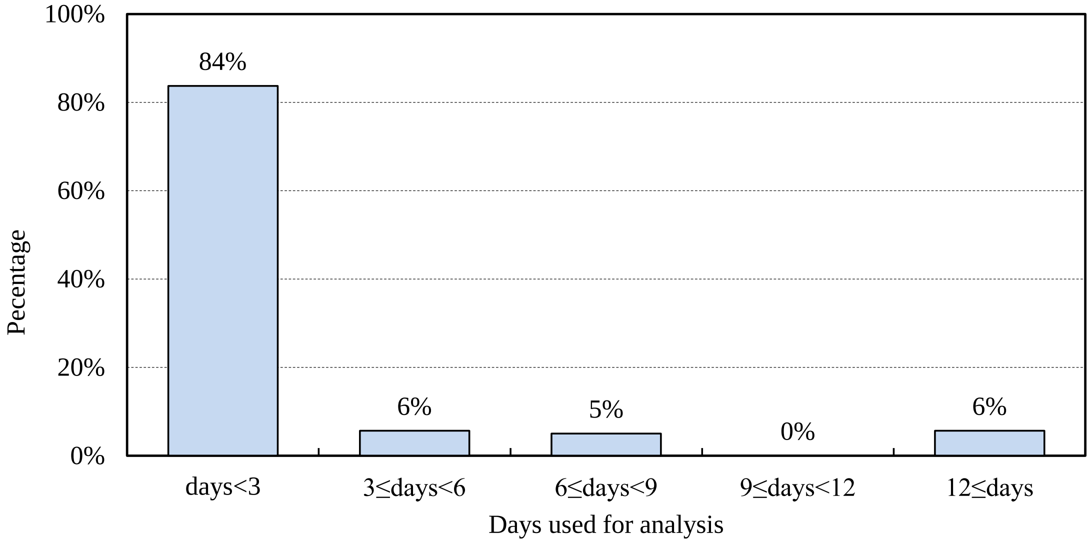


Figure 2.29 Distribution of days used for analysis

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

2.4 Comparison with past surveys

Since the beginning of EANET, the inter-laboratory comparison on wet deposition has reached the 25th survey. The percentages of data within DQO and prepared value of EC are shown in Figure 2.30. Hereafter, sample No. 221w and No. 222w are treated as high and low concentration samples, respectively.

The percentage of data within DQO for the sample No. 221w and No. 222w were 95.0% and 88.1%, respectively. As shown in this figure, low concentration samples show a tendency that the percentages of data within DQO are dependent on the prepared values of EC.

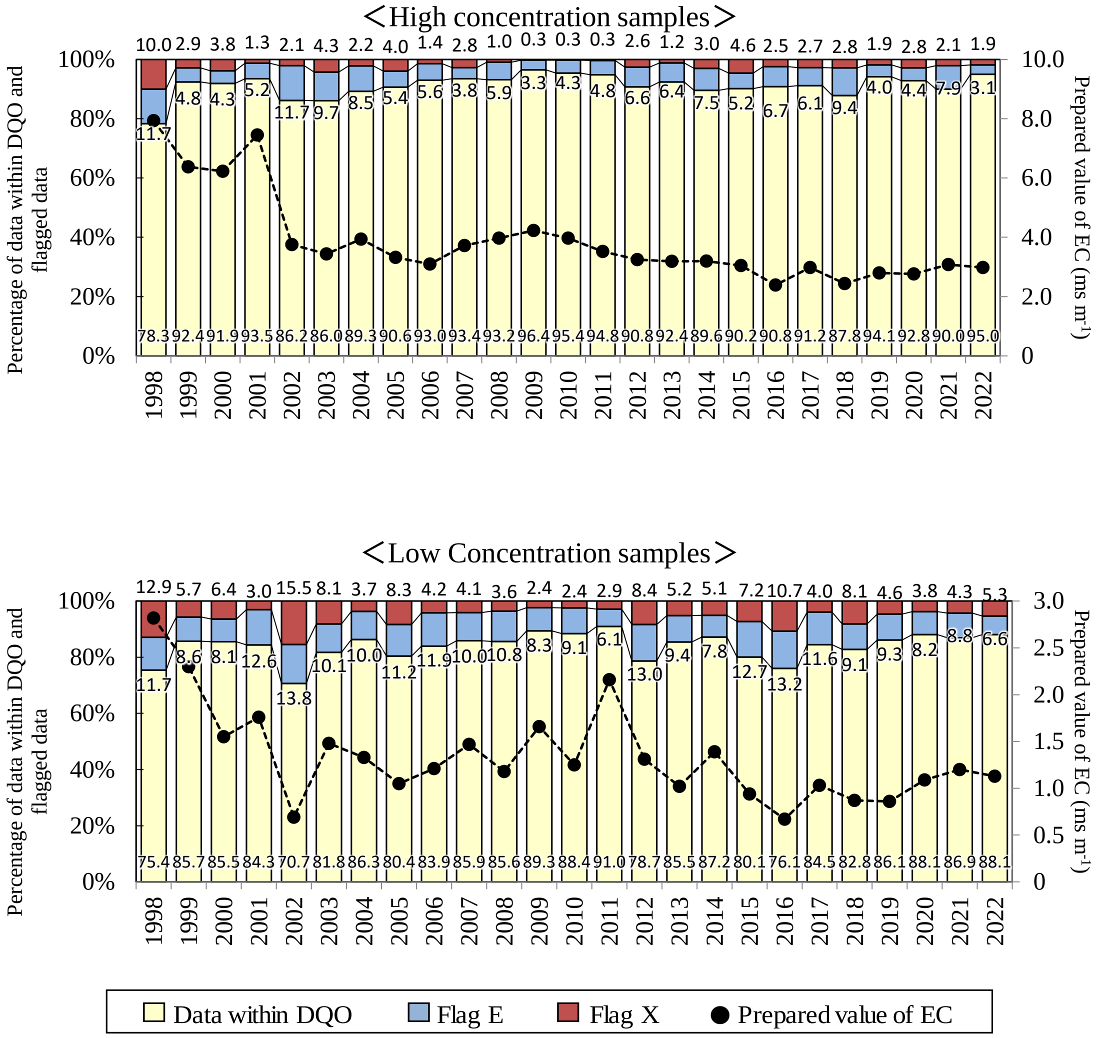


Figure 2.30 Comparison of results from the inter-laboratory comparison projects

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

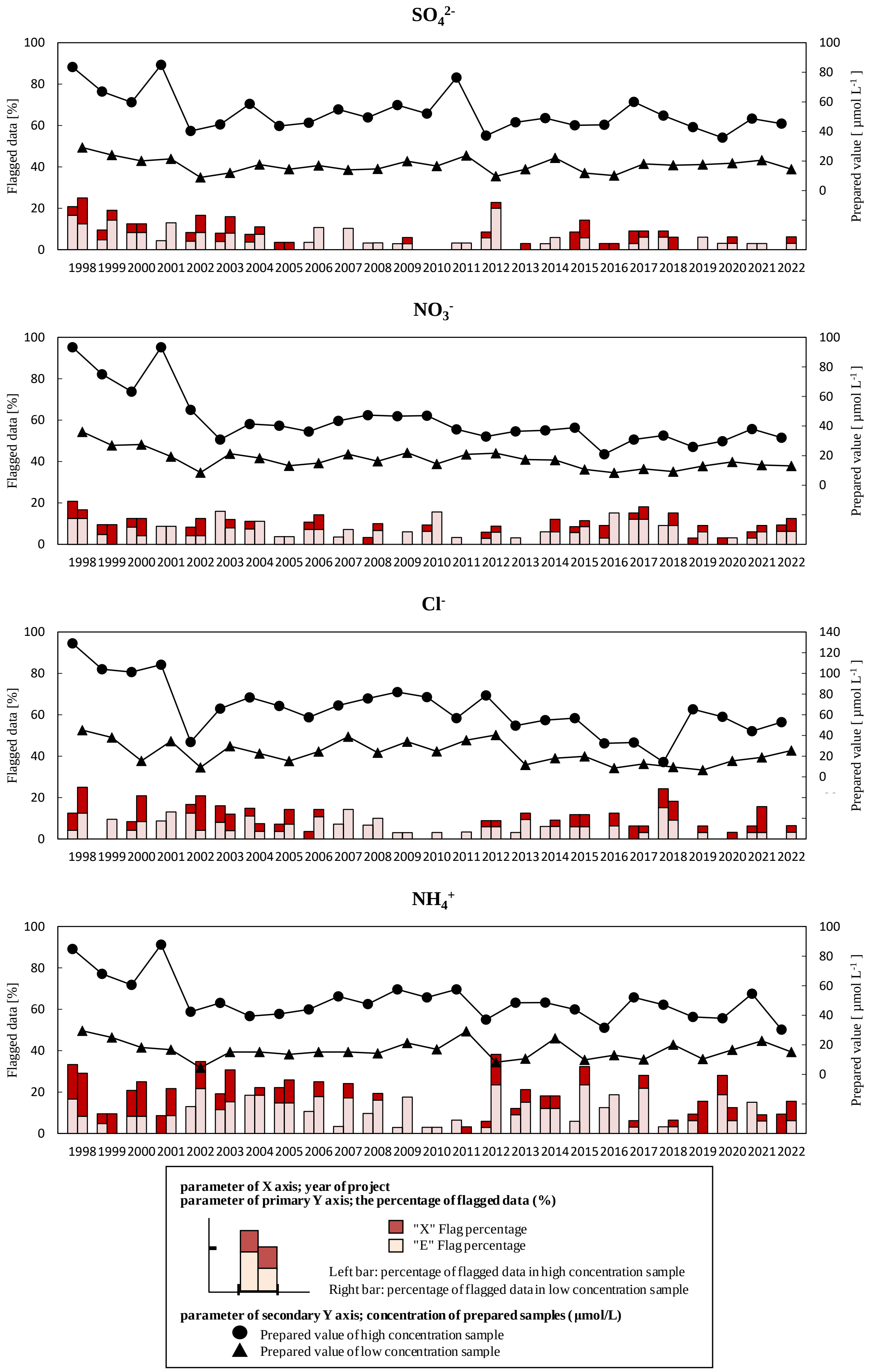


Figure 2.31 Comparison for each parameter in inter-laboratory comparison (ILC) project

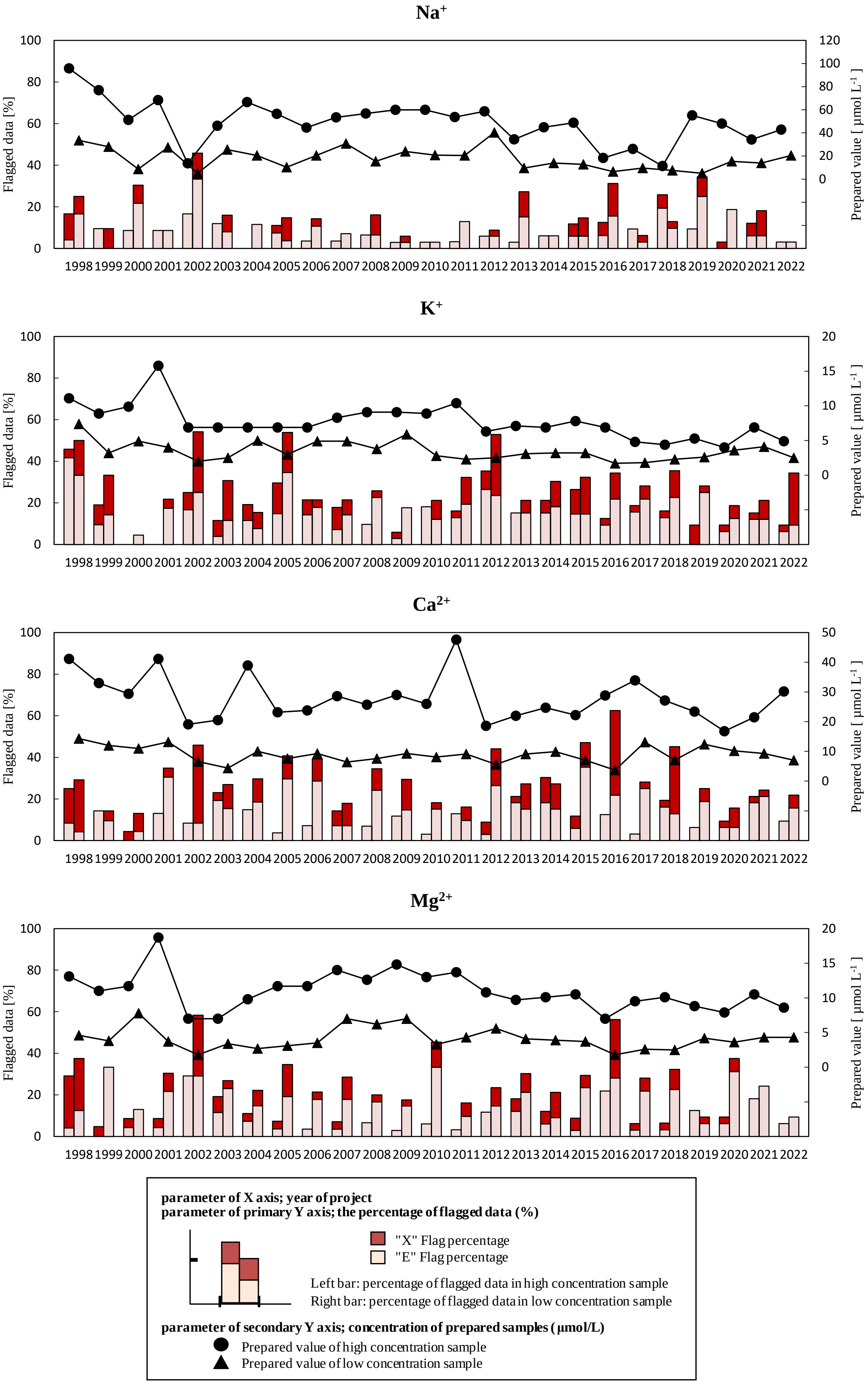


Figure 2.31 Comparison for each parameter in ILC project (continued)

As shown in figure 2.32, the total number of data in this survey was 638.

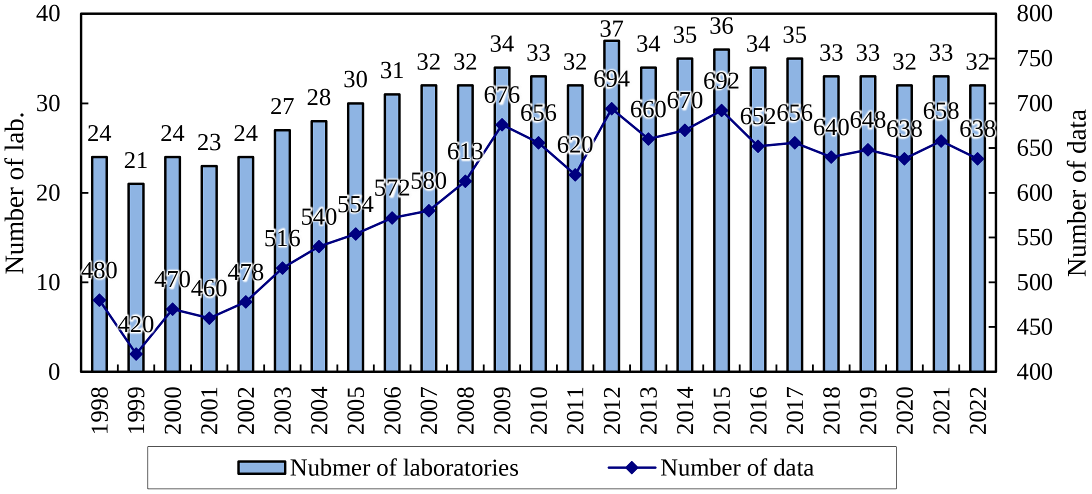


Figure 2.32 The number of participating laboratories and data in the inter-laboratory comparison projects on wet deposition

2.5 Recommendations for improvement

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

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

2.5.1 Measurement and Analysis

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

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

2.5.2 Data control

► After determining all the analytical parameters, the data check by calculating R_1 and R_2 values is important. Especially, R_1 and R_2 must meet allowable ranges according to *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. If the values exceed their allowable ranges, the data set is doubtful, and reanalysis shall be carried out after rechecking analytical instruments and analytical procedures.

► Participating laboratories are encouraged to check precision of results in prior to submission. It should be noted that precision is greatly affected by concentration. To grasp the state of precision, drawing correlation curve between concentration and precision is effective.

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

References

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

Appendix 2.1 Data precision of submitted data

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

R.S.D. = σ / Va × 100%
σ: standard deviation of result   Va: average of result

In Appendix Table 2.1.1 and Appendix Table 2.1.2, data precisions calculated from the submitted results are shown. There is a tendency that each constituent of higher concentration sample (No. 221w) shows better R.S.D. than that of lower concentration sample (No. 222w) . This suggests that R.S.D. are greatly affected by sample concentrations.

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

Appendix Table 2.1.1 Data precision (R.S.D.) of sample No. 221w

Lab. ID	pH as H^+ %	EC %	SO_4^{2-} %	NO_3^- %	Cl^- %	NH_4^+ %	Na^+ %	K^+ %	Ca^{2+} %	Mg^{2+} %
CN01	1.3	0.0	0.2	0.5	0.2	0.5	0.2	0.0	0.3	0.4
CN02	2.0	0.3	0.2	0.1	0.1	0.2	0.1	1.0	0.2	0.7
CN03	1.3	0.2	0.8	0.4	0.4	0.3	0.5	1.1	0.4	0.9
CN04	1.5	0.5	0.4	0.3	0.3	0.9	0.5	2.6	0.4	0.5
CN06	1.1	0.6	0.3	0.7	0.4	1.0	1.4	2.1	0.7	1.6
ID02	0.0	0.2	0.3	0.2	0.0	0.5	0.5	1.1	2.3	1.9
ID03	5.7	0.6	1.6	7.8	1.2	1.7	0.6	1.9	0.6	0.7
JP01	1.6	0.2	0.3	0.4	0.7	0.4	0.3	1.3	0.5	0.7
JP02	1.4	0.2	0.1	0.2	0.2	0.4	0.8	1.0	1.0	0.4
JP03	1.5	0.2	0.1	0.4	0.3	0.6	0.6	0.0	0.2	0.5
JP04	1.3	0.2	0.1	0.1	0.1	0.3	0.1	1.0	0.3	0.7
JP07	3.2	0.3	0.5	0.6	0.5	0.5	0.5	0.7	0.6	0.6
JP08	1.5	0.3	0.5	0.2	0.1	0.0	0.1	1.5	0.5	1.8
JP09	3.6	0.4	0.1	0.1	0.1	0.2	0.1	0.0	0.0	0.0
JP10	1.0	0.2	0.1	0.2	0.1	0.3	0.3	0.7	0.7	0.7
JP14	4.4	0.5	0.1	0.1	0.1	0.5	1.0	6.3	1.9	0.5
LA01	6.2	0.2	0.2	0.2	0.1	4.3	0.5	0.0	1.4	0.6
MY01	4.4	0.8	0.5	0.5	0.4	0.4	0.5	1.7	0.6	0.9
MN01	15.3	2.1	1.7	1.2	1.4	2.5	5.3	3.7	2.1	1.9
MM01	70.3	15.8	2.1	2.5	2.3	3.1	1.0	3.6	1.8	5.0
PH01	26.8	1.1	0.3	0.5	0.2	4.2	2.5	5.3	5.2	2.2
PH02	12.6	2.7	2.5	1.4	1.5	12.7	0.8	14.1	7.8	5.8
KR01	5.4	0.3	0.4	0.7	0.6	0.7	0.9	1.3	0.8	0.5
RU01	2.3	0.4	1.2	1.2	1.6	0.8	0.6	1.2	0.3	0.5
RU02	5.9	1.1	1.5	0.1	2.0	1.3	0.1	0.9	1.4	0.3
TH01	2.6	1.3	0.1	0.3	0.3	0.2	0.3	0.0	0.4	0.0
TH02	21.1	2.3	0.4	0.3	2.9	2.1	10.8	6.0	0.5	1.4
VN01	1.8	0.6	0.8	1.1	0.3	0.7	0.7	4.5	0.7	2.5
VN02	6.1	0.7	0.7	0.7	0.4	0.6	0.5	2.3	0.6	1.2
VN03	1.0	0.3	0.2	0.2	--	0.4	0.1	0.6	0.3	0.7
VN04	11.8	0.4	0.8	1.1	0.4	0.9	1.1	2.2	1.3	1.2
VN05	1.6	0.2	0.6	1.2	0.6	0.5	1.4	2.2	0.5	1.8
Number of data	32	32	32	32	31	32	32	32	32	32
Minimum	0.0	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0
25% value	1.4	0.2	0.2	0.2	0.2	0.4	0.3	0.9	0.4	0.5
Median	2.4	0.4	0.4	0.4	0.4	0.6	0.5	1.3	0.6	0.7
75% value	6.0	0.7	0.8	0.8	0.7	1.1	0.9	2.4	1.3	1.7
Maximum	70.3	15.8	2.5	7.8	2.9	12.7	10.8	14.1	7.8	5.8

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 2.1.2 Data precision (R.S.D.) of sample No. 222w

Lab. ID	pH as H^+ %	EC %	SO_4^{2-} %	NO_3^- %	Cl^- %	NH_4^+ %	Na^+ %	K^+ %	Ca^{2+} %	Mg^{2+} %
CN01	0.7	0.0	0.4	0.4	0.5	1.1	0.9	2.0	1.3	1.5
CN02	1.6	0.8	0.7	0.3	0.2	0.3	0.3	1.8	0.8	1.1
CN03	1.8	0.6	1.5	0.7	0.7	0.6	0.5	2.5	1.0	1.9
CN04	5.7	1.0	0.9	0.7	0.6	1.6	1.2	16.0	1.2	0.0
CN06	1.9	0.7	0.7	1.5	1.9	0.0	1.3	6.4	2.1	3.3
ID02	5.0	7.8	0.3	0.4	0.2	1.3	1.4	2.1	9.2	4.0
ID03	12.3	1.2	4.9	4.6	6.3	3.3	0.9	5.6	1.7	1.5
JP01	2.9	0.6	0.2	0.3	0.8	0.0	0.2	1.7	0.8	1.2
JP02	1.8	0.5	0.8	1.1	1.0	2.7	0.2	2.1	5.6	4.9
JP03	2.9	0.9	0.6	0.8	0.5	0.5	1.0	0.0	0.7	0.0
JP04	3.6	0.9	0.0	0.0	0.0	0.3	0.3	1.9	1.0	1.7
JP07	1.5	0.0	0.4	0.3	0.2	0.2	0.2	0.0	0.0	1.1
JP08	7.4	0.5	0.5	0.3	0.2	0.6	0.3	4.0	5.4	2.8
JP09	4.3	0.5	0.4	0.3	0.0	0.2	0.2	0.0	0.7	0.0
JP10	1.8	0.0	0.3	0.0	0.0	0.5	0.2	0.0	0.7	1.1
JP14	9.5	1.0	0.0	0.0	0.2	0.6	0.9	7.9	0.5	1.2
LA01	5.1	0.4	0.9	1.0	0.2	50.8	0.4	2.7	3.4	1.3
MY01	3.7	0.4	4.8	0.5	0.4	0.2	0.7	3.4	2.8	6.8
MN01	25.1	1.6	1.7	4.2	1.5	6.5	1.9	5.1	3.9	2.6
MM01	48.9	25.6	5.6	3.9	4.0	34.0	33.6	28.9	30.9	33.5
PH01	22.5	1.7	1.4	1.5	0.6	16.0	11.4	16.4	7.4	5.6
PH02	49.0	2.4	7.9	1.5	16.8	2.9	5.4	112.0	19.4	6.2
KR01	3.8	0.6	0.9	1.1	1.4	0.8	0.8	4.0	1.1	0.0
RU01	3.9	1.0	2.0	2.0	2.1	0.6	1.0	2.0	0.6	1.4
RU02	4.7	2.1	1.9	0.3	5.1	3.2	0.3	0.0	5.2	0.9
TH01	0.0	0.5	0.6	0.6	0.7	0.6	0.3	0.0	0.5	0.0
TH02	5.7	0.9	0.8	0.7	0.8	2.5	2.2	11.5	1.4	1.5
VN01	5.0	1.6	1.5	1.8	0.6	1.0	1.6	5.1	4.0	3.8
VN02	4.9	1.6	1.3	1.4	0.9	1.6	1.0	3.7	1.9	4.2
VN03	1.2	1.0	0.4	0.7	--	0.5	0.7	2.3	0.9	1.1
VN04	4.7	0.9	1.3	1.3	0.8	1.2	1.1	1.8	2.0	2.1
VN05	1.1	0.5	1.2	1.4	5.5	4.0	1.9	2.9	1.9	4.6
Number of data	32	32	32	32	31	32	32	32	32	32
Minimum	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
25% value	1.8	0.5	0.4	0.3	0.2	0.5	0.3	1.8	0.8	1.1
Median	4.1	0.9	0.8	0.7	0.7	0.9	0.9	2.6	1.5	1.5
75% value	5.7	1.3	1.5	1.4	1.5	2.7	1.4	5.3	4.0	3.9
Maximum	49.0	25.6	7.9	4.6	16.8	50.8	33.6	112.0	30.9	33.5

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 2.2.1 Deviation% from prepared values of sample No. 221w

Lab. ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
	%	%	%	%	%	%	%	%	%	%
CN01	0.4	1.0	1.3	-0.6	1.1	2.0	3.5	0.0	5.0	-1.2
CN02	0.9	0.7	1.3	0.0	2.5	-3.0	0.0	0.0	6.0	-1.2
CN03	1.7	0.3	0.4	-3.4	1.3	-1.0	-2.6	0.0	6.6	2.3
CN04	0.9	0.7	0.0	-4.0	0.0	-4.3	-1.2	-2.0	6.0	0.0
CN06	1.7	-3.0	0.9	-0.9	3.4	0.0	-3.3	2.0	1.3	-4.7
ID02	-0.4	-4.4	-2.2	-7.8	-6.4	-8.6	3.3	-6.1	0.7	-1.2
ID03	3.6	-13.4	2.2	-8.7	-4.0	-14.9	1.6	-2.0	2.6	0.0
JP01	0.0	-0.7	-0.2	0.3	-0.8	-2.6	-2.3	2.0	-5.0	-3.5
JP02	1.3	-4.4	0.7	0.3	2.3	4.3	4.7	6.1	-13.9	3.5
JP03	0.9	-1.3	0.2	-0.9	0.6	3.0	1.2	-4.1	-0.3	-4.7
JP04	0.9	-1.0	-0.4	-2.2	-0.9	1.0	-4.7	-2.0	-3.3	-4.7
JP07	1.3	-1.7	-0.7	-2.8	-0.8	-0.3	-2.3	-6.1	-6.6	-8.1
JP08	0.9	-3.7	-0.4	-0.6	0.4	-1.0	-0.2	0.0	-1.0	-1.2
JP09	2.3	-3.4	-0.4	-0.9	0.0	-1.0	0.7	-2.0	3.6	-1.2
JP10	0.6	-0.7	0.9	0.6	0.9	-2.0	0.9	-2.0	5.0	5.8
JP14	2.6	-2.3	1.8	0.3	-0.9	0.0	0.7	-2.0	1.0	-7.0
LA01	0.6	-5.7	0.4	3.4	1.9	-33.7	22.9	-22.4	1.0	-10.5
MY01	1.9	-2.7	1.8	0.0	1.3	-3.3	-0.5	-8.2	-2.0	-9.3
MN01	-3.0	-6.7	-0.7	6.9	-4.7	61.7	11.0	14.3	7.6	0.0
MM01	2.1	-40.6	-6.0	-12.5	-1.7	0.0	0.5	0.0	-5.6	-11.6
PH01	1.1	-1.0	0.2	-3.4	-3.6	3.3	-8.4	-6.1	2.3	-14.0
PH02	1.9	-8.1	-5.7	16.8	-1.9	2.3	-0.7	-65.3	12.3	8.1
KR01	0.6	-9.1	-6.8	-1.6	-1.1	-12.2	-1.9	2.0	-4.3	-1.2
RU01	-1.3	-2.0	-4.4	-4.0	1.1	-2.6	-1.9	2.0	-14.9	-4.7
RU02	-11.1	0.7	11.9	22.4	-14.8	69.3	-8.9	12.2	-28.8	17.4
TH01	3.4	-7.4	-1.3	37.4	-0.6	-11.6	-8.6	-4.1	16.9	5.8
TH02	3.2	-3.7	1.1	-1.2	2.7	-14.5	-2.8	-24.5	-13.2	-15.1
VN01	5.7	-10.7	-4.2	0.0	-0.6	-4.6	-4.9	8.2	0.7	12.8
VN02	5.3	-12.8	-3.3	0.9	0.8	-4.3	-4.7	8.2	1.0	11.6
VN03	2.6	-8.7	-2.0	-4.4	---	-5.6	-1.4	8.2	6.6	4.7
VN04	6.4	-9.4	-6.2	-1.2	-1.9	-5.0	-4.9	6.1	1.0	14.0
VN05	6.8	-7.7	-0.9	-2.5	-2.7	-7.6	-0.9	10.2	19.9	-1.2
Number of data	32	32	32	32	31	32	32	32	32	32
Average	1.4	-5.4	-0.6	0.8	-0.9	0.1	-0.5	-2.4	0.2	-0.6
Minimum	-11.1	-40.6	-6.8	-12.5	-14.8	-33.7	-8.9	-65.3	-28.8	-15.1
Maximum	6.8	1.0	11.9	37.4	3.4	69.3	22.9	14.3	19.9	17.4

Note: "---", Not measured

Appendix Table 2.2.2 Deviation% from prepared values of sample No. 222w

Lab. ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
	%	%	%	%	%	%	%	%	%	%
CN01	0.0	0.0	0.0	-3.1	0.0	8.6	4.9	0.0	7.1	2.3
CN02	0.0	1.8	2.1	-1.5	2.7	-0.7	1.5	0.0	7.1	2.3
CN03	1.2	3.5	0.7	-3.1	-1.6	6.6	12.2	4.0	7.1	7.0
CN04	1.0	3.5	1.4	-3.8	-1.2	0.7	-2.4	8.0	4.3	4.7
CN06	-1.0	-5.3	0.7	-0.8	5.5	2.6	-4.4	0.0	10.0	-4.7
ID02	2.5	-5.3	1.4	-4.6	-8.2	-6.6	2.9	-4.0	1.4	9.3
ID03	1.7	-7.1	-15.2	-8.4	-8.6	-13.2	2.0	0.0	11.4	2.3
JP01	-0.4	3.5	0.7	0.0	0.0	-2.0	-2.4	4.0	-4.3	-4.7
JP02	0.8	-1.8	1.4	-0.8	1.2	2.6	10.2	0.0	1.4	0.0
JP03	0.0	2.7	1.4	1.5	0.4	3.3	-0.5	-4.0	-4.3	-4.7
JP04	0.4	2.7	-0.7	-3.1	-0.8	1.3	-6.3	-4.0	0.0	-2.3
JP07	0.4	3.5	-2.1	-5.3	-1.2	0.7	0.5	-4.0	-8.6	-4.7
JP08	0.0	-2.7	-0.7	-3.1	-2.7	-0.7	-0.5	-4.0	4.3	0.0
JP09	3.1	-2.7	-0.7	-1.5	0.0	2.0	0.0	-4.0	0.0	-2.3
JP10	-0.4	3.5	2.1	-0.8	2.4	-0.7	1.0	-4.0	8.6	7.0
JP14	4.1	-1.8	1.4	-1.5	0.0	0.7	2.0	12.0	-5.7	-11.6
LA01	-5.0	13.3	3.4	18.3	16.9	-85.4	14.6	-28.0	15.7	-11.6
MY01	1.7	0.9	6.9	-3.1	0.4	-0.7	-2.0	-12.0	-10.0	-14.0
MN01	-3.5	-0.9	-2.8	9.2	-6.7	35.1	15.6	24.0	22.9	4.7
MM01	-12.0	26.5	-9.0	-15.3	-4.3	-9.9	-8.8	-8.0	1.4	-16.3
PH01	-3.1	0.0	-0.7	0.0	-3.9	6.0	0.5	12.0	24.3	-14.0
PH02	4.5	-2.7	-2.8	3.1	13.3	11.3	-4.4	-76.0	24.3	16.3
KR01	0.8	-5.3	-14.5	-5.3	-2.0	-21.2	-3.9	16.0	-8.6	7.0
RU01	-1.9	3.5	-4.1	-5.3	-2.4	-4.6	-3.9	4.0	-1.4	-14.0
RU02	-10.9	27.4	55.2	56.5	-31.0	39.7	-12.2	32.0	-7.1	-9.3
TH01	23.7	-1.8	-0.7	60.3	1.6	-8.6	-3.9	-8.0	45.7	11.6
TH02	1.4	-0.9	-2.8	-6.1	0.0	-15.9	-14.6	-48.0	-25.7	-23.3
VN01	5.6	-6.2	0.0	1.5	-0.8	-6.0	-4.9	60.0	1.4	0.0
VN02	4.9	-7.1	0.7	1.5	1.2	-5.3	-3.4	64.0	2.9	4.7
VN03	1.6	-8.0	2.1	-2.3	---	0.0	13.7	72.0	40.0	2.3
VN04	6.8	-5.3	-1.4	0.8	-2.7	-6.0	-6.3	56.0	0.0	-2.3
VN05	3.5	-4.4	4.8	-2.3	0.4	0.0	4.9	64.0	10.0	7.0
Number of data	32	32	32	32	31	32	32	32	32	32
Average	1.0	0.9	0.9	2.2	-1.0	-2.1	0.0	7.0	5.5	-1.6
Minimum	-12.0	-8.0	-15.2	-15.3	-31.0	-85.4	-14.6	-76.0	-25.7	-23.3
Maximum	23.7	27.4	55.2	60.3	16.9	39.7	15.6	72.0	45.7	16.3

Note: "---", Not measured

3. 18th INTER-LABORATORY COMPARISON PROJECT ON DRY DEPOSITION

3.1 Introduction

In the Inter-laboratory Comparison on dry deposition, impregnated filters which contained either $SO_4^{2-}$and Cl^-, or NH_4^+, were prepared and distributed to the participating laboratories by the Network Center (NC) in October 2021. Most of the laboratories which monitor with the filter pack method in EANET joined this activity and submitted their analytical results to the NC. These results were compared with the corresponding prepared value and statistically analyzed.

3.2 Procedures

3.2.1 Participating Laboratories

A total of 21 laboratories in charge of EANET dry deposition monitoring participated in this 18th activity and 19 laboratories submitted the results to the NC. The participating laboratories and data submission status are shown in Table 1.1.

3.2.2 Description of Samples

Two kinds of filter samples, one contained two ions (SO_4^{2-} and Cl^-), the other contained one ion (NH_4^+), were prepared and distributed to the laboratories. Blank filters, which were impregnated with K_2CO_3 or H_3PO_4 but did not contain any SO_4^{2-}, Cl^-, or NH_4^+, were also prepared and distributed. The details of the filter samples are described in Table 3.1. The analytical precision and accuracy on the individual analyte were summarized through statistical calculations of the submitted analytical results from each participating laboratory.

Table 3.1 Outline of filter samples

Name	Details	Container	Number of filters	Note
No.221d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of sulfate and chloride ions.
No.221d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions.
No.222d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of sulfate and chloride ions.

Table 3.1 Outline of filter samples (continued)

Name	Details	Container	Number of filters	Note
No.222d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions
No.223d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Blank
No.223d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	Blank

3.2.3 Analytes

All participating laboratories were expected to analyze these filter samples and to submit their values as the net quantity of each ion (SO_4^{2-}, Cl^- and NH_4^+) in microgram (μg).

3.2.4 Analytical Methodologies

The recommended procedure for sample analyses on the filter pack method is described in "*Technical Manual for Air Concentration Monitoring in East Asia*" (EANET, 2013). As each filter sample was put in a centrifuge tube, a solvent was directly poured into the tube for extraction. The extraction procedure is as follows;

(1) Sample No.221d-1, No.222d-1, No.223d-1

Add 20 mL of H_2O_2 solution (0.05% v/v) as an extracting solvent into each centrifuge tube, then shake them for 20 minutes.

(2) Sample No.221d-2, No.222d-2, No.223d-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 4ºC.

The participating laboratories were expected to use the analytical methods specified in *"Technical Manual for Wet Deposition Monitoring in East Asia – 2010"* (EANET, 2010) in Table 3.2.

Table 3.2 Analytical methods specified in the Technical Manual

Analyte	Analytical method
SO_4^{2-}, Cl^-	Ion Chromatography (preferably with suppressor) Spectrophotometry
NH_4^+	Ion Chromatography Spectrophotometry (Indophenol Blue)

3.2.5 Data Check Procedures

All participating laboratories were requested to report as the net quantity of each ion (SO_4^{2-}, Cl^- and NH_4^+) in the filter sample.

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

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

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 ($netM_{\mathrm{sol}}$) is calculated as follows:

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

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

$M_{\mathrm{sol,Sample}}$: quantity (µg) of each component in the filtrate from sample No.221d-1, No.221d-2, No.222d-1 and No.222d-2;

$M_{\mathrm{sol,Blank}}$: the median quantity (µg) in the filtrate from blank sample No.223d-1 and No.223d-2.

3.3 Results

The NC distributed the filter samples to 21 laboratories in the participating countries of EANET and received their results from 19 laboratories. The results compared to the prepared values are summarized in Table 3.3. The average, minimum, maximum, standard deviation (S.D.) and number of data (N) were calculated from each analyzed ion quantity. Outliers, defined as those results exceeding three standard deviations, excluded from the summary calculation shown in

Table 3.3 and 1 result was rejected this time.

As shown in Table 3.3, the deviations ($\Delta V/V$p) for SO_4^{2-} in Sample No.221d and Sample No.222d were -7.8% and -6.7%. The deviations for Cl^- in Sample No.221d and Sample No.222d were -19.6% and -7.3%. The deviations for NH_4^+ in Sample No.221d and Sample No.222d were -5.6% and 4.7%.

The Data Quality Objectives (DQOs) of EANET are specified that determined values are expected to fall within ±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 ±15% but not ±30%, and a flag "X" indicates that its deviation exceeds ± 30%.

Deviation (%) = (Determined value − Prepared value) / Prepared value × 100 (%) (3)

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

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

The evaluation of the results on both Samples No.221d and No.222d is described in 3.3.1 Evaluation of Laboratories' Performance (by sample). The comparison of the results for each analyte is described in 3.3.2 Comparison of Laboratories' Performance (by analyte). The evaluation of their analytical circumstance, such as analytical method, experience of personnel, and other analytical conditions is described in 3.3.3 Information on Laboratories.

Table 3.3 Summary of analytical results of the filter samples

Analyte	Prepared* (*V*p) (µg)	Average (*V*a) (µg)	Δ*V*/*V*p* (%)	S.D. (µg)	Number (N)	Minimum (µg)	Maximum (µg)
Sample No.221d							
SO_4^{2-}	11.8	10.9	-7.8	1.67	18	8.54	15.7
Cl^-	6.82	5.49	-19.6	1.75	19	0.373	7.17
NH_4^+	24.4	23.0	-5.6	6.23	19	10.1	39.0
Sample No.222d							
SO_4^{2-}	44.6	41.6	-6.7	3.57	19	33.6	45.6
Cl^-	15.4	14.3	-7.3	2.61	19	8.68	20.1
NH_4^+	53.8	51.3	-4.7	9.30	19	35.6	76.3

* Prepared: Prepared values

* Δ*V*/*V*p: (Average result (*V*a) － Prepared value (*V*p)) / Prepared value (*V*p) × 100 (%)

3.3.1 Evaluation of Laboratories' Performance (by sample)

Samples No.221d-1, No.221d-2

For Sample No.221d, 15 analytical data in 57 results were flagged E, and 9 analytical data were flagged X. The total percentage of the flagged samples was 42.1% (Figure 3.1, Table 3.4 and 3.5).

Table 3.4 Number of flagged data for Sample No.221d

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E*	7	4	4	15
Flag X*	2	4	3	9
Data within DQOs	10	11	12	33
Ratio of Flagged (%)	47.4	42.1	36.8	42.1

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

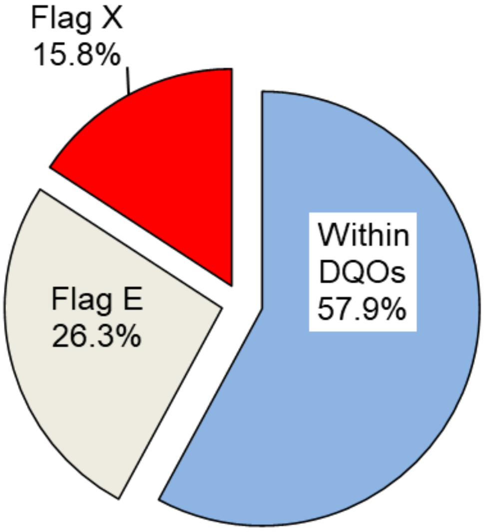


Figure 3.1 Percentage of flagged data for Sample No.221d

Table 3.5 Average analytical results of Sample No.221d

Lab. Code	SO_4^{2-} (μg)		Cl^- (μg)		NH_4^+ (μg)	
ID03	9.82	E	5.77	E	24.1	
JP01	11.8		7.09		23.9	
JP02	12.0		6.54		25.1	
JP03	12.3		6.82		23.6	
JP04	11.7		6.83		25.2	
JP08	11.0		5.93		23.9	
JP09	11.6		6.62		23.8	
JP10	11.8		7.17		22.8	
MY01	9.91	E	6.61		25.1	
MN01	11.9		6.08		39.0	X
MM01	8.96	E	5.02	E	20.0	E
PH01	10.1		5.73	E	25.0	
PH02	15.7	X	4.12	X	17.4	E
KR01	10.7		6.48		23.9	
RU01	9.05	E	4.97	E	24.0	
TH01	0.948	X	0.373	X	19.2	E
TH02	9.84	E	6.49		31.5	E
VN01	9.04	E	2.85	X	10.1	X
VN03	8.54	E	2.75	X	10.2	X

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

Flag X: 30% < | Deviation |

Samples No.222d-1, No.222d-2

For Sample No.222d, 9 analytical data in 57 results were flagged E, and 6 analytical data were flagged X. The total percentage of the flagged samples was 26.3% (Figure 3.2, Table 3.6 and 3.7).

Table 3.6 Number of flagged data for Sample No.222d

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	3	2	4	9
Flag X *	0	3	3	6
Data within DQOs	16	14	12	42
Ratio of Flagged (%)	15.8	26.3	36.8	26.3

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

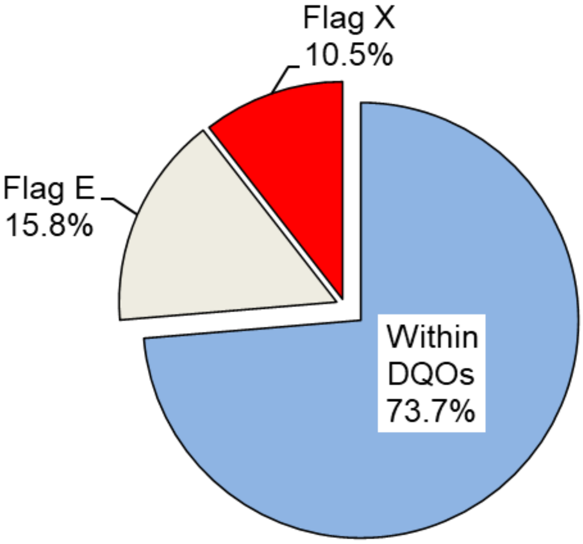


Figure 3.2 Percentage of flagged data for Sample No.222d

Table 3.7 Average analytical results of Sample No.222d

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
ID03	40.2	13.7	46.6
JP01	44.8	16.3	53.3
JP02	44.5	15.5	54.9
JP03	44.6	15.6	53.9
JP04	44.7	15.8	54.4
JP08	43.2	14.4	53.3
JP09	44.2	15.1	53.3

Table 3.7 Average analytical results of Sample No.222d (continued)

Lab. Code	SO_4^{2-} (μg)		Cl^- (μg)		NH_4^+ (μg)	
JP10	45.2		16.0		49.5	
MY01	42.6		15.3		63.0	E
MN01	45.6		15.1		76.3	X
MM01	33.6	E	13.2		53.7	
PH01	41.8		14.0		55.0	
PH02	41.1		11.5	E	36.0	X
KR01	42.2		15.3		58.4	
RU01	34.7	E	11.2	E	43.5	E
TH01	34.5	E	20.1	X	35.6	X
TH02	41.2		15.4		51.1	
VN01	40.9		8.98	X	41.3	E
VN03	40.7		8.68	X	41.1	E

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

Flag X: 30% < | Deviation |

Blank Sample (No.223d)

Each quantity of SO_4^{2-}, Cl^-, and NH_4^+ was determined for blank sample No.223d-1 and No.223d-2. Their obtained values are shown in Table 3.8. Blank values were detected in a wide range, including 0 μg.

Table 3.8 Analytical results of Blank Sample No.223d

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
ID03	0.32	1.65	1.57
JP01	0.14	1.43	0.22
JP02	0.11	1.11	0.22
JP03	0	1.27	0.02
JP04	0.14	1.42	0
JP08	0	2.52	0.98
JP09	0	1.45	0.43
JP10	0.11	1.08	0.49
MY01	1.41	2.48	1.74
MN01	0.26	2.40	1.42
MM01	0.46	3.16	3.90

Table 3.8 Analytical results of Blank Sample No.223d (continued)

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
PH01	1.98	2.36	0
PH02	3.74	2.38	0
KR01	1.09	1.79	0
RU01	0.36	1.55	2.96
TH01	0.71	1.36	0.27
TH02	0.34	1.90	0.99
VN01	0.90	1.00	0.91
VN03	1.05	1.17	1.10
Average	0.69	1.76	0.91
Median	0.34	1.55	0.49
Minimum	0.00	1.00	0.00
Maximum	3.74	3.16	3.90
Standard deviation	0.89	0.60	1.04

3.3.2 Comparison of Laboratories' Performance (by analyte)

The overviews of their results are shown in the following figures and tables for each analyte (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 3.9, 3.10 and 3.11 for each analyte.

<u>SO_4^{2-} (Sulfate)</u>

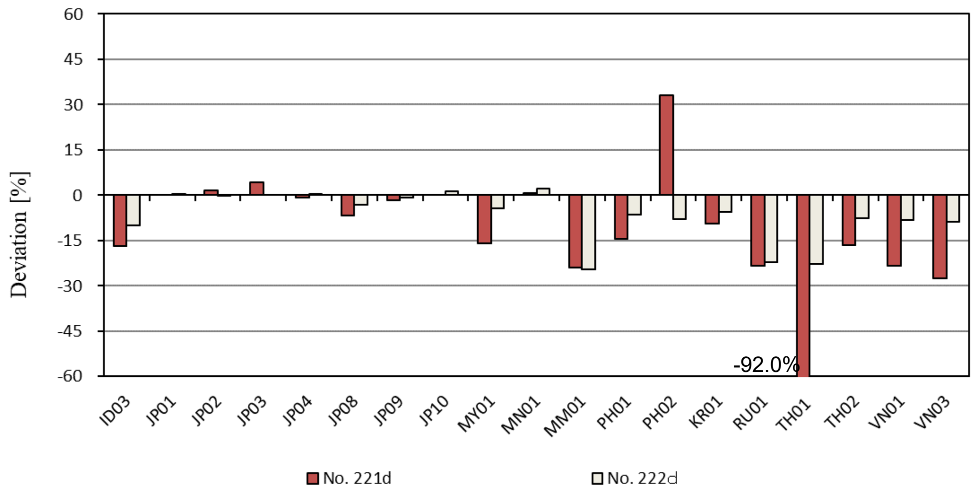


Figure 3.3 Deviation for SO_4^{2-}

Deviation (%) = (Determined value - Prepared value) / Prepared value × 100 (%)

Table 3.9 Flagged data of SO_4^{2-}

	Flag E	Flag X	Flagged (%)
Sample No.221d	7	2	47.4
Sample No.222d	3	0	15.8

All laboratories used Ion Chromatography for the determination of SO_4^{2-}. E flag appeared at 10 laboratories for Sample No.221d and No.222d. X flag appeared at 2 laboratories for Sample No.221d.

Cl$^-$ (Chloride)

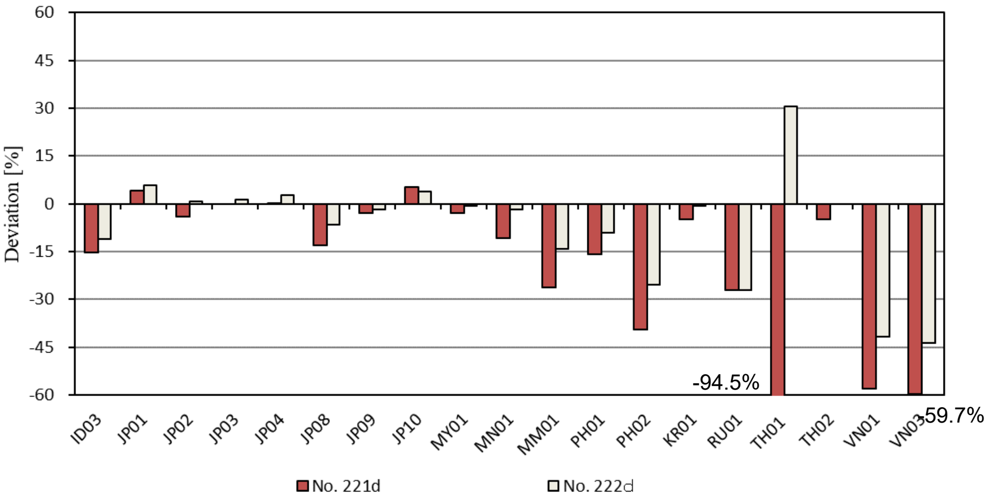


Figure 3.4 Deviation for Cl$^-$

Table 3.10 Flagged data of Cl$^-$

	Flag E	Flag X	Flagged (%)
Sample No.221d	4	4	42.1
Sample No.222d	2	3	26.3

As with the analysis of Cl$^-$, all laboratories used Ion Chromatography for the determination of Cl$^-$. E flag appeared at 6 laboratories for Sample No.221d and No.222d. X flag appeared at 7 laboratories for Sample No.221d and No. 222d.

NH_4^+ (Ammonium)

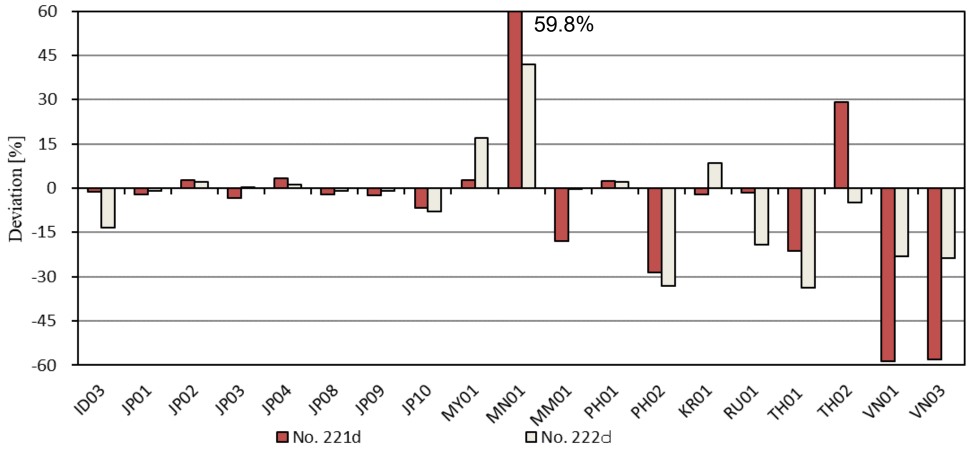


Figure 3.5 Deviation for NH_4^+

Table 3.11 Flagged data of NH_4^+

	Flag E	Flag X	Flagged (%)
Sample No.221d	4	3	36.8
Sample No.222d	4	3	36.8

Two laboratories used the spectrophotometry method. The other laboratories used Ion Chromatography for the determination of NH_4^+. E flag appeared at 8 laboratories for Sample No.221d and No.222d. X flag appeared at 6 laboratories for No.221d and No.222d.

3.3.3 Information on Laboratories

Years of staff experience

Years of staff experience are summarized in Table 3.12. A light gray color cell indicates that there is a flag for Sample No.221d or No.222d. A dark gray color cell indicates the flagged data in both Sample No.221d and No.222d.

Table 3.12 Years of staff experience

Lab. Code	SO_4^{2-}	Cl^-	NH_4^+
ID03	15	15	15
JP01	20	20	20

JP02	1	1	1
JP03	1	1	1
JP04	3	3	3
JP08	1	1	1
JP09	3	3	3
JP10	3	3	3
MY01	░ 5	5	░ 5
MN01	19	19	▓ 19
MM01	▓ 1	1	░ 1
PH01	3	3	3
PH02	░ 5/1	░ 5/1	▓ 5/1
KR01	17	17	17
RU01	▓ 20	░ 20	░ 20
TH01	▓ 1	░ 1	▓ 1
TH02	░ 24	24	░ 24
VN01	░ 9	░ 9	▓ 9
VN03	░ 18	░ 18	▓ 18

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

Flagged Data

In the results of Sample No.221d and No.222d, the total number of the flagged data was 32 (E: 21, X: 11) in the whole values (114). The number of the flagged data in each laboratory is shown in Figure 3.6. Eight laboratories met DQOs (42.1%).

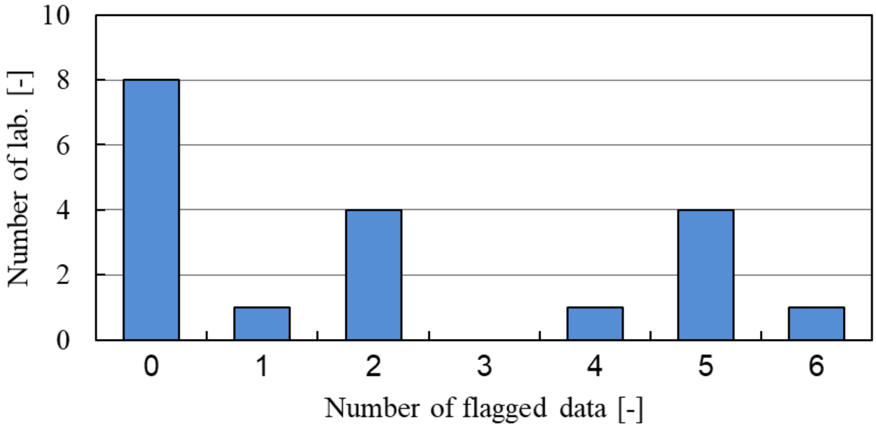


Figure 3.6 Number of flagged data and laboratories

Calibration standard solution

The ranges of the calibration standard solution in each laboratory are shown in Figure 3.7 with the prepared values and their laboratory results, which were converted in μmol L^{-1}. Each concentration of the prepared values was expected within the range of both concentrations of lowest and highest standard solutions. If the concentrations of their obtained values were not in the range of the calibration standard, laboratories should have analyzed again with the appropriate concentration range of standard solution.

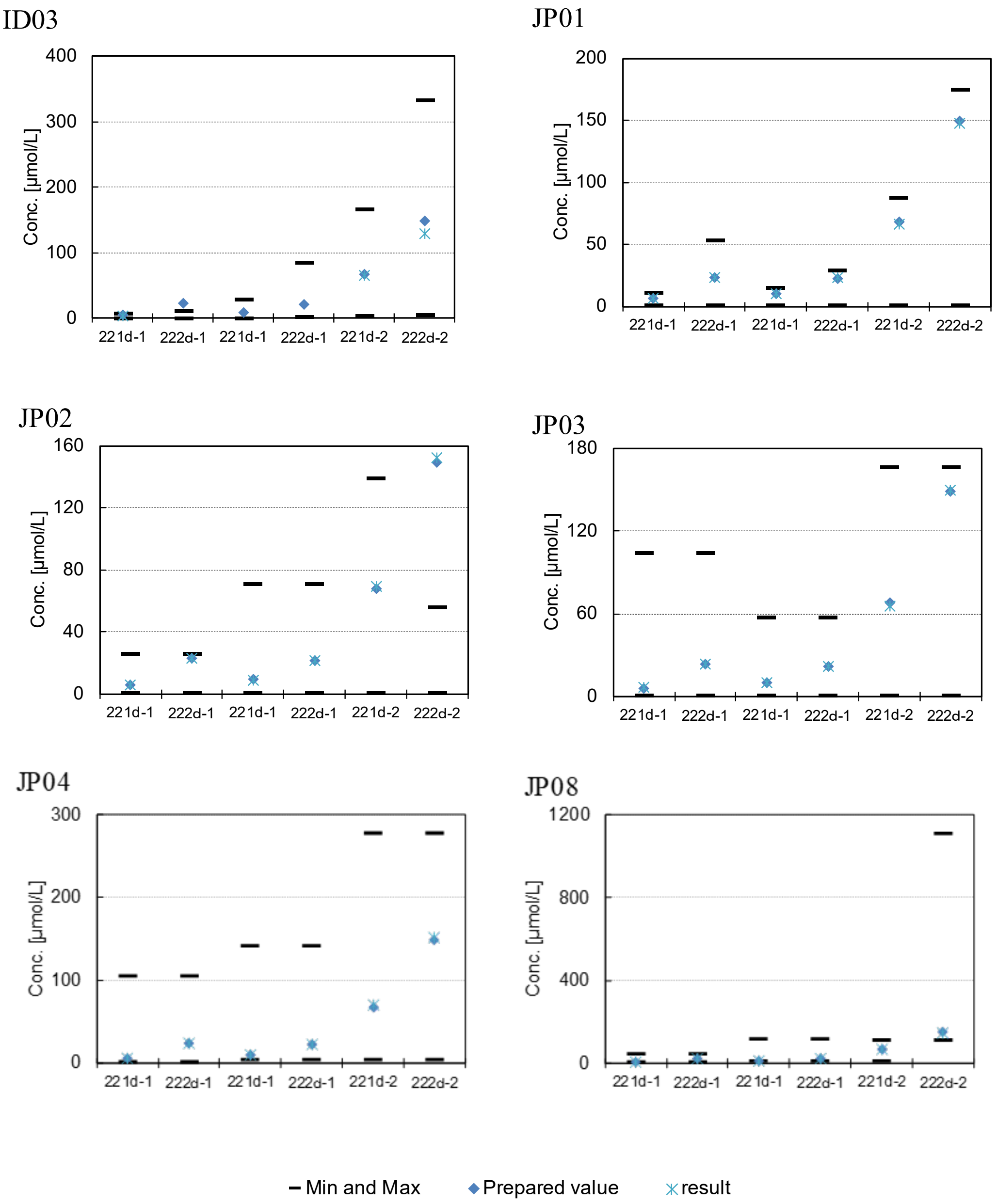


Figure 3.7 Ranges of the calibration standard solution in each laboratory

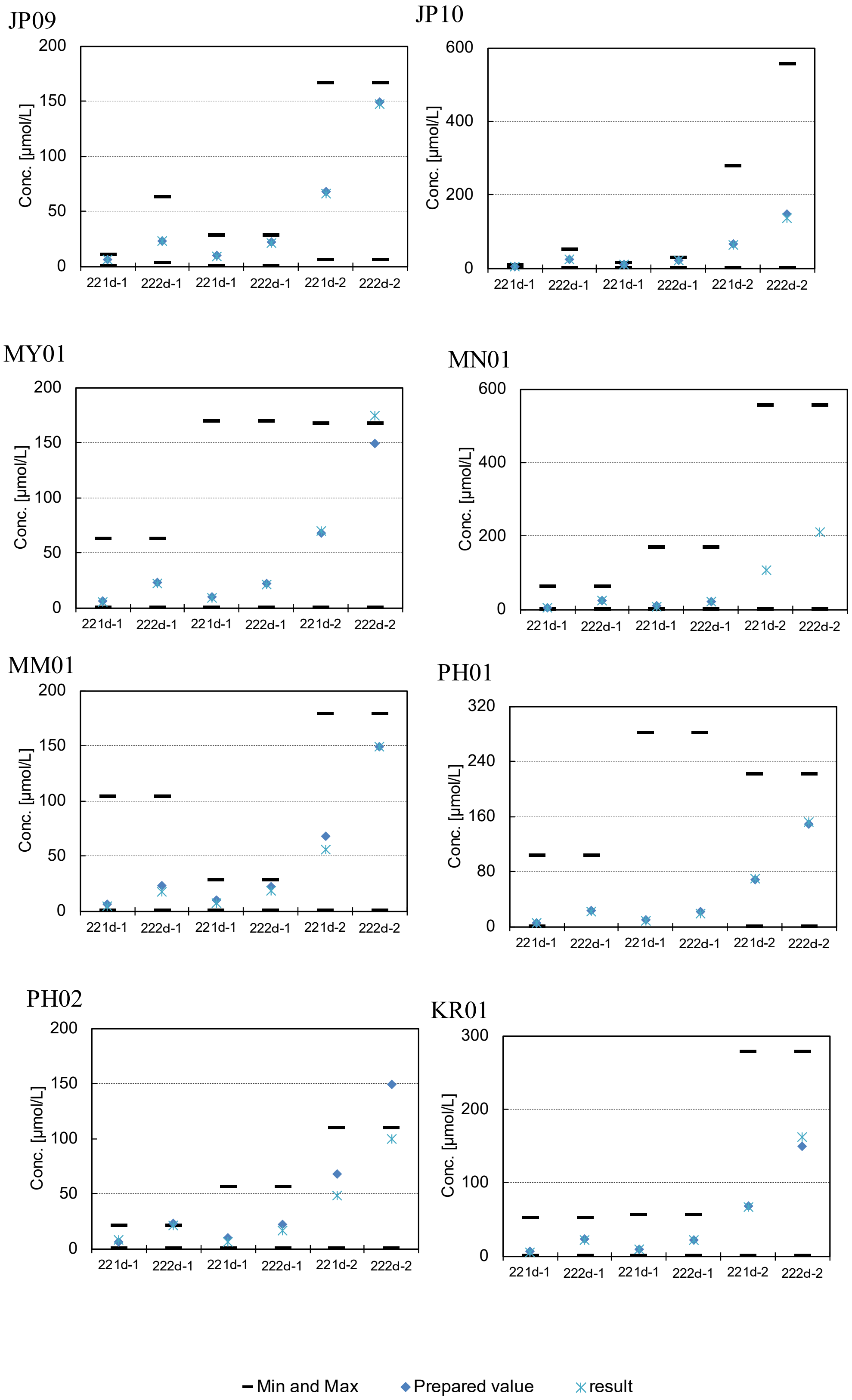


Figure 3.7 Ranges of the calibration standard solution in each laboratory (continued)

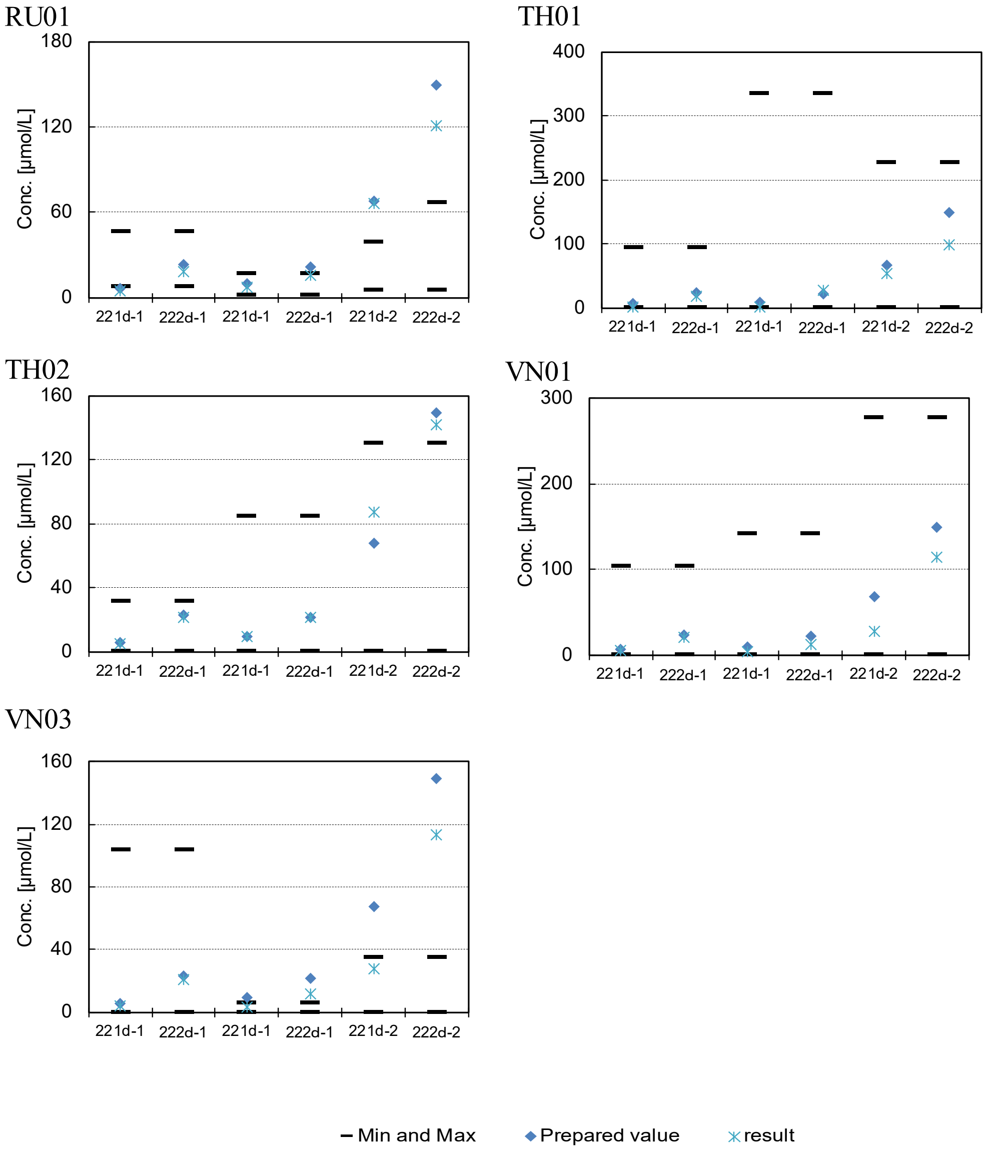


Figure 3.7 Ranges of the calibration standard solution in each laboratory (continued)

3.4 Comparison with past surveys

This Inter-laboratory Comparison on dry deposition has been implemented since 2005. The results showing the percentages of flagged data and percentages of data that were satisfied the DQOs were shown in Figure 3.8.

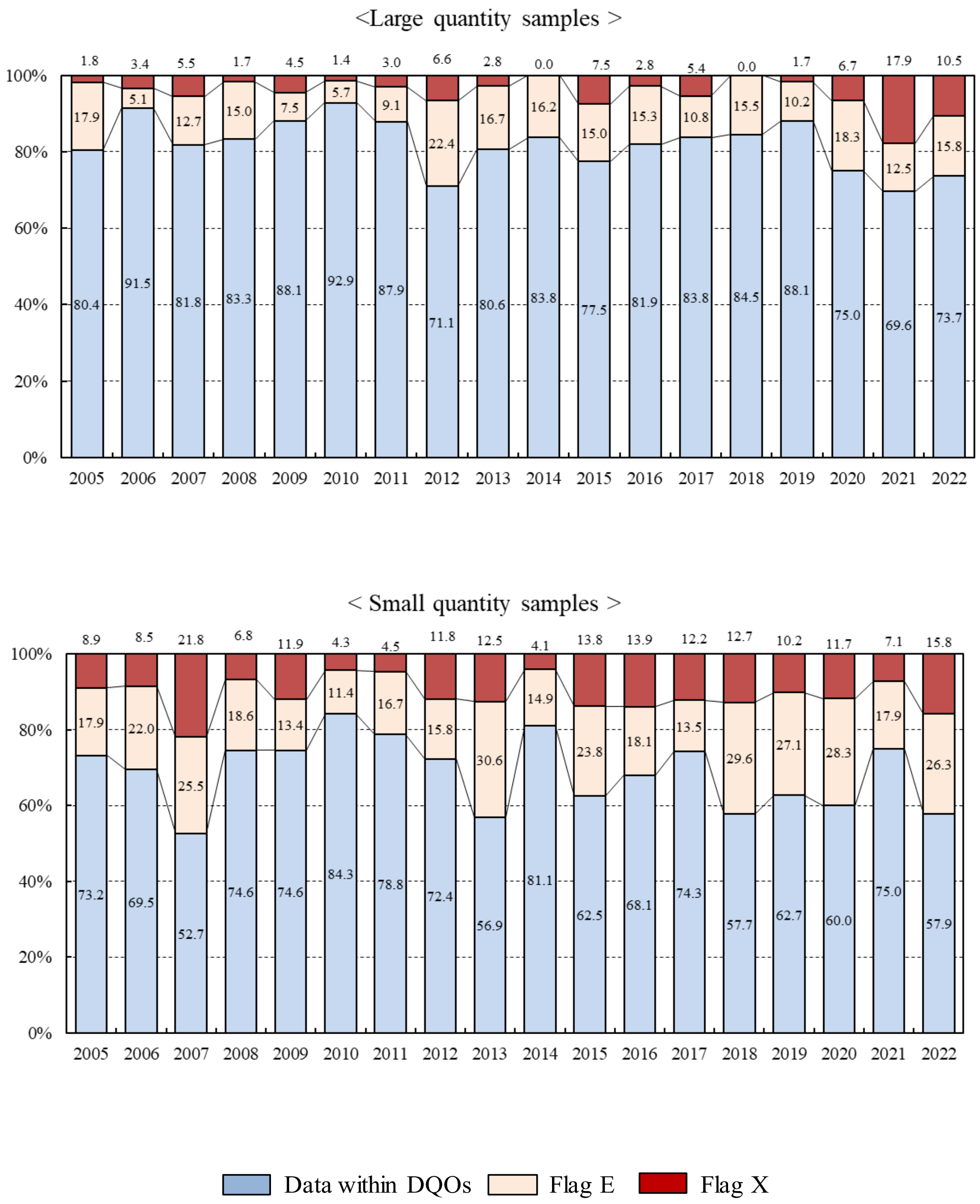


Figure 3.8 Comparison of DQOs' results for the past years

The comparison for each analyte in Inter-laboratory Comparison on dry deposition year–by-year is shown in Figure 3.9.

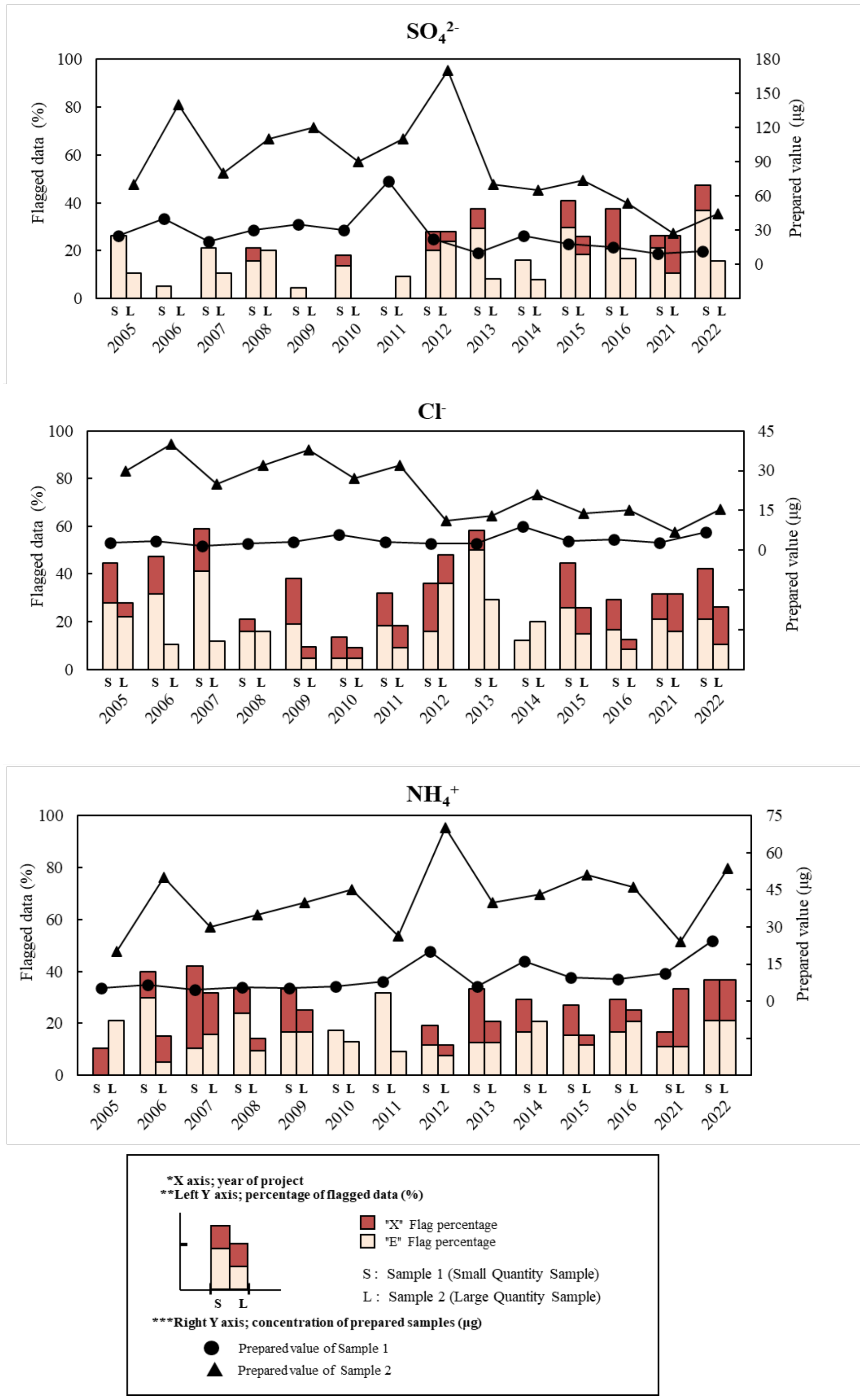


Figure 3.9 Comparison for each parameter in Inter-laboratory comparison project

3.5 Recommendations for improvement

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

3.5.1 Measurement and Analyses

► Before setting a shaker and start shaking for 20 minutes, shake each tube by hand sufficiently.

► Samples should not be diluted even though the concentration of the analytical sample exceeds that of the highest standard solution you prepared. Instead, add one or two higher standard solutions during analyses and measure its values within the calibration curve range.

► Extraction, filtration, and analyses should be done on the same day once you open the bag. In particular, special care for NH_4^+ determination. (Be aware that sample solutions may be contaminated by ammonia in a laboratory. Even each sample sets in an autosampler with a cap may be possibly contaminated by ammonia during analyses.)

► It is strongly recommended that only the interlaboratory samples should be analyzed in sequence to minimize contamination during analyses. Regular samples should not be analyzed simultaneously with the interlaboratory samples.

References

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

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

4. 24th INTER-LABORATORY COMPARISON PROJECT ON SOIL

4.1 Introduction

The Inter-Laboratory Comparison Project on Soil started in 1999 as one of the activities within the QA/QC program on Soil and Vegetation Monitoring. The inter-laboratory precision will be clarified as well as the within-laboratory and repeatability precision in the project to improve the analytical quality of the EANET laboratories. Possible factors affecting precisions have been discussed through the previous projects.

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

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

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

In the 24th project, Network Center (NC) provided two soil samples (No.221s and No.222s) to laboratories to improve the inter-laboratory precision by standardization of methods. In this report, the data from participating laboratories were evaluated statistically according to the QA/QC program for soil monitoring. The results may contribute to the assessment of the inter-laboratory variation in soil monitoring and provide useful information to improve precision of soil analysis on EANET.

4.2 Procedures

4.2.1 Participating Laboratories

Seven laboratories from four countries participated in the 24th project. The results submitted to the network center were analyzed statistically according to the QA/QC program. Names of the participating laboratories are listed in Table 1.1.

4.2.2 Description of Samples

The characteristics of the soil samples are as follows:

Sample No.221s: Andosols

Sample No.222s: Cambisols

Soil samples of No.221s and No.222s were collected under Japanese cedar (*Cryptomeria japonica*) and Japanese cypress (*Chamaecyparis obtusa*) mixed with Japanese red pine (*Pinus densiflora*) plantation, respectively, in Gunma Prefecture, Japan. Both soils were collected from B-horizon composed chiefly of soil minerals. The soils were air-dried, sieved to separate the fine earth fraction (< 2 mm), and mixed well by the following procedures; 1) the bulk sample was divided into two parts, 2) each part was mixed well, 3) the parts were joined and mixed well and 4) the sample was divided again. This procedure was repeated 15 times to ensure a completely homogeneous bulk sample. Finally, portions of 400-500 g were weighed out, packed in 500 mL plastic bottles, and then, sterilized using radioisotope (50 kGy) for distributing (exporting) to the participating countries.

4.2.3 Parameters Analyzed

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

Table 4.1 Parameters to be measured

Parameters	Unit	Mandatory or not
a) Moisture Content	wt %	M
b) pH(H_2O)	-	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

M: Mandatory items

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

4.2.4 Analytical Methodologies

All the procedures for chemical analysis were carried out basically according to the “Technical Manual for Soil and Vegetation Monitoring in East Asia” (EANET, 2000). In the respective laboratories, all the parameters were analyzed three times under the same conditions (as analyst, time, and instrument). Then, under within-laboratory-reproducibility condition (i.e., different analyst, time, and instrument), all the analytical procedures should be repeated twice.

4.2.4.1 Standardization of methods

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

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

4.2.4.2 Procedures for Ex-base cations

(1) Extract from air-dry sample with 1 M CH_3COONH_4 (pH 7.0) solution.
(2) Pipette an appropriate aliquot of the soil extract into volumetric flask and add 100 g-Sr L^{-1} solution to be 1000 mg-Sr L^{-1} as final concentration Sr ($SrCl_2$ solution eliminates the interference of the sample). And then make to volume with 1 M CH_3COONH_4 (pH 7.0). This solution is named "Prepared sample".
(3) Prepare three "prepared samples".
(4) Prepare each standard solution with diluting 1 M CH_3COONH_4 (pH 7.0) solution.
(5) Add 100 g-Sr L^{-1} solution to each standard solution to be the same concentration $SrCl_2$ as the sample.
(6) Analyze the standard solution and the prepared samples by AAS.
(7) Store the calibration curves certainly and report them together with reporting formats.
(8) Repeat the procedure 1) - 7) twice.

(9) Calculation of content in the soil

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

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

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

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

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

where,

A = Measurement values of prepared (diluted) samples (mg L^{-1})
B = Dilution ratio ($B = 2$, if 25 mL sample was diluted to 50 mL for making prepared sample.)
mcf = Moisture correction factor (Measured value)
S = Weight of air-dry sample (g)
V = Volume of extract (mL)

4.2.4.3 Procedures for Ex-acidity

(1) Extraction and titration would be carried out according to the “Technical Documents for Soil and Vegetation Monitoring in East Asia” basically.
(2) Prepare three samples. Analyze each sample and at least one blank.
(3) Repeat the procedure twice
(4) Calculation of content in the soil

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

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

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

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

where,

A_{NaOH} = Titration volume of 0.025 M NaOH solution needed for percolate (mL)
A_{HCl} = Titration volume of 0.02 M HCl solution needed for percolate (mL)
bl_{NaOH} = Titration volume of 0.025 M NaOH solution needed for blank (mL)
bl_{HCl} = Titration volume of 0.02 M HCl solution needed for blank (mL)
M_{NaOH} = Molarity of NaOH solution (mol L^{-1})
M_{HCl} = Molarity of HCl solution (mol L^{-1})
S = Weight of air-dry sample (g)
c = Aliquot factor ($c = 2$, if 50 mL percolate of 100 mL is used.)

4.2.4.4 Detection limit and quantification limit for Ex-base cation analysis

From the 21st project, it was recommended to report detection limit and quantification limit for Ex-base cations. Generally, these limit values are calculated as follows;

(1) A standard solution with the lowest concentration (Std-1 [mg L^{-1}]) should be measured for more than 5 times, and standard deviation (s.d.) of the Std-1 should be calculated.

(2) The detection limit and quantification limit are calculated from the respective formulae as follows:
Detection limit = 3*(s.d.) [mg L^{-1}]
Quantification limit = 10*(s.d.) [mg L^{-1}]

4.2.4.5 Reporting

(1) Preparation of the report
Digital formats (Microsoft Excel) are provided to the participating laboratories. Chemical properties of soil sample were calculated automatically by the formula written in the formats.

(2) Submission of the report
Entered data in digital formats and other information (e.g., calibration curve) were submitted by E-mail.

4.2.4.6 Data Checking Procedures

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

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

2) Detection of outliers to prepare the verified dataset
Evenness of within-laboratory precision (variation in each laboratory) and inter-laboratory precision (variation between 7 laboratories) were verified by Cochran and Grubbs methods, respectively. We also computed “verified” mean, median and other statistical summary from verified datasets. In inter-laboratory comparison project on soil, “verified” mean will be a good reference to assess the analyzed value of each laboratory.

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

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

Based on the above equation, inter-laboratories variance, within-laboratory-reproducibility variance, and repeatability variance were calculated, and then the precision was estimated.

4) Calculation of permissible tolerance

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

4.3 Results

4.3.1 General description of the data variability

The statistical summary is shown in Table 4.2. On the 24th inter-laboratory project, Ex-Ca, Mg, and K in 221s was higher than that in 222s, and Ex-acidity, Ex-Al, and Ex-H in 222s were higher than those in 221s. We observed large variations in the analyzed data (CVs) of Ex-base cations (approx. 2-70%), Ex-acidity (20-35%) and acid cations (10-80%) in both samples. Meanwhile, in both samples, CVs were relatively small for both pH(H_2O) and pH(KCl) (< 3%).

Table 4.2 Basic statistics of the entire dataset

Statistics	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol$_c$ kg^{-1}						
	No. 221s								
Number of Laboratories	7	7	4	4	4	4	6	6	6
Total average	4.7	4.2	1.45	0.22	0.09	0.10	3.19	2.51	0.72
Median	4.7	4.2	1.43	0.22	0.09	0.08	2.78	2.47	0.49
Maximum	5.0	4.4	1.54	0.26	0.10	0.20	5.46	3.78	1.68
Minimum	4.5	4.1	1.40	0.20	0.09	0.04	2.46	1.85	0.42
Standard deviation	0.1	0.1	0.06	0.02	0.00	0.07	1.13	0.70	0.49
CV (%)[*1]	3.0	1.9	4.4	10.6	4.2	70.2	35.3	27.7	68.3
	No. 222s								
Number of Laboratories	7	7	4	4	4	4	6	6	6
Total average	4.3	4.0	0.23	0.07	0.04	0.08	4.31	3.51	0.81
Median	4.3	4.0	0.27	0.07	0.04	0.07	3.96	3.47	0.58
Maximum	4.6	4.1	0.30	0.07	0.04	0.15	6.18	4.12	2.06
Minimum	4.2	3.8	0.11	0.06	0.04	0.03	3.80	3.03	0.39
Standard deviation	0.1	0.1	0.09	0.00	0.00	0.05	0.92	0.36	0.62
CV (%)[*1]	3.1	2.3	38.2	2.5	3.9	63.8	21.4	10.2	77.0

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

We also have an overview of the data by box-and-whisker plot (Figure 4.1) of No.221s and 222s analyzed by 7 laboratories. Box-and-whisker plot provides the six-number summaries; total average shown by an open argyle, lower quartile, median and upper quartile shown by a box and a bold line, and lowest and highest value within the range between the lower quartile minus 1.5 times the inter-quartile range and the upper quartile plus 1.5 times the inter-quartile range drawn by error bar. In addition, the values outside the error bar are shown as outliers, that is, non-parametrical outliers. The plots showed several "non-parametrical" outliers in each item. Those outliers might be due to wrong calculation, procedure, irregular contamination, and so on. Therefore, in following section, we removed these outliers by parametrically statistical method to calculate the good reference closer to true value.

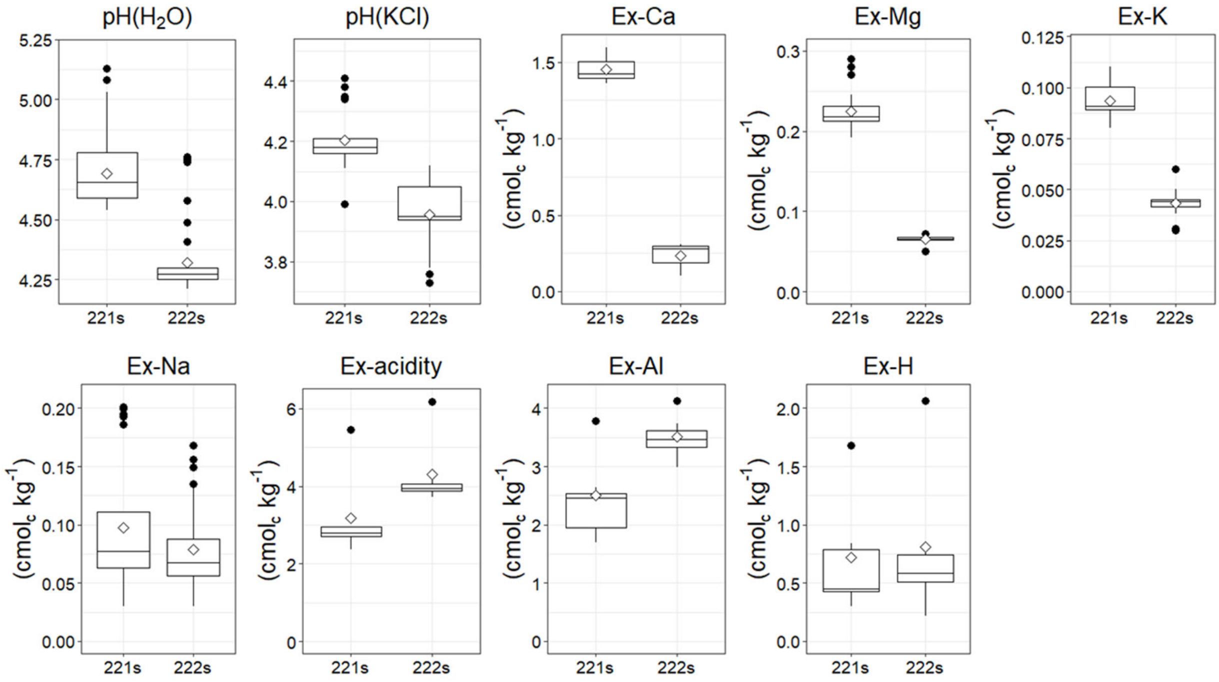


Figure 4.1 Data variability of No.221s and No.222s

4.3.2 Detection of outliers

Detection of outliers by Cochran-Grubbs methods is shown in Table 4.3. The laboratory which had a significantly large difference in repeat analyses was decided as an outlier by Cochran method (examination of the evenness of within-laboratory precision); e.g. "c" signs on "MN01" in pH(H_2O) of No.221s. Then, the rest of data were tested by Grubbs method (examination of the average value of each laboratory). In this method, the laboratory which has significantly large or small average was decided as an outlier (e.g. "g" signs on "MN01" in pH(KCl) of No. 221s). Cochran-Grubbs method detected the several outliers for each item. As a result of removing outliers, the "verified" dataset consisting of 4-6 laboratories for pH(H_2O) and pH(KCl), 3-4 laboratories in Ex-base cations and 3-5 laboratories in Ex-acidity, Al and H, and these laboratories were used for further analysis in the following section (Table 4.4).

Table 4.3 Data verification by Cochran-Grubbs tests
No. 221s

Country	Lab.	Repeat analysis	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
					cmol$_c$ kg^{-1}						
Indonesia	ID04	1st	4.8	4.2	1.57	0.20	0.10	0.19	2.71	1.92	0.79 g
		2nd	4.8	4.2	1.50	0.20	0.10	0.20	2.70	1.90	0.80 g
Mongolia	MN01	1st	4.7 c	4.4 g	NA	NA	NA	NA	5.46 g	3.78	1.68 g
		2nd	4.7 c	4.4 g	NA	NA	NA	NA	5.46 g	3.78	1.68 g
Philippines	PH01	1st	4.8 c	4.1 c	1.52	0.28 c	0.09 c	0.04	2.40 c	1.77 c	0.58 c
		2nd	5.1 c	4.4 c	1.40	0.23 c	0.11 c	0.04	2.51 c	1.94 c	0.50 c
Vietnam	VN01	1st	4.6	4.2	1.41	0.23	0.09	0.08	2.83 c	2.49	0.44
		2nd	4.6	4.2	1.40	0.23	0.09	0.08	2.86 c	2.52	0.43
	VN02	1st	4.6	4.2	NA	NA	NA	NA	2.93	2.57	0.42
		2nd	4.6	4.2	NA	NA	NA	NA	2.93	2.57	0.42
	VN04	1st	4.7	4.2	1.42	0.22	0.09	0.07	2.72	2.44	0.45
		2nd	4.7	4.2	1.38	0.22	0.09	0.07	2.72	2.44	0.44
	VN05	1st	4.5	4.1 g	NA	NA	NA	NA	NA	NA	NA
		2nd	4.6	4.1 g	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. 222s

Country	Lab.	Repeat analysis	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
					cmol$_c$ kg^{-1}						
Indonesia	ID04	1st	4.3	4.0	0.25	0.07	0.04	0.15	3.74	3.03	0.71
		2nd	4.3	4.0	0.22	0.07	0.04	0.15	3.85	3.03	0.82
Mongolia	MN01	1st	4.3	4.1	NA	NA	NA	NA	6.18 g	4.12	2.06 g
		2nd	4.3	4.1	NA	NA	NA	NA	6.18 g	4.12	2.06 g
Philippines	PH01	1st	4.5 c	3.8 c	0.10	0.07 c	0.03 c	0.03	4.01	3.35 c	0.36
		2nd	4.8 c	4.1 c	0.11	0.06 c	0.05 c	0.03	4.17	3.60 c	0.42
Vietnam	VN01	1st	4.3	4.0	0.29	0.06	0.04	0.07	3.92	3.46 c	0.59
		2nd	4.3	4.0	0.30	0.06	0.04	0.07	3.93	3.49 c	0.59
	VN02	1st	4.3	3.9	NA	NA	NA	NA	4.01	3.63	0.48
		2nd	4.3	3.9	NA	NA	NA	NA	3.99	3.63	0.48
	VN04	1st	4.3	4.0	0.30	0.07	0.04	0.07	3.88	3.34	0.58
		2nd	4.3	4.0	0.30	0.07	0.04	0.07	3.88	3.34	0.58
	VN05	1st	4.2	3.8	NA	NA	NA	NA	NA	NA	NA
		2nd	4.2	3.8	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 verified datasets in No.221s and No.222s is shown in Table 4.4. Total average of Ex-base cations in both soils decreased by verification, and the data variability (CVs) of almost all items decreased from the entire dataset. However, these variations were still too large to compare the regular monitoring data among the participating countries, accurately. The variation may include an error produced by same condition (repetition), different person, time, or instrument (within-laboratory) or different laboratories (inter-laboratory). We separated this variation in next section to detect the source of it.

Table 4.4 Basic statistics of the verified[*2] dataset

Statistics	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol$_c$ kg^{-1}						
	No. 221s								
Number of Laboratories	5	4	4	3	3	4	3	5	3
Total average	4.6	4.2	1.45	0.21	0.09	0.10	2.79	2.64	0.43
Median	4.6	4.2	1.43	0.22	0.09	0.08	2.72	2.50	0.43
Maximum	4.8	4.2	1.54	0.23	0.10	0.20	2.93	3.78	0.44
Minimum	4.5	4.2	1.40	0.20	0.09	0.04	2.70	1.91	0.42
Standard deviation	0.1	0.0	0.06	0.01	0.00	0.07	0.13	0.69	0.01
CV (%)[*1]	2.0	0.3	4.4	7.0	4.5	70.2	4.6	26.2	2.6
	No. 222s								
Number of Laboratories	6	6	4	3	3	4	5	4	5
Total average	4.3	4.0	0.23	0.07	0.04	0.08	3.94	3.53	0.56
Median	4.3	4.0	0.27	0.07	0.04	0.07	3.92	3.49	0.58
Maximum	4.3	4.1	0.30	0.07	0.04	0.15	4.09	4.12	0.76
Minimum	4.2	3.8	0.11	0.06	0.04	0.03	3.80	3.03	0.39
Standard deviation	0.0	0.1	0.09	0.00	0.00	0.05	0.11	0.46	0.14
CV (%)[*1]	0.6	2.6	38.2	2.0	4.8	63.8	2.8	13.1	24.7

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

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

4.3.4 Analysis of variance for verified data

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

1) Repeatability-precision

Repeatability-precision was enough high for all items. The CVs were <0.3% in $pH(H_2O)$ and pH(KCl), < 15% in Ex-base cations, Ex-acidity, Ex-Al and Ex-H. The result suggests that triplicate analyses were carried out under the same condition. In general, the participating laboratories could analyze the parameters with their own standard procedures and stable instruments.

2) Within-laboratory precision

CVs in within-laboratory precision for almost all parameters were smaller than CVs in repeatability precision, suggesting the average of triplicate analyses under the repeatability condition could be representative value for the analysis in a laboratory. We assumed that participating laboratories could analyze the parameters with their own standard procedures.

3) Inter-laboratories precision

The CVs in the inter-laboratories precision were less than 3% in $pH(H_2O)$ and pH(KCl). However, the CVs of the rest of the items ranged from 2 to 70%. Thus, in this inter-laboratory comparison, almost all error in each parameter was produced by different laboratories. We discussed the possible factor of the relatively high CVs in inter-laboratory precision, in the following section.

4) Calculation of permissible tolerance

The repeatability limit and within-laboratory reproducibility limit might be enough small to use as a reference value for the repeat analysis on the instrumental analysis in the respective laboratories. For assessment of temporal pH change of monitoring data at each site, participating laboratories can detect the significant change more than 0.1 pH units. Meanwhile, the result of reproducibility limit (inter-laboratories reproducibility limit) suggested that participating laboratories can detect the significant difference between the monitoring sites if the differences are more than about 0.1-0.3 for pH(H_2O) and pH(KCl), 0.01-0.25 $\mathrm{cmol_c\,kg^{-1}}$ for Ex-base cations, 0.36 $\mathrm{cmol_c\,kg^{-1}}$ for Ex-acidity, 1.9 $\mathrm{cmol_c\,kg^{-1}}$ for Ex-Al, and 0.39 $\mathrm{cmol_c\,kg^{-1}}$ for Ex-H.

Table 4.5 Analysis of variance for the verified dataset

Statistics	No. 221s								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	5	4	4	3	3	4	3	5	3
Total sum of square	19000	10000	1200	15	2.8	5.5	2500	6300	61
ST/lmd	650	420	50	0.82	0.15	0.23	140	210	3.4
Number of Laboratories	5	4	4	3	3	4	3	5	3
Number of Data	30	24	24	18	18	24	18	30	18
Total sum	140	100	35	3.9	1.7	2.3	50	79	7.8
Total average	4.6	4.2	1.45	0.21	0.09	0.10	2.79	2.64	0.43
Sum of square inter-laboratories (S_R)	0.2	0.0	0.07	0.00	0.00	0.08	0.20	11.42	0.00
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.03	0.00	0.00	0.00	0.00	0.00	0.00
Sum of square repeatablility (S_r)	0.0	0.0	0.01	0.00	0.00	0.00	0.02	0.04	0.00
Total sum of square (S_T)	0.2	0.0	0.11	0.00	0.00	0.08	0.22	11.46	0.00
Inter-laboratories degree of freedom (ϕ_R)	4	3	3	2	2	3	2	4	2
Within-laboratory degree of freedom (ϕ_{RW})	5	4	4	3	3	4	3	5	3
Repeatability degree of freedom (ϕ_r)	20	16	16	12	12	16	12	20	12
Total degree of freedom (ϕ_T)	29	23	23	17	17	23	17	29	17
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.1	0.0	0.02	0.00	0.00	0.03	0.10	2.86	0.00
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.0	0.0	0.01	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 ($s_b^2 = (V_R - V_{RW})/(2 \times 3)$)	0.0	0.0	0.00	0.00	0.00	0.00	0.02	0.48	0.00
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 ($s_R = \mathrm{SQRT}(s_r^2/(2\times3) + s_c^2/2 + s_b^2)$)	0.1	0.0	0.06	0.01	0.00	0.07	0.13	0.69	0.01
Within-laboratory standard deviation ($s_{RW} = \mathrm{SQRT}(s_r^2/3 + s_c^2)$)	0.0	0.0	0.05	0.00	0.00	0.00	0.00	0.01	0.00
Repeatability standard deviation ($s_r = \mathrm{SQRT}(s_r^2)$)	0.0	0.0	0.02	0.01	0.01	0.00	0.04	0.04	0.01
Inter-laboratories precision CV (%)	2.0	0.3	4.43	6.97	4.47	70.23	4.64	26.15	2.55
Within-laboratory precision CV (%)	0.2	0.3	3.55	1.04	1.85	2.69	0.14	0.43	0.94
Repeatability precision CV (%)	0.3	0.2	1.51	3.99	5.49	4.11	1.34	1.61	2.00
Reproducibility limit ($R = D(2, 0.95)\times s_R$)	0.3	0.0	0.18	0.04	0.01	0.19	0.36	1.93	0.03
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)\times s_{Rw}$)	0.0	0.0	0.14	0.01	0.00	0.01	0.01	0.03	0.01
Repeatability limit ($r = D(3, 0.95)\times s_r$)	0.0	0.0	0.07	0.03	0.02	0.01	0.12	0.14	0.03

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

Statistics	No. 222s								
	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	6	6	4	3	3	4	5	4	5
Total sum of square	24000	20000	32	1.4	0.60	3.6	14000	7200	280
ST/lmd	660	560	1.3	0.078	0.034	0.15	460	300	9.4
Number of Laboratories	6	6	4	3	3	4	5	4	5
Number of Data	36	36	24	18	18	24	30	24	30
Total sum	150	140	5.6	1.2	0.78	1.9	120	85	17
Total average	4.3	4.0	0.23	0.07	0.04	0.08	3.94	3.53	0.56
Sum of square inter-laboratories (S_R)	0.0	0.3	0.14	0.00	0.00	0.05	0.30	3.84	0.46
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.06	0.00	0.02
Sum of square repeatablility (S_r)	0.0	0.0	0.00	0.00	0.00	0.00	0.02	0.02	0.12
Total sum of square (S_T)	0.0	0.3	0.15	0.00	0.00	0.05	0.37	3.87	0.61
Inter-laboratories degree of freedom (ϕ_R)	5	5	3	2	2	3	4	3	4
Within-laboratory degree of freedom (ϕ_{RW})	6	6	4	3	3	4	5	4	5
Repeatability degree of freedom (ϕ_r)	24	24	16	12	12	16	20	16	20
Total degree of freedom (ϕ_T)	35	35	23	17	17	23	29	23	29
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.0	0.1	0.05	0.00	0.00	0.02	0.07	1.28	0.11
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.0	0.0	0.00	0.00	0.00	0.00	0.01	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	0.01
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2\times3)$)	0.0	0.0	0.01	0.00	0.00	0.00	0.01	0.21	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	0.01
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2\times3) + s_c^2/2 + s_b^2)$)	0.0	0.1	0.09	0.00	0.00	0.05	0.11	0.46	0.14
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.01	0.00	0.00	0.00	0.06	0.00	0.04
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.01	0.00	0.00	0.01	0.03	0.04	0.08
Inter-laboratories precision CV (%)	0.6	2.6	38.22	1.99	4.83	63.85	2.82	13.09	24.66
Within-laboratory precision CV (%)	0.3	0.1	4.89	1.04	5.56	2.61	1.56	0.07	7.03
Repeatability precision CV (%)	0.3	0.3	3.48	4.39	8.06	9.38	0.73	1.00	14.02
Reproducibility limit ($R = D(2, 0.95)\times s_R$)	0.1	0.3	0.25	0.00	0.01	0.14	0.31	1.29	0.39
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)\times s_{Rw}$)	0.0	0.0	0.03	0.00	0.01	0.01	0.17	0.01	0.11
Repeatability limit ($r = D(3, 0.95)\times s_r$)	0.0	0.0	0.03	0.01	0.01	0.02	0.09	0.12	0.26

4.3.5 Inter-laboratory variations in each parameter

To assess the precision in each laboratory and properties, scatter plots between No.221s and No.222s are shown (Figure 4.2). The plots did not include extreme outliers for eye-friendly.

1) pH

Linear correlation between No.221s and No.222s was found, suggesting the systematic errors of the inter-laboratory variation in $pH(H_2O)$ and pH(KCl). The systematic error might be caused by the condition of pure water, standard solution, or glass electrode. In addition, measuring time for the stabilization of value may lead to the variation because a carbon dioxide pressure, leakage of KCl solution from the electrode, and/or settling the clay particles in the sample tube change the ion balance in soil suspension.

2) Base cations

Because the number of participating laboratories was small this year, no correlations were found for exchangeable base cations. Laboratories that were rejected by outlier tests should pay attention to the condition of pure water, standard solutions, and so on. In the analysis of base cations, higher concentration or higher pH of extraction solution may result in an increase of the base cation concentrations. Preparing appropriate standard solutions from low to high concentrations which completely cover the concentrations of unknown samples is also important for reducing the error. Extraction solution should be used for dilution of standards to minimize the matrix effect.

3) Acidity

Similarly to base cations, no correlations were found for Ex-acidity, Ex-Al, and Ex-H. To minimize the error, the analyst should pay attention to the manipulation of titration, which was easily affected by factor of volumetric solution or end-point detection. Participating laboratories should check the standard of procedure based on the Technical Manual for Soil and Vegetation Monitoring (EANET, 2000).

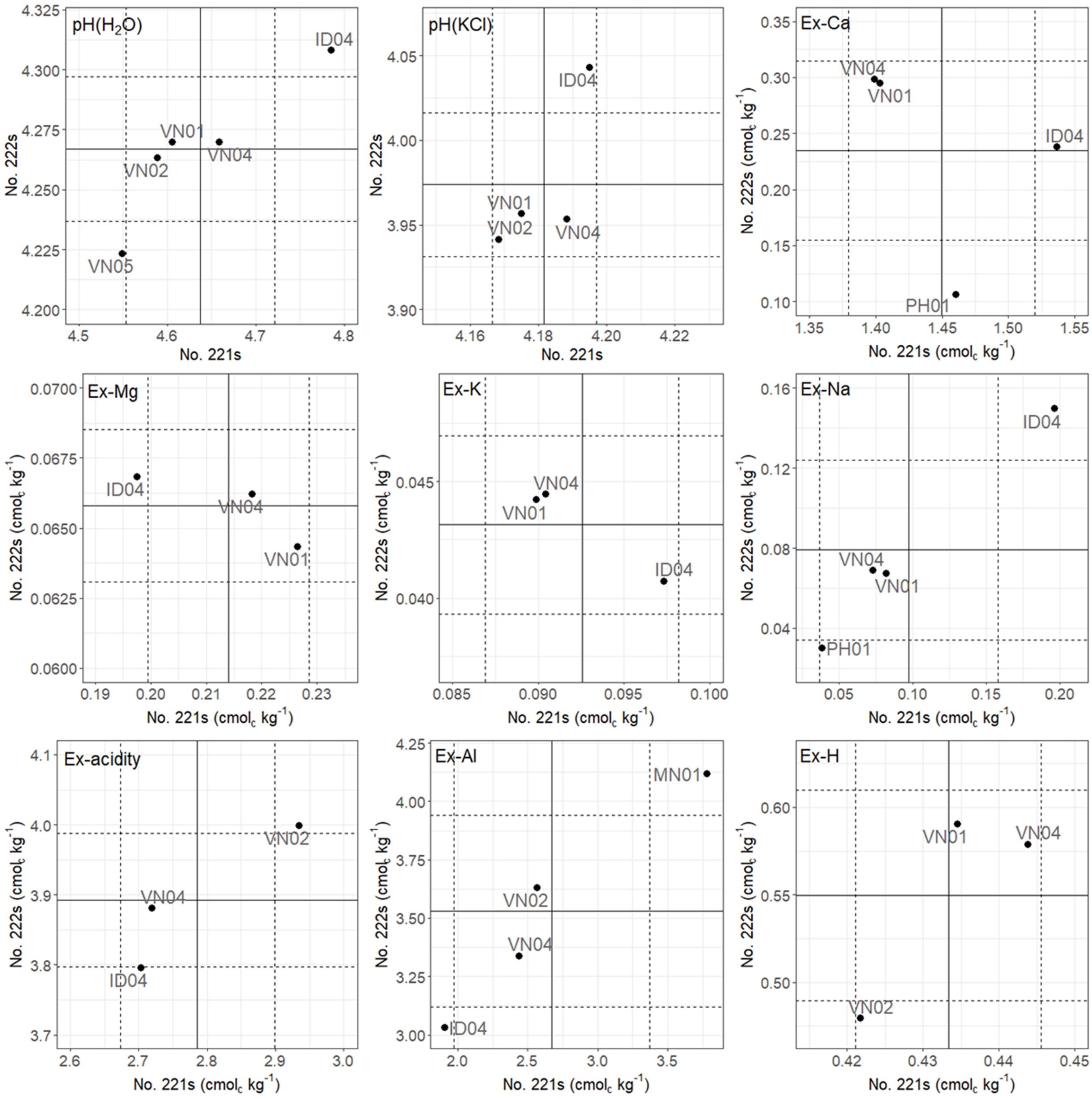


Figure 4.2 Scatter plots of each soil chemical property between No.221s and No.222s

Solid and dotted lines indicate mean and mean±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

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

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	
ID04	1	12	3	1	5	5	d
MN01	-	-	-	1	18	11	-
PH01	1	3	1	1	3	3	d
VN01	1	9	9	1	6	6	d
VN02	-	-	-	1	18	14	-
VN04	1	16	15	1	18	17	d
VN05	-	-	-	-	-	-	-

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

2) Analytical instruments and condition of instruments

Analytical instruments used for the measurement, procedures for extraction of base cations, and size of burette used for the titration method in Ex-acidity are shown in Table 4.7. All ex-base cations were analyzed by AAS. Years in use of instruments ranged from 2 to 17. Buchner funnel procedure was used in all laboratories for extraction of exchangeable base cations. No clear difference was observed among different procedures. As for the size of burette for titration of Ex-acidity, the capacities were varied from 10 to 25 mL while minimum graduates were 0.01 to 0.1.

3) Date of analysis

Dates of analysis in the respective laboratories and days used for the analysis are shown in Table 4.8. There was no significant implication between date of analysis and the data. Days used for analysis were 1 to 19 days, and interval between the first and second analyses of the repeat analyses was varied from 0 (in a same day) to 13 days. It is recommended that repeat analyses should be carried out with several-day interval (three days or more) in order to estimate actual within-laboratory reproducibility, as a supplementary instruction for the project, based on the discussion at SAC3 (The third session of the Scientific Advisory Committee on EANET).

Table 4.7 Analytical instruments and condition of the instruments for exchangeable 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		
													method	Size of burette (mL)	
			Instrument	Years[*1]	Instrument	Years		Instrument	Years	Instrument	Years			Capacity	Minimum graduate
ID04	221s	Percolation tube	AAS	8	AAS	8	La	AAS	8	AAS	8	La	Titration	25	0.05
	222s		AAS	8	AAS	8	La	AAS	8	AAS	8	La		25	0.05
MN01	221s						-						Titration	25	0.1
	222s													25	0.1
PH01	221s	Buchner funnel	AAS	2	AAS	2	La	AAS	2	AAS	2	na	Titration	10	0.05
	222s		AAS	2	AAS	2	La	AAS	2	AAS	2	na		10	0.05
VN01	221s	Buchner funnel	AAS	15	AAS	15	+	AAS	14	AAS	15	+	Titration	10	0.05
	222s		AAS	15	AAS	15	+	AAS	14	AAS	15	+		10	0.05
VN02	221s						-						Titration	10	0.05
	222s													10	0.05
VN04	221s	Buchner funnel	AAS	17	AAS	16	na	AAS	16	AAS	16	na	Titration	10	0.01
	222s		AAS	17	AAS	16	na	AAS	16	AAS	16	na		10	0.01
VN05	221s							-							
	222s														

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

Table 4.8 Date of analysis

Lab.	Repeat	pH				Ex-Ca and Mg				Ex-K and Na				Ex-acidity, Al and H			
		Start Date	Finish Date	AD	ID	Start Date	Finish Date	AD	ID	Start Date	Finish Date	AD	ID	Start Date	Finish Date	AD	ID
				Days				Days				Days				Days	
ID04	1st	2022/11/2	2022/11/2	1	7	2022/11/2	2022/11/3	2	7	2022/11/2	2022/11/3	2	7	2022/11/2	2022/11/2	1	7
	2nd	2022/11/9	2022/11/9	1		2022/11/9	2022/11/10	2		2022/11/9	2022/11/10	2		2022/11/9	2022/11/9	1	
MN01[*1]	1st	2023/2/14	2023/2/14	1	1			NA				NA		2023/2/15	2023/2/15	1	1
	2nd	2023/2/15	2023/2/15	1										2023/2/16	2023/2/16	1	
PH01	1st	2023/1/24	2023/1/24	1	6	2023/1/23	2023/2/1	10	13	2023/1/23	2023/2/1	10	13	2023/1/24	2023/1/24	1	8
	2nd	2023/1/30	2023/1/30	1		2023/1/27	2023/2/14	19		2023/1/27	2023/2/14	19		2023/2/1	2023/2/1	1	
VN01	1st	2022/12/13	2022/12/13	1	2	2022/12/13	2022/12/14	2	2	2022/12/13	2022/12/14	2	2	2022/12/13	2022/12/14	2	1
	2nd	2022/12/15	2022/12/15	1		2022/12/15	2022/12/16	2		2022/12/15	2022/12/16	2		2022/12/14	2022/12/15	2	
VN02	1st	2022/12/25	2022/12/25	1	0			NA				NA		2022/12/26	2022/12/27	2	0
	2nd	2022/12/25	2022/12/25	1										2022/12/26	2022/12/27	2	
VN04	1st	2022/12/20	2022/12/20	1	1	2022/12/20	2022/12/20	1	1	2022/12/20	2022/12/20	1	1	2022/12/20	2022/12/20	1	1
	2nd	2022/12/21	2022/12/21	1		2022/12/21	2022/12/21	1		2022/12/21	2022/12/21	1		2022/12/21	2022/12/21	1	
VN05	1st	2023/2/15	2023/2/15	1	1			NA				NA				NA	
	2nd	2023/2/16	2023/2/16	1													

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

[*1], Analysis dates were revised from the original submission by NC.

4.3.7 Detection limit and quantification limit

From the 21st project, detection limit and quantification limit for Ex-base cations were to be reported. All laboratories which analyzed Ex-base cations reported these values (Table 4.9). The range of detection limits for Ex-Ca, Ex-Mg, Ex-K and Ex-Na were 0.00-0.073, 0.001-0.076, 0.00-0.04, and 0.00-0.72 mg/L, respectively. Similarly, the range of quantification limits for Ex-Ca, Ex-Mg, Ex-K and Ex-Na were 0.01-0.242, 0.003-0.254, 0.01-0.12, 0.01-2.41 mg/L, respectively. Figure 4.3 shows the comparison between these two limit values and concentrations of soil extracts. For almost all analyzed items and laboratories, except for Na in PH01, concentrations of soil extracts were much higher than the quantification limit by one digit, suggesting 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
ID04	0.00	0.01	mg/L	0.001	0.003	mg/L	0.00	0.01	mg/L	0.00	0.01	mg/L
MN01	-	-	-	-	-	-	-	-	-	-	-	-
PH01	0.03	0.08	mg/L	0.01	0.04	mg/L	0.02	0.05	mg/L	0.72	2.41	mg/L
VN01	0.06	0.18	mg/L	0.03	0.09	mg/L	0.04	0.12	mg/L	0.02	0.06	mg/L
VN02	-	-	-	-	-	-	-	-	-	-	-	-
VN04	0.073	0.242	mg/L	0.076	0.254	mg/L	0.015	0.05	mg/L	0.015	0.05	mg/L
VN05	-	-	-	-	-	-	-	-	-	-	-	-

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

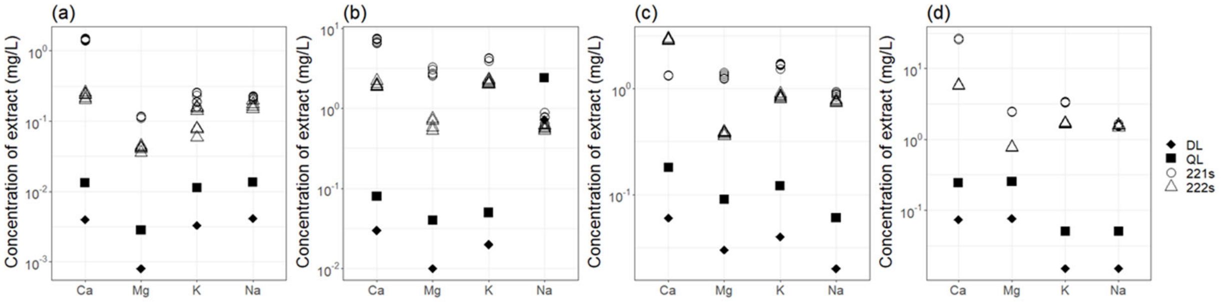


Figure 4.3 Detection limit, quantification limit and concentrations of soil extracts

(a) ID04, (b) PH01, (c) VN01, (d) VN04

DL, detection limit; QL, quantification limit

4.4 Needs for improvement of soil analysis

Figure 4.4 shows the change of outlier ratio in all properties and laboratories from 2002 to 2022. Although the ratio decreased from first experiment in 2002, this is still high (10-25% from 2003 to 2021). Both outlier ratios for 221s and 222s (2021a and b, respectively) were higher than the average outlier ratio from 2003 to 2021, which was even higher than 25%. Outliers may disturb evaluation and understanding of actual monitoring data. For inter-laboratory comparison project on soil, a decrease in the outliers is most important task in near future. Appropriate standard solution, extraction solution, dilution rate and calculation should be checked to reduce extremely different values considered as outliers.

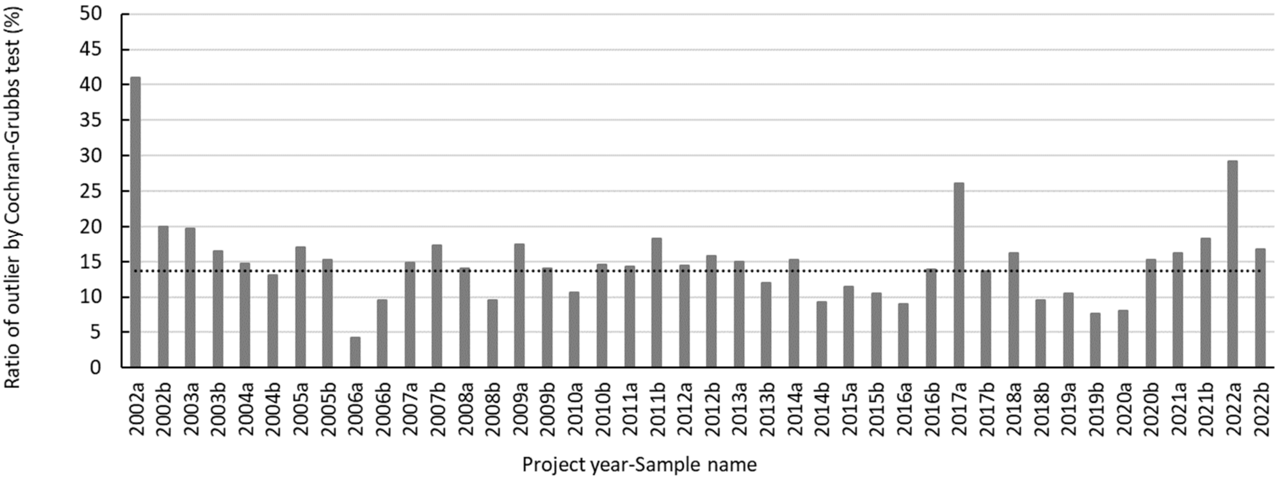


Figure 4.4 Change of the outlier ratio in all properties and laboratories from 2002 to 2022 calculated by {(*N* of entire dataset) – (*N* of verified dataset)} / (*N* of entire dataset).

'a' and 'b' show the 2 kinds of the samples in each year (*e.g.,* 221s and 222s).

The ratios from 2002 to 2021 were from *Report of Inter-Laboratory Comparison Project 2000-2020* (https://monitoring.eanet.asia/document/public/index).

Dotted line represents the average outlier ratio from 2003 to 2021.

4.5 Recommendations for improvement

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

References

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

Appendix Table 4.1 Results submitted by the laboratories (sample No. 221s)

Lab	pH(H_2O)			pH(KCl)			Ex-Ca ($\mathrm{cmol_c\,kg^{-1}}$)			Ex-Mg ($\mathrm{cmol_c\,kg^{-1}}$)			Ex-K ($\mathrm{cmol_c\,kg^{-1}}$)			Ex-Na ($\mathrm{cmol_c\,kg^{-1}}$)			Ex-Acidity ($\mathrm{cmol_c\,kg^{-1}}$)			Ex-Al ($\mathrm{cmol_c\,kg^{-1}}$)			Ex-H ($\mathrm{cmol_c\,kg^{-1}}$)		
	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
ID04	4.8	4.8	4.8	4.2	4.2	4.2	1.54	1.57	1.57	0.20	0.20	0.20	0.10	0.10	0.10	0.20	0.19	0.20	2.70	2.71	2.71	1.91	1.92	1.92	0.80	0.79	0.78
	(0.0)	(0.0)	4.8	(0.0)	(0.0)	4.2	(0.04)	(0.02)	1.60	(0.00)	(0.00)	0.19	(0.01)	(0.01)	0.09	(0.01)	(0.01)	0.19	(0.05)	(0.00)	2.71	(0.06)	(0.01)	1.92	(0.04)	(0.01)	0.78
			4.8			4.2			1.55			0.20			0.10			0.19			2.71			1.90			0.81
		4.8	4.8		4.2	4.2		1.50	1.53		0.20	0.20		0.10	0.10		0.20	0.19		2.70	2.69		1.90	1.95		0.80	0.74
		(0.0)	4.8		(0.0)	4.2		(0.02)	1.50		(0.01)	0.19		(0.01)	0.09		(0.00)	0.20		(0.08)	2.78		(0.09)	1.95		(0.06)	0.83
			4.8			4.2			1.48			0.20			0.10			0.20			2.63			1.79			0.84
MN01	4.7	4.7	4.8	4.4	4.4	4.4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	5.46	5.46	5.46	3.78	3.78	3.78	1.68	1.68	1.68
	(0.0)	(0.0)	4.7	(0.0)	(0.0)	4.4			NA			NA			NA			NA	(0.00)	(0.00)	5.46	(0.00)	(0.00)	3.78	(0.00)	(0.00)	1.68
			4.7			4.3			NA			NA			NA			NA			5.46			3.78			1.68
		4.7	4.7		4.4	4.4		NA	NA		NA	NA		NA	NA		NA	NA		5.46	5.46		3.78	3.78		1.68	1.68
		(0.0)	4.7		(0.0)	4.4			NA			NA			NA			NA		(0.00)	5.46		(0.00)	3.78		(0.00)	1.68
			4.7			4.4			NA			NA			NA			NA			5.46			3.78			1.68
PH01	5.0	4.8	4.8	4.2	4.1	4.0	1.46	1.52	1.50	0.26	0.28	0.29	0.10	0.09	0.09	0.04	0.04	0.04	2.46	2.40	2.48	1.85	1.77	1.90	0.54	0.58	0.45
	(0.1)	(0.1)	4.9	(0.2)	(0.1)	4.1	(0.07)	(0.03)	1.51	(0.03)	(0.01)	0.27	(0.01)	(0.01)	0.09	(0.00)	(0.01)	0.04	(0.08)	(0.07)	2.37	(0.14)	(0.12)	1.70	(0.15)	(0.11)	0.64
			4.8			4.1			1.55			0.28			0.08			0.03			2.36			1.70			0.64
		5.1	5.0		4.4	4.4		1.40	1.44		0.23	0.23		0.11	0.11		0.04	0.04		2.51	2.48		1.94	1.87		0.50	0.50
		(0.0)	5.1		(0.0)	4.4		(0.04)	1.36		(0.01)	0.22		(0.01)	0.10		(0.00)	0.04		(0.06)	2.58		(0.12)	2.07		(0.20)	0.30
			5.1			4.4			1.40			0.24			0.11			0.04			2.48			1.87			0.70
VN01	4.6	4.6	4.6	4.2	4.2	4.2	1.40	1.41	1.41	0.23	0.23	0.22	0.09	0.09	0.09	0.08	0.08	0.08	2.84	2.83	2.84	2.50	2.49	2.46	0.43	0.44	0.42
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.2	(0.01)	(0.01)	1.40	(0.01)	(0.02)	0.25	(0.00)	(0.00)	0.08	(0.00)	(0.00)	0.08	(0.03)	(0.02)	2.81	(0.03)	(0.02)	2.50	(0.01)	(0.01)	0.45
			4.6			4.2			1.42			0.22			0.09			0.09			2.83			2.50			0.45
		4.6	4.6		4.2	4.2		1.40	1.41		0.23	0.23		0.09	0.09		0.08	0.08		2.86	2.86		2.52	2.54		0.43	0.42
		(0.0)	4.6		(0.0)	4.2		(0.01)	1.40		(0.01)	0.22		(0.00)	0.09		(0.00)	0.08		(0.02)	2.88		(0.02)	2.50		(0.01)	0.45
			4.6			4.2			1.39			0.24			0.09			0.08			2.84			2.50			0.42
VN02	4.6	4.6	4.6	4.2	4.2	4.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.93	2.93	2.90	2.57	2.57	2.53	0.42	0.42	0.42
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.2			NA			NA			NA			NA	(0.03)	(0.03)	2.95	(0.05)	(0.06)	2.53	(0.00)	(0.00)	0.42
			4.6			4.2			NA			NA			NA			NA			2.95			2.64			0.42
		4.6	4.6		4.2	4.2		NA	NA		NA	NA		NA	NA		NA	NA		2.93	2.90		2.57	2.53		0.42	0.42
		(0.0)	4.6		(0.0)	4.2			NA			NA			NA			NA		(0.03)	2.95		(0.06)	2.53		(0.00)	0.42
			4.6			4.2			NA			NA			NA			NA			2.95			2.64			0.42
VN04	4.7	4.7	4.7	4.2	4.2	4.2	1.40	1.42	1.42	0.22	0.22	0.21	0.09	0.09	0.09	0.07	0.07	0.07	2.72	2.72	2.72	2.44	2.44	2.43	0.44	0.45	0.45
	(0.0)	(0.0)	4.7	(0.0)	(0.0)	4.2	(0.03)	(0.00)	1.42	(0.00)	(0.00)	0.22	(0.00)	(0.00)	0.09	(0.00)	(0.00)	0.07	(0.01)	(0.01)	2.72	(0.01)	(0.01)	2.45	(0.01)	(0.00)	0.45
			4.7			4.2			1.42			0.22			0.09			0.07			2.73			2.43			0.45
		4.7	4.7		4.2	4.2		1.38	1.39		0.22	0.22		0.09	0.09		0.07	0.07		2.72	2.73		2.44	2.45		0.44	0.45
		(0.0)	4.7		(0.0)	4.2		(0.01)	1.37		(0.00)	0.22		(0.00)	0.09		(0.00)	0.07		(0.01)	2.72		(0.01)	2.43		(0.01)	0.45
			4.7			4.2			1.36			0.22			0.09			0.08			2.72			2.45			0.43
VN05	4.5	4.5	4.5	4.1	4.1	4.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	(0.0)	(0.0)	4.5	(0.0)	(0.0)	4.1			NA			NA			NA			NA			NA			NA			NA
			4.6			4.1			NA			NA			NA			NA			NA			NA			NA
		4.6	4.5		4.1	4.1		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA
		(0.0)	4.5		(0.0)	4.1			NA			NA			NA			NA			NA			NA			NA
			4.6			4.1			NA			NA			NA			NA			NA			NA			NA

Appendix Table 4.2 Results submitted by the laboratories (sample No. 222s)

Lab	pH(H_2O)			pH(KCl)			Ex-Ca (cmol$_c$ kg^{-1})			Ex-Mg (cmol$_c$ kg^{-1})			Ex-K (cmol$_c$ kg^{-1})			Ex-Na (cmol$_c$ kg^{-1})			Ex-Acidity (cmol$_c$ kg^{-1})			Ex-Al (cmol$_c$ kg^{-1})			Ex-H (cmol$_c$ 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
ID04	4.3	4.3	4.3	4.0	4.0	4.1	0.24	0.25	0.27	0.07	0.07	0.07	0.04	0.04	0.04	0.15	0.15	0.16	3.80	3.74	3.74	3.03	3.03	3.02	0.76	0.71	0.72
	(0.0)	(0.0)	4.3	(0.0)	(0.0)	4.1	(0.02)	(0.01)	0.24	(0.00)	(0.00)	0.07	(0.01)	(0.01)	0.04	(0.01)	(0.01)	0.13	(0.07)	(0.02)	3.72	(0.03)	(0.02)	3.02	(0.06)	(0.01)	0.70
			4.3			4.0			0.25			0.06			0.05			0.16			3.76			3.06			0.70
		4.3	4.3		4.0	4.1		0.22	0.24		0.07	0.07		0.04	0.03		0.15	0.13		3.85	3.86		3.03	3.06		0.82	0.80
		(0.0)	4.3		(0.0)	4.0		(0.02)	0.21		(0.01)	0.06		(0.01)	0.04		(0.02)	0.15		(0.07)	3.92		(0.05)	3.06		(0.03)	0.86
			4.3			4.0			0.22			0.07			0.04			0.17			3.78			2.98			0.80
MN01	4.3	4.3	4.2	4.1	4.1	4.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	6.18	6.18	6.18	4.12	4.12	4.12	2.06	2.06	2.06
	(0.0)	(0.0)	4.3	(0.0)	(0.0)	4.1			NA			NA			NA			NA	(0.00)	(0.00)	6.18	(0.00)	(0.00)	4.12	(0.00)	(0.00)	2.06
			4.3			4.1			NA			NA			NA			NA			6.18			4.12			2.06
		4.3	4.3		4.1	4.1		NA	NA		NA	NA		NA	NA		NA	NA		6.18	6.18		4.12	4.12		2.06	2.06
		(0.0)	4.3		(0.0)	4.1			NA			NA			NA			NA		(0.00)	6.18		(0.00)	4.12		(0.00)	2.06
			4.3			4.1			NA			NA			NA			NA			6.18			4.12			2.06
PH01	4.6	4.5	4.6	3.9	3.8	3.8	0.11	0.10	0.10	0.06	0.07	0.07	0.04	0.03	0.03	0.03	0.03	0.03	4.09	4.01	4.04	3.48	3.35	3.41	0.39	0.36	0.30
	(0.2)	(0.1)	4.4	(0.2)	(0.1)	3.8	(0.01)	(0.00)	0.10	(0.01)	(0.00)	0.07	(0.01)	(0.01)	0.03	(0.00)	(0.00)	0.03	(0.09)	(0.03)	3.99	(0.17)	(0.11)	3.42	(0.15)	(0.11)	0.30
			4.5			3.7			0.10			0.07			0.04			0.03			3.99			3.22			0.49
		4.8	4.7		4.1	4.1		0.11	0.11		0.06	0.06		0.05	0.05		0.03	0.03		4.17	4.15		3.60	3.74		0.42	0.22
		(0.0)	4.8		(0.0)	4.1		(0.01)	0.12		(0.01)	0.06		(0.01)	0.06		(0.00)	0.03		(0.03)	4.20		(0.12)	3.53		(0.20)	0.62
			4.8			4.1			0.11			0.05			0.05			0.03			4.15			3.53			0.43
VN01	4.3	4.3	4.3	4.0	4.0	4.0	0.30	0.29	0.30	0.06	0.06	0.07	0.04	0.04	0.05	0.07	0.07	0.07	3.92	3.92	3.93	3.47	3.46	3.42	0.59	0.59	0.58
	(0.0)	(0.0)	4.3	(0.0)	(0.0)	4.0	(0.01)	(0.00)	0.29	(0.00)	(0.00)	0.06	(0.00)	(0.00)	0.04	(0.00)	(0.00)	0.07	(0.02)	(0.02)	3.91	(0.04)	(0.04)	3.46	(0.02)	(0.02)	0.58
			4.3			4.0			0.29			0.07			0.04			0.07			3.90			3.50			0.62
		4.3	4.3		4.0	4.0		0.30	0.30		0.06	0.06		0.04	0.04		0.07	0.07		3.93	3.91		3.49	3.46		0.59	0.58
		(0.0)	4.3		(0.0)	4.0		(0.01)	0.29		(0.00)	0.06		(0.00)	0.04		(0.00)	0.07		(0.02)	3.92		(0.05)	3.54		(0.01)	0.60
			4.3			3.9			0.31			0.07			0.05			0.07			3.94			3.46			0.60
VN02	4.3	4.3	4.3	3.9	3.9	3.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	4.00	4.01	4.01	3.63	3.63	3.60	0.48	0.48	0.51
	(0.0)	(0.0)	4.3	(0.0)	(0.0)	4.0			NA			NA			NA			NA	(0.02)	(0.00)	4.01	(0.05)	(0.06)	3.60	(0.05)	(0.06)	0.51
			4.3			3.9			NA			NA			NA			NA			4.01			3.70			0.41
		4.3	4.3		3.9	3.9		NA	NA		NA	NA		NA	NA		NA	NA		3.99	4.01		3.63	3.60		0.48	0.51
		(0.0)	4.3		(0.0)	3.9			NA			NA			NA			NA		(0.03)	4.01		(0.06)	3.60		(0.06)	0.51
			4.3			4.0			NA			NA			NA			NA			3.96			3.70			0.41
VN04	4.3	4.3	4.3	4.0	4.0	4.0	0.30	0.30	0.30	0.07	0.07	0.07	0.04	0.04	0.04	0.07	0.07	0.07	3.88	3.88	3.88	3.34	3.34	3.35	0.58	0.58	0.56
	(0.0)	(0.0)	4.2	(0.0)	(0.0)	4.0	(0.00)	(0.00)	0.30	(0.00)	(0.00)	0.07	(0.00)	(0.00)	0.04	(0.00)	(0.00)	0.07	(0.01)	(0.01)	3.88	(0.01)	(0.01)	3.33	(0.02)	(0.02)	0.60
			4.3			4.0			0.30			0.07			0.04			0.07			3.89			3.35			0.58
		4.3	4.3		4.0	4.0		0.30	0.30		0.07	0.07		0.04	0.04		0.07	0.07		3.88	3.89		3.34	3.35		0.58	0.56
		(0.0)	4.3		(0.0)	3.9		(0.00)	0.29		(0.00)	0.07		(0.00)	0.04		(0.00)	0.07		(0.01)	3.88		(0.01)	3.33		(0.02)	0.58
			4.3			4.0			0.30			0.07			0.05			0.07			3.88			3.33			0.60
VN05	4.2	4.2	4.2	3.8	3.8	3.8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	(0.0)	(0.0)	4.2	(0.0)	(0.0)	3.8			NA			NA			NA			NA			NA			NA			NA
			4.2			3.8			NA			NA			NA			NA			NA			NA			NA
		4.2	4.2		3.8	3.8		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA
		(0.0)	4.2		(0.0)	3.8			NA			NA			NA			NA			NA			NA			NA
			4.2			3.8			NA			NA			NA			NA			NA			NA			NA

5. 23rd 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

In the 23rd Project, the NC shipped an artificial inland water sample to 21 laboratories involved in the EANET activities on October 21, 2022, and most of them submitted their analytical data to the NC by February 28 2023. Participating laboratories and their identification codes are listed in Table 1.1.

5.2.2 Description of Sample

A description of the sample is given in Table 5.1.

Table 5.1 Description of the artificial inland water sample

Name	Amount of the sample	Container	Number of samples	Note
Artificial inland water sample	Approximately 1 L	Poly-ethylene bottle 1 L	One bottle	To analyze directly

The analytical parameters are shown in Table 5.2.

Table 5.2 Analytical parameters

Analytical Parameter	Reporting Units	
pH	pH units	–
EC	milli siemens per meter	$mS\ m^{-1}$
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^-	Ion Chromatography or Titration
Na^+ K^+ Ca^{2+} Mg^{2+}	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
NH_4^+	Ion Chromatography or Spectrophotometry (Indophenol blue)

5.2.4 Data Checking Procedures

a) Calculation of ion balance (R_1)

(1) Total anion equivalent concentration (A [μeq L^{-1}]) was calculated by summing the concentrations of all anions (c [μmol L^{-1}]) and alkalinity (*ALK*: μeq L^{-1}). Alkalinity was considered to be corresponded to bicarbonate ions (HCO_3^-).

$$\mathbf{A}\ [\mu eq\ L^{-1}] = \sum n\ c_{Ai}\ [\mu mol\ L^{-1}] = 2c\ (SO_4^{2-}) + c\ (NO_3^-) + c\ (Cl^-) + (ALK)$$

n, c_{Ai} : electric charge and concentration [μmol L^{-1}] of anion "i".

(2) Total cation equivalent concentration (**C** [μeq L^{-1}]) was calculated by summing the concentrations of all cations (c [μmol L^{-1}]).

$$\mathbf{C}\ [\mu eq\ L^{-1}] = \sum n\ c_{Ci}\ [\mu mol\ L^{-1}] = 10^{(6-pH)} + c\ (NH_4^+) + c\ (Na^+) + c\ (K^+) + 2c\ (Ca^{2+}) + 2c\ (Mg^{2+})$$

n, c_{Ci} : electric charge and concentration [μmol L^{-1}] of cation "i".

(3) Calculation of ion balance (R_1)

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

(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

$(C+A)$ [μeq 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 (Λcalc) is calculated as follows;

$$\Lambda\text{calc (mS m}^{-1}) = \{349.7\times10^{(6-\text{pH})} + 80.0\times2C(\text{SO}_4^{2-}) + 71.4\times C(\text{NO}_3^-) + 76.3\times C(\text{Cl}^-) + 73.5\times C(\text{NH}_4^+) + 50.1\times C(\text{Na}^+) + 73.5\times C(\text{K}^+) + 59.8\times2C(\text{Ca}^{2+}) + 53.0\times2C(\text{Mg}^{2+}) + 44.5\times(ALK)\}/10000$$

C: Molar concentrations [μmol 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 (Λcalc) to measurements (Λmeas) in electric conductivity is calculated as follows;

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

Λ 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

Λmeas[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	7.02	6.79	0.29	20	6.10	7.24
EC (mS m^{-1})	3.93	3.74	0.12	20	3.57	3.94
Alkalinity (meq L^{-1})	0.132	0.130	0.02	19	0.080	0.144
SO_4^{2-} (mg L^{-1})	5.58	5.59	0.19	20	5.22	6.00
NO_3^- (mg L^{-1})	0.68	0.65	0.04	19	0.59	0.77
Cl^- (mg L^{-1})	2.37	2.31	0.05	19	2.18	2.42
Na^+ (mg L^{-1})	3.04	3.05	0.22	20	2.62	3.79
K^+ (mg L^{-1})	0.60	0.57	0.04	19	0.51	0.64
Ca^{2+} (mg L^{-1})	1.94	1.96	0.11	19	1.74	2.20
Mg^{2+} (mg L^{-1})	0.73	0.72	0.04	19	0.64	0.78
NH_4^+ (mg L^{-1})	0.35	0.29	0.07	20	0.09	0.37

(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 ±15% but not ±30%, and the flag X is given to the value in the case that its deviation exceeds ±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	0	0	1	0	1	0	1	2	0	0	3	8	3.6%
X	0	0	2	0	0	1	0	1	1	1	2	8	3.6%
Data within DQOs	20	20	17	20	19	19	19	17	19	19	15	204	92.7%
Flagged(%)	0.0	0.0	15.0	0.0	5.0	5.0	5.0	15.0	5.0	5.0	25.0	7.3	

Flag E: 15% < |Deviation| ≦ 30%
Flag X: 30% < |Deviation|

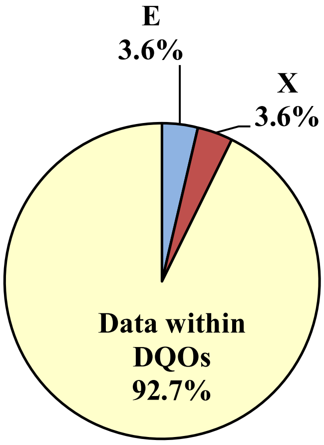


Figure 5.1 Percentage of flagged data

The data flagged by "E" shared 3.6% of all reported data, and the data flagged by "X" shared 3.6% of all reported data of samples. The NH_4^+ results were flagged most (E and X), and their percentage was 25.0%.

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

Table 5.9 Number of flagged data in each laboratory

Number of flagged data	Number of laboratories	Ratio
0	13	65%
1	3	15%
2	1	5%
3	2	10%
4	0	0%
5	1	5%
6	0	0%
7	0	0%
8	0	0%
9	0	0%
Total	20	100%

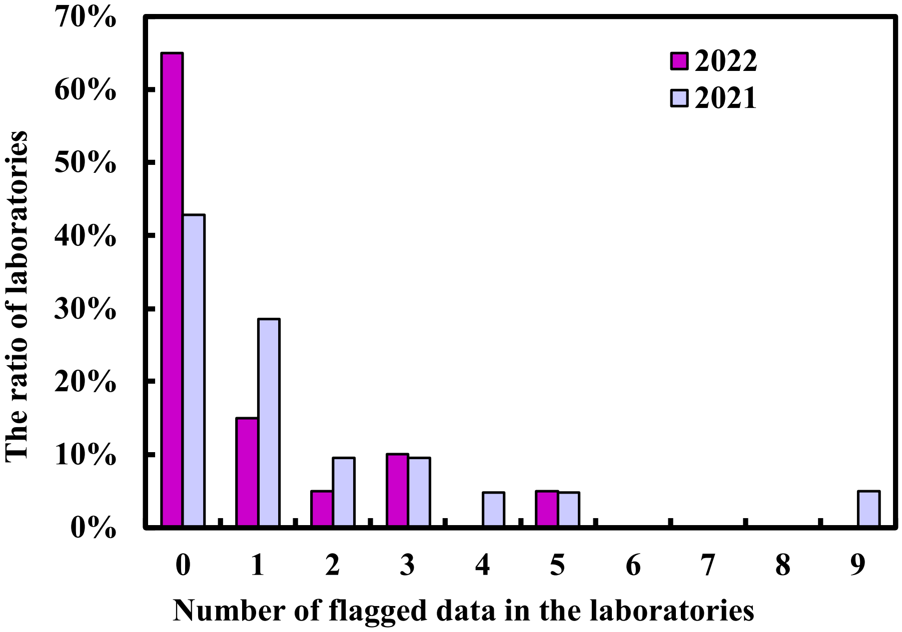


Figure 5.2 Distribution of laboratories with the number of flagged data

The percentage of the laboratories without flagged data was 65% in this attempt, while that in the last attempt (2021) was 43%. The maximum number of flagged data was five, which was submitted by one laboratory.

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

Table 5.10 Analytical Results of Sample No.221i (artificial inland aquatic environment sample : EANET in 2022)

Lab. ID	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	R1	R2
	-	mS m^{-1}	meq L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	%	%
CN01	7.01	3.90	0.136	5.75	0.67	2.42	3.21	0.62	1.98	0.72	0.32	-0.51	1.48
CN02	7.05	3.87	0.134	5.42	0.68	2.32	3.01	0.60	1.95	0.72	0.31	-0.51	-0.02
CN03	7.04	3.86	0.138	5.61	0.66	2.32	3.00	0.60	1.92	0.71	0.30	-2.18	0.52
CN04	6.97	3.89	0.132	5.59	0.64	2.38	2.99	0.59	1.97	0.73	0.33	-0.71	0.28
JP03	7.09	3.78	0.144	5.48	0.65	2.29	2.98	0.60	2.09	0.74	0.34	-0.61	2.44
JP04	7.03	3.81	0.140	5.59	0.67	2.34	2.94	0.59	1.96	0.71	0.32	-2.41	1.41
LA01	6.50	3.57	0.290 X	5.88	0.84 E	2.29	3.02	0.55	2.00	0.69	0.10 X	-22.92 I	12.35 C
MY01	6.88	3.63	0.139	5.62	0.62	2.33	2.99	0.57	1.97	0.69	0.31	-2.21	3.73
MN01	6.55	3.67	0.142	5.75	0.77	2.33	3.24	0.57	2.18	0.77	0.37	1.21	6.06
PH01	6.82	3.85	0.117	5.58	0.69	2.28	2.90	0.64	1.94	0.72	0.34	1.36	-0.45
PH02	6.48	3.74	0.080 X	5.29	0.62	2.28	3.79 E	0.59	2.20	0.78	0.09 X	15.22 I	0.63
RU01	7.08	3.94	0.117	5.56	0.61	2.28	2.62	0.52	2.72 X	0.67	0.32	4.43	-0.28
RU02	7.24	3.88	0.109 E	6.00	0.61	3.82 X	3.04	0.91 X	1.85	1.01 X	0.28 E	-0.71	5.35
TH01	7.03	3.63	0.144	5.62	0.64	2.34	3.09	0.52	2.03	0.71	0.28 E	-2.26	4.37
TH02	6.10	3.67	0.135	5.58	0.61	2.28	2.85	0.51 E	1.74	0.64	0.28 E	-5.13	1.08
VN01	6.59	3.61	0.135	5.39	0.66	2.27	3.05	0.58	1.90	0.75	0.32	0.07	3.49
VN02	6.60	3.60	0.135	5.47	0.67	2.34	3.08	0.59	1.92	0.76	0.32	-0.08	4.24
VN03	6.58	3.63	0.123	5.65	0.59	2.30	3.07	0.51 E	1.88	0.71	0.32	0.33	2.69
VN04	6.60	3.62	0.136	5.22	0.64	2.18	3.00	0.57	1.88	0.76	0.31	0.46	2.53
VN05	6.57	3.70	0.131	5.72	0.62	2.26	3.08	0.54	1.90	0.71	0.33	-0.70	2.47
Expected value	7.02	3.93	0.132	5.58	0.68	2.37	3.04	0.60	1.94	0.73	0.35	-	-

Flag E: 15% < |Deviation| ≦ 30%

Flag X: 30% < |Deviation|

I: Poor ion balance (R1)

C: Rich Conductivity agreement (R2)

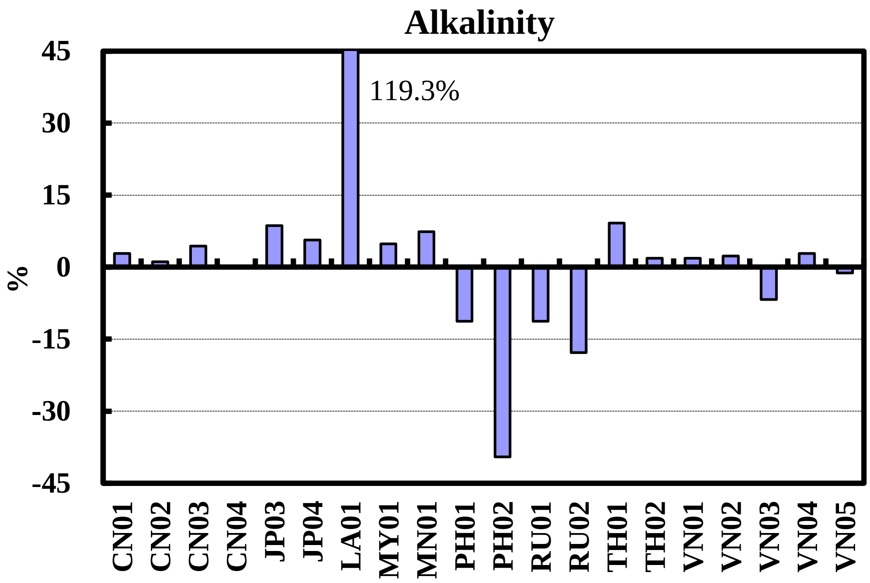


Figure 5.5 Distribution of results for alkalinity (normalized by prepared concentration)

Data of Alkalinity from 3 laboratories were flagged. The number of flagged data of alkalinity was 2 in the last attempt (2021).

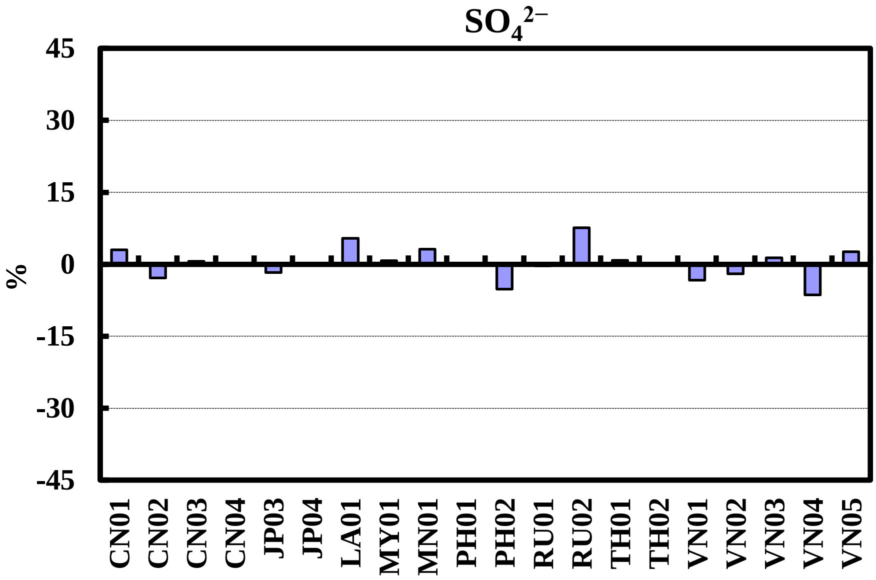


Figure 5.6 Distribution of results for SO_4^{2-} (normalized by prepared concentration)

All the submitted data of SO_4^{2-} were within DQOs.

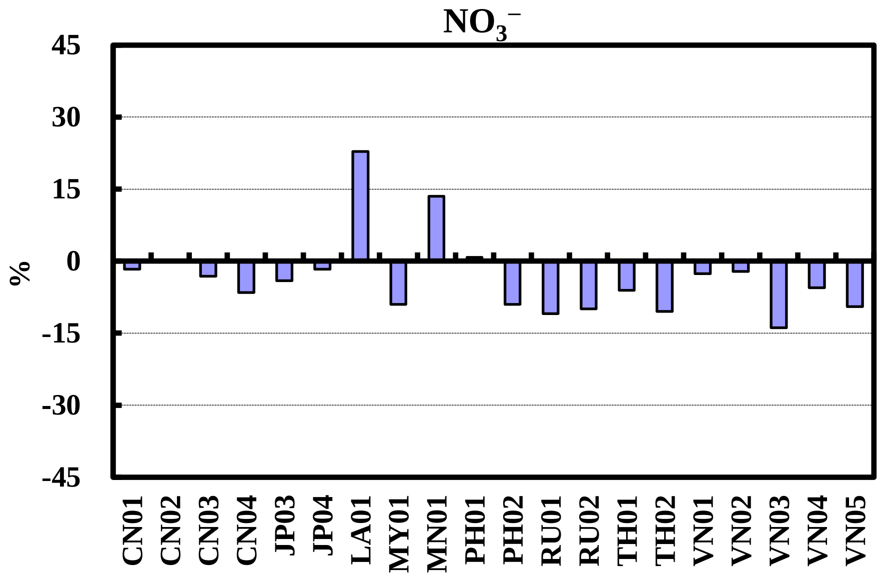


Figure 5.7 Distribution of results for NO_3^- (normalized by prepared concentration)

Except for LA01, all the submitted data of NO_3^- were within DQOs.

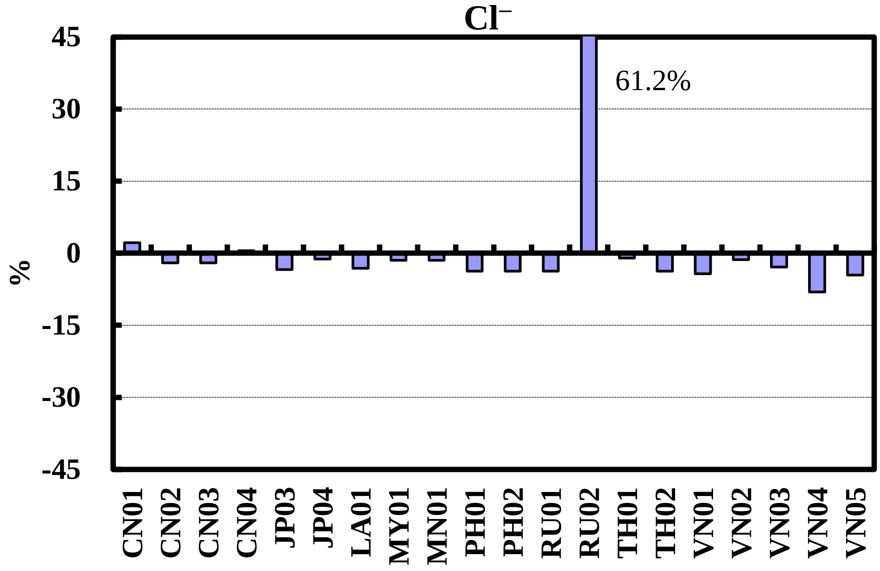


Figure 5.8 Distribution of results for Cl^- (normalized by prepared concentration)

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

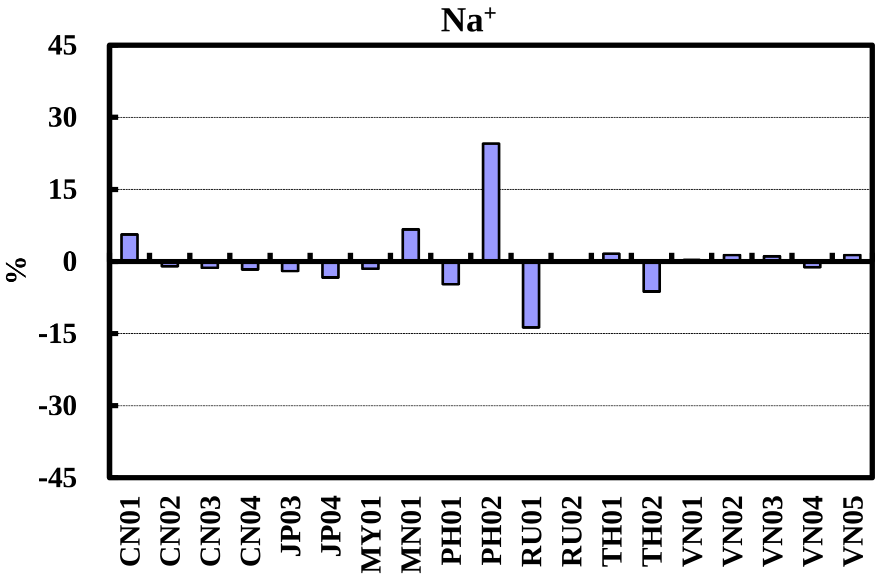


Figure 5.9 Distribution of results for Na$^+$ (normalized by prepared concentration)

Except for PH02, all the submitted data of Na$^+$ were within DQOs.

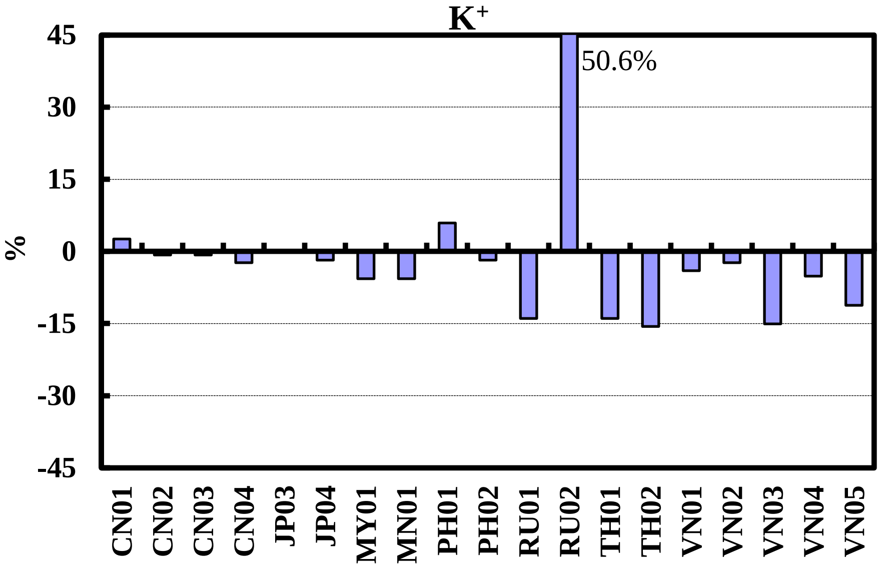


Figure 5.10 Distribution of results for K$^+$ (normalized by prepared concentration)

Except for RU02, TH02 and VN03, all the submitted data of K$^+$ were within DQOs.

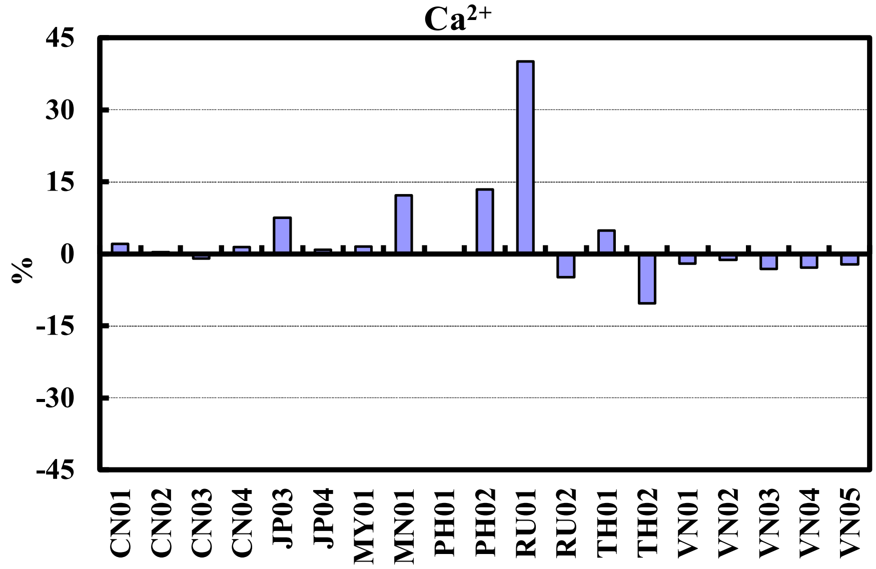


Figure 5.11 Distribution of results for Ca^{2+} (normalized by prepared concentration)

Except for RU01, all the submitted data of Ca^{2+} were within DQOs.

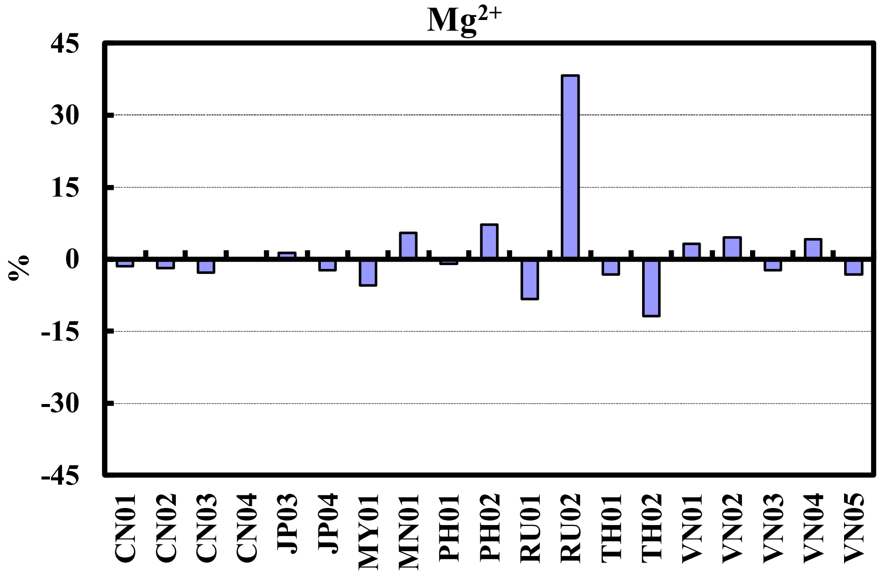


Figure 5.12 Distribution of results for Mg^{2+} (normalized by prepared concentration)

Except for RU02, all the submitted data of Mg^{2+} were within DQOs.

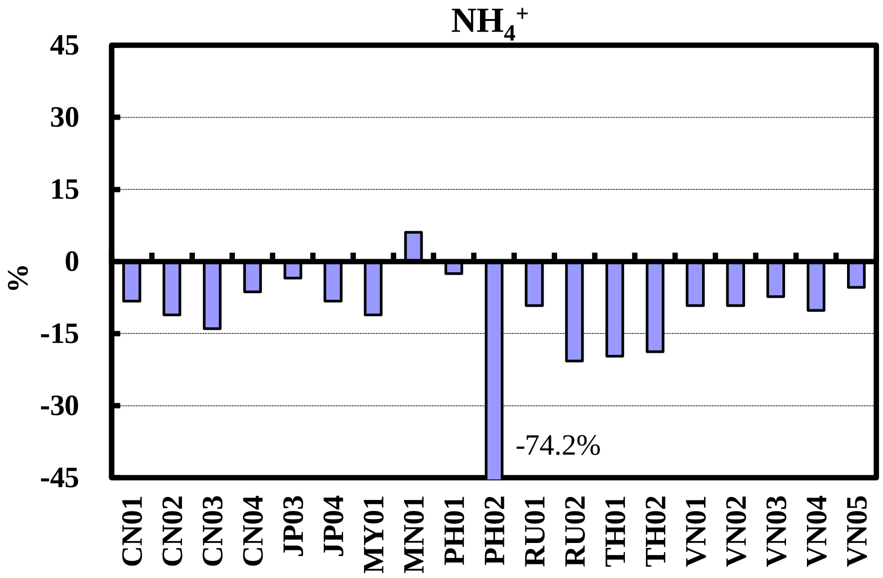


Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

Data of NH_4^+ from 4 laboratories were flagged. The number of flagged data of NH_4^+ was 8 in the last attempt(2021). Among 20 participating laboratories, 16 laboratories used ion chromatography, 4 laboratories used spectrophotometry (Indophenol) for the determination of NH_4^+. 4 laboratories with flagged data used ion chromatography, and another 1 laboratory used spectrophotometry (Indophenol) method.

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 (2021).

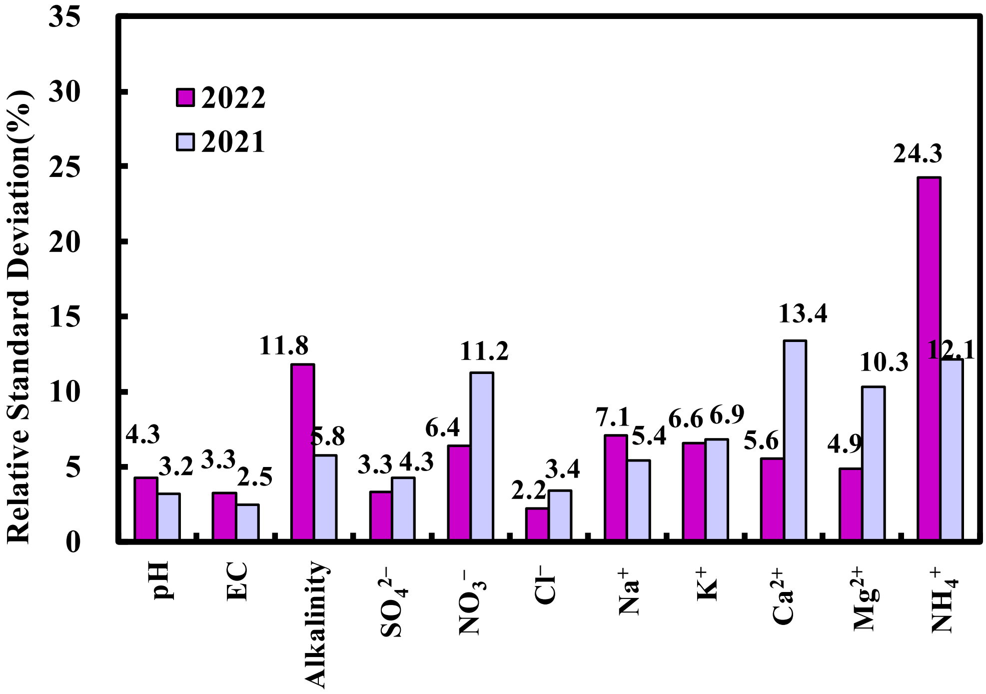


Figure 5.14 Relative standard deviation of each constituent

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

The relative standard deviation (RSD) of NO_3^-, Ca^{2+} and Mg^{2+} in 2022 were particularly lower than the last attempt(2021). On the other hand, the RSDs of Alkalinity and NH_4^+ were particularly increased in this attempt.

5.3.4 Information on laboratories

<u>Methodologies used</u>

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

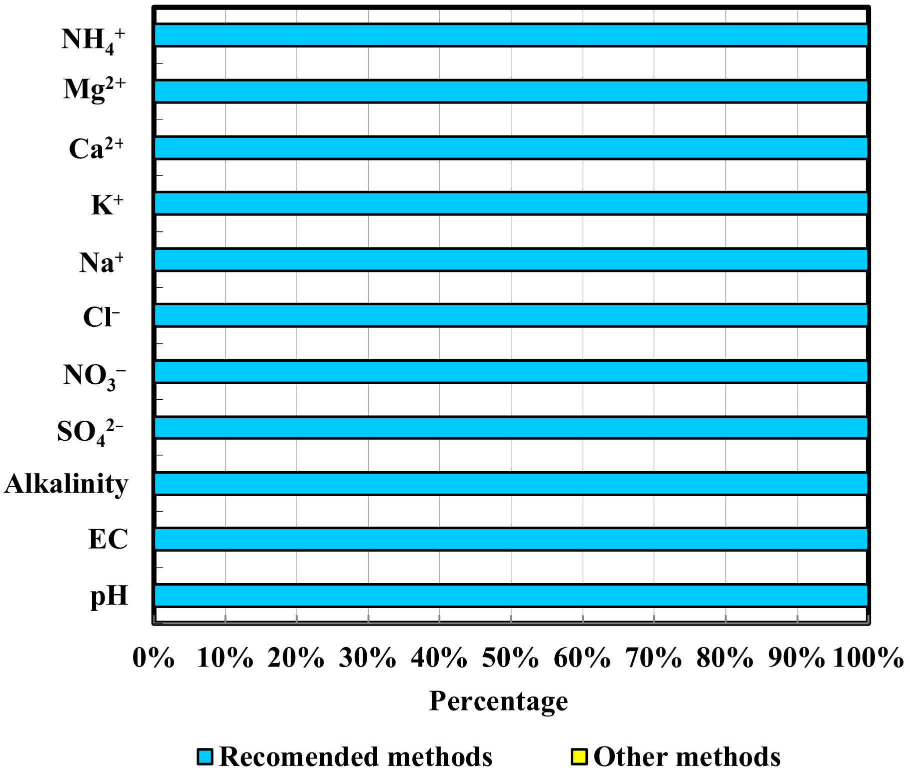


Figure 5.15 Percentage of laboratories using the recommended methods

Table 5.11 List of methods

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

Table 5.12 Analytical methods

Code	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	20										
1		20									
2			20(3)			2(1)					
3							4	4(2)	4(1)	4(1)	
4				18	18(1)	18	16(1)	16(1)	16	16	16(4)
5											
6											
7				2	2						
8											4(1)
9											
10											
Flagged E	0	0	1	0	1	0	1	2	0	0	3
Flagged X	0	0	2	0	0	1	0	1	1	1	2

▨ Recommended methods ☐ Other methods

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

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	1	A	A	A	A	A	A	A	A	A	A	A
CN02	2	A	A	A	B	B	B	B	B	B	B	B
CN03	2	A	A	A	B	B	B	B	B	B	B	B
CN04	1	A	A	A	A	A	A	A	A	A	A	A
JP03	2	A	A	B	B	B	B	B	B	B	B	B
JP04	1	A	A	A	A	A	A	A	A	A	A	A
LA01	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	2	A	A	A	A	A	A	B	B	B	B	A
PH02	2	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,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	2	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B
VN01	2	A	A	A	B	B	B	B	B	B	B	B
VN02	3	A	A	B	C	C	C	C	C	C	C	C
VN03	2	A	A	B	B	A	A	B	B	B	B	A
VN04	2	A	A	B	A	A	A	A	A	A	A	A
VN05	2	A	A	B	B	B	B	B	B	B	B	B

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

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

In many laboratories, 2 or 3 persons analyzed the sample, and usually they shared the works according to the methods such as pH, EC and ionic items.

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

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

Table 5.14 Years of experience

Unit : year

Lab.ID	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
CN01	7	7	7	7	7	7	7	7	7	7	7
CN02	4	4	4	8	8	8	8	8	8	8	8
CN03	10	10	10	1	1	1	1	1	1	1	1
CN04	16	16	16	16	16	16	16	16	16	16	16
JP03	3	3	8	8	8	8	8	8	8	8	8
JP04	12	12	12	12	12	12	12	12	12	12	12
LA01	11	11	11	11	11	11	11	11	11	11	11
MY01	10	10	10	10	10	10	1	1	1	1	1
MN01	21	21	21	24	24	24	24	24	24	24	24
PH01	6	6	6	6	6	6	2	2	2	2	6
PH02	5/1	5/1	5/1	5/1	5/1	5/1	5/1	5/1	5/1	5/1	5/1
RU01	29	29	29	9	9	9	37	37	37	37	29
RU02	17	7	7	35	1	7	17	17	17	17	42
TH01	24	24	24	24	24	24	24	24	24	24	24
TH02	24	24	24	24	24	24	24	24	24	24	24
VN01	6	6	6	9	9	9	9	9	9	9	9
VN02	16	16	18	18	18	18	18	18	18	18	18
VN03	8	8	11	11	8	8	11	11	11	11	8
VN04	19	19	18	19	19	19	19	19	19	19	19
VN05	13	13	18	18	18	18	18	18	18	18	18

▨ 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 22 times, and the results showing the percentage of flagged data and the percentage of data that satisfied the DQOs are shown in Figure 5.16.

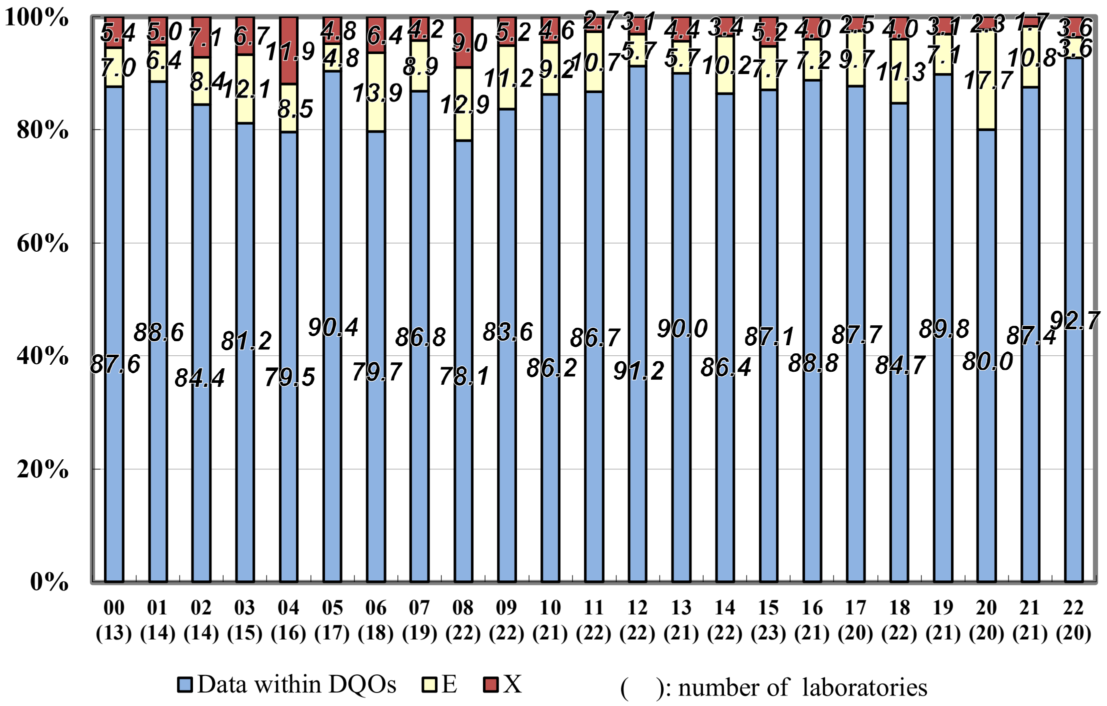


Figure 5.16 Comparison of the results from the inter-laboratory comparison projects

The percentage of data satisfied the DQOs increased from the last attempt (2021).

The values/concentrations for each parameter from the 1st to 23rd projects were compared with the percentage of flagged data in Figure 5.17.

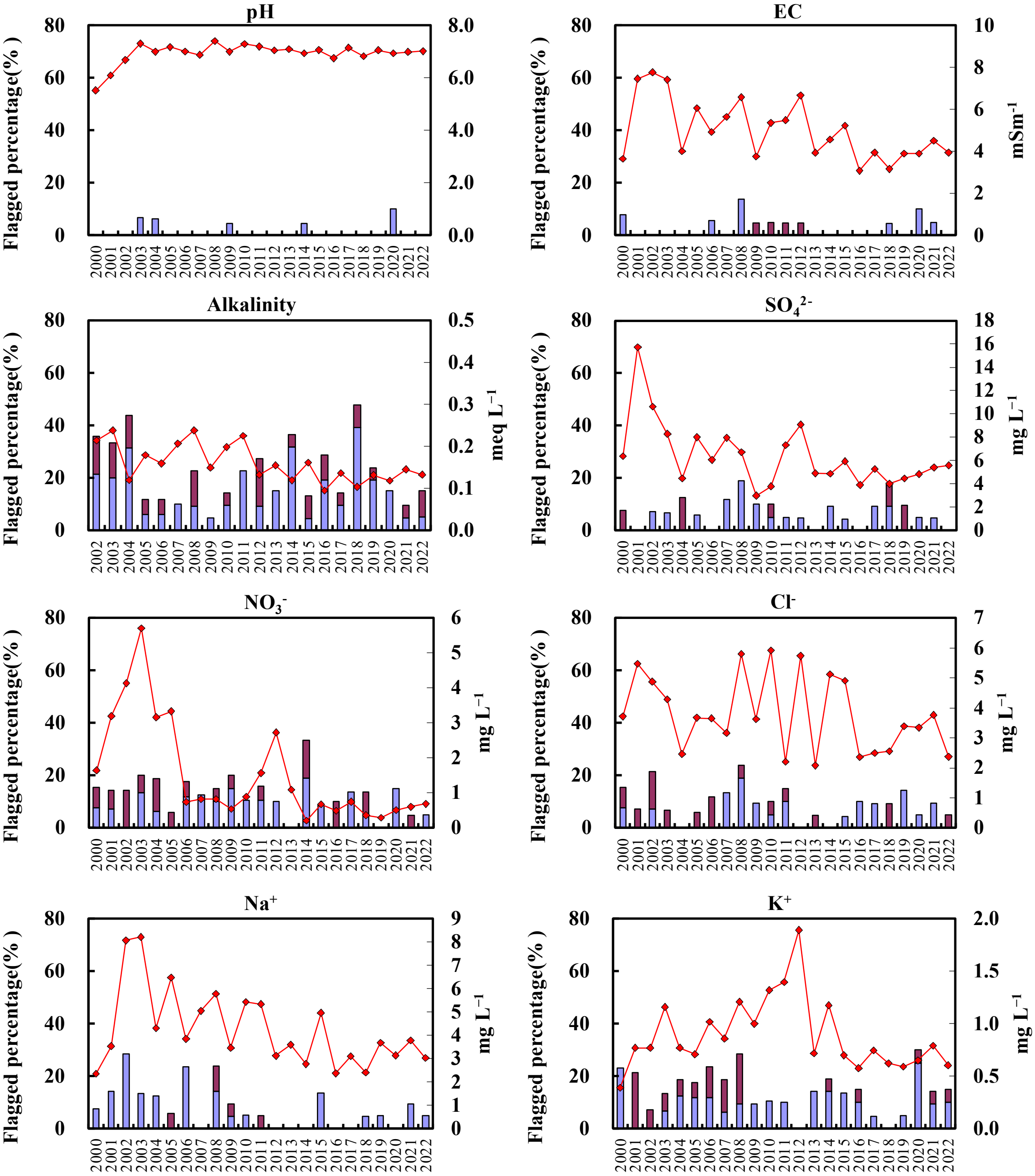
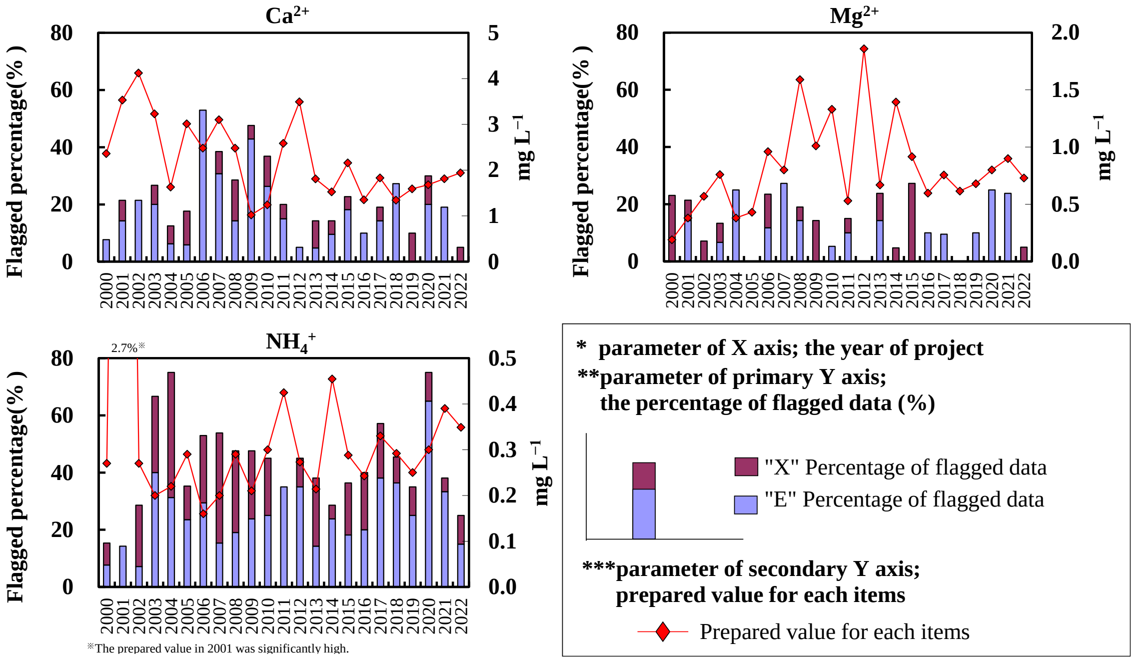


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects



※The prepared value in 2001 was significantly high.

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

There was no flagged data in pH, EC and SO_4^{2-} in this attempt. The analyses of Cl^-, Na^+, Ca^{2+}, Mg^{2+} and NH_4^+ were improved. In this attempt, flagged percentages of Alkalinity became higher than the last attempt.

Furthermore, the percentage of flagged data was larger in NH_4^+ than for other parameters in every survey except for the 1st- 2nd project. Therefore, in the inland water analysis, it is necessary to pay more attention to NH_4^+.

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.

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

Appendix Table 5.1 Results submitted by the laboratories

Lab. ID	pH -	EC (mS m^{-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	7.01	3.90	0.136	5.75	0.67	2.42	3.21	0.62	1.98	0.72	0.32
CN02	7.05	3.87	0.134	5.42	0.68	2.32	3.01	0.60	1.95	0.72	0.31
CN03	7.04	3.86	0.138	5.61	0.66	2.32	3.00	0.60	1.92	0.71	0.30
CN04	6.97	3.89	0.132	5.59	0.64	2.38	2.99	0.59	1.97	0.73	0.33
JP03	7.09	3.78	0.144	5.48	0.65	2.29	2.98	0.60	2.09	0.74	0.34
JP04	7.03	3.81	0.140	5.59	0.67	2.34	2.94	0.59	1.96	0.71	0.32
LA01	6.50	3.57	0.290	5.88	0.84	2.29	3.02	0.55	2.00	0.69	0.10
MY01	6.88	3.63	0.139	5.62	0.62	2.33	2.99	0.57	1.97	0.69	0.31
MN01	6.55	3.67	0.142	5.75	0.77	2.33	3.24	0.57	2.18	0.77	0.37
PH01	6.82	3.85	0.117	5.58	0.69	2.28	2.90	0.64	1.94	0.72	0.34
PH02	6.48	3.74	0.080	5.29	0.62	2.28	3.79	0.59	2.20	0.78	0.09
RU01	7.08	3.94	0.117	5.56	0.61	2.28	2.62	0.52	2.72	0.67	0.32
RU02	7.24	3.88	0.109	6.00	0.61	3.82	3.04	0.91	1.85	1.01	0.28
TH01	7.03	3.63	0.144	5.62	0.64	2.34	3.09	0.52	2.03	0.71	0.28
TH02	6.10	3.67	0.135	5.58	0.61	2.28	2.85	0.51	1.74	0.64	0.28
VN01	6.59	3.61	0.135	5.39	0.66	2.27	3.05	0.58	1.90	0.75	0.32
VN02	6.60	3.60	0.135	5.47	0.67	2.34	3.08	0.59	1.92	0.76	0.32
VN03	6.58	3.63	0.123	5.65	0.59	2.30	3.07	0.51	1.88	0.71	0.32
VN04	6.60	3.62	0.136	5.22	0.64	2.18	3.00	0.57	1.88	0.76	0.31
VN05	6.57	3.70	0.131	5.72	0.62	2.26	3.08	0.54	1.90	0.71	0.33
Expected value	7.02	3.93	0.132	5.58	0.68	2.37	3.04	0.60	1.94	0.73	0.35
Number of data	20	20	20	20	20	20	20	20	20	20	20
Average	6.79	3.74	0.14	5.59	0.66	2.38	3.05	0.59	2.00	0.74	0.29
Minimum	6.10	3.57	0.08	5.22	0.59	2.18	2.62	0.51	1.74	0.64	0.09
Maximum	7.24	3.94	0.29	6.00	0.84	3.82	3.79	0.91	2.72	1.01	0.37

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	-0.1	-0.7	2.8	3.0	-1.7	2.2	5.6	2.6	2.1	-1.4	-8.3
CN02	0.4	-1.4	1.1	-2.8	-0.2	-2.0	-1.0	-0.7	0.4	-1.9	-11.1
CN03	0.3	-1.7	4.4	0.6	-3.1	-2.0	-1.3	-0.7	-1.0	-2.8	-14.0
CN04	-0.7	-0.9	0.1	0.2	-6.5	0.5	-1.6	-2.4	1.4	-0.1	-6.3
JP03	1.0	-3.7	8.6	-1.7	-4.1	-3.4	-2.0	-0.2	7.6	1.3	-3.5
JP04	0.2	-3.0	5.6	0.2	-1.7	-1.2	-3.3	-1.8	0.9	-2.3	-8.3
LA01	-7.4	-9.2	119.3	5.4	22.8	-3.2	-0.7	-9.0	3.0	-5.5	-71.3
MY01	-2.0	-7.6	4.9	0.8	-9.0	-1.5	-1.5	-5.7	1.6	-5.5	-11.1
MN01	-6.7	-6.5	7.4	3.2	13.5	-1.5	6.7	-5.7	12.2	5.4	6.1
PH01	-2.8	-2.0	-11.3	0.1	0.8	-3.7	-4.7	5.9	-0.1	-1.0	-2.5
RU01	0.8	0.3	-11.3	-0.3	-11.0	-3.7	-13.7	-14.0	40.1	-8.3	-9.2
RU02	3.1	-1.2	-17.8	7.6	-10.0	61.2	0.1	50.6	-4.8	38.3	-20.7
TH01	0.1	-7.5	9.1	0.8	-6.1	-1.0	1.6	-14.0	4.8	-3.3	-19.7
TH02	-13.1	-6.5	1.8	0.0	-10.5	-3.7	-6.3	-15.6	-10.3	-11.9	-18.8
VN01	-6.1	-8.1	1.8	-3.3	-2.6	-4.3	0.3	-4.0	-2.0	3.1	-9.2
VN02	-5.9	-8.3	2.3	-2.0	-2.1	-1.3	1.3	-2.4	-1.2	4.5	-9.2
VN03	-6.2	-7.5	-6.7	1.4	-13.9	-2.9	1.1	-15.1	-3.1	-2.3	-7.3
VN04	-6.0	-7.7	2.8	-6.4	-5.6	-8.1	-1.2	-5.1	-2.9	4.0	-10.2
VN05	-6.4	-5.8	-1.2	2.6	-9.5	-4.6	1.3	-11.2	-2.2	-3.3	-5.4
Minimum	-13.1	-9.2	-39.5	-6.4	-13.9	-8.1	-13.7	-15.6	-10.3	-11.9	-74.2
Maximum	3.1	0.3	119.3	7.6	22.8	61.2	24.6	50.6	40.1	38.3	6.1
Average	-3.3	-4.7	4.2	0.2	-3.5	0.6	0.3	-2.5	3.0	0.7	-15.7

6. ACKNOWLEDGEMENT

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7. CONTACT INFORMATION

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