

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

Report of the Inter-laboratory Comparison Project 2019

22nd Inter-laboratory Comparison Project on Wet Deposition

15th Inter-laboratory Comparison Project on Dry Deposition

21st Inter-laboratory Comparison Project on Soil

20th Inter-laboratory Comparison Project on Inland Aquatic Environment

December 2020
Network Center for EANET

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1. INTRODUCTION

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

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

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

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

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

This report presented the results of the 22nd Inter-laboratory Comparison Project on wet deposition, 15th Inter-laboratory Comparison Project on dry deposition, 21st Inter-laboratory Comparison Project on soil, and 20th 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.

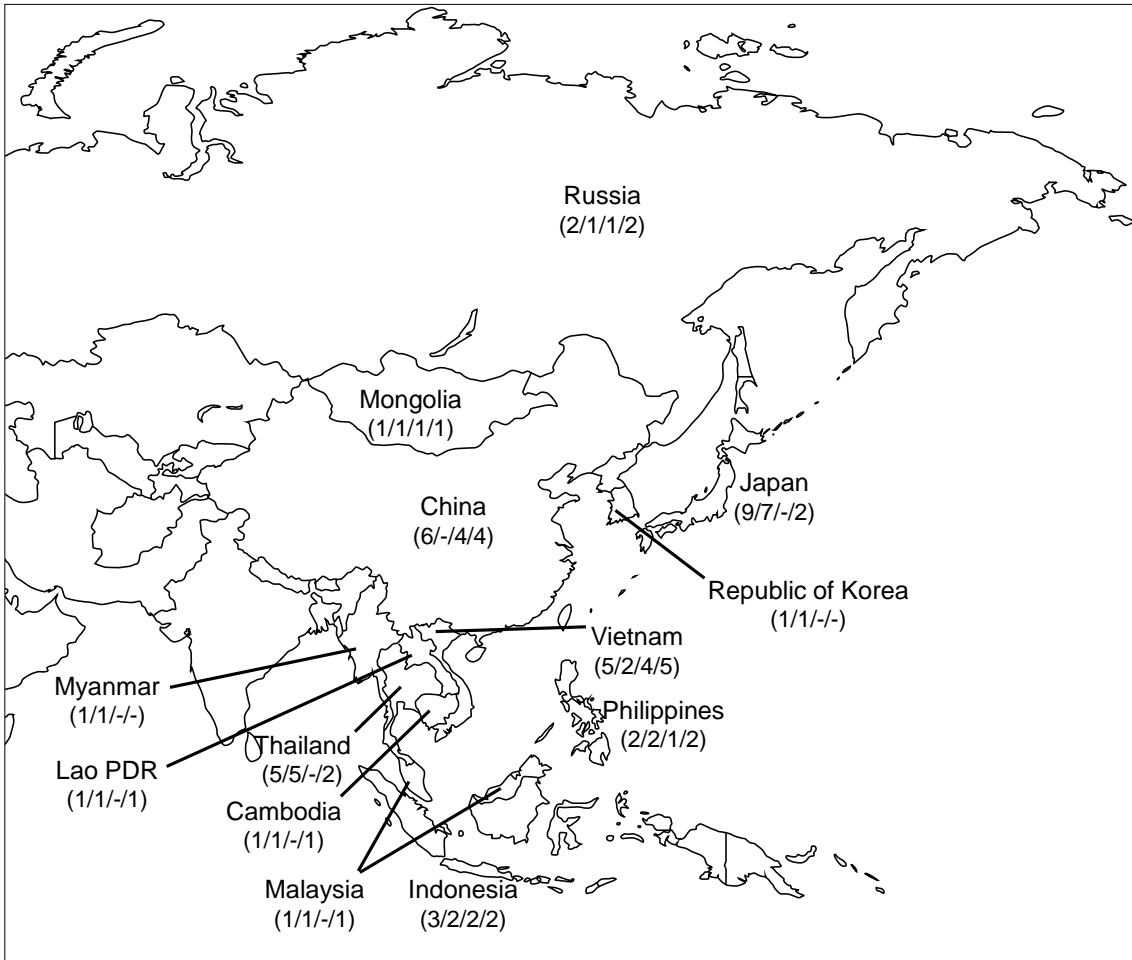


Figure 1.1 Number of participating laboratories in 2019

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

Table 1.1 Participating laboratories and data submission status

Participating laboratories	Code	Data submission			
		Wet	Dry	Soil	IAE
Cambodia Department of Environment Pollution Control, Ministry of Environment	KH01				
China Zhuhai Environmental Monitoring Center Station Xiamen Environmental Monitoring Station Xi'an Environmental Monitoring Center Station Chongqing Ecological and Environmental Monitoring Center Wuzhishan City Ecological Environment Protection Monitoring Station Lijiang Environmental Monitoring Station	CN01 CN02 CN03 CN04 CN05 CN06	✓ ✓ ✓ ✓ ✓ ✓		✓ ✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓ ✓
Indonesia Environmental Management Center (EMC), Ministry of Environment and Forestry Climatology, Meteorological and Geophysical Agency (BMKG) Indonesian National Institute of Aeronautic and Space (LAPAN) Indonesian Soil Research Institute (ISRI) Research Center for Water Resources (RCWR), Agency for Research and Development, Ministry of Public Works	ID01 ID02 ID03 ID04 ID05	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓
Japan Institute of Environmental Sciences, Hokkaido Research Organization Niigata Prefectural Institute of Public Health and Environmental Sciences Nagano Environmental Conservation Research Institute Gifu Prefectural Research Institute for Health and Environmental Sciences Kochi Prefectural Institute of Health and Environment Okinawa Prefectural Institute of Health and Environment Asia Center for Air Pollution Research (ACAP) Japan Environmental Sanitation Center (JESC) Ishikawa Prefectural Institute of Public Health and Environmental Science Nagasaki Prefectural Institute of Environment and Public Health	JP01 JP02 JP03 JP04 JP07 JP08 JP09 JP10 JP13 JP14	✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓		✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓
Lao PDR Division of Environmental Quality Monitoring and Analysis (DEQMA), Natural Resource and Environment Research Institute (NRERI), Ministry of Natural Resource and Environment (MoNRE)	LA01	✓	✓		✓
Malaysia Division of Environmental Health, Department of Chemistry (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) Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR)	PH01 PH02	✓ ✓	✓ ✓	✓ ✓	✓ ✓
Republic of Korea National Institute of Environment Research (NIER)	KR01	✓	✓		
Russia Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB) Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	RU01 RU02	✓ ✓	✓ ✓	✓ ✓	✓ ✓
Thailand Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MONRE) Environmental Research and Training Center (ERTC), Department of Environmental Quality Promotion Chemistry Department, Science Faculty, Chiangmai University (CMU) Khon Kaen University (KKU) King Mongkut's University of Technology Thonburi (KMUTT)	TH01 TH02 TH04 TH05 TH06	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓		✓ ✓ ✓ ✓ ✓
Vietnam Environmental Laboratory - Center for Environmental Research - Vietnam Institute of Meteorology, Hydrology and Environment (IMHEN)- MoNRE Mid- Central Regional Hydro Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE Sub-Institute of HydroMeteorology and Climate Change(SIHYMECC) Center for Hydro-Meteorological and Environmental Networks, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE Southern Region Hydro-Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	VN01 VN02 VN03 VN04 VN05	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓

Total number of submitted data : 33 20 13 21

Table 1.2 Laboratories in charge of the analysis of each monitoring site in EANET (2019)

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	<i>KHA001</i>			Sras Srang Lake	<i>KHI002</i>	KH01	KH01					
China	Chingqing Xi'an Xiamen Zhuhai Wuzhishan Lijiang	<i>CNA003</i> <i>CNA004</i> <i>CNA005</i> <i>CNA007</i> <i>CNA008</i> <i>CNA009</i> <i>CNA010</i> <i>CNA011</i> <i>CNA012</i> <i>CNA013</i> <i>CNA014</i>	Ji Yunshan Dabagou Xiaoping Zhuxiandong	<i>CNS004</i> <i>CNS007</i> <i>CNS009</i> <i>CNS011</i>	Ji Yunshan Lake Jiwozi River Xiaoping Dam Zhuxiandong Stream	<i>CNI004</i> <i>CNI007</i> <i>CNI209</i> <i>CNI111</i>	CN04 CN04 CN03 CN03 CN02 CN02 CN01 CN01 CN05 CN06		CN04 CN03 CN02 CN02 CN01		CN04 CN03 CN02 CN01	CN04 CN03 CN02 CN01	
Indonesia	Jakarta Serpong Kototabang Bandung Maros Jembrana Lombok	<i>IDA001</i> <i>IDA002</i> <i>IDA003</i> <i>IDA004</i> <i>IDA005</i> <i>IDA006</i> <i>IDA007</i>	Bogor Research Forest	<i>IDS002</i>	Patengang Lake Gunung Lake	<i>IDI004</i> <i>IDI006</i>	ID02 ID01 ID02 ID03 ID02 ID02 ID02	ID02 ID01 ID03	ID01		ID01 ID01		
Japan	Rishiri Ochiishi Sado-seki Happo Ijira Okii Yusuhara Hedo Ogasawara Tokyo Niigata-maki Tsushima	<i>JPA001</i> <i>JPA002</i> <i>JPA004</i> <i>JPA005</i> <i>JPA006</i> <i>JPA007</i> <i>JPA009</i> <i>JPA010</i> <i>JPA011</i> <i>JPA012</i> <i>JPA013</i> <i>JPA014</i>	Sekido-san Horyu-zan Ijira Yamato	<i>JPS005</i> <i>JPS105</i> <i>JPS006</i> <i>JPS106</i>	Futago-ike Lake Ijira Lake	<i>IPI005</i> <i>IPI006</i>	JP01 JP09 JP09 JP03 JP09 JP07 JP08 JP10 JP10 JP02 JP14	JP01 JP09 JP02 JP03 JP09 JP09 JP08 JP10 JP10 JP09	JP13 JP13 JP04 JP04		JP03 JP04		
Lao PDR	Vientiane	<i>LAA001</i>			Nam Hum Lake	<i>LAI001</i>	LA01	LA01					LA01
Malaysia	Petaling Jaya Tanah Rata Danum Valley Kuching	<i>MYA001</i> <i>MYA002</i> <i>MYA003</i> <i>MYA004</i>	Pasoh Reserve Forest 1 / 2 UPMKB Rehabilitated Forest Planted in 1991 / 2008	<i>MYS001</i> <i>MYS101</i> <i>MYS005</i> <i>MYS105</i>	Semenyih Dam Tembaling River	<i>MYI001</i> <i>MYI003</i>	MY01 MY01 MY01 MY01	MY01 MY01 MY01			MY01 MY01		MY01 MY01
Mongolia	Ulaanbaatar Terelj	<i>MNA001</i> <i>MNA002</i>	Bogdkhan Mountain Terelj Mountain	<i>MNS001</i> <i>MNS002</i>	Terelj River	<i>MNI002</i>	MN01 MN01	MN01 MN01	MN01 MN01				MN01 MN01
Myanmar	Yangon Mandalay	<i>MMA001</i> <i>MMA002</i>					MM01	MM01					
Philippines	Metro Manila Los Baños Mt. Sto. Tomas	<i>PHA001</i> <i>PHA002</i> <i>PHA003</i>	La Mesa Watershed Mt. Makiling UP Quezon, Land Grant Boneco Long Term Ecological Research Site	<i>PHS001</i> <i>PHS002</i> <i>PHS102</i> <i>PHS003</i>	Pandin Lake Ambulalakaw River	<i>PHI102</i> <i>PHI003</i>	PH01 PH01 PH02	PH01 PH01 PH02			PH01 PH02		PH01 PH02
Republic of Korea	Kanghwa Cheju (Kosan) Imsil	<i>KRA003</i>	Mt. Naejang	<i>KRS003</i>			KR01 KR01 KR01	KR01 KR01 KR01	KR01				
Russia	Mondy Listvyanka Irkutsk Primorskaya	<i>RUA001</i> <i>RUA002</i> <i>RUA003</i> <i>RUA004</i>	Ilchir Lake Okinskoe Lake Solar Observatory Bolshie Koty Pereemnya river Catchment Irkutsk Primorskaya	<i>RUS001</i> <i>RUS101</i> <i>RUS201</i> <i>RUS002</i> <i>RUS102</i> <i>RUS003</i> <i>RUS004</i>	Pereemnya River Komarovka River	<i>RUI102</i> <i>RUI004</i>	RU01 RU01 RU01 RU02	RU01 RU01 RU01 RU01			RU01 RU01 RU01 RU01	RU01 RU01	
Thailand	Bangkok Samutprakarn Pathumthani Khanchanaburi Chiang Mai Nakhon Ratchasima	<i>THA001</i> <i>THA002</i> <i>THA003</i> <i>THA004</i> <i>THA005</i> <i>THA006</i> <i>THA007</i> <i>THA008</i> <i>THA009</i>	Vachiralongkorn Dam Vachiralongkorn Puyue	<i>THS004</i> <i>THS104</i>	Vachiralongkorn Dam	<i>THI004</i>	TH01 TH01 TH02 TH01 TH02 TH05	TH01 TH01 TH02 TH01 TH04 TH05	TH06 TH06		TH01 TH01 TH06 TH01	TH01	
Vietnam	Hanoi Hoa Binh Cuc Phuong Da Nang Can Tho Ho Chi Minh Yen Bai	<i>VNA001</i> <i>VNA002</i> <i>VNA003</i> <i>VNA004</i> <i>VNA005</i> <i>VNA006</i> <i>VNA007</i>	Cave of Heaven Thang Ranh	<i>VNS002</i> <i>VNS102</i>	Hoa Binh Reservoir	<i>VNI002</i>	VN01 VN01 VN04 VN02 VN03 VN03 VN01	VN01 VN01 VN03 VN03 VN01	VN01 VN01 VN01		VN01 VN01 VN01	VN01 VN01	

* FP: Filter pack method

2. 22nd INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

2.1 Introduction

In the 22nd 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 2019. Their analytical results were required to be submitted to the NC by 28 February 2020.

2.2 Procedures

2.2.1 Participating laboratories

The NC distributed the artificial rainwater samples to 38 laboratories in charge of chemical analysis in 13 countries of EANET. 33 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. 191w No. 192w	100 mL each	Polypropylene bottle 100 mL	One bottle each	- Fixed quantity of reagents are dissolved in deionized water - Samples do not include other ions than shown in Table 2.2

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

Table 2.2 Prepared values/concentrations of analytical parameters*

	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
	-	mS m ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹
No. 191w	4.89	2.80	42.9	25.9	65.2	38.9	55.2	5.3	23.4	8.8
No. 192w	5.46	0.86	17.6	13.0	6.6	10.4	5.1	2.6	12.4	4.2

* For 100 times diluted samples.

2.2.3 Analytical methods and data checking procedures

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

All participating laboratories were expected to analyze the diluted samples for the following 10 parameters; pH, EC, concentrations of SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺.

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

Table 2.3 Analytical methods specified in the Technical Manual

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

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

Calculation of ion balance (R₁)

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

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

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

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

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

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

- (3) Calculation of ion balance (R₁)

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

- (4) R₁ 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 R₁ 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 R₁ in different concentration ranges

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

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

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

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

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

(2) Electrical conductivity comparison (R₂) was calculated as follows;

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

Λ meas : measured conductivity

(3) R₂ calculated by the above equation was compared with allowable ranges specified in the Technical Manual which are shown in Table 2.5. If R₂ 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 R₂ 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 33 laboratories in the participating countries of EANET.

Basic statistics of submitted data summarized in Table 2.6 was calculated for each parameter of the artificial rainwater samples such as: average (Va), minimum (Min.), maximum (Max.), standard deviation (S.D.), and number of data (N). The outliers, exceeding three standard deviations, were excluded from the calculation. As shown in Table 2.6, the range of $\Delta V/V_p$ between -4.3% to 3.0% for sample No. 191w, and -8.1% to 6.7% for sample No. 192w.

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

Sample No. 191w							
Constituents	Prepared (Vp)	Average (Va)	$\Delta V/V_p$ *1 %	S.D.	N	Min.	Max.
pH	4.89	5.04	3.0	0.17	32	4.74	5.53
EC [mS m ⁻¹]	2.80	2.68	-4.3	0.11	32	2.30	2.85
SO ₄ ²⁻ [μmol L ⁻¹]	42.9	42.9	0.0	1.40	32	40.0	46.6
NO ₃ ⁻ [μmol L ⁻¹]	25.9	25.4	-1.8	0.77	32	23.2	26.7
Cl ⁻ [μmol L ⁻¹]	65.2	64.3	-1.3	1.88	32	60.6	68.2
NH ₄ ⁺ [μmol L ⁻¹]	38.9	38.6	-0.7	2.34	31	31.9	46.1
Na ⁺ [μmol L ⁻¹]	55.2	55.9	1.2	3.66	31	46.7	66.6
K ⁺ [μmol L ⁻¹]	5.3	5.2	-1.9	0.53	31	3.7	7.2
Ca ²⁺ [μmol L ⁻¹]	23.4	24.0	2.6	1.52	31	20.5	27.5
Mg ²⁺ [μmol L ⁻¹]	8.8	8.6	-2.0	0.72	32	6.5	10.4
Sample No. 192w							
Constituents	Prepared (Vp)	Average (Va)	$\Delta V/V_p$ *1 %	S.D.	N	Min.	Max.
pH	5.46	5.43	-0.5	0.13	32	5.17	5.74
EC [mS m ⁻¹]	0.86	0.89	3.7	0.03	32	0.82	0.95
SO ₄ ²⁻ [μmol L ⁻¹]	17.6	17.3	-1.9	0.80	32	14.6	18.8
NO ₃ ⁻ [μmol L ⁻¹]	13.0	12.6	-3.2	0.70	32	10.1	13.5
Cl ⁻ [μmol L ⁻¹]	6.6	6.5	-1.9	0.37	31	5.0	7.1
NH ₄ ⁺ [μmol L ⁻¹]	10.4	10.4	0.0	1.71	31	3.7	14.5
Na ⁺ [μmol L ⁻¹]	5.1	5.4	6.7	1.09	31	3.7	9.8
K ⁺ [μmol L ⁻¹]	2.6	2.4	-8.1	0.24	31	1.9	2.9
Ca ²⁺ [μmol L ⁻¹]	12.4	12.9	3.9	1.39	31	8.2	15.4
Mg ²⁺ [μmol L ⁻¹]	4.2	4.1	-1.3	0.31	31	3.3	4.7

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 $\pm 15\%$ of deviation from V_p . In this report, analytical data of the artificial rainwater samples were compared with V_p , and the data exceed DQO were marked with flags. The flag “E” indicates that the deviation from V_p exceeds $\pm 15\%$ but not $\pm 30\%$, and the flag “X” indicates that the deviation from V_p exceeds $\pm 30\%$.

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

The results were evaluated by the following three aspects:

- i) Comparison of concentration dependence on level of their concentration
– sample No. 191w and No. 192w,
- ii) Comparison of individual parameters,
- iii) Comparison of circumstances of chemical analysis in each participating laboratory.

Evaluation of analytical data on both sample No. 191w and No. 192w 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. 191w

The number and percentage of the flagged data for sample No. 191w are shown in Table 2.7. 13 analytical data out of 324 were flagged by "E". And 6 analytical data out of 324 were flagged by "X". Data flagged by "E" and "X" shared 5.9 percent of all the submitted data for sample No. 191w.

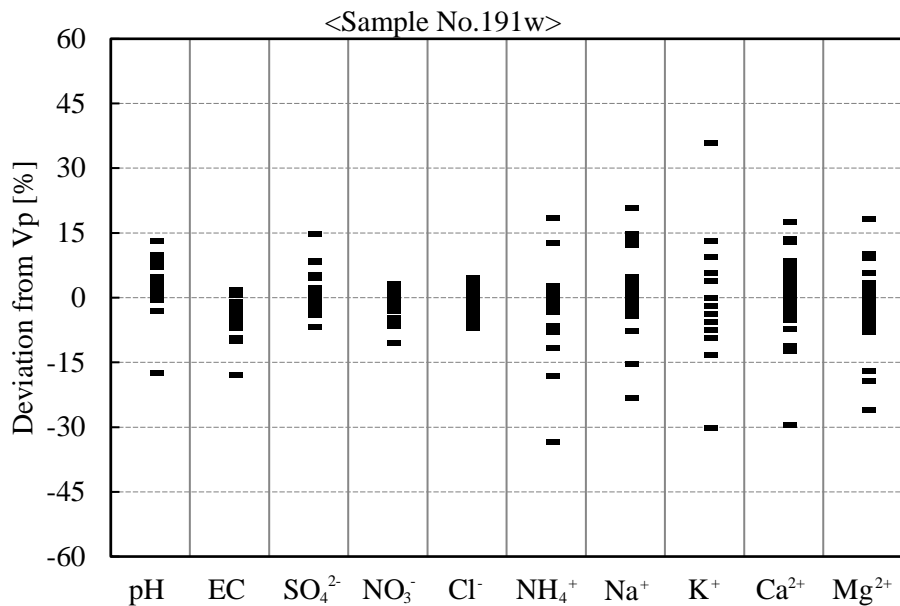
The data normalized by prepared value in each parameter are shown in Figure 2.1.

Table 2.7 Number of flagged data for the Sample No. 191w

Characterization of data	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total
Data within DQO	32	31	33	32	32	29	29	29	30	28	305
Data with flag E ^{*1}	1	1	0	0	0	2	3	0	2	4	13
Data with flag X ^{*2}	0	1	0	1	0	1	0	3	0	0	6
Flagged data [%]	3.0	6.1	0.0	3.0	0.0	9.4	9.4	9.4	6.3	12.5	5.9

(Total data = 324)

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



Three plots are out of upper scale. EC:101.4%, NO₃⁻: 162.5%, K⁺: 109.4%

Figure 2.1 Distribution of the data normalized by prepared value in each parameter for sample No. 191w

The parameter which had the most flags was Mg²⁺. The analytical data submitted by the participating laboratories are shown in Table 2.8 with flags.

Table 2.8 Analytical Results of Sample No. 191w

Lab. ID*1	pH	EC mS m ⁻¹	SO ₄ ²⁻ μmol L ⁻¹	NO ₃ ⁻ μmol L ⁻¹	Cl ⁻ μmol L ⁻¹	NH ₄ ⁺ μmol L ⁻¹	Na ⁺ μmol L ⁻¹	K ⁺ μmol L ⁻¹	Ca ²⁺ μmol L ⁻¹	Mg ²⁺ μmol L ⁻¹	R ₁ %	R ₂ %
CN01	5.07	2.67	42.3	25.2	64.8	37.9	57.2	4.9	24.1	9.1	0.1	-0.7
CN02	4.97	2.74	41.7	25.5	65.4	38.3	54.3	5.1	24.0	8.8	-0.1	-0.9
CN03	4.99	2.82	42.7	26.4	66.0	38.3	54.4	4.9	24.0	8.4	-1.5	-2.2
CN04	4.98	2.85	42.9	26.3	66.0	37.6	56.4	5.1	23.5	8.2	-1.5	-2.6
CN05	5.02	2.71	41.2	24.5	64.9	39.4	62.0	4.9	24.1	9.6	3.2	-0.4
CN06	5.01	2.62	42.8	26.0	65.1	37.8	57.0	5.3	24.6	8.9	0.0	1.5
ID01	4.98	2.73	42.4	24.7	62.6	39.0	55.7	5.3	22.8	8.2	0.1	-1.3
ID02	5.02	2.60	42.1	25.4	64.9	35.8	55.2	5.0	24.3	8.6	-0.9	0.8
ID03	5.12	2.30 E	44.9	25.7	62.2	39.7	54.3	4.8	21.7	7.3 E	-3.9	5.7
JP01	5.01	2.76	43.0	26.2	63.9	39.7	57.8	5.8	26.4	9.0	2.2	-0.4
JP02	4.94	2.72	42.9	25.4	64.2	38.6	53.6	5.0	22.5	8.9	-1.1	-0.2
JP03	4.92	2.75	43.8	26.7	67.0	38.5	55.0	5.3	23.7	8.5	-1.7	0.8
JP04	4.93	2.73	42.4	25.5	64.3	39.1	52.9	5.3	22.2	8.3	-1.3	-0.5
JP07	4.98	2.72	43.1	25.4	65.1	38.9	54.6	5.2	23.0	8.1	-1.5	-0.5
JP08	4.94	2.74	43.6	26.3	66.1	39.3	55.2	5.3	27.5 E	8.9	1.2	1.4
JP09	5.00	2.77	43.0	25.8	64.7	38.4	55.3	5.3	23.2	8.9	-0.9	-1.6
JP10	4.87	2.77	43.9	26.5	66.1	38.1	56.6	5.3	24.4	9.0	0.0	1.5
JP14	5.03	2.73	42.5	25.7	63.1	38.1	55.2	5.5	23.3	8.6	-0.5	-1.7
LA01	4.97	2.60	43.0	25.5	62.7	---	---	---	---	---	---	---
MY01	4.86	2.73	41.7	25.6	64.5	34.4	53.8	5.2	24.1	8.7	-0.2	0.6
MN01	5.10	2.64	41.2	25.3	60.6	46.1 E	52.9	3.7 X	20.5	6.5 E	-1.1	-2.2
MM01	5.53	2.63	49.2	24.2	68.2	39.7	54.9	5.1	23.1	8.6	-6.9	-1.5
PH01	4.90	2.73	43.4	26.1	65.3	25.9 X	57.0	7.2 X	26.6	8.2	-1.7	0.4
KR01	4.74	2.75	40.0	24.2	61.5	43.8	55.9	4.6	25.2	8.5	6.8	3.4
RU01	4.90	2.68	42.3	23.2	60.6	38.4	54.5	5.3	24.1	9.7	2.9	0.9
RU02	4.04 E	5.64 X	46.6	68.0 X	61.1	31.9 E	42.4 E	11.1 X	20.8	10.4 E	3.6	1.2
TH01	4.86	2.72	42.4	25.1	64.3	36.4	55.1	4.9	24.7	8.4	0.6	1.3
TH02	4.92	2.73	43.6	25.8	64.8	38.3	55.4	5.6	16.5 E	7.1 E	-5.7	-1.1
VN01	5.32	2.52	41.8	25.5	65.6	38.7	63.4	5.1	25.1	8.8	1.4	0.6
VN02	5.37	2.54	41.9	25.4	63.9	38.5	62.7	5.0	25.4	9.0	1.7	-0.4
VN03	5.29	2.69	45.2	24.5	---	39.4	50.9	5.1	25.4	9.3	---	---
VN04	5.36	2.54	41.5	25.6	67.3	38.9	66.6 E	5.1	24.9	8.6	1.7	0.3
VN05	5.24	2.52	46.5	24.3	61.9	40.0	46.7 E	6.0	24.7	8.8	-4.0	0.6
Vp	4.89	2.80	42.9	25.9	65.2	38.9	55.2	5.3	23.4	8.8	-0.1	-0.1
N of data	33	33	33	33	32	32	32	32	32	32		
Within DQO	32	31	33	32	32	29	29	29	30	28		
Flag E	1	1	0	0	0	2	3	0	2	4		
Flag X	0	1	0	1	0	1	0	3	0	0		

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

"I", Poor ion balance (R₁); "C", Poor conductivity agreement (R₂); "----", Not measured; "Vp", Prepared values of parameters;

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

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

2) Sample No. 192w

The number and percentage of the flagged data for sample No. 192w are shown in Table 2.9. 30 analytical data out of 324 were flagged by "E". 15 analytical data out of 324 were flagged by "X". Data marked with flags shared up to 13.9 percent of all the submitted data for sample No. 192w.

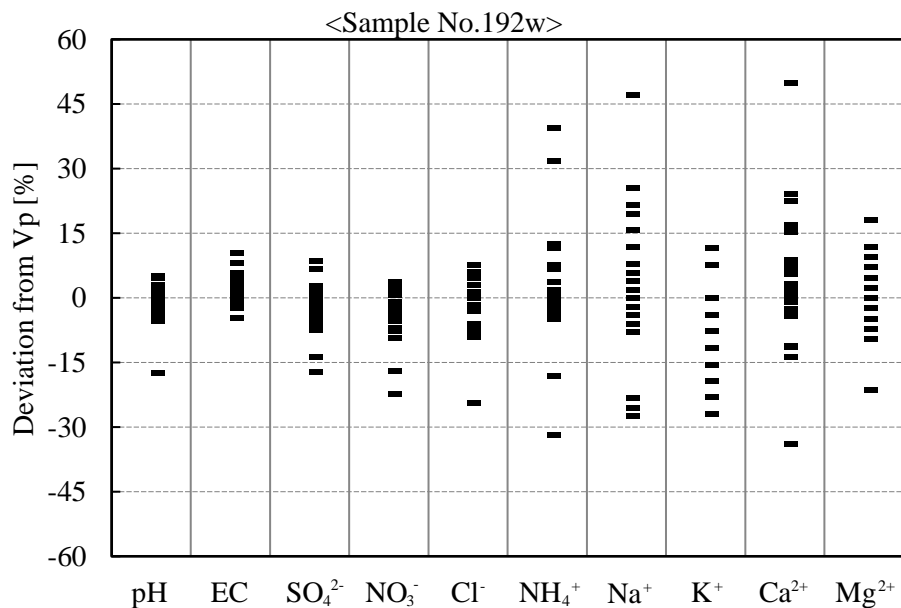
The normalized data by prepared value in each parameter are shown in Figure 2.2.

Table 2.9 Number of flagged data for the sample No. 192w

Characterization of data	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total
Data within DQO	32	32	31	30	30	27	21	23	24	29	279
Data with flag E ^{*1}	1	0	2	2	1	0	8	8	6	2	30
Data with flag X ^{*2}	0	1	0	1	1	5	3	1	2	1	15
Flagged data [%]	3.0	3.0	6.1	9.1	6.3	15.6	34.4	28.1	25.0	9.4	13.9

(Total data = 324)

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



Eight plots are out of upper scale. EC:198.8%, NO₃⁻: 175.4%, Cl⁻: 324.2%, NH₄⁺: -88.5%, -64.4%, Na⁺: 360.8%, K⁺: 230.8%, Mg²⁺: -90.5%

Figure 2.2 Distribution of the data normalized by prepared value for each parameter for sample No. 192w

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

Table 2.10 Analytical Results of Sample No. 192w

Lab. ID*1	pH	EC mS m ⁻¹	SO ₄ ²⁻ μmol L ⁻¹	NO ₃ ⁻ μmol L ⁻¹	Cl ⁻ μmol L ⁻¹	NH ₄ ⁺ μmol L ⁻¹	Na ⁺ μmol L ⁻¹	K ⁺ μmol L ⁻¹	Ca ²⁺ μmol L ⁻¹	Mg ²⁺ μmol L ⁻¹	R ₁ %	R ₂ %
CN01	5.52	0.86	17.2	13.5	7.0	11.7	7.5 X	2.3	13.1	4.3	3.9	0.7
CN02	5.42	0.90	17.7	13.1	6.5	10.6	5.7	2.6	12.5	4.2	1.0	-1.2
CN03	5.47	0.95	18.1	12.9	6.5	11.1	5.5	2.4	12.6	4.2	0.3	-4.3
CN04	5.48	0.91	17.5	12.7	6.5	11.2	5.7	2.2 E	12.7	4.1	1.6	-3.0
CN05	5.63	0.87	16.8	13.1	6.5	10.8	4.8	2.6	13.2	4.6	2.7	-2.8
CN06	5.51	0.89	17.8	13.2	6.5	11.1	5.9 E	2.5	13.1	4.2	1.7	-1.3
ID01	5.36	0.95	17.5	11.8	6.9	10.6	5.0	2.5	11.0	4.2	-0.8	-4.6
ID02	5.21	0.87	17.8	13.4	6.8	10.2	5.1	2.5	14.5 E	4.5	5.2	6.3
ID03	5.43	0.82	17.7	12.0	6.6	10.4	5.0	2.4	10.7	4.0	-2.9	1.1
JP01	5.44	0.93	17.7	13.4	6.6	10.3	5.0	2.5	14.3 E	4.3	2.8	-2.1
JP02	5.39	0.89	17.6	12.6	6.0	10.2	4.9	2.2 E	11.9	4.2	-0.2	-1.6
JP03	5.32	0.93	17.8	13.3	6.8	10.0	5.1	2.4	12.0	4.0	-1.3	-1.6
JP04	5.37	0.89	17.3	12.8	6.5	10.2	5.5	2.4	12.1	4.0	0.6	-0.9
JP07	5.31	0.91	17.3	12.4	6.4	10.0	4.7	2.3	12.6	3.8	1.2	-1.1
JP08	5.39	0.91	17.9	13.2	6.5	10.1	5.4	2.6	18.6 X	4.7	10.7 I	2.9
JP09	5.48	0.90	17.7	12.9	6.7	10.5	5.2	2.6	12.4	4.3	0.0	-2.4
JP10	5.30	0.91	18.0	12.7	6.1	10.0	5.2	2.5	13.2	4.4	2.8	0.7
JP14	5.56	0.89	17.6	12.8	7.1	10.2	5.9 E	2.8	12.5	4.1	-0.2	-2.8
LA01	5.44	0.84	17.5	12.5	6.5	---	---	---	---	---	---	---
MY01	5.17	0.93	16.6	12.9	6.5	7.1 X	5.0	2.3	12.3	3.8	0.7	-0.3
MN01	5.71	0.86	16.9	12.9	6.2	13.7 X	9.8 X	2.0 E	12.4	3.3 E	5.3	-2.1
MM01	5.74	0.88	18.8	12.3	6.4	11.1	6.4 E	2.9	14.4 E	4.4	3.0	-1.5
PH01	5.32	0.91	17.0	12.5	6.4	1.2 X	6.2 E	2.3	15.4 E	4.1	0.6	-2.8
KR01	5.29	0.88	16.3	11.8	6.0	14.5 X	5.2	1.9 E	12.8	3.8	8.6 I	1.6
RU01	5.36	0.90	17.3	12.1	5.0 E	9.9	5.3	2.8	13.1	4.3	5.0	-1.4
RU02	4.48 E	2.57 X	21.0 E	35.8 X	28.0 X	3.7 X	23.5 X	8.6 X	12.6	0.4 X	-5.4	-5.0
TH01	5.25	0.84	17.4	12.5	6.4	11.1	4.9	2.3	12.8	3.9	3.3	5.1
TH02	5.45	0.89	17.8	12.7	6.4	10.1	5.7	2.6	8.2 X	3.3 E	-9.8	-5.1
VN01	5.52	0.85	16.7	12.7	6.8	10.0	3.7 E	2.1 E	13.4	4.2	1.0	-1.4
VN02	5.56	0.87	17.1	12.7	6.8	9.9	3.8 E	2.0 E	13.5	4.2	0.1	-2.7
VN03	5.46	0.95	15.2	10.8 E	---	10.4	6.1 E	2.1 E	15.2 E	4.5	---	---
VN04	5.56	0.86	16.4	12.4	6.7	10.0	3.8 E	2.1 E	13.3	4.2	1.7	-3.0
VN05	5.41	0.89	14.6 E	10.1 E	6.2	11.6	5.7	2.4	15.4 E	4.4	16.3 I	-2.3
Vp	5.46	0.86	17.6	13.0	6.6	10.4	5.1	2.6	12.4	4.2	0.0	0.0
N of data	33	33	33	33	32	32	32	32	32	32		
Within DQO	32	32	31	30	30	27	21	23	24	29		
Flag E	1	0	2	2	1	0	8	8	6	2		
Flag X	0	1	0	1	1	5	3	1	2	1		

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

"I", Poor ion balance (R₁); "C", Poor conductivity agreement (R₂); "---", Not measured; "Vp", Prepared values of parameters;

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

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

3) Comparison of high and low concentration sample

The percentage of the flagged data for sample No. 191w and 192w are shown in Figure 2.3. The percentage of the data within the DQO for sample No. 191w and 192w were 94.1% and 86.1% respectively. The difference between both samples was 8.0%. In this project, the total number of flagged data was 64 (E: 43, X: 21) among the whole set of 648 data.

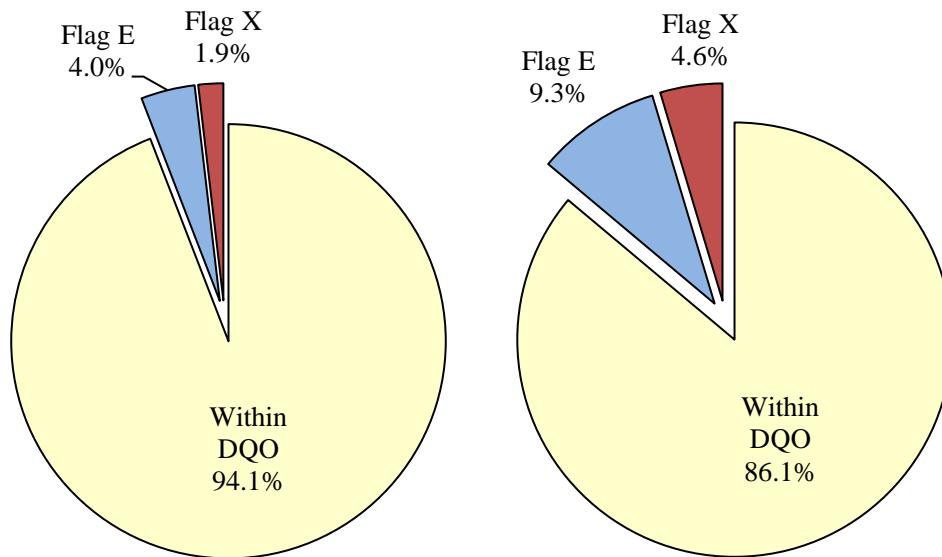


Figure 2.3 Percentage of flagged data for sample No. 191w and No. 192w (Left: No. 191w, Right: No. 192w)

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 11, which corresponds to 33.3% of all the participating laboratories.

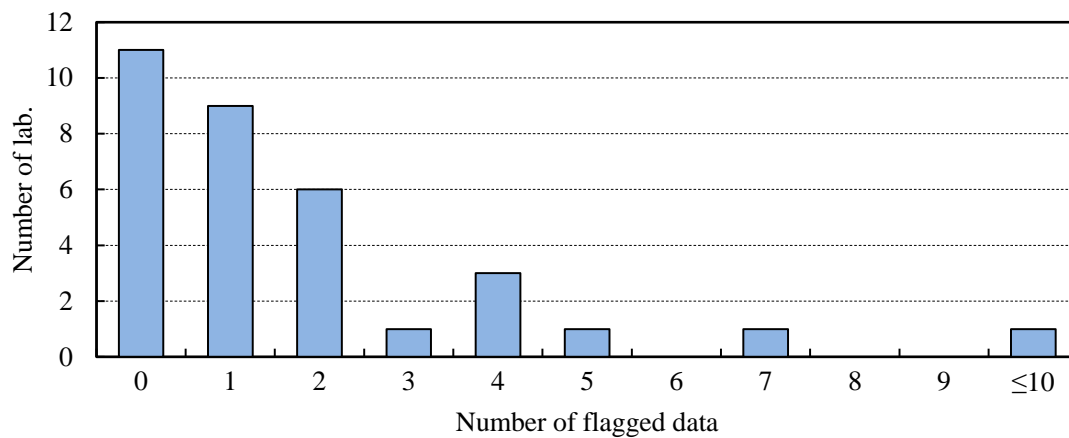


Figure 2.4 Distribution of the number of laboratory (by number of flags)

2.3.2 Evaluation of laboratories' performance (by analytical parameter)

The data normalized by V_p are shown in Figures 2.5 through 2.24 for each parameter. In scatter diagrams (lower figures), bold line means the prepared values of sample No. 191w and 192w, broken lines and dotted lines showed the values of $V_p \pm 15\%$ and $V_p \pm 30\%$ respectively.

1) pH

All participating laboratories used pH meter with glass electrode method for the measurement of pH. The data of sample No.191w from RU02 and the data of sample No.192w from RU02 were marked with flag “E”.

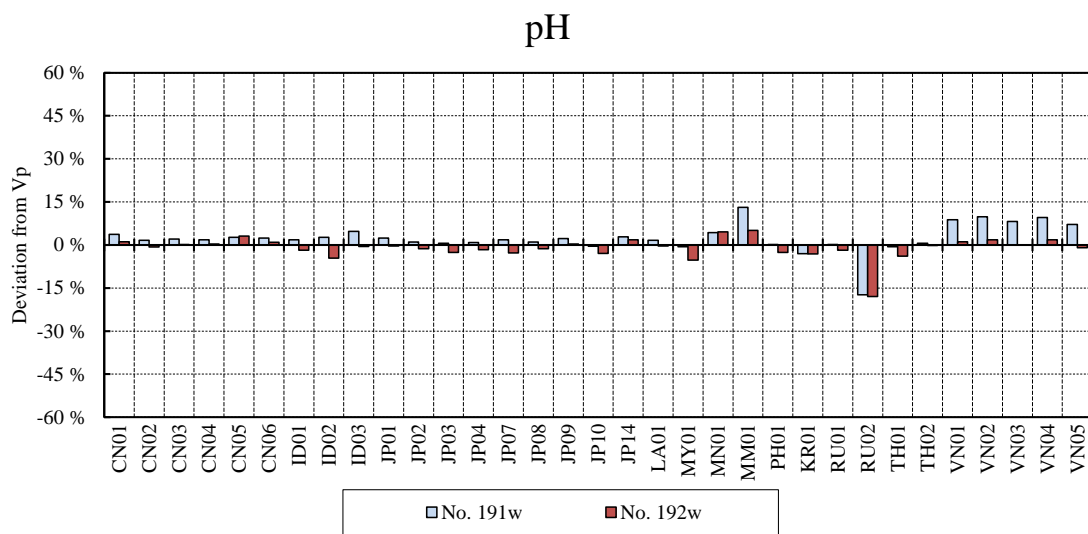


Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)

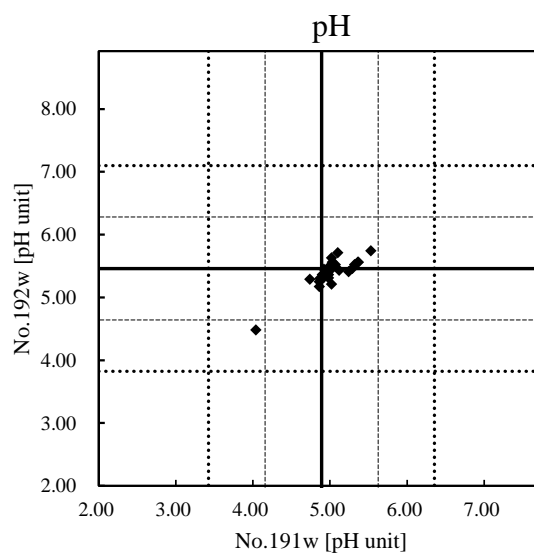


Figure 2.6 Scatter diagram for pH

2) EC

All participating laboratories used conductivity cell method for the measurement of EC. The data of sample No.191w from ID03 was marked with flag “E”. Additionally, the data of sample No.191w from RU02 and the data of sample No. 192w from RU02 were marked with flag “X”.

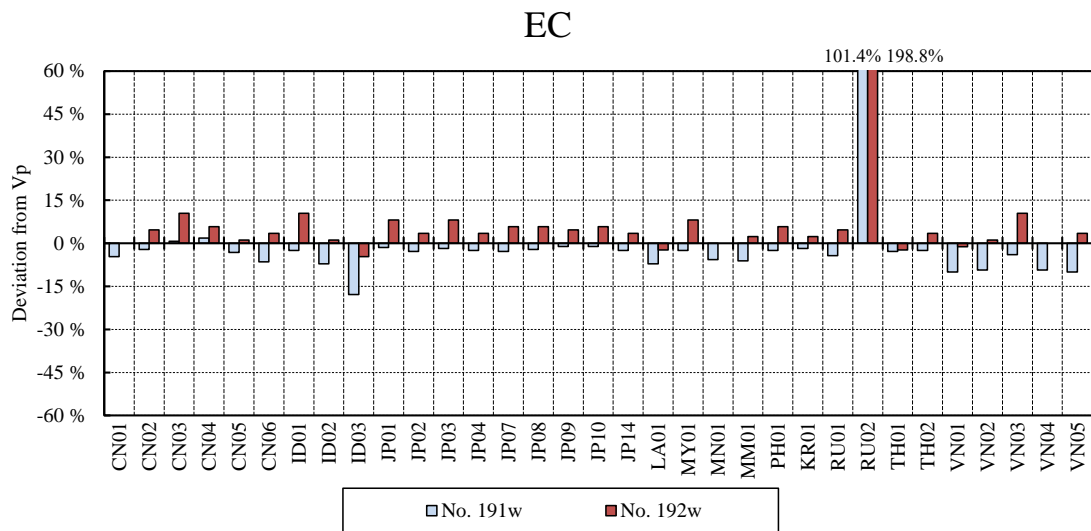


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)

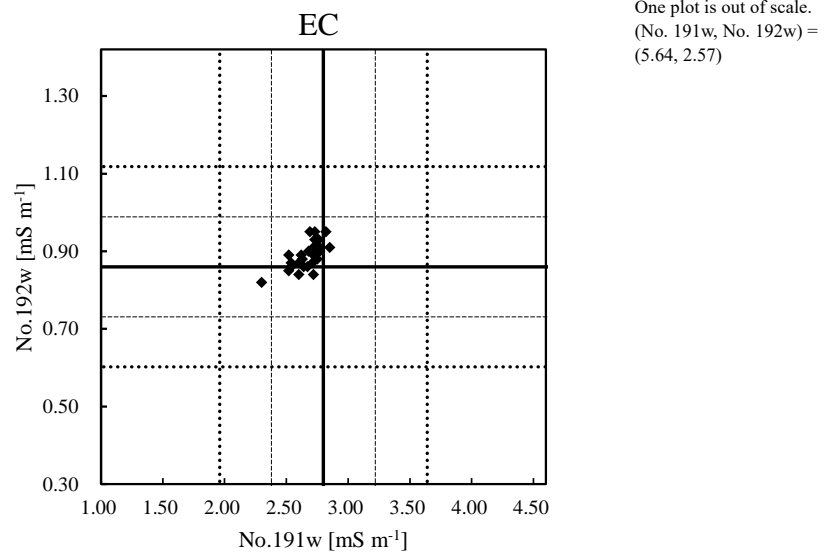


Figure 2.8 Scatter diagram for EC

3) SO_4^{2-}

The data of sample No.191w from 2 laboratories (RU02 and VN05) were marked with flag “E”.

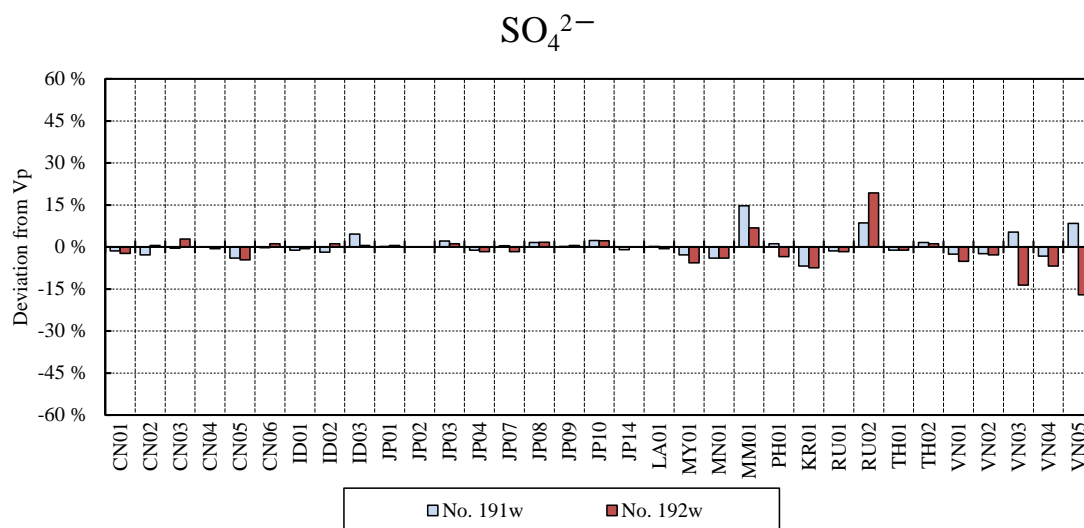


Figure 2.9 Deviation from prepared value for SO_4^{2-} (normalized by prepared value)

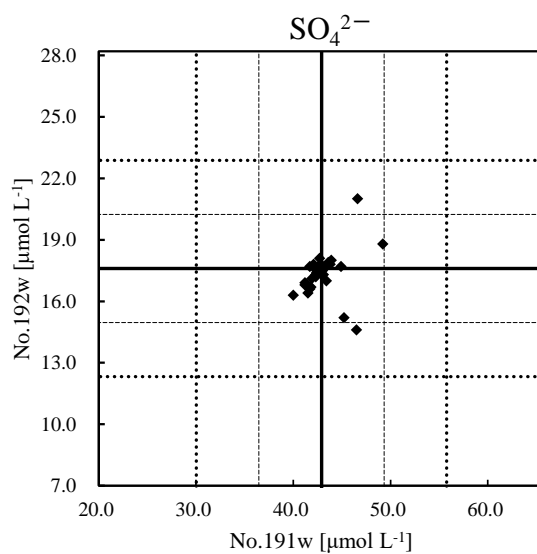


Figure 2.10 Scatter diagram for SO_4^{2-}

4) NO₃⁻

The data of sample No. 192w from 2 laboratories (VN03 and VN05) were marked with flag “E”. Additionally, the data of sample No. 191w from RU02 and the data of sample No.192w from RU02 were marked with flag “X”.

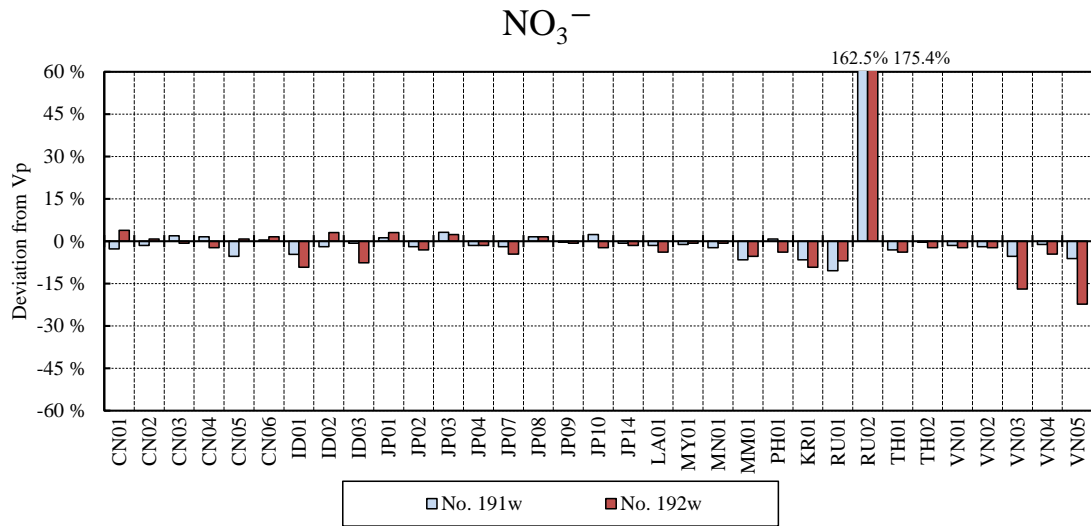


Figure 2.11 Deviation from prepared value for NO₃⁻ (normalized by prepared value)

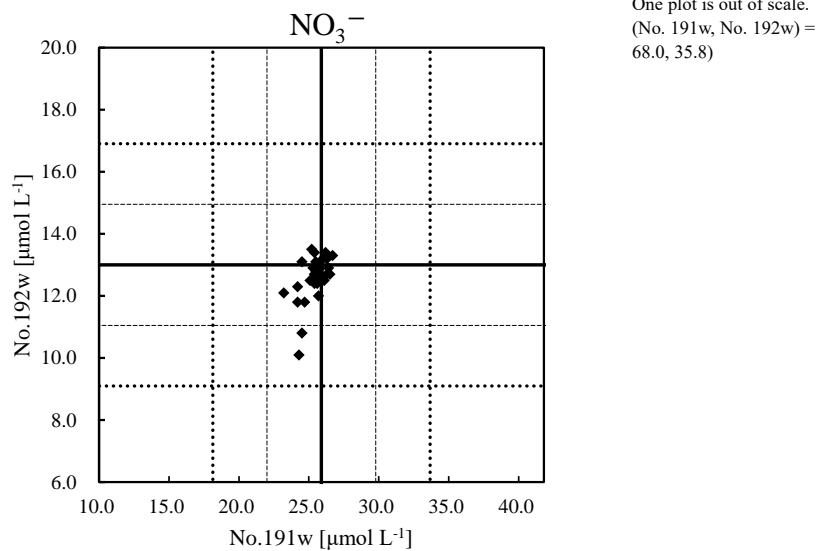


Figure 2.12 Scatter diagram for NO₃⁻

5) Cl⁻

The data of sample No. 192w from RU01 was marked with flag “E”. Additionally, the data of sample No.192w from RU02 was marked with flag “X”.

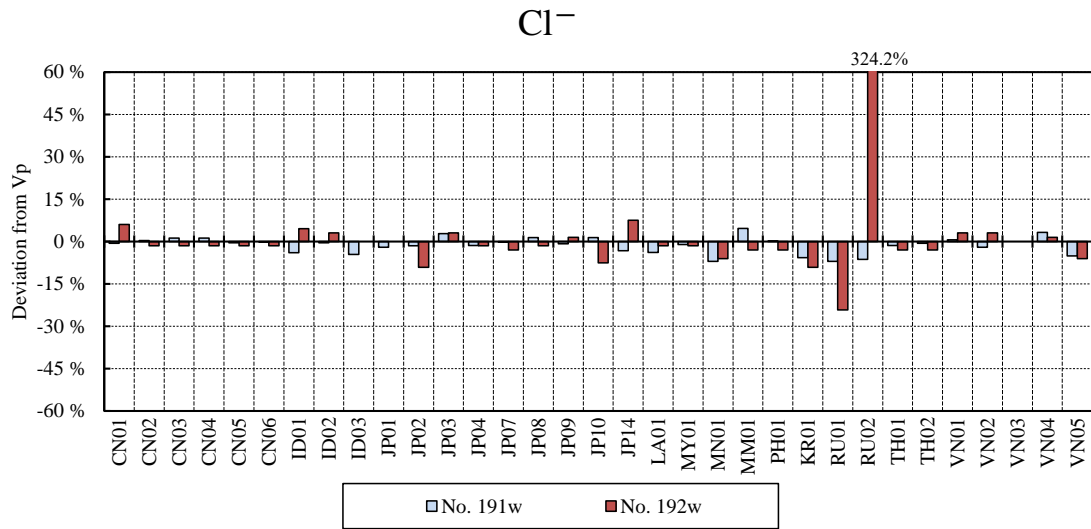


Figure 2.13 Deviation from prepared value for Cl⁻ (normalized by prepared value)

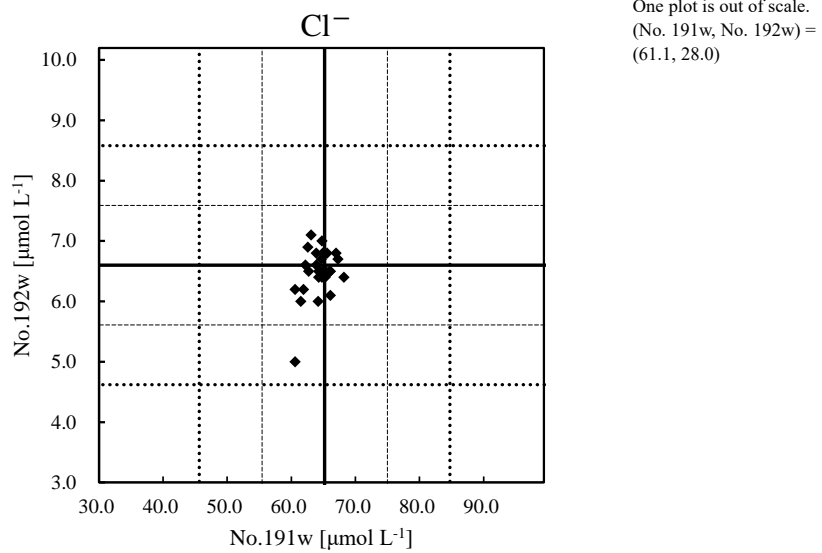


Figure 2.14 Scatter diagram for Cl⁻

6) NH_4^+

The data of sample No. 191w from 2 laboratories (MN01 and RU02) were marked with flag “E”. Additionally, the data of sample No.191w from PH01 and the data of sample No.192w from 5 laboratories (MY01, MN01, PH01, KR01 and RU02) were marked with flag “X”.

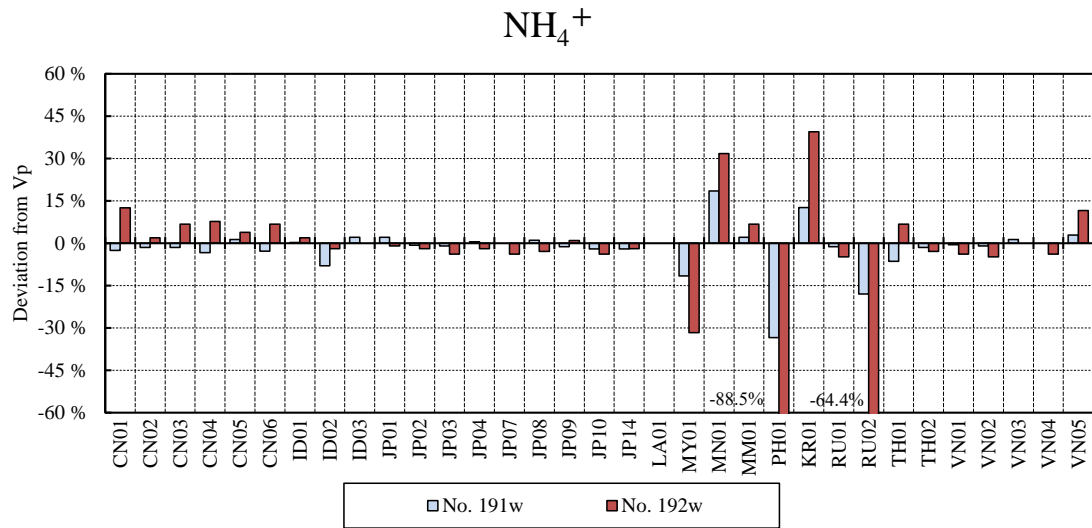
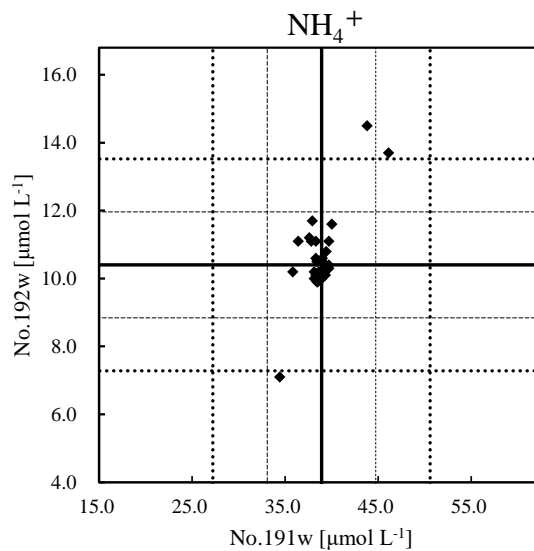


Figure 2.15 Deviation from prepared value for NH_4^+ (normalized by prepared value)



Two plots are out of scale.
(No. 191w, No. 192w) =
(25.9, 1.2), (31.9, 3.7)

Figure 2.16 Scatter diagram for NH_4^+

7) Na⁺

The data of sample No. 191w from 3 laboratories (RU02, VN04 and VN05) and the data of sample No. 192w from 8 laboratories (CN06, JP14, MM01, PH01, VN01, VN02, VN03 and VN04) were marked with flag “E”. Additionally, the data of sample No. 192w from 3 laboratories (CN01, MN01 and RU02) were marked with flag “X”.

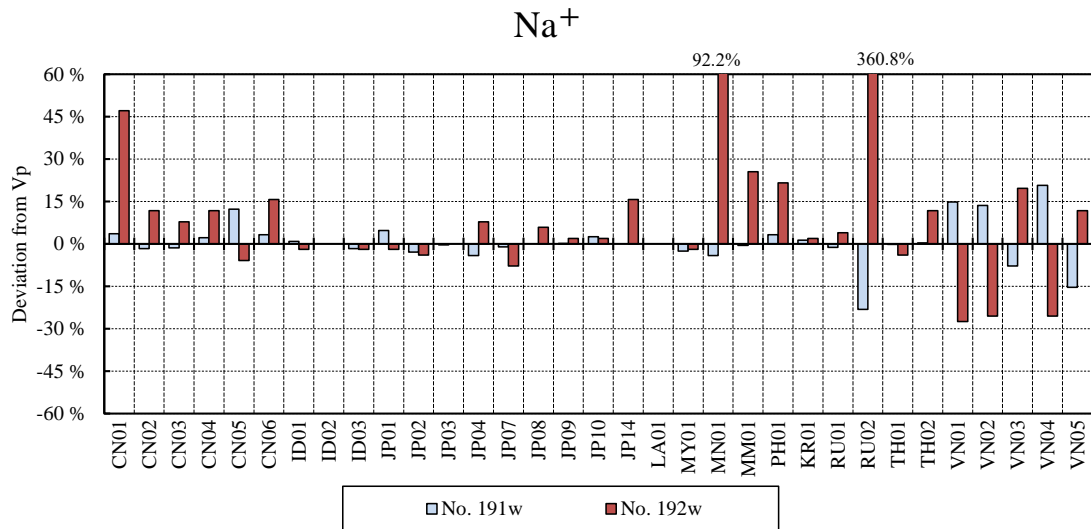


Figure 2.17 Deviation from prepared value for Na⁺ (normalized by prepared value)

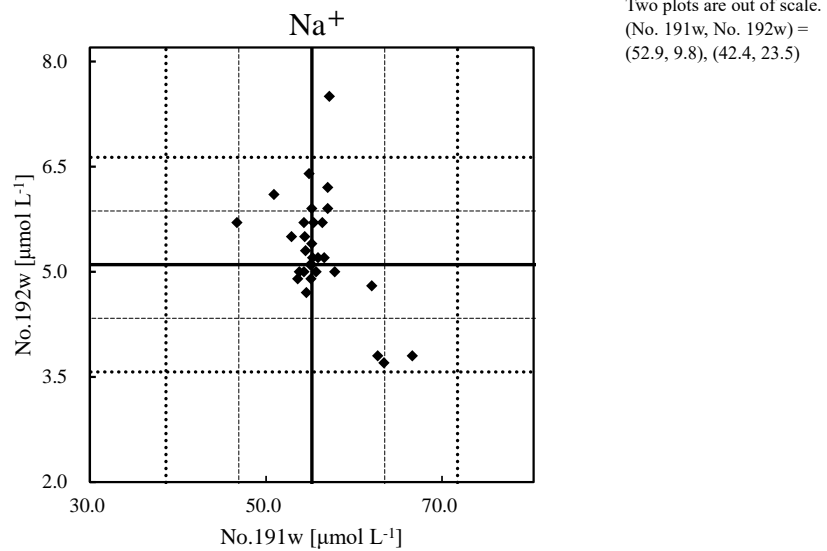


Figure 2.18 Scatter diagram for Na⁺

8) K⁺

The data of sample No. 192w from 8 laboratories (CN04, JP02, MN01, KR01, VN01, VN02, VN03 and VN04) were marked with flag “E”. Additionally, the data of sample No.191w from 3 laboratories (MN01, PH01 and RU02) and the data of sample No. 192w from RU02 were marked with flag “X”.

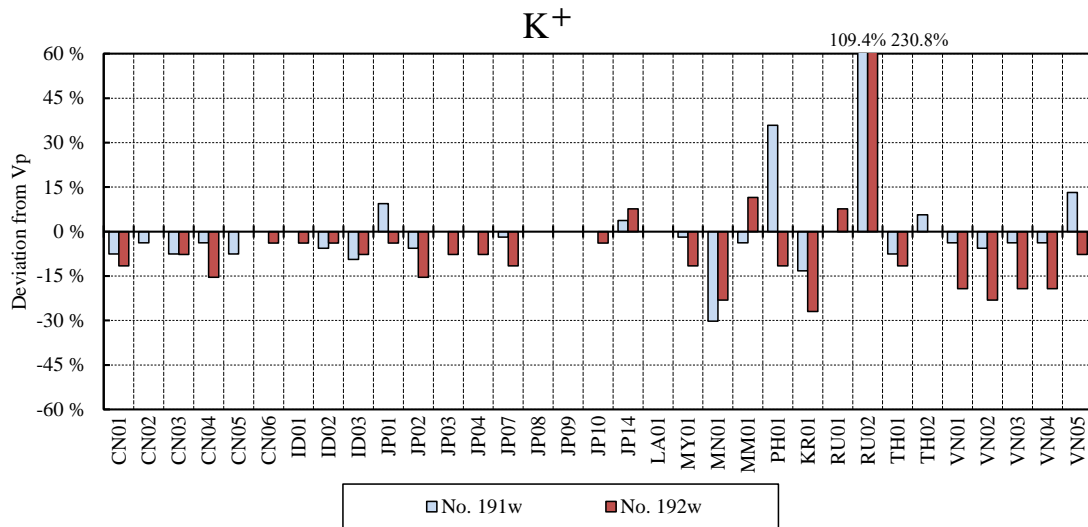


Figure 2.19 Deviation from prepared value for K⁺ (normalized by prepared value)

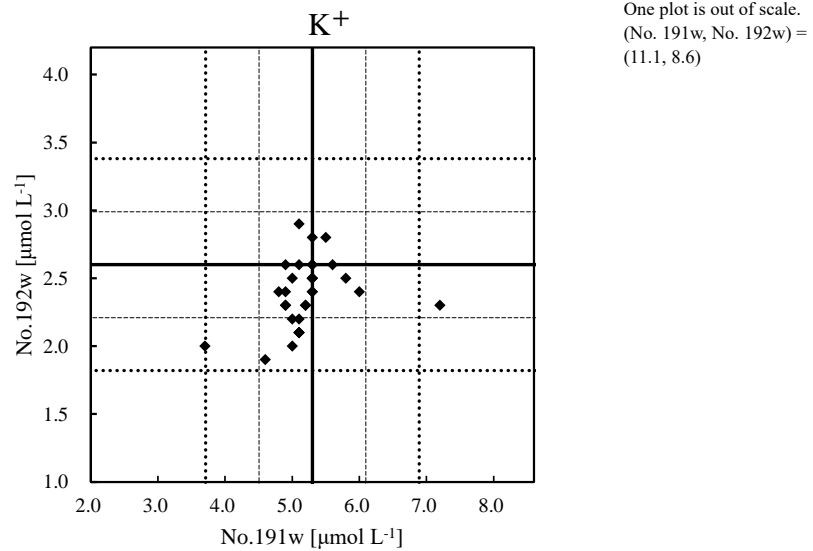


Figure 2.20 Scatter diagram for K⁺

9) Ca²⁺

The data of sample No. 191w from 2 laboratories (JP08 and TH02) and the data of sample No. 192w from 6 laboratories (ID02, JP01, MM01, PH01, VN03 and VN05) were marked with flag “E”. Additionally, the data of sample No.192w from 2 laboratories (JP08 and TH02) were marked with flag “X”.

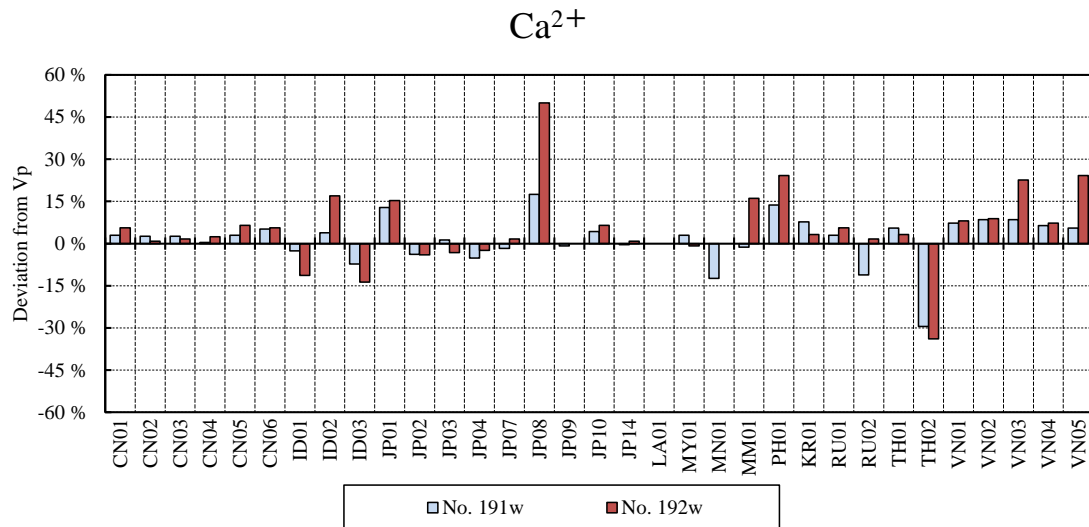


Figure 2.21 Deviation from prepared value for Ca²⁺ (normalized by prepared value)

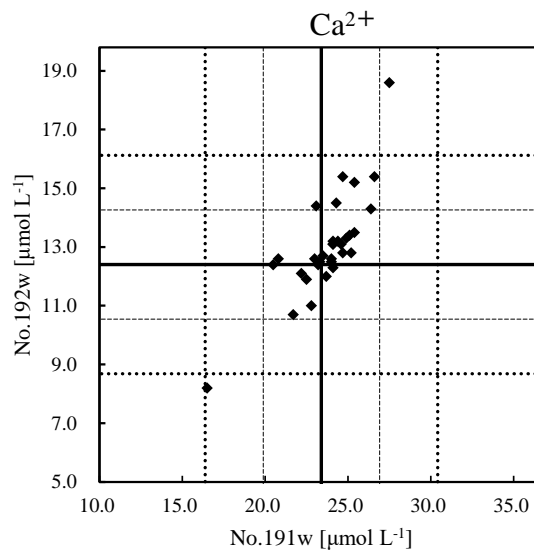


Figure 2.22 Scatter diagram for Ca²⁺

10) Mg²⁺

The data of sample No. 191w from 4 laboratories (ID03, MN01, RU02 and TH02) and the data of sample No. 192w from 2 laboratories (MN01 and TH02) were marked with flag “E”. Additionally, the data of sample No. 192w from RU02 was marked with flag “X”.

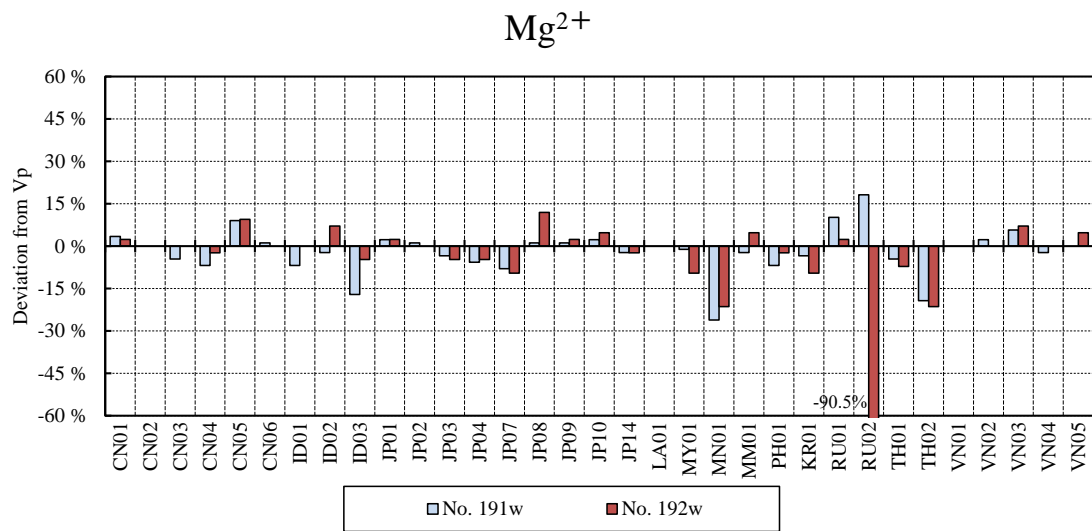


Figure 2.23 Deviation from prepared value for Mg²⁺ (normalized by prepared value)

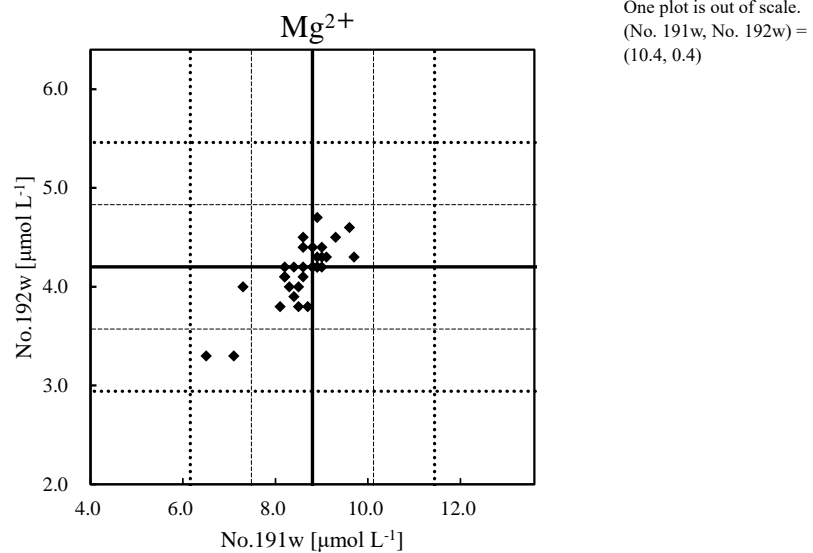


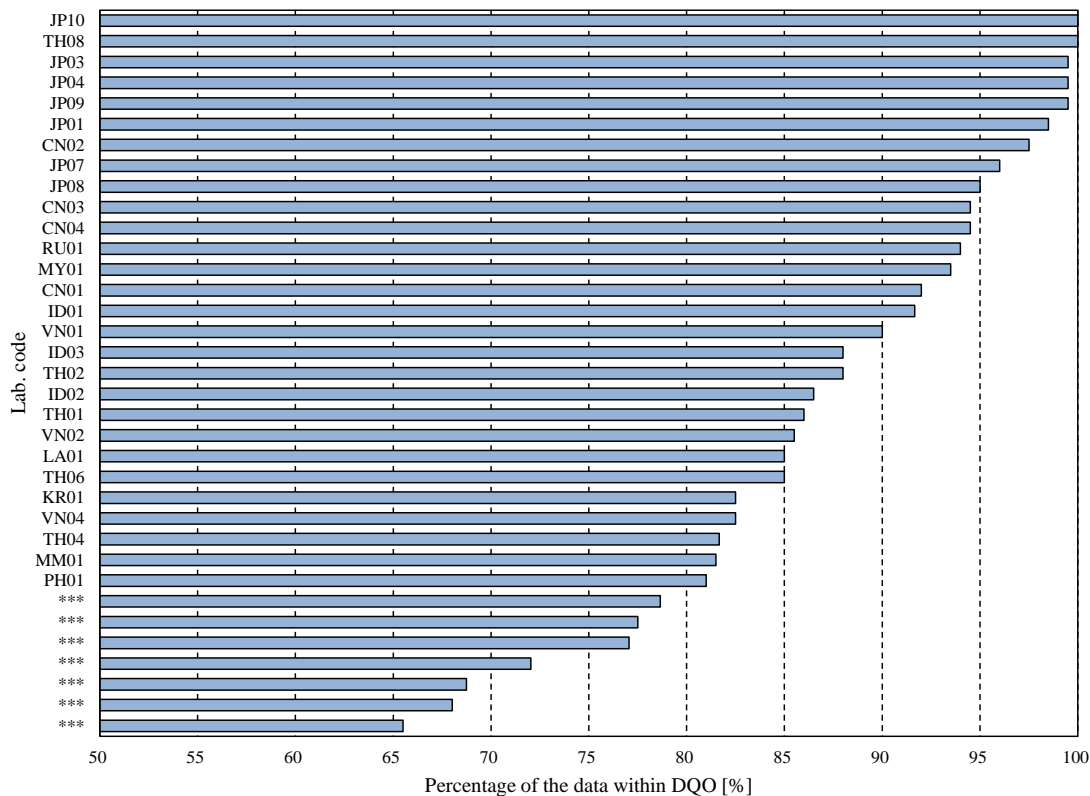
Figure 2.24 Scatter diagram for Mg²⁺

11) Scatter diagrams

Most of constituents showed positive correlation between the submitted pairs of results of sample No. 191w and 192w. 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 2010 to 2019. While all of the analytical data of 2 laboratories (JP10 and TH08*) were satisfied DQO, 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%.
 TH08*: Ion parameters are not included in the percentage of TH08.

Figure 2.25 Percentage of the data within DQO for each participating laboratory (2010-2019)

2.3.3 Sample and analysis evaluation

The concentrations of the analytical parameters in the samples for this survey were fixed on the basis of the reference to monitoring data on wet deposition in EANET. Two samples were not

distinguished as high or low concentration samples when they were distributed to participating laboratories. Ions (including pH as H⁺) concentrations of sample No. 191w were higher than those of No. 192w.

The relative standard deviations (R.S.D.) of each parameter for sample No. 191w and No. 192w are shown in the Figure 2.26. The R.S.D. values of sample No. 192w were higher than sample No.191w except for pH, EC, K⁺ and Mg²⁺. The difference between the R.S.D. values for sample No.191w and sample No. 192w were large in NH₄⁺ and Na⁺. The R.S.D. of Na⁺ for sample No. 192w was the highest in this survey.

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

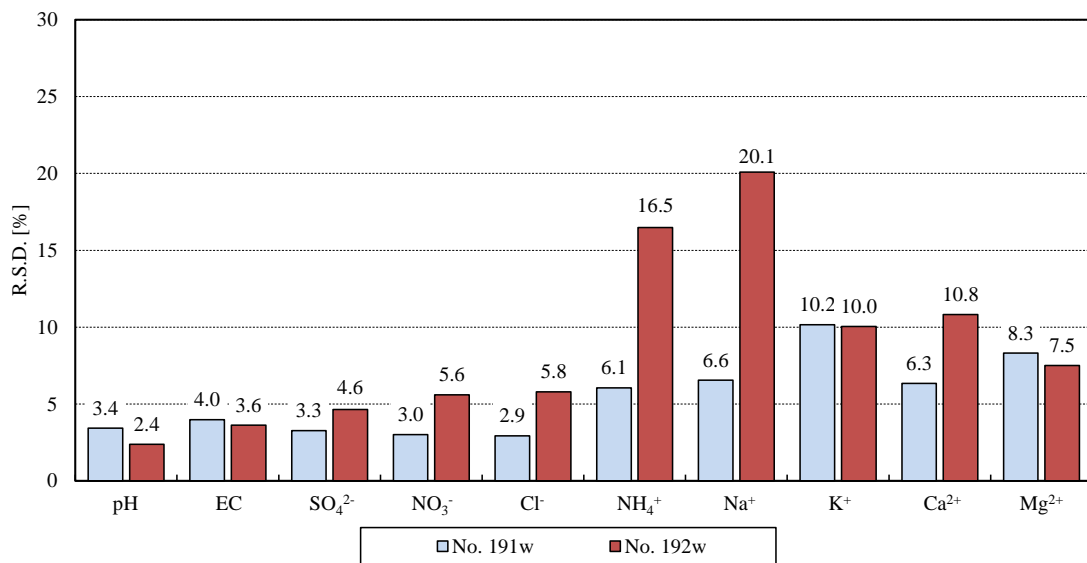


Figure 2.26 Relative standard deviations (R.S.D.) of each parameter

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” and “C” mean individuals of analysts in each laboratory who carried out analyses. In 19 laboratories, same analyst carried out the analyses for all parameters. Clear relationship between the number of analysts and flagged data was not suggested.

Table 2.11 Number of analysts

Lab. ID	Total	pH	EC	SO 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	1	A	A	A	A	A	A	A	A	A	A
CN04	1	A	A	A	A	A	A	A	A	A	A
CN05	2	A	A	B	B	B	B	B	B	B	B
CN06	2	A	A	B	B	B	B	B	B	B	B
ID01	3	A	A	B	B	B	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	1	A	A	A	A	A	A	A	A	A	A
JP07	1	A	A	A	A	A	A	A	A	A	A
JP08	1	A	A	A	A	A	A	A	A	A	A
JP09	1	A	A	A	A	A	A	A	A	A	A
JP10	1	A	A	A	A	A	A	A	A	A	A
JP14	1	A	A	A	A	A	A	A	A	A	A
LA01	1	A	A	A	A	A	---	---	---	---	---
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	2	A	A	B	B	B	B	B	B	B	B
MM01	1	A	A	A	A	A	A	A	A	A	A
PH01	1	A	A	A	A	A	A	A	A	A	A
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	B	A	A	A	A	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. 191w or No. 192w was marked with flag "E" or "X";

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

"---", Not measured

Total of 282 data out of 648 were analyzed by the analysts whose experience was less than 5 years. The number corresponds to 43.5% of all the submitted data. Clear relationship between the years of experience and flagged data was not suggested.

Table 2.12 Years of experience

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
CN01	3	3	3	3	3	3	3	3	3	3
CN02	2	2	14	14	14	14	14	14	14	14
CN03	2	2	2	2	2	2	2	2	2	2
CN04	11	11	11	11	11	11	11	11	11	11
CN05	2	2	2	2	2	2	2	2	2	2
CN06	2	2	2	2	2	2	2	2	2	2
ID01	5	5	1	1	1	1	1	1	1	1
ID02	6	6	13	13	13	13	13	13	13	13
ID03	11	11	11	11	11	11	11	11	11	11
JP01	16	16	16	16	16	16	16	16	16	16
JP02	1	1	1	1	1	1	1	1	1	1
JP03	2	2	2	2	2	2	2	2	2	2
JP04	5	5	5	5	5	5	5	5	5	5
JP07	1	1	1	1	1	1	1	1	1	1
JP08	1	1	1	1	1	1	1	1	1	1
JP09	1	1	1	1	1	1	1	1	1	1
JP10	1	1	1	1	1	1	1	1	1	1
JP14	1	1	1	1	1	1	1	1	1	1
LA01	1	1	1	1	1	---	---	---	---	---
MY01	6	6	10	10	10	7	7	7	7	7
MN01	12	12	16	16	16	16	16	16	16	16
MM01	6	6	6	6	6	6	6	6	6	6
PH01	5	5	5	5	5	5	5	5	5	5
KR01	1	1	1	1	1	1	1	1	1	1
RU01	21	21	19	19	19	21	21	21	21	21
RU02	5	5	5	5	5	5	2	2	2	2
TH01	10	10	9	9	9	9	9	9	9	9
TH02	22	22	22	22	22	22	22	22	22	22
VN01	3	3	6	6	6	6	6	6	6	6
VN02	10	10	6	6	6	6	6	6	6	6
VN03	5	5	7	5	---	5	7	7	7	7
VN04	15	15	13	13	13	13	13	13	13	13
VN05	6	6	12	12	12	12	12	12	12	12

Note: Light mesh, Analytic data of sample No. 191w or No. 192w 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 specified methods described in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. RU02 used Titrimetry for the analyses of Cl^- . In addition, RU01 and RU02 used Spectrophotometry with Nessler's Reagent for the analyses of NH_4^+ . The specified methods are shown in Table 2.3. Analytical methods used for the measurement in the participating laboratories are shown in Table 2.13. Clear relationship between analytical methods and flagged data was not suggested.

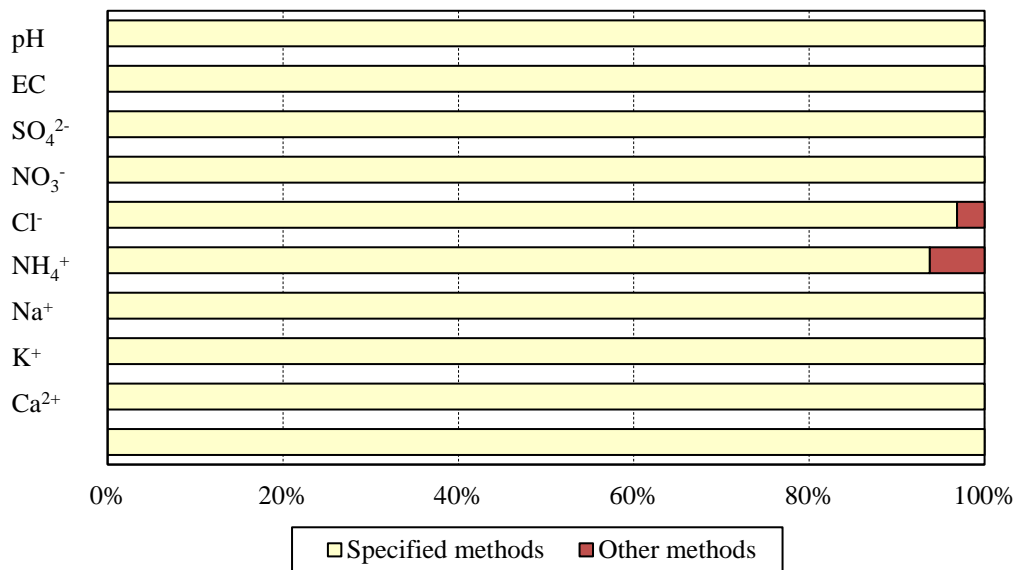


Figure 2.27 Percentage of laboratories that use the specified methods

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
CN05	IC	IC	IC	IC	IC	IC	IC	IC
CN06	IC	IC	IC	IC	IC	IC	IC	IC
ID01	IC	IC	IC	IC	IC	IC	IC	IC
ID02	IC	IC	IC	IC	IC	IC	IC	IC
ID03	IC	IC	IC	IC	IC	IC	IC	IC
JP01	IC	IC	IC	IC	IC	IC	IC	IC
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	---	---	---	---	---
MY01	IC	IC	IC	IC	IC	IC	IC	IC
MN01	IC	IC	IC	IC	IC	IC	IC	IC
MM01	IC	IC	IC	IC	IC	IC	IC	IC
PH01	IC	IC	IC	IC	IC	IC	IC	IC
KR01	IC	IC	IC	IC	IC	IC	IC	IC
RU01	IC	IC	IC	SP	AAS	AAS	AAS	AAS
RU02	SP	SP	TI	SP	AAS	AAS	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

AES: Atomic Emission Spectrometry

TI: Titrimetry

AAS: Atomic Absorption Spectrometry

SP: Spectrophotometry

3) Date of analysis

Figure 2.28 shows the distribution of “Start date” and “Finish date” of analysis in the participating laboratories. In total, 54% of all the submitted data was determined within the year of 2019, and 9% was finished after the deadline of data submission in this project.

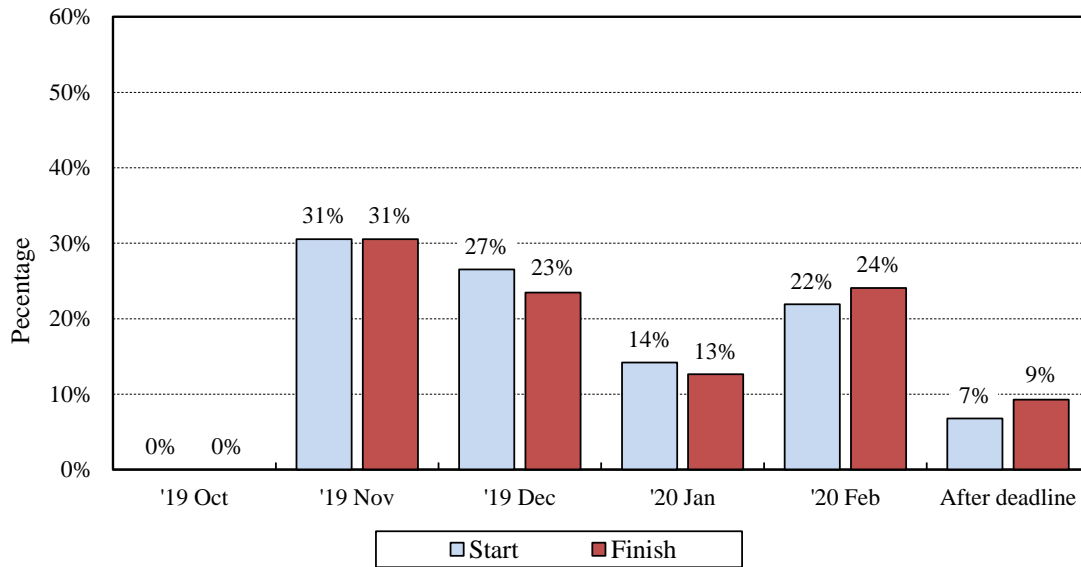


Figure 2.28 Distribution of start date and finish date of analysis

Figure 2.29 shows how many days were needed to determine the analytical data in the participating laboratories. Most analytical data were obtained within less than 3 days.

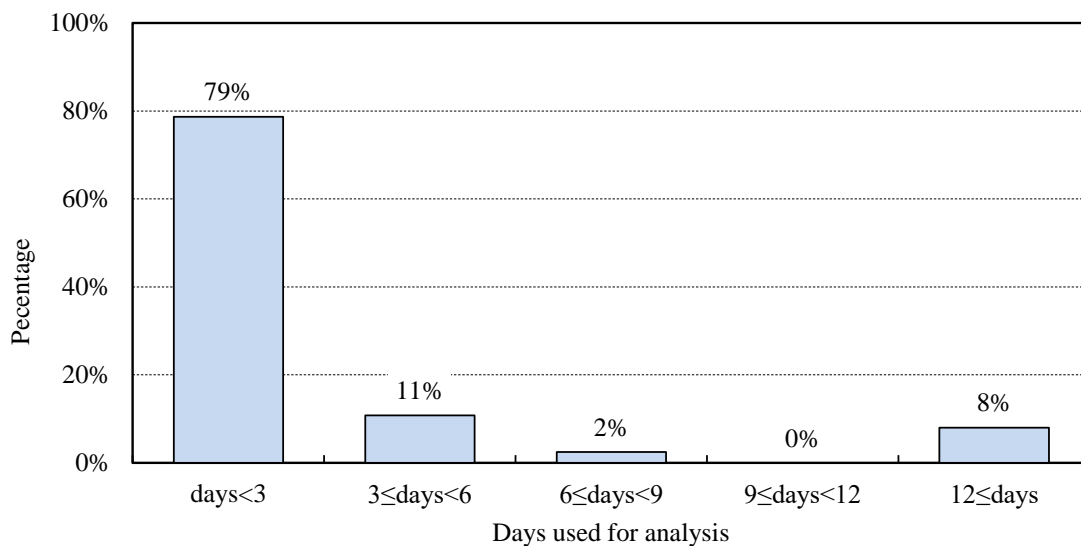


Figure 2.29 Distribution of days used for analysis

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

2.4 Comparison with past surveys

Since the beginning of EANET, inter-laboratory comparison on wet deposition reached the 22nd survey. The percentages of data within DQO and prepared value of EC are shown in Figure 2.30. Hereafter, sample No. 191w and sample No. 192w were treated as high and low concentration samples respectively.

The percentage of data within DQO for the sample No. 191w and No. 192w were 94.1% and 86.1% respectively. As shown in this figure, there is a tendency that the percentages of data within DQO depend on prepared values of EC in low concentration samples.

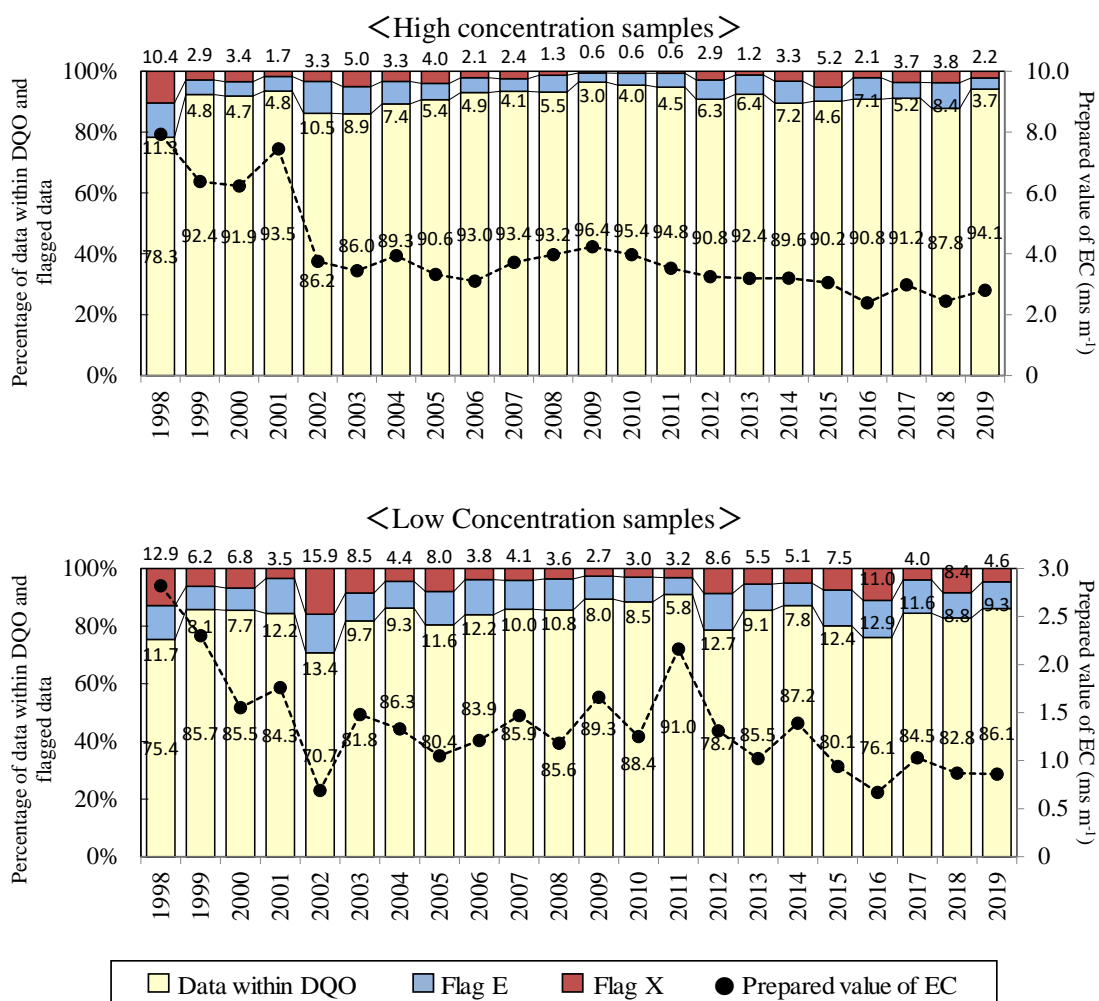


Figure 2.30 Comparison of results from the inter-laboratory comparison projects

Figure 2.31 shows the trend of the prepared values and the percentage of the flagged data. The percentages of the flagged data are relatively high in cations than anions through the series of surveys. The percentage of the flagged data of anions in 2019 was improved than 2018 even considering the concentration differences.

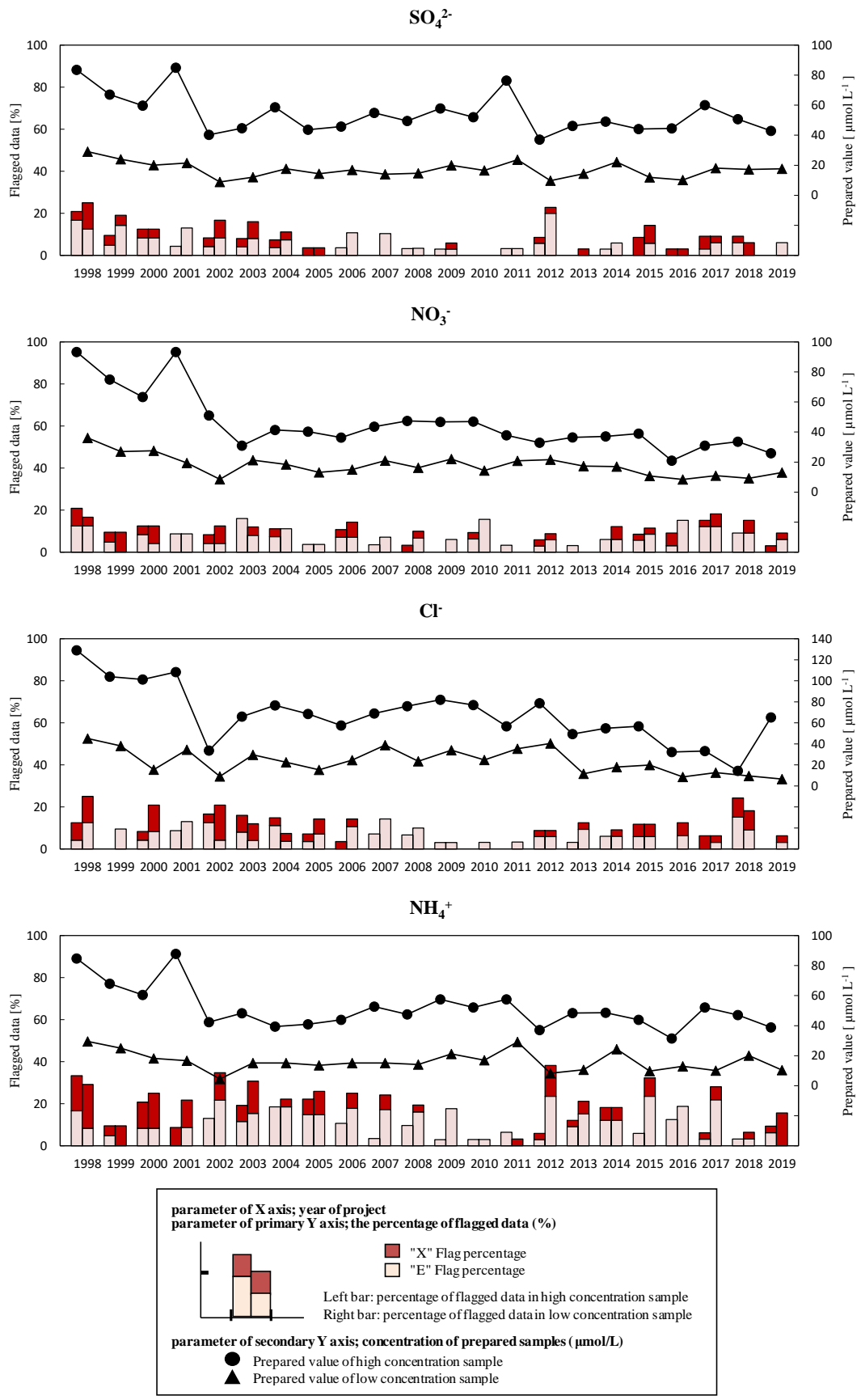


Figure 2.31 Comparison for each parameter in inter-laboratory comparison (ILC) project

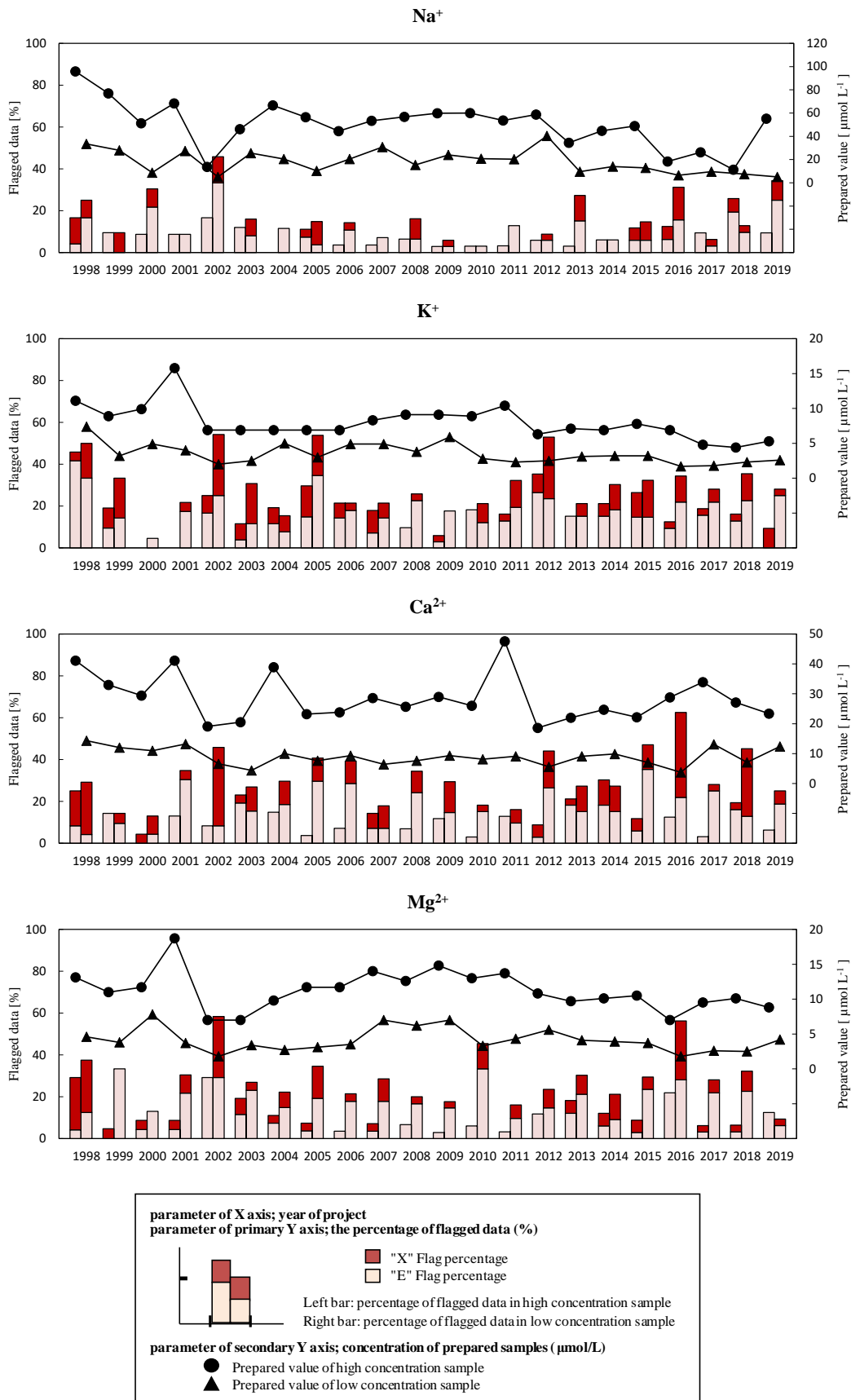


Figure 2.31 Comparison for each parameter in ILC project (continued)

As shown in figure 2.32, the total number of data in this survey was 648.

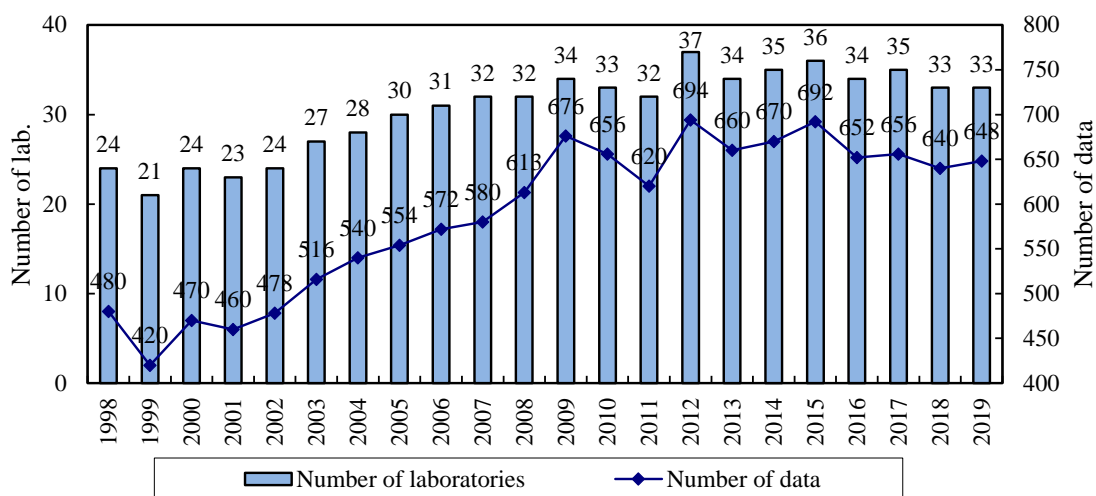


Figure 2.32 The number of participating laboratories and data in the inter-laboratory comparison projects on wet deposition

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.

2.5.2 Data control

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

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

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

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

References

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

Appendix 2.1 Data precision of submitted data

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

$$\text{R.S.D.} = \sigma / \bar{V}_a \times 100\%$$

σ : standard deviation of result

\bar{V}_a : average of result

In Appendix Table 2.1.1 and Appendix Table 2.1.2, data precisions calculated from the submitted results are shown. Sample No. 191w of higher concentration had a tendency to show better R.S.D. than sample No. 192w of lower concentration in each constituent. It was suggested that R.S.D. was greatly affected by sample concentration.

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

Appendix Table 2.1.1 Data precision (R.S.D.) of sample No. 191w

Lab. ID	pH as H ⁺ %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	NH ₄ ⁺ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %
CN01	9.0	0.9	0.3	0.3	0.3	0.8	0.7	3.2	0.8	0.4
CN02	2.9	0.2	0.2	0.4	0.1	0.1	0.1	1.0	0.2	0.4
CN03	1.6	0.2	0.3	0.2	0.1	0.3	0.2	0.7	0.4	0.0
CN04	1.7	0.6	0.1	0.3	0.9	0.4	0.4	0.0	1.2	0.6
CN05	1.6	0.2	0.3	0.1	0.2	0.0	0.4	0.0	0.7	1.4
CN06	2.8	0.4	0.2	0.4	0.7	1.1	0.1	2.8	0.2	3.3
ID01	2.7	1.2	1.4	1.4	2.9	1.2	2.2	1.4	2.2	2.1
ID02	11.8	0.0	0.6	0.3	0.4	1.0	1.0	1.0	1.3	2.5
ID03	3.3	1.0	0.6	0.6	0.7	1.1	0.6	3.3	1.4	1.7
JP01	2.4	0.6	0.6	0.6	0.6	0.7	0.6	2.1	1.1	0.6
JP02	3.0	0.6	0.4	0.5	0.4	0.5	0.2	2.3	3.2	6.7
JP03	1.1	0.3	0.2	0.5	0.3	0.3	0.2	0.0	0.7	0.0
JP04	1.1	0.2	0.3	0.3	0.2	0.4	0.4	1.9	0.7	0.8
JP07	7.4	0.4	1.3	1.3	1.2	0.7	1.0	1.7	0.9	0.9
JP08	6.9	0.9	0.3	0.3	0.2	0.5	1.4	0.8	1.0	1.1
JP09	2.3	0.3	0.1	0.1	0.1	0.1	0.1	0.0	0.2	0.0
JP10	1.6	0.2	0.2	0.3	0.2	0.3	0.2	0.0	0.3	0.0
JP14	4.4	0.7	0.3	0.3	0.3	0.3	0.6	4.6	0.7	0.8
LA01	13.1	0.6	0.9	2.2	0.6	--	--	--	--	--
MY01	5.6	0.3	0.4	0.3	0.7	0.8	0.7	1.3	0.5	1.0
MN01	7.5	1.5	2.4	1.9	1.7	7.1	1.3	10.9	2.0	3.1
MM01	46.3	1.9	15.4	4.4	5.7	0.7	0.3	3.4	0.8	2.5
PH01	2.5	0.4	0.5	1.0	0.2	5.8	2.9	20.3	5.3	3.9
KR01	13.3	1.1	1.0	1.1	1.1	0.7	0.9	1.5	1.0	1.4
RU01	3.1	1.1	3.6	4.7	3.8	1.6	0.2	0.0	0.4	0.3
RU02	17.0	0.8	3.6	2.0	3.1	7.0	4.8	8.7	4.5	7.4
TH01	3.7	0.8	0.1	0.2	0.1	0.1	0.1	1.4	0.7	0.5
TH02	2.2	0.8	0.5	1.2	0.3	0.6	0.2	5.5	0.3	0.0
VN01	4.1	1.1	0.4	0.7	0.4	0.9	0.5	3.8	1.0	2.9
VN02	2.3	0.3	0.3	0.6	0.3	0.4	0.4	2.2	0.5	2.1
VN03	2.2	0.0	0.2	0.4	--	0.1	0.5	0.7	0.6	1.4
VN04	8.6	1.0	0.2	0.2	0.1	0.1	0.1	0.7	0.1	0.6
VN05	2.3	0.1	1.3	3.1	0.5	2.0	1.6	1.2	3.4	2.3
Number of data	33	33	33	33	32	32	32	32	32	32
Minimum	1.1	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.0
25% value	2.3	0.3	0.2	0.3	0.2	0.3	0.2	0.7	0.5	0.5
Median	3.0	0.6	0.4	0.5	0.4	0.7	0.5	1.5	0.7	1.1
75% value	7.4	0.9	0.9	1.2	0.8	1.0	0.9	3.2	1.2	2.3
Maximum	46.3	1.9	15.4	4.7	5.7	7.1	4.8	20.3	5.3	7.4

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. 192w

Lab. ID	pH as H ⁺ %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	NH ₄ ⁺ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %
CN01	4.7	1.1	0.6	0.6	1.0	1.4	1.4	5.5	1.1	1.2
CN02	2.6	0.7	0.5	0.4	2.0	0.5	0.6	1.3	0.6	0.8
CN03	1.6	1.1	0.3	0.3	0.5	0.9	0.6	2.1	1.0	1.2
CN04	2.4	0.0	0.3	0.0	0.0	0.9	0.0	2.0	0.0	0.0
CN05	1.9	0.5	0.5	0.7	0.0	2.4	0.0	2.5	0.5	0.0
CN06	4.4	1.1	0.4	0.5	0.8	0.0	0.9	2.0	0.5	6.7
ID01	4.9	0.7	2.1	1.5	4.9	1.8	6.7	14.2	4.8	1.7
ID02	4.3	0.0	0.5	0.4	0.7	1.3	1.7	0.0	1.0	1.1
ID03	8.6	1.1	1.3	1.4	1.1	3.2	0.9	1.4	10.4	4.8
JP01	2.7	1.6	0.6	1.1	2.7	0.5	0.7	2.0	1.9	2.6
JP02	7.4	1.1	0.2	0.4	0.8	0.9	0.9	1.5	3.2	1.7
JP03	1.5	0.0	0.5	0.8	0.5	0.5	0.7	1.9	0.7	0.0
JP04	2.0	1.0	1.0	1.0	0.8	1.4	3.2	2.8	1.0	2.8
JP07	3.4	0.7	0.5	0.7	0.0	0.5	0.9	0.0	0.4	1.3
JP08	6.7	0.9	0.3	0.3	0.7	0.7	8.7	2.3	1.7	1.5
JP09	2.5	0.9	0.3	0.4	0.8	0.6	0.0	0.0	0.3	0.0
JP10	3.2	0.8	0.7	0.7	0.8	0.5	1.9	2.0	1.9	1.1
JP14	11.0	2.2	0.7	0.8	1.4	1.4	5.2	3.9	1.1	1.2
LA01	19.6	0.6	3.1	5.8	2.5	--	--	--	--	--
MY01	4.1	0.7	1.0	0.4	0.8	1.2	4.3	2.6	0.9	1.6
MN01	18.7	1.3	2.7	2.2	2.9	2.2	20.3	7.5	2.8	2.0
MM01	44.4	5.0	2.5	5.0	2.9	3.8	14.0	3.0	5.8	2.9
PH01	2.3	0.6	0.5	4.6	15.2	17.1	17.9	22.0	6.3	11.4
KR01	15.6	1.3	0.9	1.5	1.0	0.6	1.4	3.9	1.0	1.9
RU01	4.0	1.4	3.7	3.6	6.2	1.7	1.0	0.0	0.6	0.8
RU02	7.9	3.1	2.2	7.7	7.4	12.9	6.8	6.3	11.2	30.0
TH01	3.2	0.5	0.3	0.0	0.8	0.3	0.0	2.1	0.3	0.9
TH02	5.0	0.6	0.2	0.5	0.8	1.3	8.6	8.8	0.0	1.5
VN01	4.5	2.0	1.2	1.7	1.7	2.4	3.6	6.8	0.9	3.7
VN02	1.8	1.0	0.7	1.3	1.3	1.6	4.2	5.9	0.9	2.3
VN03	2.9	0.0	0.3	0.5	--	0.5	1.4	1.6	0.7	1.7
VN04	7.3	2.3	0.2	0.3	0.5	0.4	1.3	2.3	0.4	1.0
VN05	1.8	0.0	5.3	5.3	1.4	5.5	2.1	6.3	3.9	2.5
Number of data	33	33	33	33	32	32	32	32	32	32
Minimum	1.5	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
25% value	2.5	0.6	0.3	0.4	0.7	0.5	0.8	1.8	0.6	1.1
Median	4.1	0.9	0.6	0.7	0.9	1.2	1.4	2.3	1.0	1.6
75% value	7.3	1.3	1.2	1.5	2.1	1.9	4.5	5.6	2.2	2.5
Maximum	44.4	5.0	5.3	7.7	15.2	17.1	20.3	22.0	11.2	30.0

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. 191w

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
	%	%	%	%	%	%	%	%	%	%
CN01	3.7	-4.6	-1.4	-2.7	-0.6	-2.6	3.6	-7.5	3.0	3.4
CN02	1.6	-2.1	-2.8	-1.5	0.3	-1.5	-1.6	-3.8	2.6	0.0
CN03	2.0	0.7	-0.5	1.9	1.2	-1.5	-1.4	-7.5	2.6	-4.5
CN04	1.8	1.8	0.0	1.5	1.2	-3.3	2.2	-3.8	0.4	-6.8
CN05	2.7	-3.2	-4.0	-5.4	-0.5	1.3	12.3	-7.5	3.0	9.1
CN06	2.5	-6.4	-0.2	0.4	-0.2	-2.8	3.3	0.0	5.1	1.1
ID01	1.8	-2.5	-1.2	-4.6	-4.0	0.3	0.9	0.0	-2.6	-6.8
ID02	2.7	-7.1	-1.9	-1.9	-0.5	-8.0	0.0	-5.7	3.8	-2.3
ID03	4.7	-17.9	4.7	-0.8	-4.6	2.1	-1.6	-9.4	-7.3	-17.0
JP01	2.5	-1.4	0.2	1.2	-2.0	2.1	4.7	9.4	12.8	2.3
JP02	1.0	-2.9	0.0	-1.9	-1.5	-0.8	-2.9	-5.7	-3.8	1.1
JP03	0.6	-1.8	2.1	3.1	2.8	-1.0	-0.4	0.0	1.3	-3.4
JP04	0.8	-2.5	-1.2	-1.5	-1.4	0.5	-4.2	0.0	-5.1	-5.7
JP07	1.8	-2.9	0.5	-1.9	-0.2	0.0	-1.1	-1.9	-1.7	-8.0
JP08	1.0	-2.1	1.6	1.5	1.4	1.0	0.0	0.0	17.5	1.1
JP09	2.2	-1.1	0.2	-0.4	-0.8	-1.3	0.2	0.0	-0.9	1.1
JP10	-0.4	-1.1	2.3	2.3	1.4	-2.1	2.5	0.0	4.3	2.3
JP14	2.9	-2.5	-0.9	-0.8	-3.2	-2.1	0.0	3.8	-0.4	-2.3
LA01	1.6	-7.1	0.2	-1.5	-3.8	---	---	---	---	---
MY01	-0.6	-2.5	-2.8	-1.2	-1.1	-11.6	-2.5	-1.9	3.0	-1.1
MN01	4.3	-5.7	-4.0	-2.3	-7.1	18.5	-4.2	-30.2	-12.4	-26.1
MM01	13.1	-6.1	14.7	-6.6	4.6	2.1	-0.5	-3.8	-1.3	-2.3
PH01	0.2	-2.5	1.2	0.8	0.2	-33.4	3.3	35.8	13.7	-6.8
KR01	-3.1	-1.8	-6.8	-6.6	-5.7	12.6	1.3	-13.2	7.7	-3.4
RU01	0.2	-4.3	-1.4	-10.4	-7.1	-1.3	-1.3	0.0	3.0	10.2
RU02	-17.4	101.4	8.6	162.5	-6.3	-18.0	-23.2	109.4	-11.1	18.2
TH01	-0.6	-2.9	-1.2	-3.1	-1.4	-6.4	-0.2	-7.5	5.6	-4.5
TH02	0.6	-2.5	1.6	-0.4	-0.6	-1.5	0.4	5.7	-29.5	-19.3
VN01	8.8	-10.0	-2.6	-1.5	0.6	-0.5	14.9	-3.8	7.3	0.0
VN02	9.8	-9.3	-2.3	-1.9	-2.0	-1.0	13.6	-5.7	8.5	2.3
VN03	8.2	-3.9	5.4	-5.4	---	1.3	-7.8	-3.8	8.5	5.7
VN04	9.6	-9.3	-3.3	-1.2	3.2	0.0	20.7	-3.8	6.4	-2.3
VN05	7.2	-10.0	8.4	-6.2	-5.1	2.8	-15.4	13.2	5.6	0.0
Number of data	33	33	33	33	32	32	32	32	32	32
Average	2.4	-1.1	0.4	3.1	-1.3	-1.8	0.5	1.6	1.5	-2.0
Minimum	-17.4	-17.9	-6.8	-10.4	-7.1	-33.4	-23.2	-30.2	-29.5	-26.1
Maximum	13.1	101.4	14.7	162.5	4.6	18.5	20.7	109.4	17.5	18.2

Note: "---", Not measured

Appendix Table 2.2.2 Deviation% from prepared values of sample No. 192w

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
	%	%	%	%	%	%	%	%	%	%
CN01	1.1	0.0	-2.3	3.8	6.1	12.5	47.1	-11.5	5.6	2.4
CN02	-0.7	4.7	0.6	0.8	-1.5	1.9	11.8	0.0	0.8	0.0
CN03	0.2	10.5	2.8	-0.8	-1.5	6.7	7.8	-7.7	1.6	0.0
CN04	0.4	5.8	-0.6	-2.3	-1.5	7.7	11.8	-15.4	2.4	-2.4
CN05	3.1	1.2	-4.5	0.8	-1.5	3.8	-5.9	0.0	6.5	9.5
CN06	0.9	3.5	1.1	1.5	-1.5	6.7	15.7	-3.8	5.6	0.0
ID01	-1.8	10.5	-0.6	-9.2	4.5	1.9	-2.0	-3.8	-11.3	0.0
ID02	-4.6	1.2	1.1	3.1	3.0	-1.9	0.0	-3.8	16.9	7.1
ID03	-0.5	-4.7	0.6	-7.7	0.0	0.0	-2.0	-7.7	-13.7	-4.8
JP01	-0.4	8.1	0.6	3.1	0.0	-1.0	-2.0	-3.8	15.3	2.4
JP02	-1.3	3.5	0.0	-3.1	-9.1	-1.9	-3.9	-15.4	-4.0	0.0
JP03	-2.6	8.1	1.1	2.3	3.0	-3.8	0.0	-7.7	-3.2	-4.8
JP04	-1.6	3.5	-1.7	-1.5	-1.5	-1.9	7.8	-7.7	-2.4	-4.8
JP07	-2.7	5.8	-1.7	-4.6	-3.0	-3.8	-7.8	-11.5	1.6	-9.5
JP08	-1.3	5.8	1.7	1.5	-1.5	-2.9	5.9	0.0	50.0	11.9
JP09	0.4	4.7	0.6	-0.8	1.5	1.0	2.0	0.0	0.0	2.4
JP10	-2.9	5.8	2.3	-2.3	-7.6	-3.8	2.0	-3.8	6.5	4.8
JP14	1.8	3.5	0.0	-1.5	7.6	-1.9	15.7	7.7	0.8	-2.4
LA01	-0.4	-2.3	-0.6	-3.8	-1.5	---	---	---	---	---
MY01	-5.3	8.1	-5.7	-0.8	-1.5	-31.7	-2.0	-11.5	-0.8	-9.5
MN01	4.6	0.0	-4.0	-0.8	-6.1	31.7	92.2	-23.1	0.0	-21.4
MM01	5.1	2.3	6.8	-5.4	-3.0	6.7	25.5	11.5	16.1	4.8
PH01	-2.6	5.8	-3.4	-3.8	-3.0	-88.5	21.6	-11.5	24.2	-2.4
KR01	-3.1	2.3	-7.4	-9.2	-9.1	39.4	2.0	-26.9	3.2	-9.5
RU01	-1.8	4.7	-1.7	-6.9	-24.2	-4.8	3.9	7.7	5.6	2.4
RU02	-17.9	198.8	19.3	175.4	324.2	-64.4	360.8	230.8	1.6	-90.5
TH01	-3.8	-2.3	-1.1	-3.8	-3.0	6.7	-3.9	-11.5	3.2	-7.1
TH02	-0.2	3.5	1.1	-2.3	-3.0	-2.9	11.8	0.0	-33.9	-21.4
VN01	1.1	-1.2	-5.1	-2.3	3.0	-3.8	-27.5	-19.2	8.1	0.0
VN02	1.8	1.2	-2.8	-2.3	3.0	-4.8	-25.5	-23.1	8.9	0.0
VN03	0.0	10.5	-13.6	-16.9	---	0.0	19.6	-19.2	22.6	7.1
VN04	1.8	0.0	-6.8	-4.6	1.5	-3.8	-25.5	-19.2	7.3	0.0
VN05	-0.9	3.5	-17.0	-22.3	-6.1	11.5	11.8	-7.7	24.2	4.8
Number of data	33	33	33	33	32	32	32	32	32	32
Average	-1.0	9.6	-1.2	2.2	8.3	-2.8	17.8	-0.6	5.3	-4.1
Minimum	-17.9	-4.7	-17.0	-22.3	-24.2	-88.5	-27.5	-26.9	-33.9	-90.5
Maximum	5.1	198.8	19.3	175.4	324.2	39.4	360.8	230.8	50.0	11.9

Note: "---", Not measured

3. 15th 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 2019. 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 25 laboratories in charge of EANET dry deposition monitoring participated in this 15th activity and 20 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.191d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of sulfate and chloride ions.
No.191d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions.
No.192d-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.192d-2	Acid (H ₃ PO ₄) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions
No.193d-1	Alkali (K ₂ CO ₃) impregnated filter	Polyethylene centrifuge tube	3	Blank
No.193d-2	Acid (H ₃ PO 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 (SO₄²⁻, Cl⁻ and NH₄⁺) 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.191d-1, No.192d-1, No.193d-1

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

(2) Sample No.191d-2, No.192d-2, No.193d-2

Add 20 mL of pure water (EC<0.15 mS m⁻¹) as an extracting solvent into each centrifuge tube, then shake them for 20 minutes.

(3) Filtration

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

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

The participating laboratories were expected to use the analytical methods specified in “*Technical Manual for Wet Deposition Monitoring in East Asia – 2010*” (EANET, 2010) in Table 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 (SO₄²⁻, Cl⁻ and NH₄⁺) in the filter sample.

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

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

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

C_{sol} : concentration of each component in the filtrate (mg L⁻¹);

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

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

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

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

$M_{sol, Sample}$: quantity (μg) of each component in the filtrate from sample No.191d-1, No.191d-2, No.192d-1 and No.192d-2;

$M_{sol, Blank}$: the median quantity (μg) in the filtrate from blank sample No.193d-1 and No.193d-2.

3.3 Results

The NC distributed the filter samples to 25 laboratories in the participating countries of EANET, and received their results from 20 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, should be rejected before their calculation 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.191d and Sample No.192d were -7.7% and -5.3%. The deviations for Cl^- in Sample No.191d and Sample No.192d were -6.0% and -6.9%. The deviations for NH_4^+ in Sample No.191d and Sample No.192d were 3.3% and -0.4%.

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

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

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

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

The evaluation of the results on both Samples No.191d and No.192d 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)	$\Delta V/V_p^*$ (%)	S.D. (μg)	Number (N)	Minimum (μg)	Maximum (μg)
<u>Sample No.191d</u>							
SO_4^{2-}	7.02	6.48	-7.7	1.19	20	4.32	9.03
Cl^-	3.02	2.84	-6.0	0.30	19	2.20	3.50
NH_4^+	9.45	9.77	3.3	1.47	19	7.60	12.7
<u>Sample No.192d</u>							
SO_4^{2-}	70.1	66.4	-5.3	3.38	20	57.0	71.0
Cl^-	17.1	15.9	-6.9	1.21	20	12.4	17.5
NH_4^+	58.3	58.1	-0.4	7.54	19	42.5	79.7

* Prepared: Prepared values

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

3.3.1 Evaluation of Laboratories' Performance (by sample)

Samples No.191d-1, No.191d-2

For Sample No.191d, 16 analytical data in 59 results were flagged E, and 6 analytical data were flagged X. The total percentage of the flagged samples was 37.3 % (Figure 3.1, Table 3.4 and 3.5).

Table 3.4 Number of flagged data for Sample No.191d

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	7	5	4	16
Flag X *	2	1	3	6
Data within DQOs	11	14	12	37
Ratio of Flagged (%)	45.0	30.0	36.8	37.3

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

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

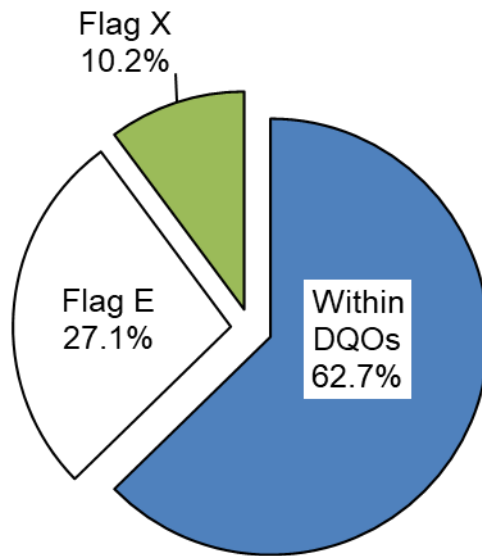


Figure 3.1 Percentage of flagged data for Sample No.191d

Table 3.5 Average analytical results of Sample No.191d

Lab. Code	SO ₄ ²⁻ (µg)	Cl ⁻ (µg)	NH ₄ ⁺ (µg)
ID01	8.12 E	2.72	10.4
ID03	7.08	3.04	9.48
JP01	6.81	2.66	9.02
JP02	6.88	2.87	9.70
JP03	7.16	2.87	9.66
JP04	6.78	2.93	9.37
JP08	7.06	2.89	9.13
JP09	6.79	2.74	9.33
JP10	6.11	2.87	8.99
LA01	7.55	4.20 X	--
MY01	5.37 E	3.50 E	11.0 E
MN01	5.81 E	3.00	12.4 X
MM01	5.30 E	3.21	7.68 E
PH01	4.99 E	2.56 E	8.75
KR01	4.32 X	2.20 E	7.60 E
RU01	6.44	2.44 E	10.5
TH01	5.51 E	3.12	9.47
TH02	4.57 X	2.39 E	7.88 E

Table 3.5 Average analytical results of Sample No.191d (continued)

Lab. Code	SO ₄ ²⁻ (µg)	Cl ⁻ (µg)	NH ₄ ⁺ (µg)
VN01	7.85	3.02	12.7 X
VN02	9.03 E	2.90	12.5 X

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

-- : No result

Samples No.192d-1, No.192d-2

For Sample No.192d, 6 analytical data in 59 results were flagged E, and 1 analytical datum was flagged X. The total percentage of the flagged samples was 11.9 % (Figure 3.2, Table 3.6 and 3.7).

Table 3.6 Number of flagged data for Sample No.192d

	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	Total
Flag E*	2	2	2	6
Flag X*	0	0	1	1
Data within DQOs	18	18	16	52
Ratio of Flagged (%)	10.0	10.0	15.8	11.9

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

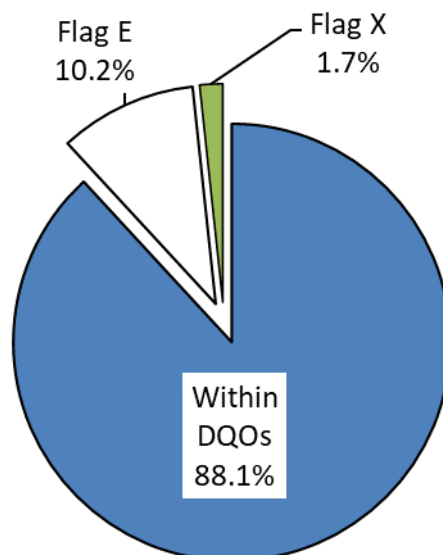


Figure 3.2 Percentage of flagged data for Sample No.192d

Table 3.7 Average analytical results of Sample No.192d

Lab. Code	SO ₄ ²⁻ (µg)	Cl ⁻ (µg)	NH ₄ ⁺ (µg)
ID01	66.5	15.6	42.5 E
ID03	66.2	16.9	62.2
JP01	67.2	16.7	54.3
JP02	69.4	16.7	59.1
JP03	70.0	17.0	57.3
JP04	69.2	16.7	59.1
JP08	69.6	17.0	57.6
JP09	67.9	16.6	57.9
JP10	71.0	16.9	53.0
LA01	68.2	12.4 E	--
MY01	67.8	17.5	79.7 X
MN01	64.9	15.0	61.1
MM01	64.5	14.9	62.4
PH01	67.1	15.3	52.2
KR01	58.9 E	15.3	43.8 E
RU01	64.3	14.3 E	62.0
TH01	64.8	16.6	61.4
TH02	57.0 E	14.6	56.3
VN01	66.0	16.2	61.2
VN02	67.2	16.1	60.5

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

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

--: No result

Blank Sample (No.193d)

Each quantity of SO_4^{2-} , Cl^- , and NH_4^+ was determined for blank sample No.193d-1 and No.193d-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 Sample No.193d (blank)

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
ID01	0.00	0.91	4.64
ID03	0.22	1.40	2.01
JP01	0.07	0.49	0.08
JP02	0.07	0.56	0.24
JP03	0.00	0.93	0.00
JP04	0.13	0.83	0.08
JP08	0.00	1.12	0.00
JP09	0.01	0.85	0.39
JP10	0.11	0.88	0.09
LA01	0.05	7.80	--
MY01	0.47	1.60	0.35
MN01	0.06	0.80	0.40
MM01	0.02	3.76	3.52
PH01	0.51	1.11	2.72
KR01	0.71	3.12	16.2
RU01	0.00	0.00	1.07
TH01	0.67	1.82	3.18
TH02	0.61	2.38	5.83
VN01	0.57	0.83	0.61
VN02	0.00	1.82	0.32
Average	0.21	1.65	2.20
Median	0.07	1.02	0.40
Minimum	0.00	0.00	0.00
Maximum	0.71	7.80	16.2
Standard deviation	0.26	1.66	3.71

-- : No result

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.

SO_4^{2-} (Sulfate)

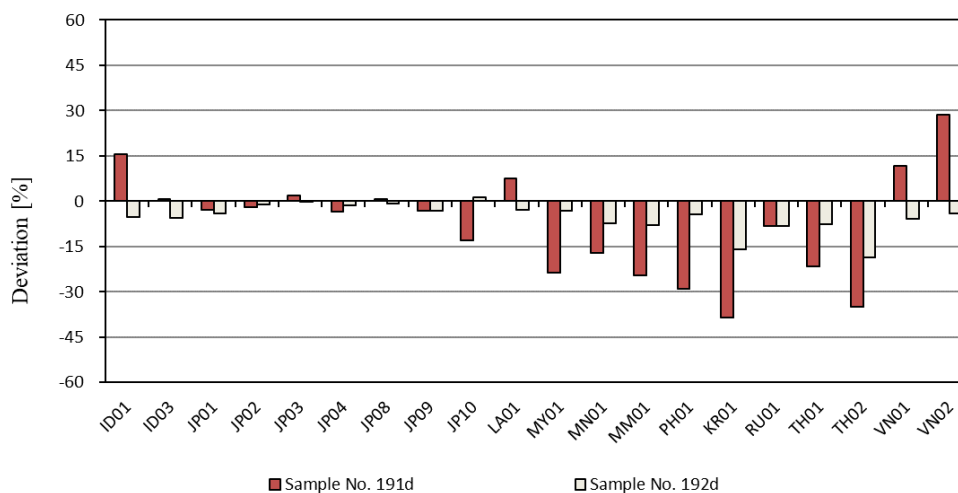


Figure 3.3 Deviation for SO_4^{2-}

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

Table 3.9 Flagged data of SO_4^{2-}

	Flag E	Flag X	Flagged (%)
Sample No.191d	7	2	45.0
Sample No.192d	2	0	10.0

All laboratories used Ion Chromatography for the determination of SO_4^{2-} . E flag appeared at 9 laboratories for Sample No.191d and No.192d. X flag appeared at 2 laboratories for Sample No.191d.

Cl⁻ (Chloride)

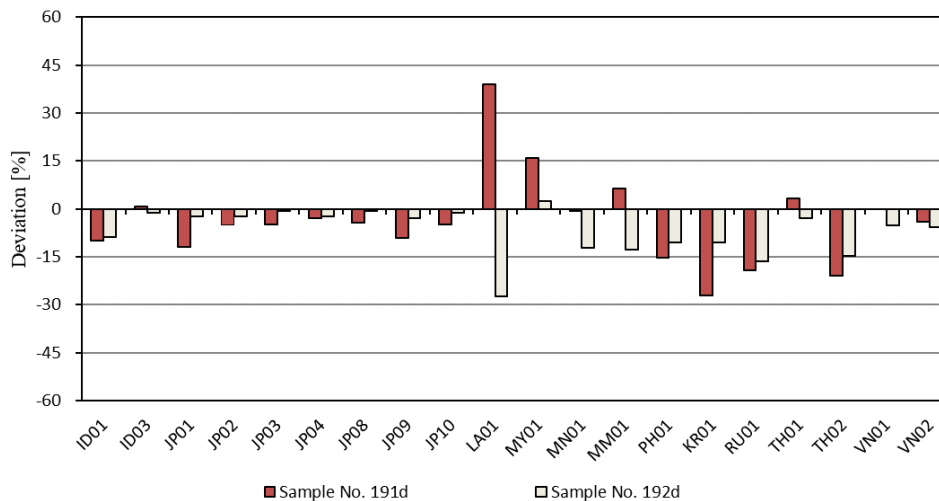


Figure 3.4 Deviation for Cl⁻

Table 3.10 Flagged data of Cl⁻

	Flag E	Flag X	Flagged (%)
Sample No.191d	5	1	30.0
Sample No.192d	2	0	10.0

As with the analysis of Cl⁻, all laboratories used Ion Chromatography for the determination of Cl⁻. E flag appeared at 7 laboratories for Sample No.191d and No.192d. X flag appeared at 1 laboratory for Sample No.191d.

NH₄⁺ (Ammonium)

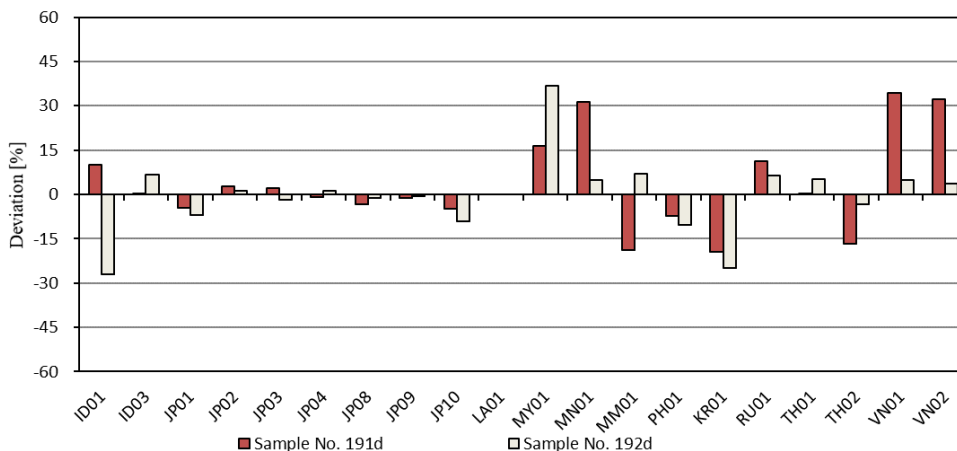


Figure 3.5 Deviation for NH₄⁺

Table 3.11 Flagged data of NH₄⁺

	Flag E	Flag X	Flagged (%)
Sample No.191d	4	3	36.8
Sample No.192d	2	1	15.8

All laboratories used Ion Chromatography for the determination of NH₄⁺. E flag appeared at 6 laboratories for Sample No.191d and No.192d. X flag appeared at 4 laboratories for Sample No. 191d and No.192d.

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.191d or No.192d. A dark gray color cell indicates the flagged data in both Sample No.191d and No.192d.

Table 3.12 Years of staff experience (unit: year)

Lab. Code	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺
ID01	1	1	1
ID03	10	10	10
JP01	16	16	16
JP02	1	1	1
JP03	2	2	2
JP04	5	5	5
JP08	1	1	1
JP09	1	1	1
JP10	1	1	1
LA01	1	1	--
MY01	7	7	7
MN01	16	16	16
MM01	6	6	6
PH01	1	1	1
KR01	1	1	1
RU01	19	19	19
TH01	9	9	9
TH02	22	22	22

Table 3.12 Years of staff experience (unit: year) (continued)

Lab. Code	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺
VN01	6	6	6
VN02	6	6	6

 : One sample is flagged.

 : Two samples are flagged.

Flagged Data

In the results of Sample No.191d and No.192d, the total number of the flagged data was 29 (E: 22, X: 7) in the whole values (118). The number of the flagged data in each laboratory is shown in Figure 3.6. Six laboratories met DQOs (25%).

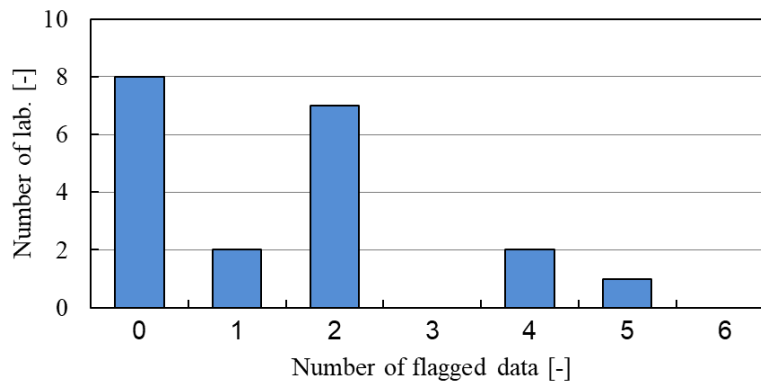
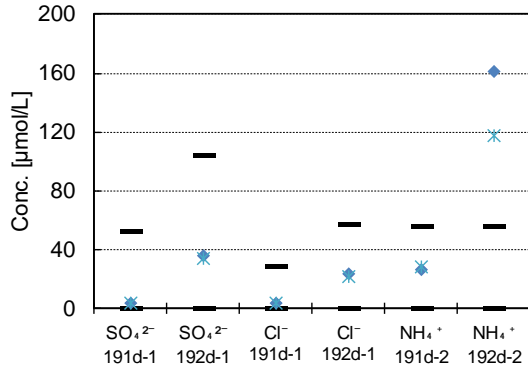


Figure 3.6 Number of flagged data and laboratories

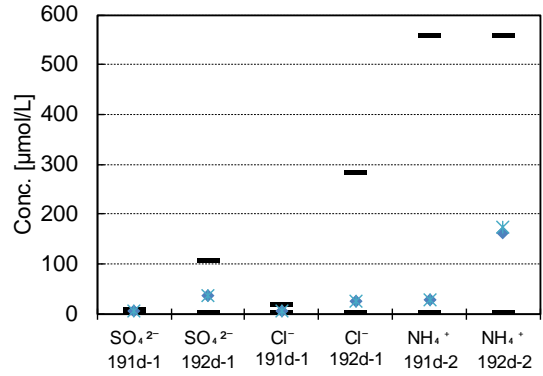
Calibration standard solution

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

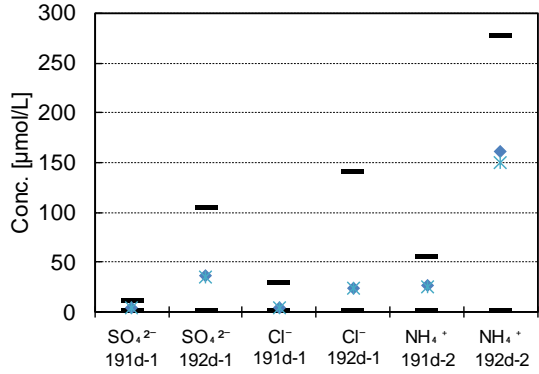
ID01



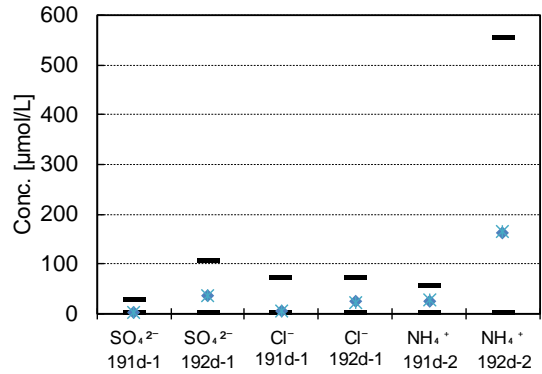
ID03



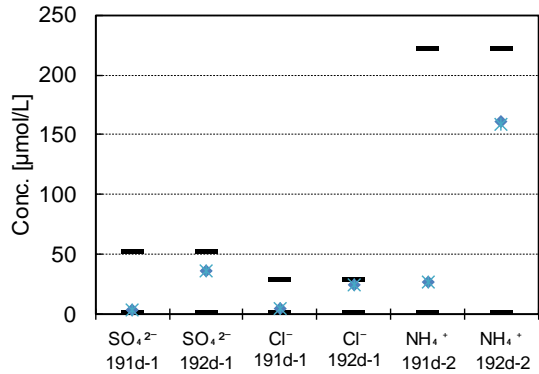
JP01



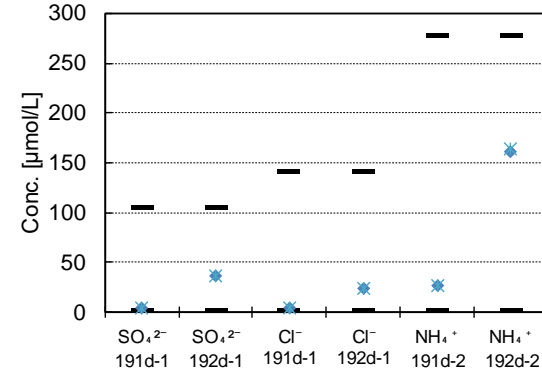
JP02



JP03



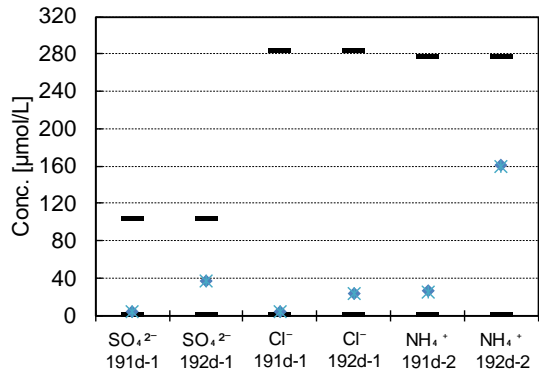
JP04



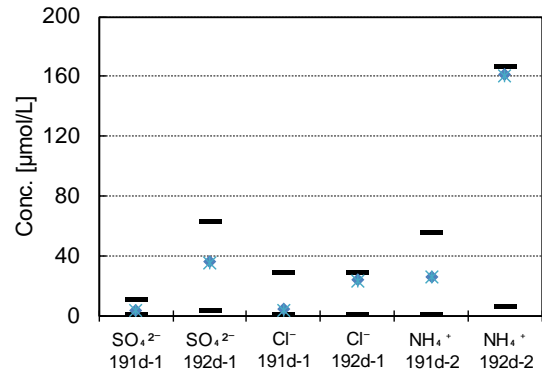
— Min and Max ◆ Prepared value ✕ result

Figure 3.7 Ranges of the calibration standard solution in each laboratory

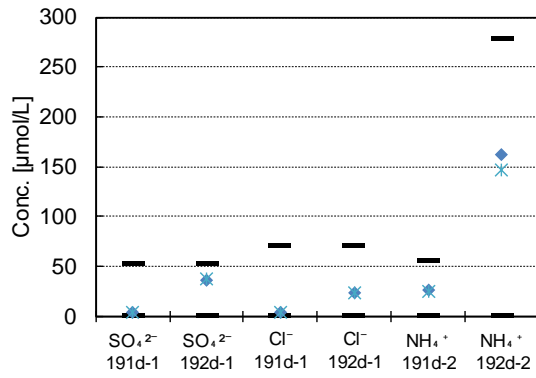
JP08



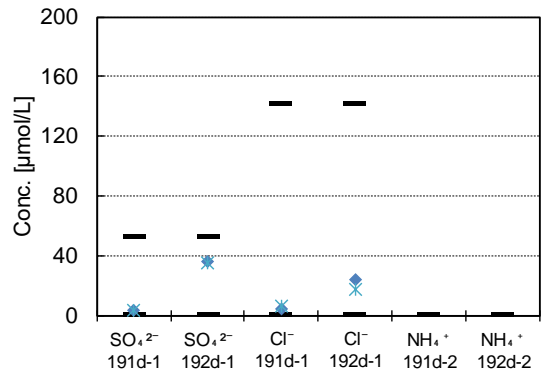
JP09



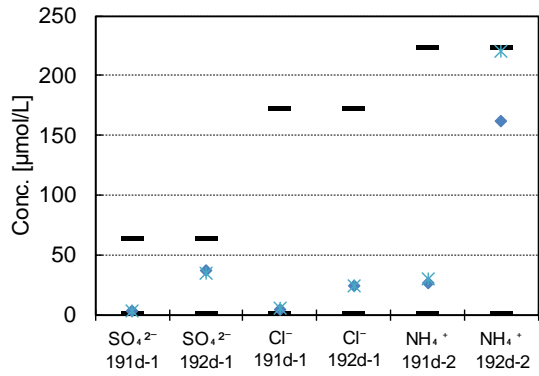
JP10



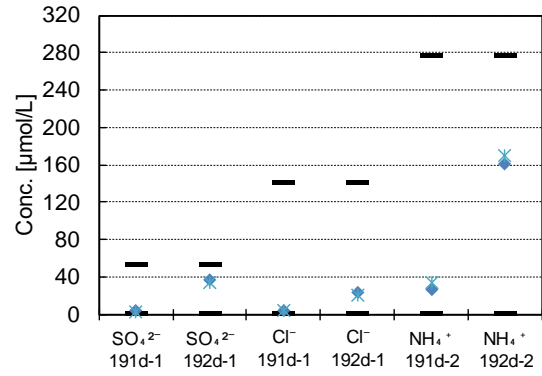
LA01



MY01



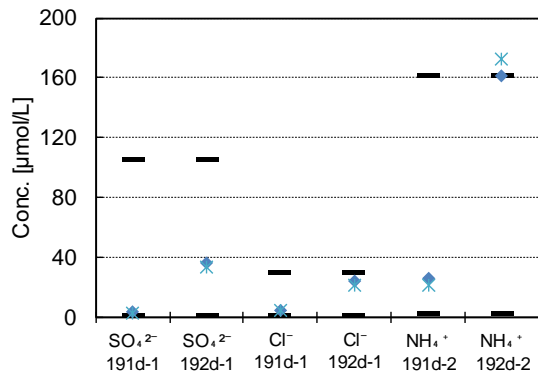
MN01



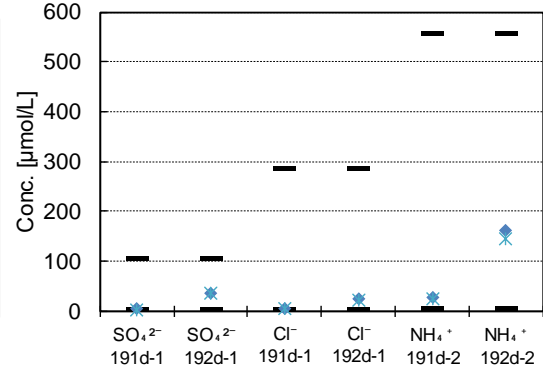
— Min and Max ◆ Prepared value ✕ result

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

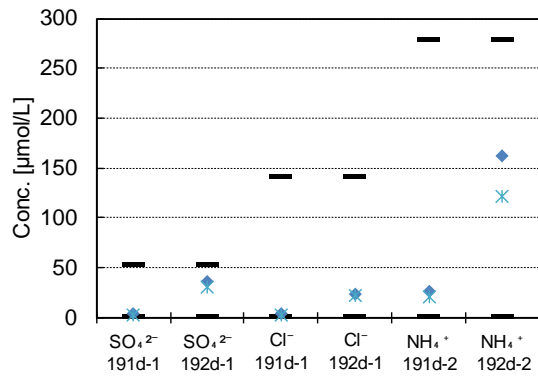
MM01



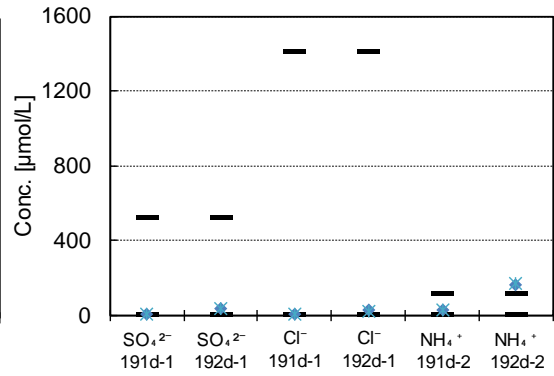
PH01



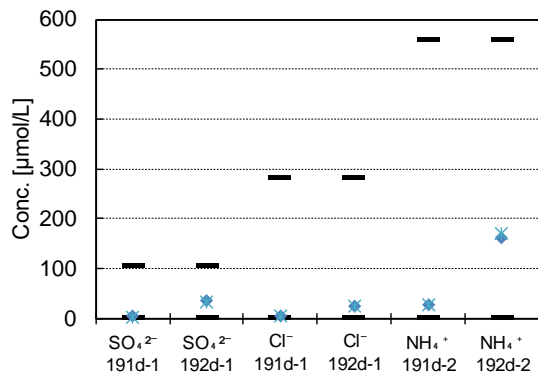
KR01



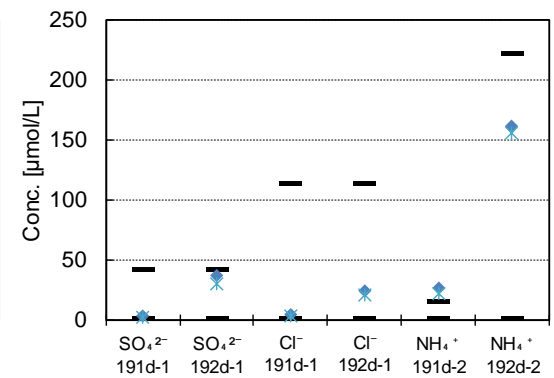
RU01



TH01



TH02



— Min and Max ◆ Prepared value ✕ result

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

VN01

VN02

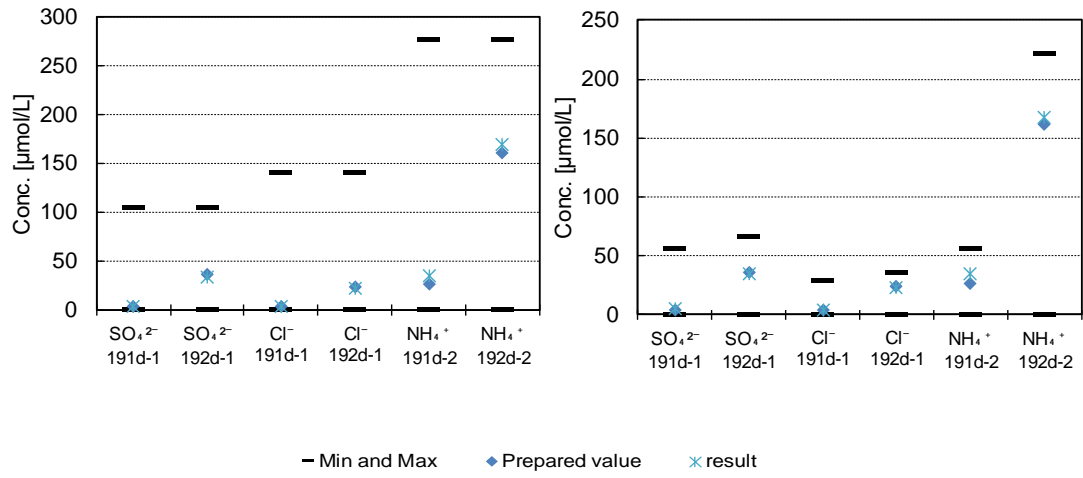


Figure 3.7 Ranges of the calibration standard solution in each laboratory (continued)

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.

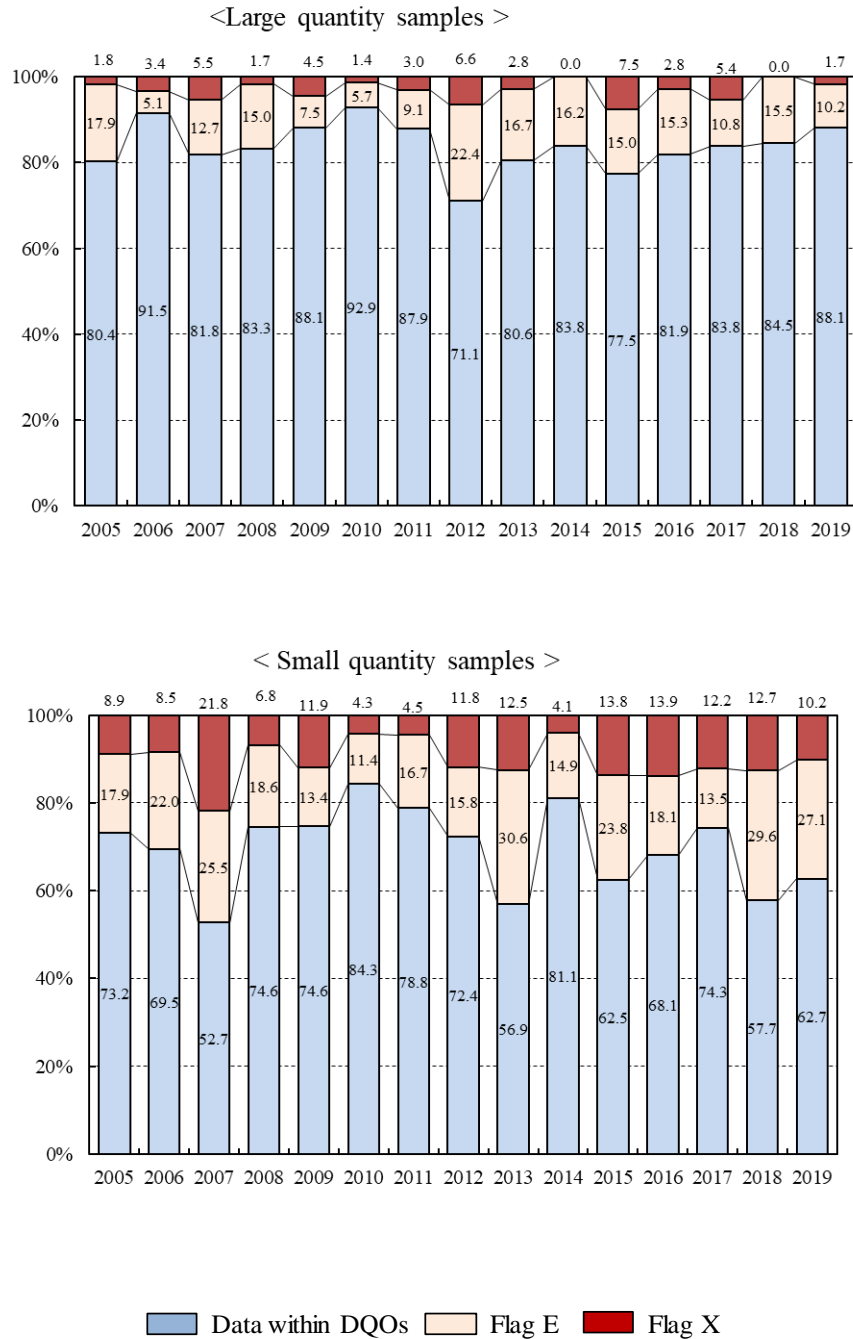


Figure 3.8 Comparison of DQOs' results for the past years

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

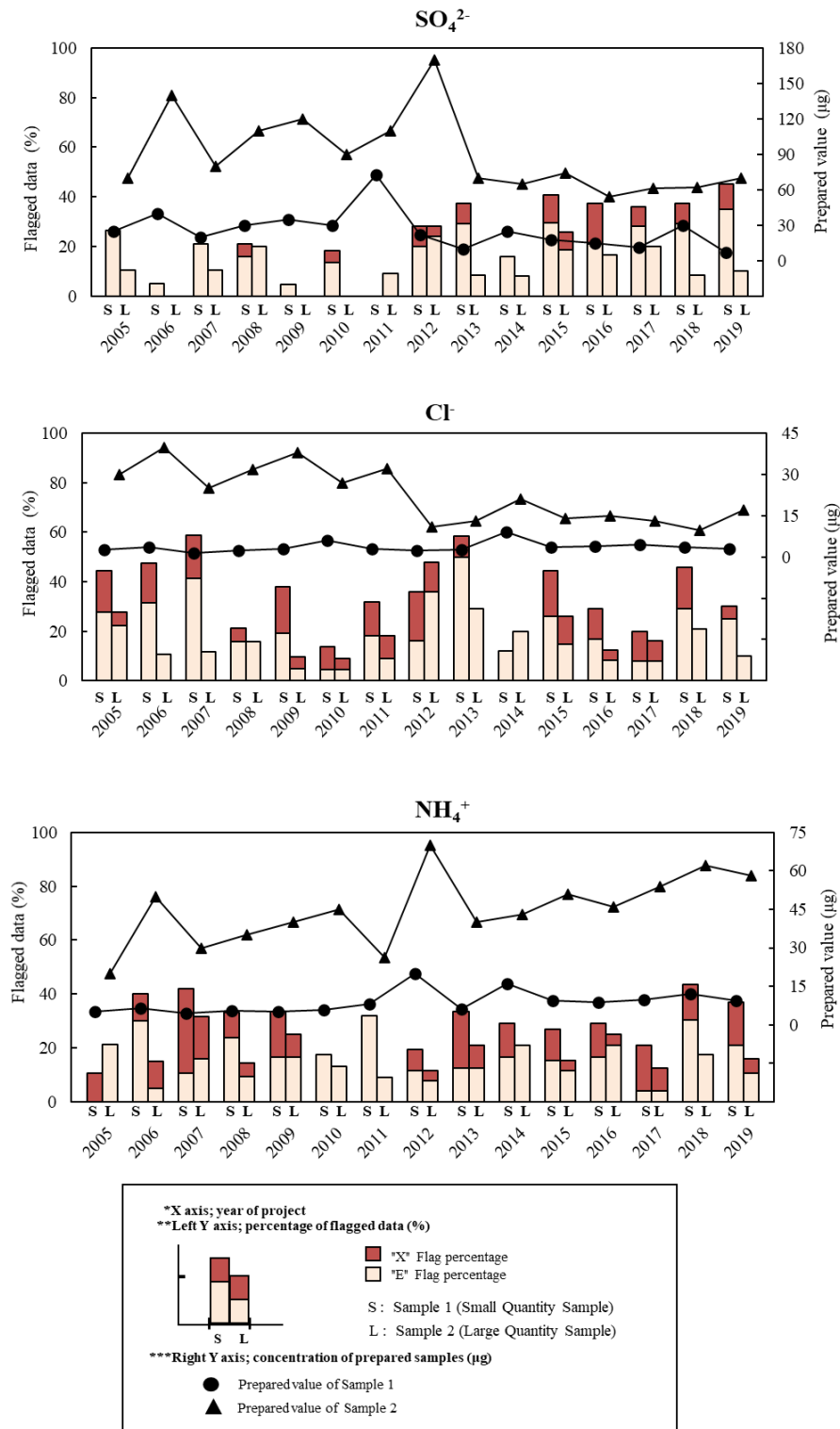


Figure 3.9 Comparison for each parameter in Inter-laboratory comparison project

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. 21st INTER-LABORATORY COMPARISON PROJECT ON SOIL

4.1 Introduction

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

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

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

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

In the 21st project, Network Center (NC) provided two soil samples (No.191s and No.192s) to laboratories to improve the inter-laboratory precision further more by standardization of methods. In this report, the data from participating laboratories were evaluated statistically according to the QA/QC program for soil monitoring. The results may contribute to the assessment of 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

Thirteen laboratories of 6 countries participated in the 21st 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.191s: Andosols

Sample No.192s: Cambisols

Soils for sample No.191s and No.192s were collected under mixed plantation of Japanese cedar (*Cryptomeria japonica*) and Japanese cypress (*Chamaecyparis obtusa*) and Japanese cedar plantation, respectively, in Tochigi 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	No.191s and 192s
a) Moisture Content	wt %	M
b) pH(H ₂ O)	-	M
c) pH(KCl)	-	M
d) Exchangeable Ca ²⁺	cmol _c kg ⁻¹	M
e) Exchangeable Mg ²⁺	cmol _c kg ⁻¹	M
f) Exchangeable K ⁺	cmol _c kg ⁻¹	M
g) Exchangeable Na ⁺	cmol _c kg ⁻¹	M
h) Exchangeable acidity	cmol _c kg ⁻¹	M
i) Exchangeable Al ³⁺	cmol _c kg ⁻¹	M
j) Exchangeable H ⁺	cmol _c kg ⁻¹	M

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 **1M CH₃COONH₄ (pH 7.0)** for analysis of Ex-Ca, Mg, K and Na. Then, 1M CH₃COONH₄ (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 1M CH₃COONH₄ (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 (SrCl₂ solution eliminates the interference of the sample). And then make to volume with 1M CH₃COONH₄ (pH 7.0). This solution is named “Prepared sample”.
- (3) Prepare three “prepared samples”.
- (4) Prepare each standard solution with diluting 1M CH₃COONH₄ (pH 7.0) solution.
- (5) Add 100 g-Sr L⁻¹ solution to each standard solution to be the same concentration SrCl₂ as the sample.
- (6) Analyze the standard solution and the prepared samples by AAS.
- (7) Store the calibration curves certainly and report them together with reporting formats.
- (8) Repeat the procedure 1) - 7) twice.

(9) Calculation of content in the soil

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

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

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

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

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

Where

A = 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:

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

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

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

Where

A_{NaOH} = 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 12 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 21st inter-laboratory project, all analyzed items [i.e., pH(H₂O), pH(KCl), Ex-base cations (Ex-Ca, Ex-Mg, Ex-K and Ex-Na), Ex-acidity, and acid cations (Ex-Al and Ex-H)] were largely different between two samples; pH and Ex-base cations were higher in No.192s than in No.191s, and Ex-acidity was lower in 192s than in 191s. We observed the large variations in the analyzed data (CVs) of Ex-base cations (approx. 20-80%), Ex-acidity (20-30%) and acid cations (20-40%) in both samples. Meanwhile, in both samples, CVs were relatively small for both pH(H₂O) and pH(KCl) (2-5%).

Table 4.2 Basic statistics of the entire dataset

Statistics	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol _c kg ⁻¹						
No. 191s									
Number of Laboratories	13	13	10	10	10	10	13	13	13
Total average	4.5	4.2	0.19	0.08	0.08	0.05	3.95	3.25	0.72
Median	4.6	4.2	0.09	0.08	0.07	0.04	3.74	3.05	0.75
Maximum	4.6	4.3	0.47	0.12	0.23	0.09	5.60	4.48	1.12
Minimum	4.3	4.0	0.07	0.06	0.05	0.02	3.09	2.42	0.27
Standard deviation	0.1	0.1	0.15	0.02	0.05	0.02	0.68	0.59	0.22
CV (%) ^{*1}	2.2	2.4	78.9	25.0	62.5	40.0	17.2	18.2	30.6
No. 192s									
Number of Laboratories	13	13	10	10	10	10	13	13	13
Total average	5.1	4.3	4.79	0.59	0.49	0.15	2.27	1.65	0.62
Median	5.1	4.2	4.90	0.59	0.48	0.14	2.11	1.42	0.66
Maximum	5.3	4.9	5.81	0.74	0.82	0.20	4.33	3.98	0.89
Minimum	4.9	3.9	3.86	0.45	0.35	0.10	1.78	1.19	0.34
Standard deviation	0.1	0.2	0.74	0.11	0.14	0.03	0.66	0.73	0.17
CV (%) ^{*1}	2.0	4.7	15.4	18.6	28.6	20.0	29.1	44.2	27.4

*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.191s and 192s analyzed by 13 laboratories. Box-and-whisker plot provides the six-number summaries; total average

shown by an open argyle, lower quartile, median and upper quartile shown by a box and a bold line, and lowest and highest value within the range between the lower quartile minus 1.5 times the inter-quartile range and the upper quartile plus 1.5 times the inter-quartile range drawn by error bar. In addition, the values outside the error bar are shown as outliers, that is, non-parametrical outliers. The plots showed several “non-parametrical” outliers in each property. Those outliers might be due to wrong calculation, procedure, irregular contamination, and so on. Therefore, in following section, we removed these outliers by parametrically statistical method to calculate the good reference closer to true value.

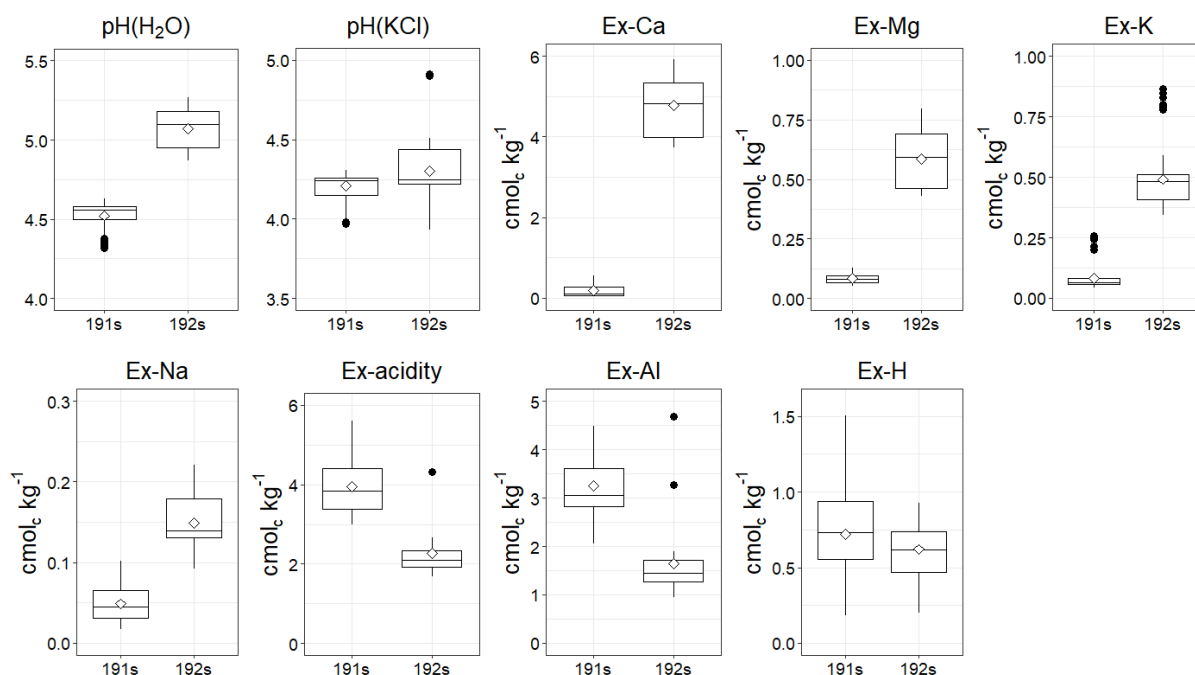


Figure 4.1 Data variability of No.191s and No.192s

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 “VN05” in pH(H₂O) of No.191s. 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 “ID01” in pH(KCl) of No. 191s). Cochran-Grubbs method detected the several outliers for each parameter. As a result of removing outliers, the “verified” dataset consisting of 12-13 laboratories in pH(H₂O) and pH(KCl), 7-10 laboratories in Ex-base cations and 11-13 laboratories in Ex-acidity, Al and H were used for further analysis in the following section (Table 4.4).

**Table 4.3 Data verification by Cochran-Grubbs tests
No. 191s**

Country	Lab.	Repeat analysis	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
cmol _c kg ⁻¹											
China	CN01	1st	4.6	4.2	0.08	0.09	0.06	0.04	3.08	2.81	0.27
		2nd	4.6	4.2	0.07	0.09	0.07	0.04	3.10	2.83	0.27
	CN02	1st	4.6	4.3	0.10	0.09	0.08	0.06	3.59	2.86	0.73
		2nd	4.6	4.3	0.10	0.09	0.08	0.06	3.63	2.90	0.73
	CN03	1st	4.6	4.3	0.09	0.08	0.08	0.05	3.67	2.99	0.68
		2nd	4.6	4.3	0.09	0.08	0.09	0.05	3.67	2.97	0.70
	CN04	1st	4.6	4.3	0.07	0.07	0.06	0.03	3.20	2.66	0.54
		2nd	4.6	4.3	0.07	0.07	0.07	0.03	3.23	2.65	0.58
Indonesia	ID01	1st	4.3	4.0 g	0.07	0.06	0.08	0.04	4.04	3.06	0.97
		2nd	4.3	4.0 g	0.07	0.06	0.08	0.04	3.96	3.03	0.92
	ID04	1st	4.4	4.1	0.40 c	0.08	0.25 c	0.09	3.29	2.43	0.86
		2nd	4.4	4.1	0.37 c	0.09	0.21 c	0.09	3.39	2.41	0.98
Mongolia	MN01	1st	4.6	4.2	NA	NA	NA	NA	5.60	4.48	1.12
		2nd	4.6	4.2	NA	NA	NA	NA	5.60	4.48	1.12
Philippines	PH01	1st	4.5	4.1	0.07	0.06	0.06	0.02	3.38 c	2.91 c	0.61 c
		2nd	4.6	4.2	0.07	0.06	0.06	0.03	3.66 c	2.76 c	0.90 c
Russia	RU01	1st	4.4	4.2	0.53 c	0.08 c	0.05	0.02	4.07 c	3.51 c	0.51
		2nd	4.4	4.2	0.42 c	0.05 c	0.05	0.02	3.42 c	2.79 c	0.53
Vietnam	VN01	1st	4.6	4.2	0.28	0.12	0.06	0.07	4.46	3.79	0.71
		2nd	4.6	4.2	0.28	0.13	0.06	0.07	4.46	3.75	0.80
	VN02	1st	4.5	4.2	NA	NA	NA	NA	4.43	3.97	0.52
		2nd	4.5	4.2	NA	NA	NA	NA	4.43	4.02	0.52
	VN04	1st	4.6	4.3	0.28	0.11	0.06	0.07	4.44	3.66	0.85
		2nd	4.6	4.2	0.27	0.12	0.05	0.06	4.44	3.66	0.85
	VN05	1st	4.5 c	4.2	NA	NA	NA	NA	4.24	3.51	0.73
		2nd	4.6 c	4.3	NA	NA	NA	NA	4.25	3.51	0.77

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. 192s**

Country	Lab.	Repeat analysis	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
cmol _c kg ⁻¹											
China	CN01	1st	5.2	4.2	5.34	0.71 c	0.59	0.18	1.80	1.20	0.60
		2nd	5.2	4.2	5.23	0.77 c	0.58	0.18	1.76	1.18	0.58
	CN02	1st	5.3	4.3	5.79	0.73	0.52	0.19	2.28	1.85	0.43
		2nd	5.3	4.3	5.82	0.73	0.51	0.19	2.22	1.81	0.41
	CN03	1st	5.2	4.2	5.21	0.70	0.49	0.20	1.86	1.42	0.43
		2nd	5.2	4.2	5.22	0.70	0.50	0.21	1.86	1.42	0.43
	CN04	1st	5.2	4.2	5.01	0.63	0.50	0.14	1.94	1.24	0.70
		2nd	5.2	4.2	4.82	0.62	0.48	0.14	1.94	1.33	0.61
Indonesia	ID01	1st	5.0	4.0	5.73	0.59	0.47	0.12	2.36	1.61	0.74
		2nd	5.0	3.9	5.75	0.59	0.47	0.12	2.32	1.61	0.71
	ID04	1st	5.0	4.1	4.51	0.55	0.41	0.14	1.97	1.27	0.71
		2nd	5.0	4.1	3.92	0.54	0.41	0.15	1.91	1.23	0.68
Mongolia	MN01	1st	5.2	4.9 g	NA	NA	NA	NA	4.33 g	3.28 c	0.47
		2nd	5.2	4.9 g	NA	NA	NA	NA	4.33 g	4.68 c	0.47
Philippines	PH01	1st	5.1	4.1	3.96	0.45	0.85 g	0.09	1.84	1.26	0.41
		2nd	5.1	4.1	4.06	0.45	0.79 g	0.11	1.83	1.56	0.28
Russia	RU01	1st	4.9	4.2	5.13	0.62 c	0.46	0.14	2.64 c	1.89	0.72
		2nd	4.9	4.3	4.65	0.55 c	0.40	0.12	2.28 c	1.63	0.62
Vietnam	VN01	1st	5.0	4.5	3.94	0.44 c	0.34	0.14	2.26	1.44	0.83
		2nd	5.0	4.5	3.88	0.46 c	0.35	0.14	2.24	1.54	0.73
	VN02	1st	4.9	4.4	NA	NA	NA	NA	2.38	1.75	0.57
		2nd	4.9	4.4	NA	NA	NA	NA	2.38	1.75	0.57
	VN04	1st	5.0	4.5	3.90	0.44	0.34	0.14	2.11	1.24	0.89
		2nd	4.9	4.5	3.83	0.45	0.35	0.13	2.11	1.24	0.89
	VN05	1st	5.1	4.2	NA	NA	NA	NA	2.03	1.24	0.77
		2nd	5.1	4.3	NA	NA	NA	NA	2.08	1.24	0.85

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.191s and No.192s is shown in Table 4.4. Total average of Ex-base cations in both soils were largely 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 ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol _c kg ⁻¹						
No. 191s									
Number of Laboratories	12	12	8	9	9	10	11	11	12
Total average	4.5	4.2	0.13	0.09	0.07	0.05	4.01	3.29	0.72
Median	4.6	4.2	0.08	0.09	0.06	0.04	4.00	3.05	0.74
Maximum	4.6	4.3	0.28	0.12	0.08	0.09	5.60	4.48	1.12
Minimum	4.3	4.1	0.07	0.06	0.05	0.02	3.09	2.42	0.27
Standard deviation	0.1	0.1	0.09	0.02	0.01	0.02	0.73	0.63	0.23
CV (%) ^{*1}	2.2	2.4	69.2	22.2	14.3	40.0	18.2	19.1	31.9
No. 192s									
Number of Laboratories	13	12	10	7	9	10	11	12	13
Total average	5.1	4.3	4.79	0.58	0.45	0.15	2.07	1.46	0.62
Median	5.1	4.2	4.90	0.59	0.47	0.14	2.06	1.42	0.66
Maximum	5.3	4.5	5.81	0.73	0.58	0.20	2.38	1.83	0.89
Minimum	4.9	3.9	3.86	0.45	0.35	0.10	1.78	1.19	0.34
Standard deviation	0.1	0.2	0.74	0.11	0.08	0.03	0.21	0.23	0.17
CV (%) ^{*1}	2.0	4.7	15.4	19.0	17.8	20.0	10.1	15.8	27.4

*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 properties. The CVs were around 0.5% in both pH(H₂O) and pH(KCl), < 11% 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. It was suggested that the average of triplicate analyses under the repeatability condition could be representative value for the analysis in a laboratory. We assumed that participating laboratories could analyze the parameters with their own standard procedures.

3) Inter-laboratories precision

The CVs in the inter-laboratories precision were less than 4% in pH(H₂O) and pH(KCl). However, the CVs of the rest of the items ranged from 10 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 0.3 for pH(H₂O), 0.4 for pH(KCl), 0.04-2.1 cmol_c kg⁻¹ for Ex-base cations, 2.1 cmol_c kg⁻¹ for Ex-acidity, 1.8 cmol_c kg⁻¹ for Ex-Al, and .0.6 cmol_c kg⁻¹ for Ex-H.

Table 4.5 Analysis of variance for the verified dataset

Statistics	No. 191s								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	12	12	8	9	9	10	11	11	12
Total sum of square	110000	93000	38	22	13	8.6	70000	47000	2700
ST/lmd	1500	1300	0.80	0.41	0.24	0.14	1100	720	37
Number of Laboratories	12	12	8	9	9	10	11	11	12
Number of Data	72	72	48	54	54	60	66	66	72
Total sum	330	300	6.2	4.7	3.6	2.9	260	220	52
Total average	4.5	4.2	0.13	0.09	0.07	0.05	4.01	3.29	0.72
Sum of square inter-laboratories (S _R)	0.6	0.2	0.35	0.02	0.01	0.03	32.10	24.16	3.50
Sum of square within-laboratory (S _{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.03	0.01	0.04
Sum of square repeatability (S _r)	0.0	0.0	0.00	0.00	0.00	0.00	0.10	0.23	0.31
Total sum of square (S _T)	0.6	0.2	0.36	0.02	0.01	0.03	32.23	24.40	3.85
Inter-laboratories degree of freedom (φ _R)	11	11	7	8	8	9	10	10	11
Within-laboratory degree of freedom (φ _{RW})	12	12	8	9	9	10	11	11	12
Repeatability degree of freedom (φ _r)	48	48	32	36	36	40	44	44	48
Total degree of freedom (φ _T)	71	71	47	53	53	59	65	65	71
Inter-laboratories variance (V _R = S _R /φ _R)	0.1	0.0	0.05	0.00	0.00	0.00	3.21	2.42	0.32
Within-laboratory variance (V _{RW} = S _{RW} /φ _{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability variance (V _r = S _r /φ _r)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Laboratory component of variance (s _b ² = (V _R -V _{RW})/(2×3))	0.0	0.0	0.01	0.00	0.00	0.00	0.53	0.40	0.05
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	0.01	0.01
Inter-laboratories standard deviation (s _R = SQRT((s _b ² /(2×3) + s _c ² /2 + s _b ²)))	0.1	0.1	0.09	0.02	0.01	0.02	0.73	0.63	0.23
Within-laboratory standard deviation (s _{RW} = SQRT((s _r ² /3 + s _c ²)))	0.0	0.0	0.00	0.00	0.00	0.00	0.03	0.02	0.03
Repeatability standard deviation (s _r = SQRT(s _r ²))	0.0	0.0	0.01	0.00	0.01	0.00	0.05	0.07	0.08
Inter-laboratories precision CV (%)	2.0	1.2	71.32	25.32	18.95	46.91	18.25	19.27	32.03
Within-laboratory precision CV (%)	0.2	0.1	2.81	3.34	5.33	5.18	0.72	0.58	4.72
Repeatability precision CV (%)	0.4	0.4	4.31	5.41	8.71	8.46	1.18	2.18	11.09
Reproducibility limit (R = D(2, 0.95)×s _R)	0.3	0.1	0.26	0.06	0.04	0.06	2.05	1.78	0.64
Within-laboratory-reproducibility limit (R _w = D(2, 0.95)×s _{RW})	0.0	0.0	0.01	0.01	0.01	0.01	0.08	0.05	0.09
Repeatability limit (r = D(3, 0.95)×s _r)	0.1	0.1	0.02	0.02	0.02	0.01	0.16	0.24	0.26

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

Statistics	No. 192s								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	13	12	10	7	9	10	11	12	13
Total sum of square	160000	94000	82000	600	600	80	19000	11000	2300
ST/lmd	2000	1300	1400	14	11	1.3	280	150	30
Number of Laboratories	13	12	10	7	9	10	11	12	13
Number of Data	78	72	60	42	54	60	66	72	78
Total sum	400	310	290	25	25	8.9	140	100	48
Total average	5.1	4.3	4.79	0.58	0.45	0.15	2.07	1.46	0.62
Sum of square inter-laboratories (S_R)	1.1	1.5	29.75	0.45	0.29	0.06	2.72	3.55	2.01
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.99	0.00	0.01	0.00	0.02	0.28	0.08
Sum of square repeatability (S_r)	0.0	0.0	1.42	0.01	0.00	0.00	0.11	0.37	0.22
Total sum of square (S_T)	1.1	1.5	32.16	0.46	0.30	0.06	2.85	4.20	2.30
Inter-laboratories degree of freedom (ϕ_R)	12	11	9	6	8	9	10	11	12
Within-laboratory degree of freedom (ϕ_{RW})	13	12	10	7	9	10	11	12	13
Repeatability degree of freedom (ϕ_r)	52	48	40	28	36	40	44	48	52
Total degree of freedom (ϕ_T)	77	71	59	41	53	59	65	71	77
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.1	0.1	3.31	0.08	0.04	0.01	0.27	0.32	0.17
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.0	0.0	0.10	0.00	0.00	0.00	0.00	0.02	0.01
Repeatability variance ($V_r = S_r/\phi_r$)	0.0	0.0	0.04	0.00	0.00	0.00	0.00	0.01	0.00
Laboratory component of variance ($s_b^2 = (V_R - V_{RW})/(2 \times 3)$)	0.0	0.0	0.53	0.01	0.01	0.00	0.04	0.05	0.03
Within-laboratory component of variance ($s_c^2 = (V_{RW} - V_r)/3$)	0.0	0.0	0.02	0.00	0.00	0.00	0.00	0.01	0.00
Repeatability component of variance ($s_r^2 = V_r$)	0.0	0.0	0.04	0.00	0.00	0.00	0.00	0.01	0.00
Inter-laboratories standard deviation ($s_R = \text{SQRT}(s_b^2/(2 \times 3) + s_c^2/2 + s_r^2)$)	0.1	0.2	0.74	0.11	0.08	0.03	0.21	0.23	0.17
Within-laboratory standard deviation ($s_{RW} = \text{SQRT}(s_r^2/3 + s_c^2)$)	0.0	0.0	0.18	0.00	0.01	0.01	0.03	0.09	0.05
Repeatability standard deviation ($s_r = \text{SQRT}(s_r^2)$)	0.0	0.0	0.19	0.01	0.01	0.01	0.05	0.09	0.06
Inter-laboratories precision CV (%)	2.4	3.5	15.51	19.16	17.18	22.62	10.29	15.92	26.91
Within-laboratory precision CV (%)	0.2	0.2	3.80	0.52	3.23	3.94	1.21	6.01	7.38
Repeatability precision CV (%)	0.5	0.5	3.94	2.54	1.40	3.41	2.44	6.06	10.41
Reproducibility limit ($R = D(2, 0.95) \times s_R$)	0.3	0.4	2.08	0.31	0.22	0.09	0.60	0.65	0.47
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95) \times s_{RW}$)	0.0	0.0	0.51	0.01	0.04	0.02	0.07	0.24	0.13
Repeatability limit ($r = D(3, 0.95) \times s_r$)	0.1	0.1	0.62	0.05	0.02	0.02	0.17	0.29	0.21

4.3.5 Inter-laboratory variations in each parameter

To assess the precision in each laboratories and properties, we show scatter plots between No.191s and No.192s with its “verified” mean indicated by solid line (Figure 4.2). As a guide for comparison, mean \pm standard deviation was added by dotted lines. The plots did not include extreme outliers for eye-friendly.

1) pH

Linear correlation between No.191s and No.192s was found, which suggests the systematic errors of the inter-laboratory variation in pH(H₂O) 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

Linear correlations were not observed for Ex-Ca and Ex-Mg, suggesting random errors in some laboratories. The errors might be caused by a calculation procedure, operation of the equipment, the

contamination, and/or quality of ammonium acetate (extraction solution). Linear correlation between the samples for Ex-K and Ex-Na suggested the errors might be caused by the condition of pure waters, standard solution 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. To prepare 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

Linear correlations of the plots for Ex-Acidity and Ex-Al seemed to indicate the systematic error of inter-laboratory variation. The error might be derived from the manipulation of titration by each analyst, which is easily affected by factor of volumetric solution or end-point detection. On the other hand, linear correlations were not observed for Ex-H, suggesting random errors in some laboratories. Participating laboratories should check the standard of procedure based on the Technical Manual for Soil and Vegetation Monitoring (EANET, 2000).

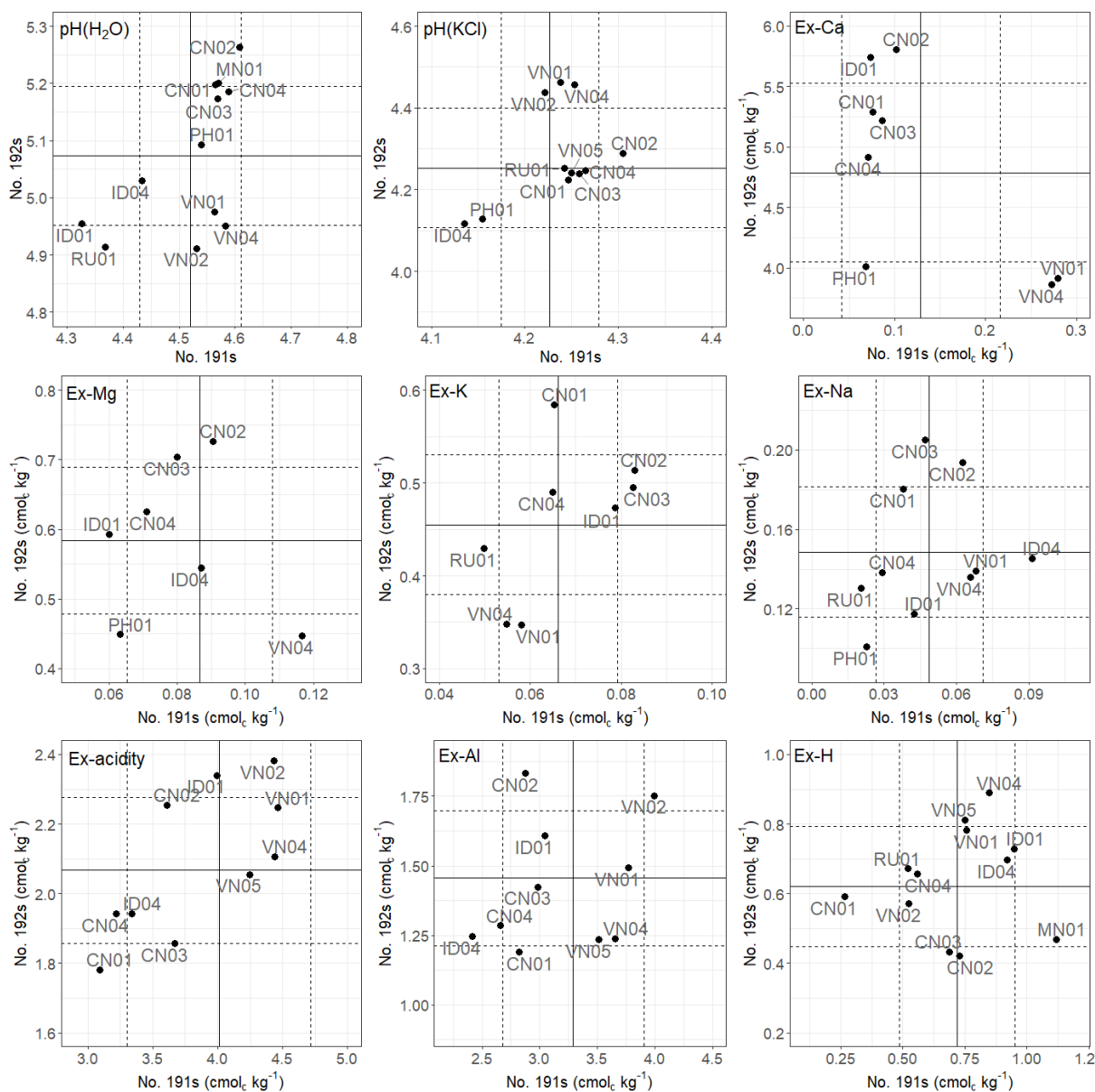


Figure 4.2 Scatter plots of each soil chemical property between No.191s and No.192s

Solid and dotted lines indicate mean and mean \pm S.D. of verified datasets, respectively.

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

Table 4.6 Number and experience of analyst

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience		Number of analyst	Years of experience		
		Chemical	Soil		Chemical	Soil	
CN01	1	5	5	1	5	5	s
CN02	1	14	14	1	14	14	s
CN03	1	2	2	1	9	9	d
CN04	1	13	11	1	13	11	s
ID01	1	13	10	1	13	10	s
ID04	1	37	35	1	1	1	d
MN01	-	-	-	1	25	25	-
PH01	1	5	1	1	6	1	d
RU01	1	34	21	1	19	16	d
VN01	1	3	3	1	3	3	s
VN02	-	-	-	1	15	11	-
VN04	1	13	12	1	16	15	d
VN05	-	-	-	1	16	15	-

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. Ex-base cations were analyzed either AAS, ICP-AES or ICP-OES. Years in use of instruments ranged from 2 to 34. Automatic extractor for extraction of exchangeable base cations was used in one laboratory, while percolation tube procedures, Buchner funnel procedures, and centrifuge procedures were used in 3 laboratories, respectively. No clear difference was observed among data obtained by different procedures. As for the size of burette for titration of Ex-acidity, the capacities were varied from 5 to 50 mL while minimum graduates were 1/800 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 8 days, and interval between the first and second analyses of the repeat analyses was varied from 0 (in a same day) to 29 days. It was suggested 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). Some laboratories reported unreasonable date of analysis in the original submission, which was revised by the suggest from NC. Analysis dates should be reported with care in the style of “yyyy/mm/dd”, which is indicated in reporting files.

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			
		Instrument		Years*1		Instrument		Years		Instrument		Years		Instrument		Years		method	
		Instrument	Years	Instrument	Years	Instrument	Years	Instrument	Years	Instrument	Years	Instrument	Years	Instrument	Years	Instrument	Years	Capacity	Minimum graduate
CN01	No.191	Centrifuge	AAS	14	AAS	14	La	AAS	14	AAS	14	AAS	14	La	Titration	10	0.1		
	No.192		AAS	14	AAS	14	La	AAS	14	AAS	14	AAS	14	La	Titration	10	0.1		
CN02	No.191	Percolation tube	AAS	14	AAS	14	Sr	AAS	14	AAS	14	AAS	14	Sr	Titration	25	0.1		
	No.192		AAS	14	AAS	14	Sr	AAS	14	AAS	14	AAS	14	Sr	Titration	25	0.1		
CN03	No.191	Automatic extractor	AAS	6	AAS	6	Sr	AAS	6	AAS	6	AAS	6	+	Titration	5	1/800		
	No.192		AAS	6	AAS	6	Sr	AAS	6	AAS	6	AAS	6	+	Titration	5	1/800		
CN04	No.191	Percolation tube	ICP-AES	9	ICP-AES	9	+	ICP-AES	9	ICP-AES	9	ICP-AES	9	+	Titration	25	0.1		
	No.192		ICP-AES	9	ICP-AES	9	+	ICP-AES	9	ICP-AES	9	ICP-AES	9	+	Titration	25	0.1		
ID01	No.191	Centrifuge	AAS	14	AAS	14	Sr	AAS	14	AAS	14	AAS	14	Sr	Titration	25	0.05		
	No.192		AAS	14	AAS	14	Sr	AAS	14	AAS	14	AAS	14	Sr	Titration	25	0.05		
ID04	No.191	Percolation tube	AAS	5	AAS	5	La	AAS	5	AAS	5	AAS	5	La	Titration	50	0.02		
	No.192		AAS	5	AAS	5	La	AAS	5	AAS	5	AAS	5	La	Titration	50	0.02		
MN01	No.191						-								Titration	25	0.1		
	No.192						-								Titration	25	0.1		
PH01	No.191	Buchner funnel	ICP-OES	6	ICP-OES	6	na	ICP-OES	6	ICP-OES	6	ICP-OES	6	na	Titration	25	0.05		
	No.192		ICP-OES	6	ICP-OES	6	na	ICP-OES	6	ICP-OES	6	ICP-OES	6	na	Titration	25	0.05		
RU01	No.191	Centrifuge	AAS	2	AAS	34	La	AAS	34	AAS	34	AAS	34	na	Titration	10	0.1		
	No.192		AAS	2	AAS	34	La	AAS	34	AAS	34	AAS	34	na	Titration	10	0.1		
VN01	No.191	Buchner funnel	AAS	12	AAS	12	+	AAS	12	AAS	12	AAS	10	+	Titration	10	0.05		
	No.192		AAS	12	AAS	12	+	AAS	12	AAS	12	AAS	10	+	Titration	10	0.05		
VN02	No.191						-								Titration	10	0.05		
	No.192						-								Titration	10	0.05		
VN04	No.191	Buchner funnel	AAS	14	AAS	14	na	AAS	14	AAS	14	AAS	14	+	Titration	10	0.01		
	No.192		AAS	14	AAS	14	na	AAS	14	AAS	14	AAS	14	+	Titration	10	0.01		
VN05	No.191						-								Titration	10	0.01		
	No.192						-								Titration	10	0.01		

*1, years in use of instrument; -, not measured; AAS, atomic absorption spectrometry; ICP, inductively coupled plasma; na, not added; +, not reported.

Table 4.8 Date of analysis

Lab.	Repeat	pH			Ex-Ca and Mg			Ex-K and Na			Ex-acidity, Al and H		
		Start Date	Finish Date	AD ID Days	Start Date	Finish Date	AD ID Days	Start Date	Finish Date	AD ID Days	Start Date	Finish Date	AD ID Days
CN01	1st	2020/5/20	2020/5/20	1 3	2020/5/21	2020/5/28	8 0	2020/5/21	2020/5/28	8 0	2019/11/14	2019/11/14	1 4
	2nd	2020/5/23	2020/5/23	1 1	2020/5/21	2020/5/28	8 8	2020/5/21	2020/5/28	8 8	2019/11/18	2019/11/18	1 1
CN02	1st	2020/2/19	2020/2/19	1 1	2020/2/19	2020/2/20	2 1	2020/2/19	2020/2/20	2 1	2020/2/21	2020/2/21	1 3
	2nd	2020/2/20	2020/2/20	1 1	2020/2/20	2020/2/21	2 2	2020/2/20	2020/2/21	2 2	2020/2/24	2020/2/24	1 1
CN03	1st	2020/1/7	2020/1/7	1 1	2020/1/9	2020/1/9	1 1	2020/1/9	2020/1/9	1 1	2020/1/9	2020/1/9	1 1
	2nd	2020/1/8	2020/1/8	1 1	2020/1/10	2020/1/10	1 1	2020/1/10	2020/1/10	1 1	2020/1/10	2020/1/10	1 1
CN04	1st	2019/12/16	2019/12/17	2 2	2019/12/23	2019/12/24	2 17	2019/12/23	2019/12/24	2 17	2019/12/17	2019/12/17	1 4
	2nd	2019/12/18	2019/12/19	2 2	2020/1/9	2020/1/10	2 2	2020/1/9	2020/1/10	2 2	2019/12/21	2019/12/21	1 1
ID01 ^{*1}	1st	2019/12/4	2019/12/4	1 26	2020/1/2	2020/1/8	7 0	2020/1/2	2020/1/8	7 0	2019/12/12	2019/12/12	1 18
	2nd	2019/12/30	2019/12/30	1 1	2020/1/2	2020/1/8	7 7	2020/1/2	2020/1/8	7 7	2019/12/30	2019/12/30	1 1
ID04	1st	2019/11/20	2019/11/20	1 29	2019/11/20	2019/11/20	1 5	2019/11/20	2019/11/20	1 5	2019/11/20	2019/11/20	1 5
	2nd	2019/12/19	2019/12/19	1 1	2019/11/25	2019/11/25	1 1	2019/11/25	2019/11/25	1 1	2019/11/25	2019/11/25	1 1
MN01 ^{*1}	1st	2019/12/3	2019/12/3	1 0			NA			NA	2019/12/4	2019/12/4	1 0
	2nd	2019/12/3	2019/12/3	1 1							2019/12/4	2019/12/4	1 1
PH01	1st	2020/2/13	2020/2/13	1 4	2020/2/21	2020/2/21	1 4	2020/2/21	2020/2/21	1 4	2020/2/18	2020/2/18	1 4
	2nd	2020/2/17	2020/2/17	1 1	2020/2/25	2020/2/25	1 1	2020/2/25	2020/2/25	1 1	2020/2/22	2020/2/22	1 1
RU01	1st	2020/2/20	2020/2/20	1 4	2020/2/20	2020/2/27	8 0	2020/2/20	2020/2/27	8 0	2020/2/20	2020/2/20	1 5
	2nd	2020/2/24	2020/2/24	1 1	2020/2/24	2020/2/27	4 4	2020/2/24	2020/2/27	4 4	2020/2/25	2020/2/25	1 1
VN01	1st	2019/11/20	2019/11/20	1 2	2019/11/20	2019/11/21	2 2	2019/11/20	2019/11/21	2 2	2019/11/24	2019/11/25	2 2
	2nd	2019/11/22	2019/11/22	1 1	2019/11/22	2019/11/23	2 2	2019/11/22	2019/11/23	2 2	2019/11/26	2019/11/27	2 2
VN02	1st	2019/12/25	2019/12/25	1 0			NA			NA	2019/12/26	2019/12/27	2 0
	2nd	2019/12/25	2019/12/25	1 1							2019/12/26	2019/12/27	2 2
VN04	1st	2019/12/3	2019/12/3	1 1	2019/12/3	2019/12/3	1 1	2019/12/3	2019/12/3	1 1	2019/12/3	2019/12/3	1 1
	2nd	2019/12/4	2019/12/4	1 1	2019/12/4	2019/12/4	1 1	2019/12/4	2019/12/4	1 1	2019/12/4	2019/12/4	1 1
VN05	1st	2020/1/5	2020/1/6	2 0			NA			NA	2020/1/5	2020/1/6	2 0
	2nd	2020/1/6	2020/1/6	1 1							2020/1/6	2020/1/6	1 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.

4.3.7 Detection limit and quantification limit

From 21st project, detection limit and quantification limit for Ex-base cations should be reported. Around one fourth of participating laboratories reported these values (Table 4.9). The range of detection limits for Ex-Ca, Ex-Mg, Ex-K and Ex-Na were 0.002-0.07, 0.01-0.03, 0.01-0.03, and 0.01-0.05 mg/L, respectively. Similarly, the range of quantification limits for Ex-Ca, Ex-Mg, Ex-K and Ex-Na were 0.067-0.2, 0.04-0.1, 0.067-0.1, 0.05-0.15 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, concentrations of soil extracts were much higher than quantification limit by one digit, suggesting analyses of Ex-base cations were conducted with enough spare 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
CN01	-	-	-	-	-	-	-	-	-	-	-	-
CN02	-	-	-	-	-	-	-	-	-	-	-	-
CN03	-	-	-	-	-	-	-	-	-	-	-	-
CN04	-	-	-	-	-	-	-	-	-	-	-	-
ID01	-	-	-	-	-	-	-	-	-	-	-	-
ID04	-	-	-	-	-	-	-	-	-	-	-	-
MN01	-	-	-	-	-	-	-	-	-	-	-	-
PH01	0.0492	-	mg/L	-	-	-	-	-	-	-	-	-
RU01	0.002	0.2	mg/L	0.01	0.04	mg/L	0.01	0.1	mg/L	0.01	0.1	mg/L
VN01	0.07	0.2	mg/L	0.03	0.1	mg/L	0.03	0.1	mg/L	0.05	0.15	mg/L
VN02	-	-	-	-	-	-	-	-	-	-	-	-
VN04	0.02	0.067	mg/L	0.015	0.05	mg/L	0.02	0.067	mg/L	0.015	0.05	mg/L
VN05	-	-	-	-	-	-	-	-	-	-	-	-

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

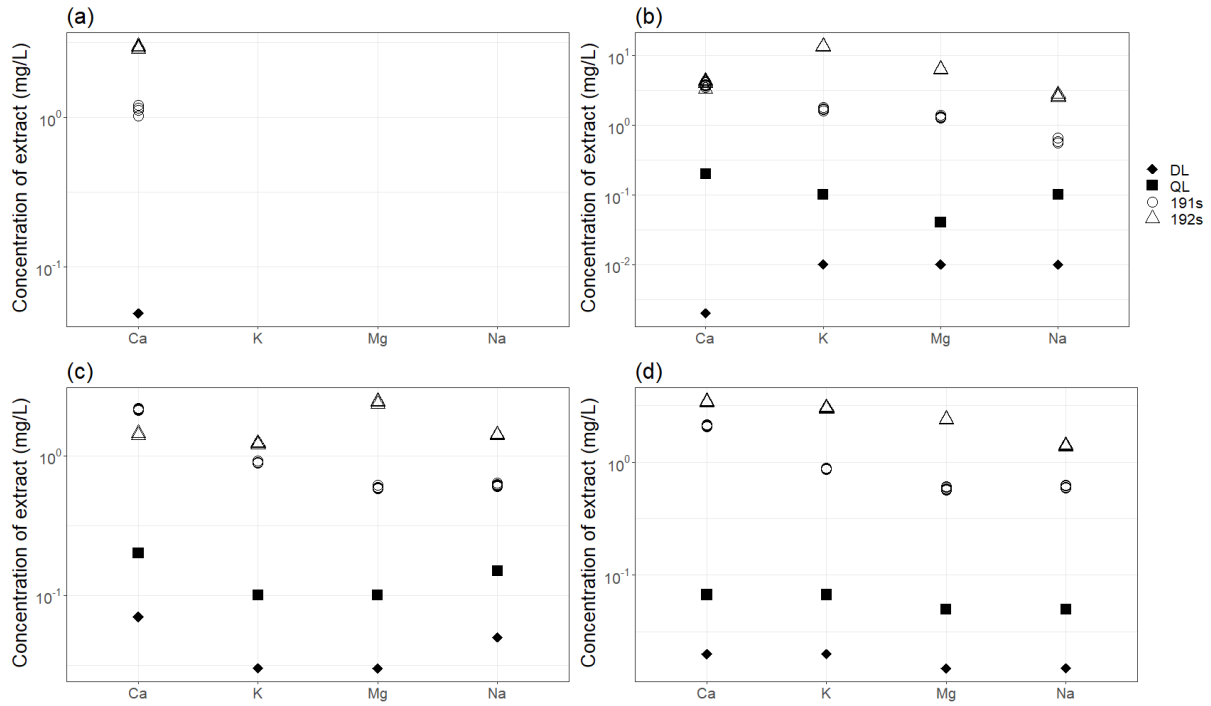


Figure 4.3 Detection limit, quantification limit and concentrations of soil extracts

(a) PH01, (b) RU01, (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 2019 [the ratio is calculated by $\{(N \text{ of entire dataset}) - (N \text{ of verified dataset})\} / (N \text{ of entire dataset})$]. Although the ratio decreased from first experiment in 2002, this is still high (10-25% from 2003 to 2019). The outlier ratio in 2019 was lower than the average outlier ratio from 2003 to 2018, which was around 14%. 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.

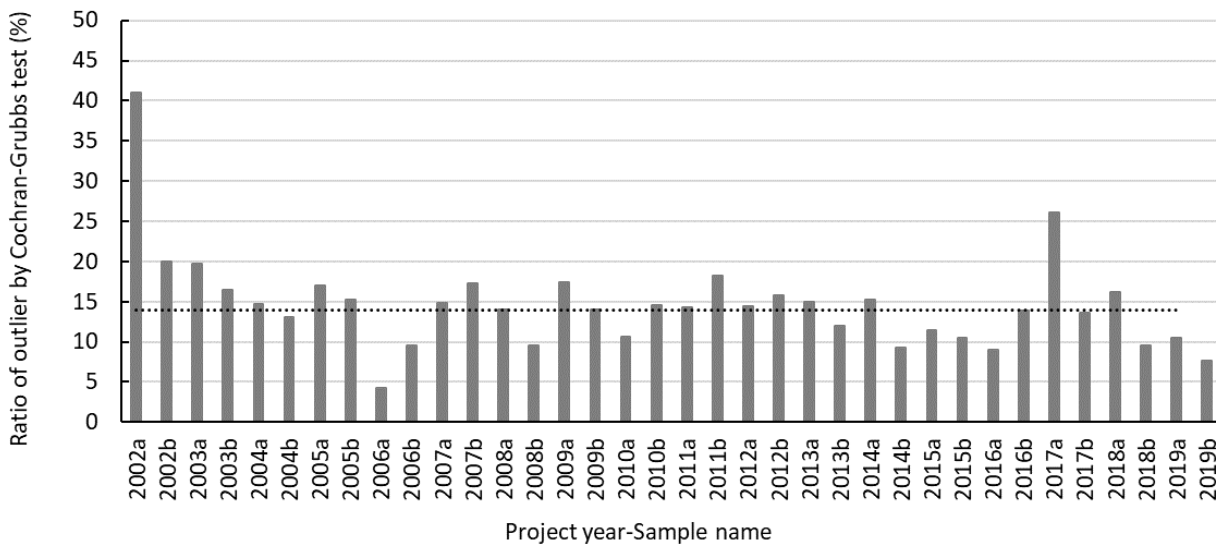


Figure 4.4 Change of the outlier ratio in all properties and laboratories from 2002 to 2019 calculated by $\{(N \text{ of entire dataset}) - (N \text{ of verified dataset})\} / (N \text{ of entire dataset})$.

‘a’ and ‘b’ show the 2 kinds of the samples in each year (e.g. 191s and 192s).

The ratios from 2002 to 2018 were from *Report of Inter-Laboratory Comparison Project 2000-2018* (<https://monitoring.eanet.asia/document/public/index>).

Dotted line represents the average outlier ratio from 2003 to 2018.

4.5 Recommendations

Reducing the outliers (about 10% of all data) in exchangeable base and acid cations will be considered firstly. In addition, the precision for the samples with low concentrations should be improved. The condition of standard solution, extraction 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. 191s)

Lab	pH(H ₂ O)			pH(KCl)			Ex-Ca (cmol kg ⁻¹)			Ex-Mg (cmol kg ⁻¹)			Ex-K (cmol kg ⁻¹)			Ex-Na (cmol kg ⁻¹)			Ex-Acidity (cmol kg ⁻¹)			Ex-Al (cmol kg ⁻¹)			Ex-H (cmol kg ⁻¹)		
	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat
CN01	4.6	4.6	4.6	4.2	4.2	4.3	0.08	0.08	0.09	0.09	0.09	0.09	0.07	0.06	0.07	0.04	0.04	0.05	3.09	3.08	3.00	2.82	2.81	2.75	2.27	2.27	0.24
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.2	(0.01)	(0.01)	0.07	(0.00)	(0.00)	0.09	(0.01)	(0.01)	0.06	(0.01)	(0.01)	0.03	(0.07)	(0.07)	3.12	(0.05)	(0.06)	2.88	(0.05)	(0.04)	0.24
			4.6			4.3			0.08			0.09			0.06			0.04			3.12			2.81			0.31
			4.6			4.2			0.07			0.09			0.07			0.04			3.10			2.83			0.18
			(0.0)			(0.0)			(0.02)			(0.00)			(0.00)			(0.00)			(0.09)			(0.04)			(0.07)
			4.6			4.2			0.09			0.09			0.07			0.04			3.12			2.81			0.31
CN02	4.6	4.6	4.6	4.3	4.3	4.3	0.10	0.10	0.10	0.09	0.09	0.09	0.08	0.08	0.08	0.06	0.06	0.06	3.61	3.59	3.59	2.88	2.86	2.86	0.73	0.73	0.73
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.3	(0.00)	(0.00)	0.10	(0.00)	(0.00)	0.09	(0.00)	(0.00)	0.08	(0.00)	(0.00)	0.06	(0.04)	(0.00)	3.59	(0.06)	(0.00)	2.86	(0.08)	(0.00)	0.73
			4.6			4.3			0.10			0.09			0.08			0.06			3.59			2.86			0.73
			4.6			4.3			0.10			0.09			0.08			0.06			3.63			2.90			0.60
			(0.0)			(0.0)			(0.00)			(0.00)			(0.00)			(0.00)			(0.06)			(0.08)			(0.12)
			4.6			4.3			0.10			0.09			0.08			0.06			3.70			2.86			0.84
CN03	4.6	4.6	4.6	4.3	4.3	4.3	0.09	0.09	0.10	0.08	0.08	0.08	0.08	0.08	0.07	0.05	0.05	0.04	3.67	3.67	3.67	2.98	2.99	2.94	0.69	0.68	0.73
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.3	(0.00)	(0.01)	0.08	(0.00)	(0.00)	0.08	(0.01)	(0.01)	0.07	(0.01)	(0.01)	0.04	(0.00)	(0.00)	3.67	(0.04)	(0.06)	3.05	(0.04)	(0.06)	0.62
			4.6			4.3			0.09			0.08			0.09			0.05			3.67			2.99			0.68
			4.6			4.3			0.09			0.08			0.09			0.05			3.67			2.97			0.70
			(0.0)			(0.0)			(0.00)			(0.00)			(0.01)			(0.00)			(0.00)			(0.03)			(0.03)
			4.6			4.3			0.09			0.08			0.10			0.05			3.67			2.99			0.68
CN04	4.6	4.6	4.6	4.3	4.3	4.3	0.07	0.07	0.07	0.07	0.07	0.07	0.06	0.06	0.06	0.03	0.03	0.02	3.22	3.20	3.22	2.66	2.66	2.70	0.56	0.54	0.53
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.3	(0.00)	(0.01)	0.08	(0.00)	(0.00)	0.07	(0.00)	(0.00)	0.06	(0.00)	(0.00)	0.03	(0.02)	(0.02)	3.20	(0.06)	(0.07)	2.71	(0.05)	(0.06)	0.49
			4.6			4.3			0.07			0.07			0.06			0.03			3.19			2.59			0.60
			4.6			4.3			0.07			0.07			0.07			0.03			3.23			2.70			0.55
			(0.0)			(0.0)			(0.00)			(0.00)			(0.00)			(0.00)			(0.02)			(0.06)			(0.04)
			4.6			4.3			0.07			0.08			0.07			0.03			3.22			2.66			0.56
ID01	4.3	4.3	4.3	4.0	4.0	4.0	0.07	0.07	0.07	0.06	0.06	0.06	0.08	0.08	0.09	0.04	0.04	0.04	4.00	4.04	4.04	3.05	3.06	3.06	0.95	0.97	0.97
	(0.0)	(0.0)	4.3	(0.0)	(0.0)	4.0	(0.00)	(0.00)	0.07	(0.00)	(0.00)	0.06	(0.01)	(0.01)	0.07	(0.00)	(0.00)	0.04	(0.07)	(0.00)	4.04	(0.04)	(0.00)	3.06	(0.05)	(0.00)	0.97
			4.3			4.0			0.08			0.06			0.08			0.04			4.03			3.06			0.97
			4.3			4.0			0.07			0.06			0.09			0.04			3.96			3.07			0.92
			(0.0)			(0.0)			(0.00)			(0.00)			(0.01)			(0.00)			(0.08)			(0.06)			(0.07)
			4.3			4.0			0.07			0.06			0.08			0.04			3.91			3.07			0.84
ID04	4.4	4.4	4.4	4.1	4.1	4.1	0.39	0.40	0.39	0.09	0.08	0.08	0.23	0.25	0.25	0.09	0.09	0.09	3.34	3.29	3.41	2.42	2.43	2.38	0.92	0.86	1.02
	(0.0)	(0.0)	4.5	(0.0)	(0.0)	4.1	(0.02)	(0.02)	0.42	(0.01)	(0.01)	0.10	(0.02)	(0.01)	0.24	(0.01)	(0.01)	0.08	(0.10)	(0.11)	3.27	(0.11)	(0.15)	2.30	(0.16)	(0.23)	0.97
			4.4			4.2			0.41			0.07			0.26			0.10			3.19			2.60			0.60
			4.4			4.1			0.37			0.37			0.21			0.09			3.39			2.41			0.97
			(0.0)			(0.0)			(0.01)			(0.01)			(0.01)			(0.01)			(0.07)			(0.08)			(0.02)
			4.5			4.2			0.38			0.08			0.20			0.10			3.33			2.33			1.00
MN01	4.6	4.6	4.6	4.2	4.2	4.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	5.60	5.60	5.60	4.48	4.48	4.48	1.12	1.12	1.12
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.2			NA			NA			NA			NA	(0.00)	(0.00)	5.60	(0.00)	(0.00)	4.48	(0.00)	(0.00)	1.12
			4.6			4.2			NA			NA			NA			NA			5.60			4.48			1.12
			4.6			4.2			NA			NA			NA			NA			5.60			4.48			1.12
			(0.0)			(0.0)			NA			NA			NA			NA			(0.00)			(0.00)			(0.00)
			4.6			4.2			NA			NA			NA			NA			5.60			4.48			1.12

Appendix Table 4.1 continued

Lab	pH(H ₂ O)			pH(KCl)			Ex-Ca (cmol kg ⁻¹)			Ex-Mg (cmol kg ⁻¹)			Ex-K (cmol kg ⁻¹)			Ex-Na (cmol kg ⁻¹)			Ex-Acidity (cmol kg ⁻¹)			Ex-Al (cmol kg ⁻¹)			Ex-H (cmol kg ⁻¹)				
	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat		
PH01	4.5	4.5	4.6	4.2	4.1	4.1	0.07	0.07	0.07	0.06	0.06	0.06	0.06	0.06	0.06	0.02	0.02	0.02	3.52	3.38	3.25	2.83	2.91	3.27	0.76	0.61	0.25		
	(0.0)	(0.0)	4.5	(0.0)	(0.0)	4.2	(0.00)	(0.00)	0.07	(0.00)	(0.00)	0.07	(0.00)	(0.00)	0.06	(0.01)	(0.00)	0.02	(0.19)	(0.13)	3.38	(0.44)	(0.31)	2.72	(0.42)	(0.31)	0.80		
			4.5			4.2			0.07			0.06			0.06			0.02			3.51			2.72			0.80		
			4.6			4.2			0.07			0.06			0.06			0.03			3.66			3.11			0.90	0.73	
			(0.0)			(0.0)			(0.00)			(0.00)			(0.00)			(0.00)			(0.11)			(0.60)			(0.53)	1.50	
			4.5			4.2			0.07			0.06			0.06			0.02			3.57			3.11			0.48		
RU01	4.4	4.4	4.4	4.2	4.2	4.3	0.47	0.53	0.48	0.06	0.08	0.07	0.05	0.05	0.05	0.02	0.02	0.02	3.74	4.07	4.12	3.15	3.51	3.51	0.52	0.51	0.49		
	(0.0)	(0.0)	4.4	(0.0)	(0.0)	4.2	(0.07)	(0.04)	0.54	(0.01)	(0.00)	0.08	(0.01)	(0.00)	0.06	(0.00)	(0.00)	0.02	(0.37)	(0.09)	4.12	(0.41)	(0.00)	3.51	(0.04)	(0.04)	0.56		
			4.4			4.3			0.56			0.08			0.06			0.02			3.97			3.51			0.49		
			4.4			4.2			0.42			0.05			0.05			0.02			3.42			2.79			0.53	0.55	
			(0.0)			(0.0)			(0.02)			(0.00)			(0.00)			(0.00)			(0.10)			(0.20)			(0.05)	0.47	
			4.4			4.2			0.40			0.05			0.04			0.02			3.36			2.68			0.55		
VN01	4.6	4.6	4.6	4.2	4.2	4.2	0.28	0.28	0.28	0.12	0.12	0.12	0.06	0.06	0.06	0.07	0.07	0.07	4.46	4.46	4.48	3.77	3.79	3.75	0.76	0.71	0.80		
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.3	(0.00)	(0.00)	0.28	(0.00)	(0.00)	0.12	(0.00)	(0.00)	0.06	(0.00)	(0.00)	0.07	(0.03)	(0.04)	4.42	(0.10)	(0.08)	3.88	(0.11)	(0.08)	0.67		
			4.5			4.2			0.28			0.12			0.06			0.07			4.48			3.75			0.67		
			4.6			4.2			0.28			0.13			0.06			0.07			4.46			3.75			0.80	0.67	
			(0.0)			(0.0)			(0.00)			(0.00)			(0.00)			(0.00)			(0.04)			(0.13)			(0.13)	0.80	
			4.6			4.2			0.28			0.12			0.06			0.07			4.48			3.61			0.94		
VN02	4.5	4.5	4.5	4.2	4.2	4.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	4.43	4.43	4.39	4.00	3.97	3.93	0.52	0.52	0.52		
	(0.0)	(0.0)	4.5	(0.0)	(0.0)	4.2			NA			NA			NA			NA	(0.03)	(0.04)	4.45	(0.07)	(0.08)	4.06	(0.00)	(0.00)	0.52		
			4.5			4.2			NA			NA			NA			NA			4.45			3.93			0.52		
			4.5			4.2			NA			NA			NA			NA			4.43			4.02			0.52	0.52	
			(0.0)			(0.0)			NA			NA			NA			NA			(0.04)			4.39			(0.08)	3.93	0.52
			4.5			4.2			NA			NA			NA			NA			4.45			4.06			0.52		
VN04	4.6	4.6	4.6	4.3	4.3	4.2	0.27	0.28	0.28	0.12	0.11	0.12	0.05	0.06	0.06	0.07	0.07	0.07	4.44	4.44	4.42	3.66	3.66	3.61	0.85	0.85	0.94		
	(0.0)	(0.1)	4.5	(0.0)	(0.0)	4.3	(0.01)	(0.00)	0.28	(0.00)	(0.00)	0.11	(0.00)	(0.00)	0.06	(0.00)	(0.00)	0.07	(0.03)	(0.04)	4.48	(0.07)	(0.08)	3.61	(0.11)	(0.15)	0.94		
			4.6			4.3			0.28			0.11			0.06			0.07			4.42			3.75			0.67		
			4.6			4.3			0.27			0.12			0.05			0.06			4.44			3.66			0.85	0.94	
			(0.0)			(0.0)			(0.00)			(0.00)			(0.00)			(0.00)			(0.04)			4.42			(0.08)	3.61	0.80
			4.6			4.3			0.27			0.12			0.05			0.06			4.42			3.75			0.80		
VN05	4.5	4.5	4.5	4.3	4.2	4.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	4.25	4.24	4.24	3.51	3.51	3.47	0.75	0.73	0.77		
	(0.0)	(0.0)	4.5	(0.0)	(0.0)	4.2			NA			NA			NA			NA	(0.01)	(0.02)	4.26	(0.07)	(0.07)	3.47	(0.05)	(0.07)	0.77		
			4.5			4.2			NA			NA			NA			NA			4.23			3.60			0.64		
			4.6			4.3			NA			NA			NA			NA			4.25			3.51			0.77	0.77	
			(0.0)			(0.0)			NA			NA			NA			NA			(0.01)			(0.07)			(0.00)	0.77	
			4.6			4.3			NA			NA			NA			NA			4.24			3.47			0.77		

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Appendix Table 4.2 Results submitted by the laboratories (sample No. 192s)

Lab	pH(H ₂ O)			pH(KCl)			Ex-Ca (cmol kg ⁻¹)			Ex-Mg (cmol kg ⁻¹)			Ex-K (cmol kg ⁻¹)			Ex-Na (cmol kg ⁻¹)			Ex-Acidity (cmol kg ⁻¹)			Ex-Al (cmol kg ⁻¹)			Ex-H (cmol kg ⁻¹)			
	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	
CN01	5.2	5.2	5.2	4.2	4.2	4.2	5.29	5.34	5.36	0.74	0.71	0.63	0.58	0.59	0.59	0.18	0.18	0.18	1.78	1.80	1.85	1.19	1.20	1.27	0.59	0.60	0.58	
	(0.0)	(0.0)	5.2	(0.0)	(0.0)	4.2	(0.07)	(0.02)	5.36	(0.06)	(0.08)	0.73	(0.00)	(0.00)	0.59	(0.00)	(0.00)	0.18	(0.04)	(0.05)	1.80	(0.04)	(0.06)	1.16	(0.02)	(0.03)	0.63	
			5.2			4.2			5.32			0.77			0.58			0.18			1.75			1.16			0.58	
			5.2			4.2			5.17			0.77			0.80			0.18			1.75			1.16			0.58	
			(0.0)			(0.0)			(0.06)			(0.04)			(0.00)			(0.00)			(0.03)			(0.03)			(0.00)	0.58
CN02	5.3	5.3	5.3	4.3	4.3	4.3	5.81	5.79	5.80	0.73	0.73	0.74	0.51	0.52	0.52	0.19	0.19	0.19	2.25	2.28	2.32	1.83	1.85	1.85	0.42	0.43	0.46	
	(0.0)	(0.0)	5.3	(0.0)	(0.0)	4.3	(0.04)	(0.01)	5.79	(0.01)	(0.01)	0.72	(0.00)	(0.00)	0.51	(0.00)	(0.00)	0.19	(0.05)	(0.05)	2.32	(0.05)	(0.00)	1.85	(0.06)	(0.05)	0.46	
			5.3			4.3			5.78			0.72			0.52			0.19			2.22			1.85			0.37	
			5.3			4.3			5.78			0.73			0.73			0.19			2.22			1.74			0.41	0.49
			(0.0)			(0.0)			(0.05)			(0.00)			(0.00)			(0.00)			(0.00)			(0.07)			(0.07)	0.37
CN03	5.2	5.2	5.2	4.2	4.2	4.2	5.22	5.21	5.24	0.70	0.70	0.69	0.49	0.49	0.50	0.20	0.20	0.19	1.86	1.86	1.86	1.42	1.42	1.39	0.43	0.43	0.46	
	(0.0)	(0.0)	5.2	(0.0)	(0.0)	4.2	(0.05)	(0.03)	5.19	(0.01)	(0.02)	0.72	(0.01)	(0.01)	0.49	(0.01)	(0.01)	0.20	(0.00)	(0.00)	1.86	(0.02)	(0.03)	1.44	(0.02)	(0.03)	0.42	
			5.2			4.2			5.21			0.71			0.49			0.21			1.86			1.44			0.42	
			5.2			4.2			5.22			0.70			0.50			0.21			1.86			1.44			0.43	0.42
			(0.0)			(0.0)			(0.07)			(0.02)			(0.00)			(0.01)			(0.00)			(0.03)			(0.03)	0.42
CN04	5.2	5.2	5.2	4.2	4.2	4.2	4.91	5.01	4.80	0.63	0.63	0.62	0.49	0.50	0.48	0.14	0.14	0.14	1.94	1.94	1.90	1.29	1.24	1.21	0.66	0.70	0.69	
	(0.0)	(0.0)	5.2	(0.0)	(0.0)	4.3	(0.19)	(0.21)	5.22	(0.01)	(0.01)	0.62	(0.01)	(0.02)	0.51	(0.00)	(0.00)	0.14	(0.03)	(0.04)	1.97	(0.06)	(0.05)	1.30	(0.06)	(0.03)	0.67	
			5.2			4.3			5.03			0.64			0.50			0.14			1.94			1.21			0.73	
			5.2			4.2			4.95			0.62			0.64			0.14			1.94			1.32			0.61	0.67
			(0.0)			(0.0)			(0.14)			(0.01)			(0.01)			(0.00)			(0.04)			(0.02)			(0.05)	0.58
ID01	5.0	5.0	5.0	3.9	4.0	4.0	5.74	5.73	5.91	0.59	0.59	0.60	0.47	0.47	0.47	0.12	0.12	0.12	2.34	2.36	2.36	1.61	1.61	1.58	0.73	0.74	0.77	
	(0.0)	(0.0)	5.0	(0.0)	(0.0)	4.0	(0.13)	(0.17)	5.70	(0.01)	(0.00)	0.59	(0.01)	(0.01)	0.48	(0.00)	(0.00)	0.12	(0.05)	(0.00)	2.36	(0.05)	(0.05)	1.67	(0.05)	(0.05)	0.68	
			5.0			4.0			5.58			0.59			0.47			0.12			2.36			1.58			0.77	
			5.0			3.9			5.85			0.59			0.61			0.12			2.32			1.61			0.71	0.69
			(0.0)			(0.0)			(0.11)			(0.01)			(0.01)			(0.00)			(0.07)			(0.05)			(0.06)	0.78
ID04	5.0	5.0	5.0	4.1	4.1	4.1	4.21	4.51	4.39	0.54	0.55	0.56	0.41	0.41	0.41	0.15	0.14	0.15	1.94	1.97	2.01	1.25	1.27	1.20	0.70	0.71	0.82	
	(0.0)	(0.0)	5.1	(0.0)	(0.1)	4.1	(0.35)	(0.11)	4.60	(0.02)	(0.02)	0.53	(0.00)	(0.00)	0.42	(0.01)	(0.01)	0.14	(0.05)	(0.05)	1.99	(0.07)	(0.07)	1.34	(0.07)	(0.09)	0.65	
			5.0			4.1			4.53			0.56			0.41			0.14			1.92			1.27			0.65	
			5.0			4.1			3.92			0.54			0.55			0.15			1.91			1.29			0.63	
			(0.0)			(0.1)			(0.17)			(0.02)			(0.02)			(0.00)			(0.04)			(0.07)			(0.05)	0.72
MN01	5.2	5.2	5.2	4.9	4.9	4.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	4.33	4.33	4.33	3.98	3.28	3.28	0.47	0.47	0.47	
	(0.0)	(0.0)	5.2	(0.0)	(0.0)	4.9			NA			NA			NA			NA	(0.00)	(0.00)	4.33	(0.77)	(0.00)	3.28	(0.00)	(0.00)	0.47	
			5.2			4.9			NA			NA			NA			NA			4.33			3.28			0.47	
			5.2			4.9			NA			NA			NA			NA			(0.00)			4.68			(0.00)	0.47
			(0.0)			(0.0)			NA			NA			NA			NA			(0.00)			4.68			(0.00)	0.47

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Appendix Table 4.2 continued

Lab	pH(H ₂ O)			pH(KCl)			Ex-Ca (cmol kg ⁻¹)			Ex-Mg (cmol kg ⁻¹)			Ex-K (cmol kg ⁻¹)			Ex-Na (cmol kg ⁻¹)			Ex-Acidity (cmol kg ⁻¹)			Ex-Al (cmol kg ⁻¹)			Ex-H (cmol kg ⁻¹)			
	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	
PH01	5.1	5.1	5.1	4.1	4.1	4.1	4.01	3.96	4.00	0.45	0.45	0.44	0.82	0.85	0.87	0.10	0.09	0.09	1.83	1.84	1.93	1.41	1.26	1.41	0.34	0.41	0.33	
	(0.0)	(0.0)	5.1	(0.0)	(0.0)	4.1	(0.08)	(0.04)	3.97	(0.02)	(0.01)	0.45	(0.03)	(0.02)	0.83	(0.01)	(0.00)	0.10	(0.11)	(0.08)	1.82	(0.28)	(0.27)	1.41	(0.14)	(0.15)	0.33	
			5.1			4.1			3.91			0.44			0.85			0.09			1.76			0.94			0.58	
			5.1			4.1			4.06			0.45			0.79			0.11			1.83			1.56			0.28	0.20
			(0.0)			(0.0)			(0.08)			(0.03)			(0.01)			(0.00)			(0.15)			(0.22)			(0.13)	0.20
			5.1			4.1			4.06			0.43			0.79			0.11			1.69			1.34			0.43	0.43
RU01	4.9	4.9	4.9	4.3	4.2	4.2	4.89	5.13	5.31	0.58	0.62	0.62	0.43	0.46	0.46	0.13	0.14	0.13	2.46	2.64	2.62	1.76	1.89	1.89	0.67	0.72	0.69	
	(0.0)	(0.0)	4.9	(0.0)	(0.0)	4.2	(0.53)	(0.71)	4.35	(0.04)	(0.00)	0.62	(0.03)	(0.01)	0.45	(0.01)	(0.01)	0.13	(0.20)	(0.02)	2.62	(0.14)	(0.00)	1.89	(0.06)	(0.03)	0.74	
			4.9			4.3			5.74			0.63			0.46			0.15			2.66			1.89			0.74	
			4.9			4.3			4.47			0.55			0.40			0.12			2.28			1.63			0.62	0.60
			(0.0)			(0.0)			(0.17)			(0.00)			(0.00)			(0.00)			(0.03)	2.31		(0.00)	1.63		(0.04)	0.66
			4.9			4.3			4.65			0.55			0.40			0.12			2.26			1.63			0.60	0.60
VN01	5.0	5.0	5.0	4.5	4.5	4.5	3.91	3.94	3.90	0.45	0.44	0.44	0.35	0.34	0.34	0.14	0.14	0.14	2.25	2.26	2.26	1.49	1.44	1.39	0.78	0.83	0.93	
	(0.0)	(0.0)	5.0	(0.0)	(0.0)	4.5	(0.07)	(0.09)	4.05	(0.01)	(0.00)	0.44	(0.00)	(0.00)	0.34	(0.00)	(0.00)	0.14	(0.04)	(0.06)	2.20	(0.08)	(0.06)	1.50	(0.10)	(0.12)	0.69	
			5.0			4.5			3.88			0.44			0.34			0.14			2.31			1.43			0.88	
			5.0			4.5			3.88			0.46			0.35			0.14			2.24			1.54			0.73	0.81
			(0.0)			(0.0)			(0.00)			(0.00)			(0.00)			(0.00)			(0.03)	2.26		(0.07)	1.50		(0.07)	0.69
			5.0			4.5			3.88			0.46			0.35			0.14			2.20			1.62			0.69	0.69
VN02	4.9	4.9	4.9	4.4	4.4	4.4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.38	2.38	2.40	1.75	1.75	1.71	0.57	0.57	0.57	
	(0.0)	(0.0)	4.9	(0.0)	(0.0)	4.4			NA			NA			NA			NA	(0.03)	(0.03)	2.40	(0.06)	(0.07)	1.71	(0.00)	(0.00)	0.57	
			4.9			4.4			NA			NA			NA			NA			2.34			1.83			0.57	0.57
			4.9			4.4			NA			NA			NA			NA			2.38			1.75			0.57	0.57
			(0.0)			(0.0)			NA			NA			NA			NA			(0.03)	2.40		(0.07)	1.83		(0.00)	0.57
			4.9			4.4			NA			NA			NA			NA			2.40			1.71			0.57	0.57
VN04	5.0	5.0	5.1	4.5	4.5	4.4	3.86	3.90	3.86	0.45	0.44	0.44	0.35	0.34	0.34	0.14	0.14	0.14	2.11	2.11	2.09	1.24	1.24	1.16	0.89	0.89	0.93	
	(0.1)	(0.1)	4.9	(0.0)	(0.0)	4.5	(0.05)	(0.04)	3.93	(0.00)	(0.00)	0.45	(0.00)	(0.00)	0.35	(0.00)	(0.00)	0.14	(0.03)	(0.03)	2.14	(0.06)	(0.07)	1.27	(0.06)	(0.07)	0.81	
			4.9			4.5			3.90			0.44			0.34			0.14			2.09			1.27			0.93	
			4.9			4.5			3.83			0.45			0.35			0.13			2.11			1.24			0.89	0.93
			(0.0)			(0.1)			3.83			(0.00)			(0.00)			(0.00)			(0.03)	2.15		(0.07)	1.28		(0.07)	0.81
			4.9			4.4			3.81			0.45			0.36			0.13			2.09			1.16			0.93	0.93
VN05	5.1	5.1	5.1	4.2	4.2	4.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.06	2.03	2.03	1.24	1.24	1.16	0.81	0.77	0.81	
	(0.0)	(0.0)	5.1	(0.0)	(0.0)	4.2			NA			NA			NA			NA	(0.03)	(0.00)	2.03	(0.06)	(0.07)	1.27	(0.07)	(0.07)	0.81	
			5.1			4.2			NA			NA			NA			NA			2.03			1.27			0.69	0.69
			5.1			4.3			NA			NA			NA			NA			2.08			1.24			0.85	0.81
			(0.0)			(0.0)			NA			NA			NA			NA			(0.00)	2.08		(0.07)	1.27		(0.07)	0.81
			5.1			4.3			NA			NA			NA			NA			2.08			1.16			0.81	0.93

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5. 20th INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENTT

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 20th Project, the NC shipped an artificial inland water sample to 23 laboratories involved in the EANET activities on October 18, 2019, and most of them submitted their analytical data to the NC by February 29, 2020. 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 1L	Poly-ethylene bottle 1L	One bottle	To analyze directly

The analytical parameters are shown in Table 5.2.

Table 5.2 Analytical parameters

Analytical Parameter	Reporting Units	
pH	pH units	–
EC	milli siemens per meter	mS m ⁻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 pH4.8)
SO ₄ ²⁻ NO ₃ ⁻	Ion Chromatography or Spectrophotometry
Cl ⁻	Ion Chromatography or Titration
Na ⁺ K ⁺	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
Ca ²⁺ Mg ²⁺	
NH ₄ ⁺	Ion Chromatography or Spectrophotometry (Indophenol blue)

5.2.4 Data Checking Procedures

a) Calculation of ion balance (R_1)

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

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

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

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

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

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

(3) Calculation of ion balance (R_1)

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

(4) R_1 , which is calculated using the above equation, should be compared with allowable ranges in Table 5.5. Re-measurement, check with standard solutions, and/or inspection of calibration

curves should be undertaken, when R_1 is not within the range.

Table 5.5 Allowable ranges for R_1 in different concentration ranges

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

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

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

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

C : Molar concentrations [$\mu\text{mol L}^{-1}$] of ions in the parenthesis; each constant value was ionic equivalent conductance at 25 degrees centigrade. Alkalinity considered to be corresponded to bicarbonate ions (HCO_3^-).

(2) Ratio (R_2) of calculations (A_{calc}) to measurements (A_{meas}) in electric conductivity is calculated as follows;

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

A_{meas} : measured conductivity

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

Table 5.6 Allowable ranges for R_2 in different concentration ranges

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

5.3 Results

5.3.1 Outline of Results

Table 5.7 shows the summary of the analytical results. The outliers, defined as those results exceeding three standard deviations, were excluded from calculations in Table 5.7. Each average of submitted data agreed well with the corresponding prepared value/concentration. Original data from the laboratories are shown in Table 5.10 and APPENDIX table 5.1.

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

Constituents	Prepared	Average	S.D.	N	Min.	Max.
pH	7.06	6.90	0.19	21	6.46	7.22
EC (mS m ⁻¹)	3.88	3.79	0.11	21	3.60	3.96
Alkalinity (meq L ⁻¹)	0.131	0.132	0.02	21	0.090	0.163
SO ₄ ²⁻ (mg L ⁻¹)	4.48	4.31	0.47	20	2.39	4.65
NO ₃ ⁻ (mg L ⁻¹)	0.29	0.28	0.02	21	0.25	0.31
Cl ⁻ (mg L ⁻¹)	3.39	3.35	0.26	21	2.84	3.97
Na ⁺ (mg L ⁻¹)	3.68	3.66	0.25	20	3.24	4.37
K ⁺ (mg L ⁻¹)	0.59	0.55	0.03	20	0.50	0.63
Ca ²⁺ (mg L ⁻¹)	1.59	1.56	0.13	19	1.09	1.75
Mg ²⁺ (mg L ⁻¹)	0.68	0.66	0.03	19	0.58	0.71
NH ₄ ⁺ (mg L ⁻¹)	0.25	0.22	0.05	19	0.04	0.29

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

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

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

Table 5.8 Number of flagged data

Flag*	pH	EC	Alkalinity	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total	Ratio
E	0	0	4	0	0	3	1	1	0	2	5	16	7.1%
X	0	0	1	2	0	0	0	0	2	0	2	7	3.1%
Data within DQOs	21	21	16	19	21	18	19	19	18	18	13	203	89.8%
Flagged(%)	0.0	0.0	23.8	9.5	0.0	14.3	5.0	5.0	10.0	10.0	35.0	10.2	

Flag E: 15% < |Deviation| ≤ 30%

Flag X: 30% < |Deviation|

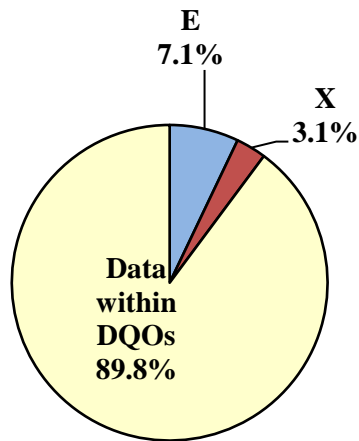


Figure 5.1 Percentage of flagged data

The data flagged by "E" shared 7.1% of all reported data, and the data flagged by "X" shared 3.1% of all reported data of samples. The NH₄⁺ results were flagged most (E and X), and their percentage was 35.0%.

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	57%
1	3	13%
2	4	17%
3	1	4%
4	1	4%
5	1	4%
6	0	0%
7	0	0%
8	0	0%
9	0	0%
Total	23	100%

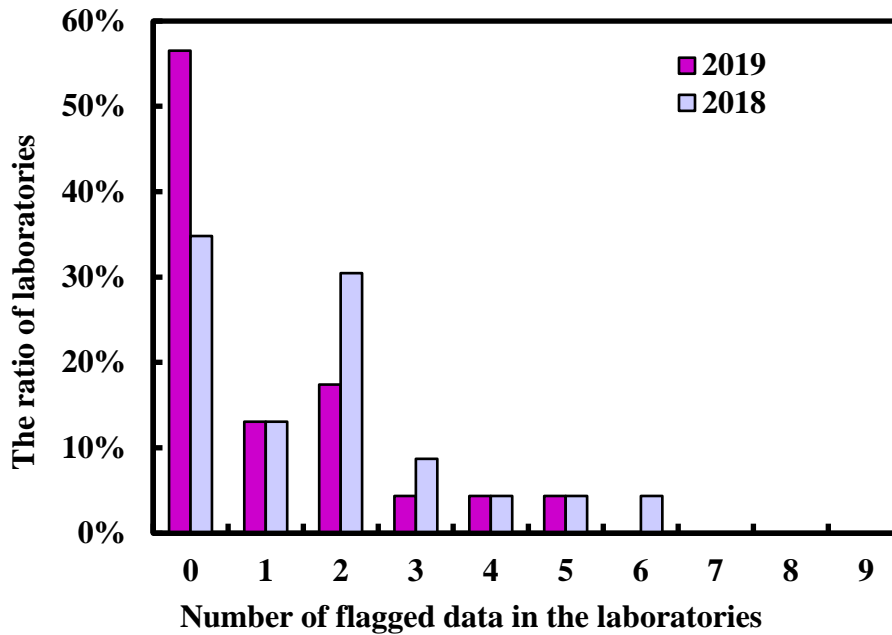


Figure 5.2 Distribution of laboratories with the number of flagged data

The percentage of the laboratories without flagged data was 57% in this attempt, while that in the last attempt (2018) was 35%. 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.191i (artificial inland aquatic environment sample : EANET in 2019)

Lab. ID	pH	EC mS m ⁻¹	Alkalinity meq L ⁻¹	SO ₄ ²⁻ mg L ⁻¹	NO ₃ ⁻ mg L ⁻¹	Cl ⁻ mg L ⁻¹	Na ⁺ mg L ⁻¹	K ⁺ mg L ⁻¹	Ca ²⁺ mg L ⁻¹	Mg ²⁺ mg L ⁻¹	NH ₄ ⁺ mg L ⁻¹	R1 %	R2 %
CN01	7.01	3.81	0.143	4.44	0.30	3.35	3.66	0.59	1.58	0.71	0.29 E	-0.98	1.76
CN02	6.99	3.80	0.125	4.46	0.30	3.34	3.57	0.57	1.58	0.68	0.24	0.15	0.15
CN03	6.99	3.87	0.130	4.44	0.30	3.34	3.63	0.54	1.57	0.67	0.24	-0.47	-0.47
CN04	6.98	3.88	0.135	4.44	0.26	3.32	3.63	0.56	1.57	0.69	0.24	-0.62	-0.36
ID01	6.89	3.87	0.163 E	4.33	0.29	2.99	3.64	0.57	1.65	0.61	0.19 E	-4.00	-0.04
ID05	7.22	3.60	0.157 E	2.39 X	0.26	3.97 E	3.58	0.55	0.90 X	0.62	0.49 X	-4.79	0.10
JP03	7.08	3.77	0.143	4.59	0.31	3.29	3.63	0.57	1.63	0.66	0.22	-2.47	1.90
JP04	7.19	3.77	0.141	4.48	0.29	3.34	3.60	0.59	1.62	0.67	0.24	-1.84	1.67
LA01	6.75	3.77	0.090 X	0.31 X	0.25	3.23							
MY01	6.86	3.92	0.143	4.54	0.29	3.39	3.75	0.56	1.58	0.64	0.22	-2.55	0.06
MN01	6.46	3.64	0.140	4.65	0.28	3.42	3.69	0.50	1.58	0.61	0.26	-3.13	3.77
PH01	6.91	3.79	0.139	4.33	0.27	3.45	3.43	0.55	1.61	0.69	0.04 X	-4.54	-0.32
RU01	6.96	3.81	0.120	4.23	0.27	3.57	3.51	0.55	1.50	0.65	0.22	-0.95	-1.05
RU02	6.79	3.87	0.110 E	3.94	0.26	3.91 E	3.50	0.63	1.53	0.65	0.24	0.88	-1.61
TH01	7.13	3.86	0.133	4.30	0.25	3.16	3.64	0.51	1.75	0.68	0.22	1.71	-0.51
TH02	6.69	3.73	0.092 E	4.55	0.27	3.35	3.64	0.57	1.09 X	0.50 E	0.21 E	-0.98	-3.70
VN01	6.65	3.63	0.134	4.40	0.29	3.37	4.11	0.54	1.62	0.67	0.22	2.32	4.36
VN02	6.70	3.64	0.133	4.39	0.30	3.37	3.92	0.54	1.65	0.69	0.23	1.85	3.85
VN03	6.96	3.96	0.130	4.43	0.31	2.84 E	3.37	0.54	1.56	0.67	0.22	-0.28	-4.05
VN04	6.69	3.64	0.133	4.43	0.27	3.37	4.37 E	0.53	1.53	0.66	0.21 E	3.12	4.42
VN05	6.98	3.93	0.140	4.39	0.31	2.94	3.24	0.50 E	1.45	0.58 E	0.19 E	-5.85	-4.50
Expected value	7.06	3.88	0.131	4.48	0.29	3.39	3.68	0.59	1.59	0.68	0.25	-	-

Flag E: 15% < |Deviation| ≤ 30%

Flag X: 30% < |Deviation|

I: Poor ion balance (R1)

C: Rich Conductivity agreement (R2)

blank: not analyzed

5.3.2 Evaluation of laboratories' performance (by analytical parameters)

The laboratories' performances are presented below in Figures from 5.3 to 5.13 for each analytical parameter. The results received from each laboratory are normalized by the prepared values to evaluate deviation from the prepared values.

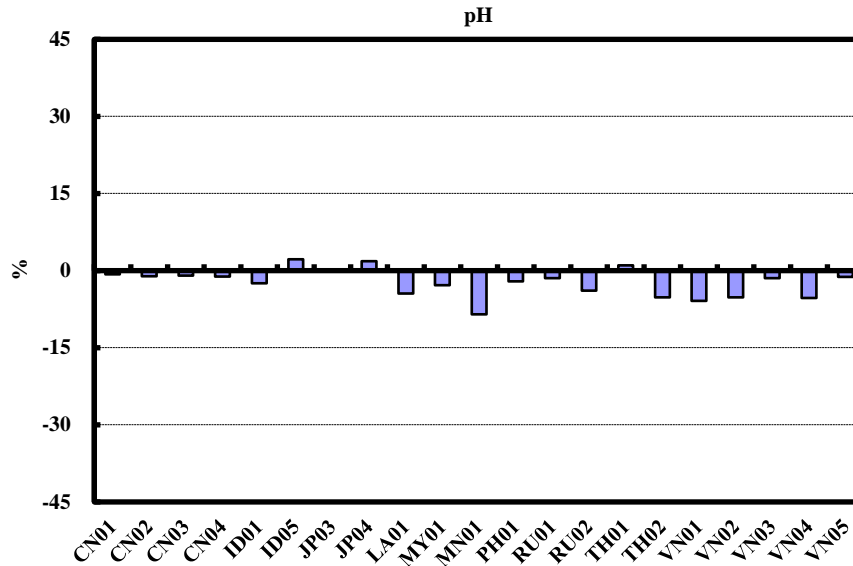


Figure 5.3 Distribution of results for pH (normalized by the prepared value)

All the submitted data of pH were within DQO, 15%. Most of them were lower than the prepared value.

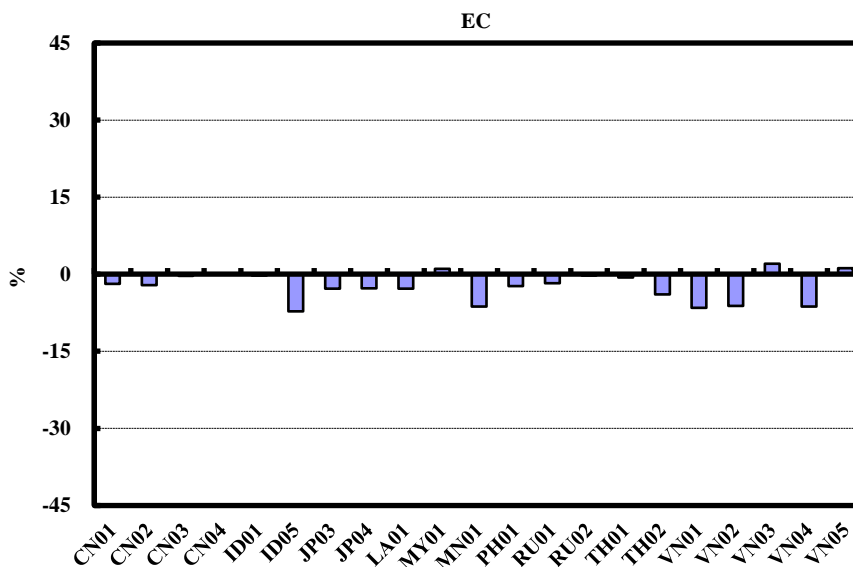


Figure 5.4 Distribution of results for EC (normalized by the prepared value)

All the submitted data of EC were within DQO, 15%. Most of them were lower than the prepared value.

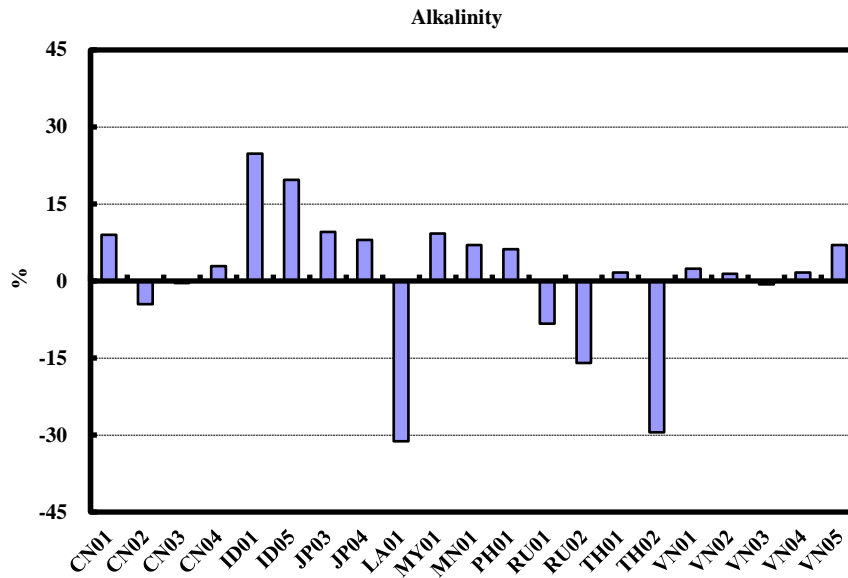


Figure 5.5 Distribution of results for alkalinity (normalized by prepared concentration)

Data of alkalinity from 5 laboratories were flagged and one of them were deviated more than 30%. The number of flagged data of alkalinity was 11 in the last attempt (2018). The flagged data decreased.

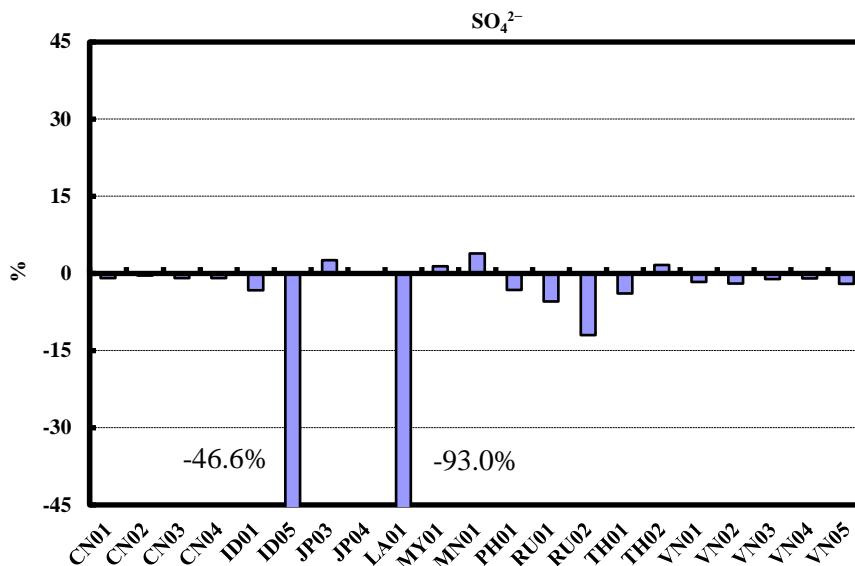


Figure 5.6 Distribution of results for SO₄²⁻ (normalized by prepared concentration)

Except for ID05 and LA01, all the submitted data of SO₄²⁻ were within DQOs.

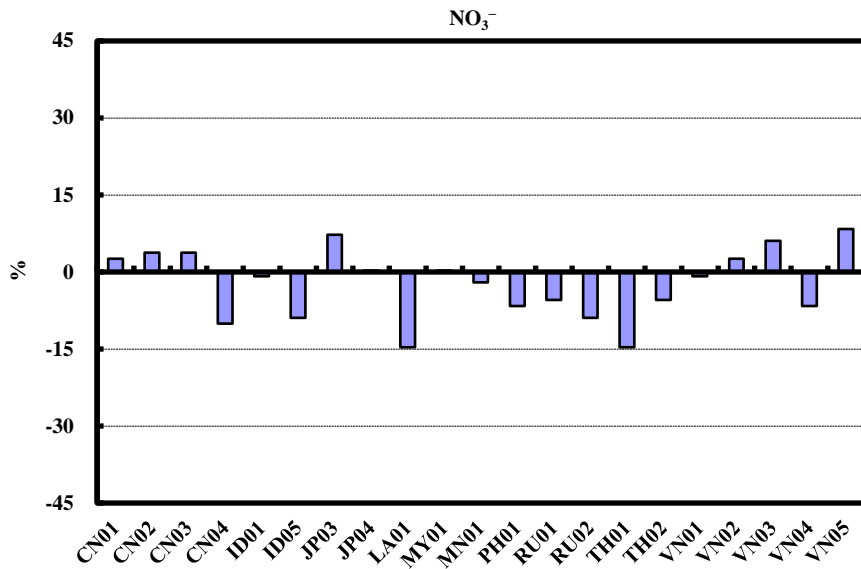


Figure 5.7 Distribution of results for NO₃⁻ (normalized by prepared concentration)

All the submitted data of NO₃⁻ were within DQO, 15%. Most of them were lower than the prepared value.

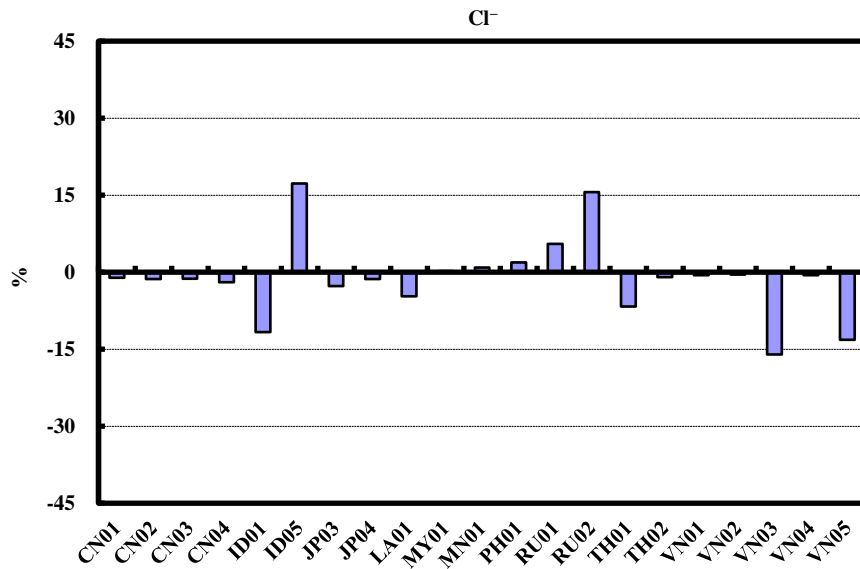


Figure 5.8 Distribution of results for Cl⁻ (normalized by prepared concentration)

Except for ID05, RU02 and VN03, all the submitted data of Cl⁻ were within DQOs.

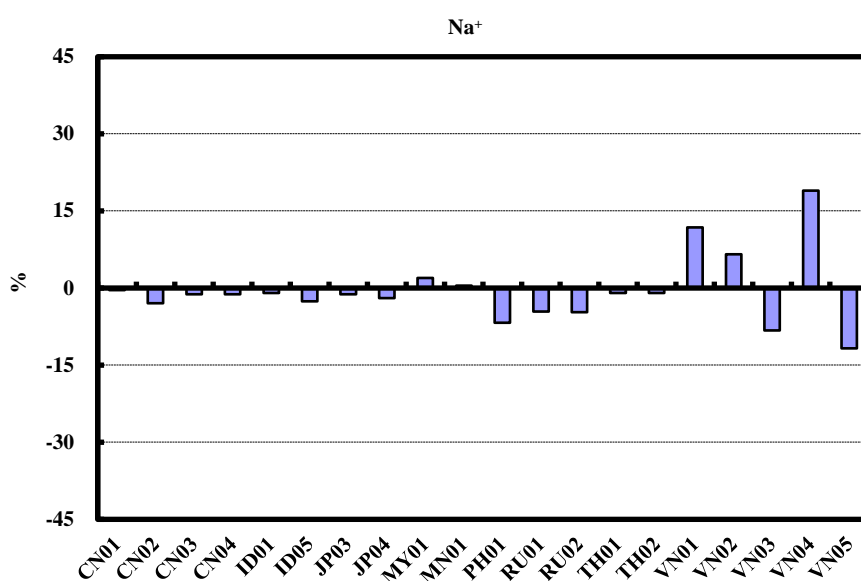


Figure 5.9 Distribution of results for Na⁺ (normalized by prepared concentration)

Except for VN04, all the submitted data of Na⁺ were within DQOs.

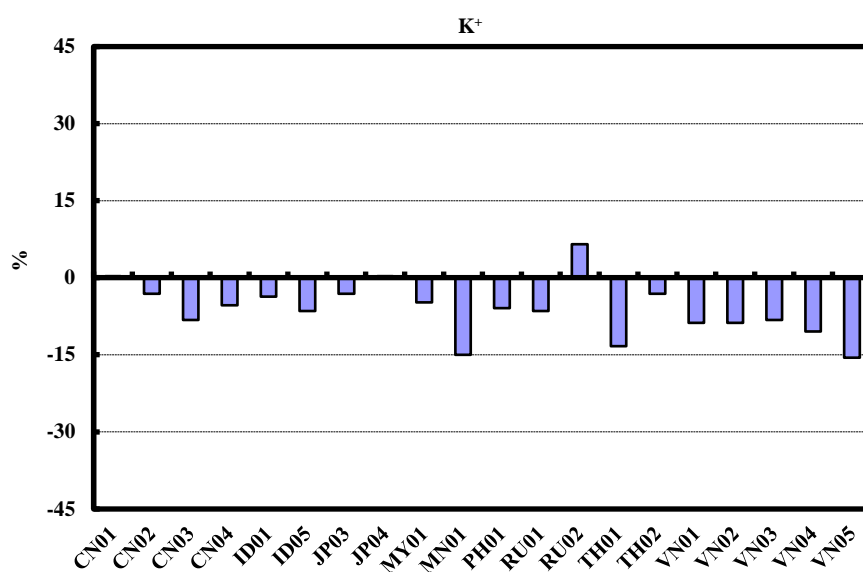


Figure 5.10 Distribution of results for K⁺ (normalized by prepared concentration)

Except for VN05, all the submitted data of K⁺ were within DQOs.

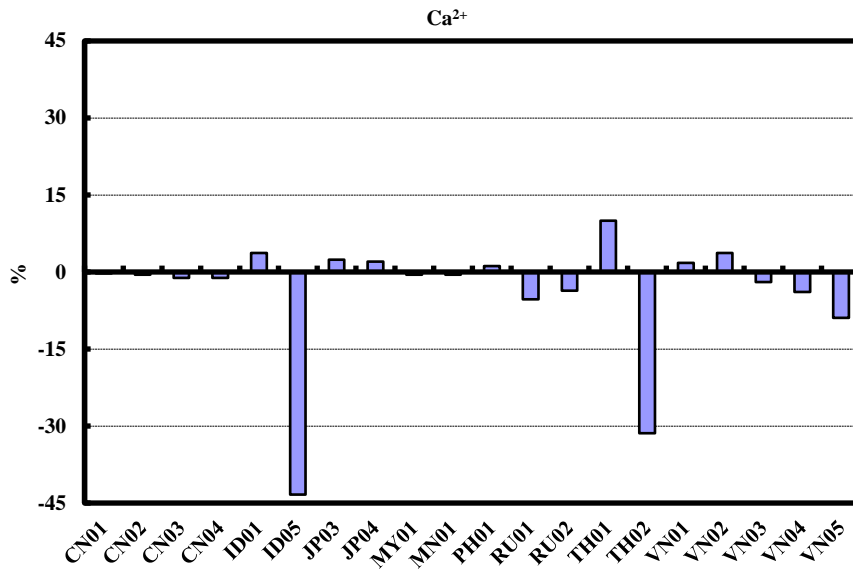


Figure 5.11 Distribution of results for Ca²⁺ (normalized by prepared concentration)

Except for ID05 and TH02, all the submitted data of Ca²⁺ were within DQOs.

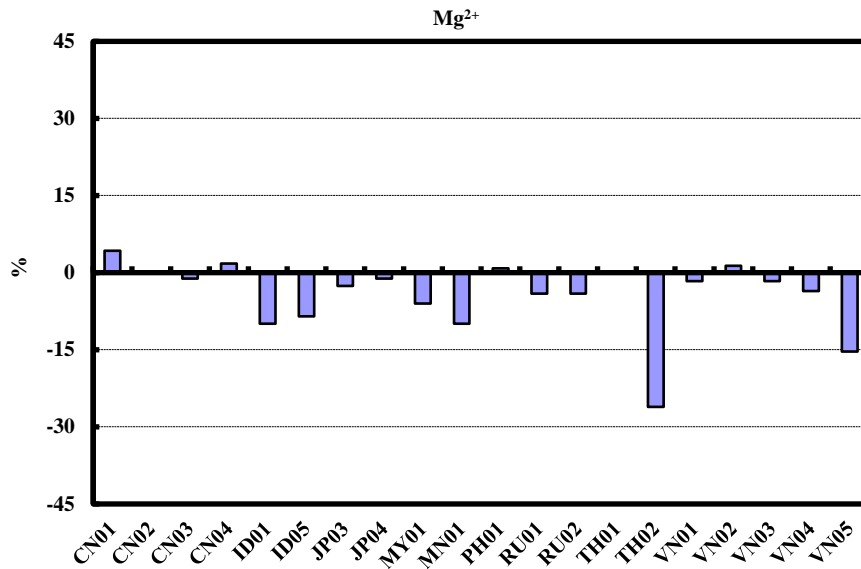


Figure 5.12 Distribution of results for Mg²⁺ (normalized by prepared concentration)

Except for TH02 and VN05, all the submitted data of Mg²⁺ were within DQOs.

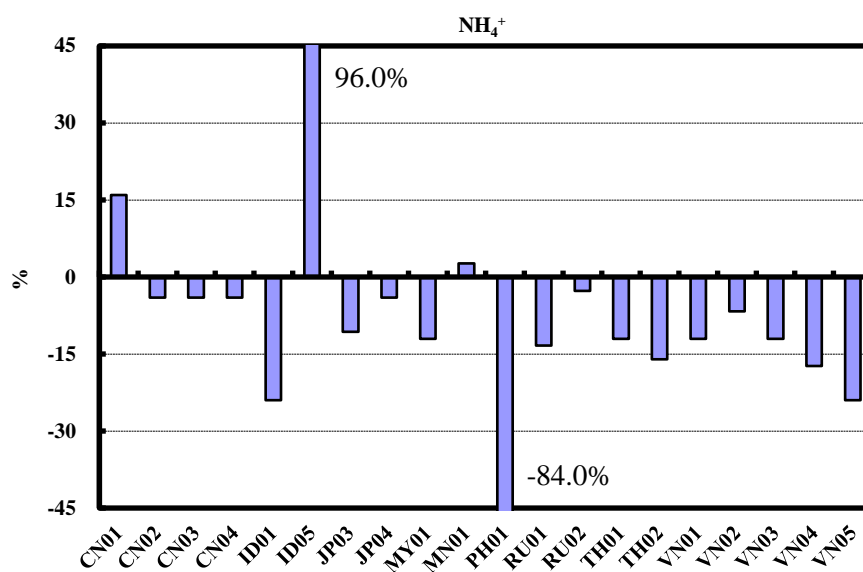


Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

Data of NH_4^+ from 7 laboratories were flagged, and 2 of them were deviated more than 30%. Among 21 participating laboratories, 17 laboratories used ion chromatography, 4 laboratories used spectrophotometry (Indophenol) for the determination of NH_4^+ . 6 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 (2018).

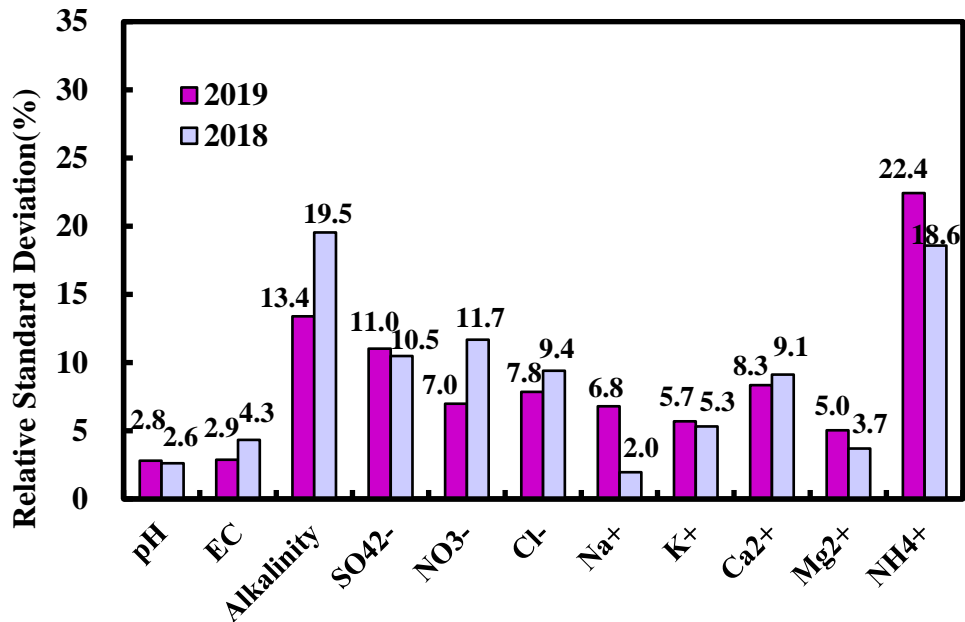


Figure 5.14 Relative standard deviation of each constituent

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

The relative standard deviation (RSD) of alkalinity and NO₃⁻ in 2019 were particularly lower than the last attempt. On the other hand, the RSDs of Na⁺, and NH₄⁺ increased remarkably in this attempt .

5.3.4 Information on laboratories

Methodologies used

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

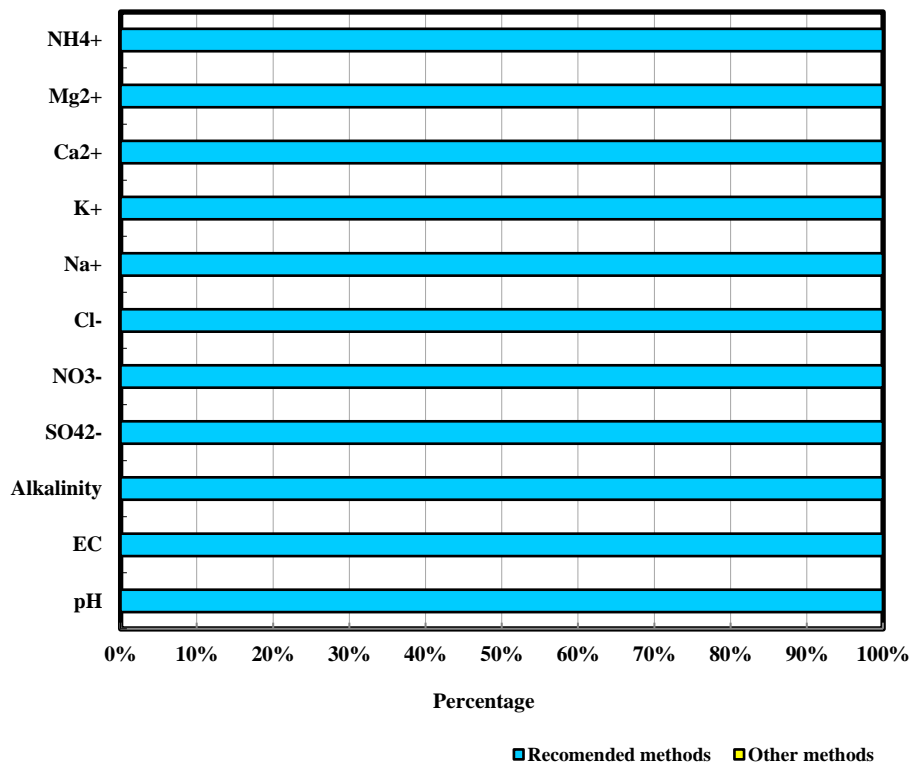


Figure 5.15 Percentage of laboratories using the recommended methods

Table 5.11 List of methods

Code	Method
0	pH meter with electrode
1	Conductivity cell
2	Titration
3	Atomic absorption / Flame (emission) photometry
4	Ion chromatography
5	Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP - AES)
6	Calculation
7	Spectrophotometry
8	Spectrophotometry (Indophenol blue)
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	Graphite Furnace Atomic Absorption spectrometry (GFAA)
11	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	21										
1		21									
2			21(5)			3(3)					
3							4	4	4(1)	4	
4				18(1)	18	18	16(1)	16(1)	16(1)	16(2)	16(6)
5											
6											
7				3(1)	3						
8											4(1)
9											
10											
11											
Flagged E	0	0	4	0	0	3	1	1	0	2	5
Flagged X	0	0	1	2	0	0	0	0	2	0	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	3	A	A	B	C	C	C	C	C	C	C	C
CN03	1	A	A	A	A	A	A	A	A	A	A	A
CN04	1	A	A	A	A	A	A	A	A	A	A	A
ID01	3	A	A	B	C	C	C	C	C	C	C	C
ID05	6	A	B	C	B	D	D	E	E	F	F	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					
MY01	3	A	A	B	C	C	C	B	B	B	B	B
MN01	2	A	A	A	B	B	B	B	B	B	B	B
PH01	2	A	B	B	A	A	A	A	A	A	A	A
RU01	3	A	A	A	B	B	B	C	C	C	C	A
RU02	7	A	B	C	D	E	C	F	F	F	F	G
TH01	1	A	A	A	A	A	A	A	A	A	A	A
TH02	1	A	A	A	A	A	A	A	A	A	A	A
VN01	2	A	A	A	B	B	B	B	B	B	B	B
VN02	3	A	A	B	C	C	C	C	C	C	C	C
VN03	2	A	A	B	B	A	A	B	B	B	B	A
VN04	3	A	A	B	C	C	C	C	C	C	C	C
VN05	2	A	A	A	B	B	B	B	B	B	B	B

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

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

blank: not analyzed

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

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

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

Table 5.14 Years of experience

Lab.ID	pH	EC	Alkalinity	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Unit : year
											NH ₄ ⁺
CN01	3	3	3	3	3	3	3	3	3	3	3
CN02	10	10	2	14	14	14	14	14	14	14	14
CN03	2	2	2	2	2	2	2	2	2	2	2
CN04	13	13	13	13	13	13	13	13	13	13	13
ID01	21	21	1	1	1	1	1	1	1	1	1
ID05	2	6	7	6	2	2	7	7	4	4	2
JP03	4	4	5	5	5	5	5	5	5	5	5
JP04	17	17	17	17	17	17	17	17	17	17	17
LA01	8	8	8	8	8	8					
MY01	6	6	7	10	10	10	7	7	7	7	7
MN01	18	18	18	21	21	21	21	21	21	21	21
PH01	5	5	5	5	5	5	5	5	5	5	5
RU01	26	26	26	24	24	24	34	34	34	34	26
RU02	15	6	5	33	1	5	25	25	25	25	40
TH01	21	21	21	21	21	21	21	21	21	21	21
TH02	22	22	22	22	22	22	22	22	22	22	22
VN01	3	3	3	6	6	6	6	6	6	6	6
VN02	13	13	15	15	15	15	15	15	15	15	15
VN03	5	5	8	8	5	5	8	8	8	8	5
VN04	16	16	16	13	14	14	14	14	14	14	14
VN05	6	6	6	15	15	15	15	15	15	15	15

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

1 year means experienced with one year or less.

blank: not analyzed

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

5.4. Comparison with past surveys

The inter-laboratory comparison projects of the EANET have been carried out 20 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.

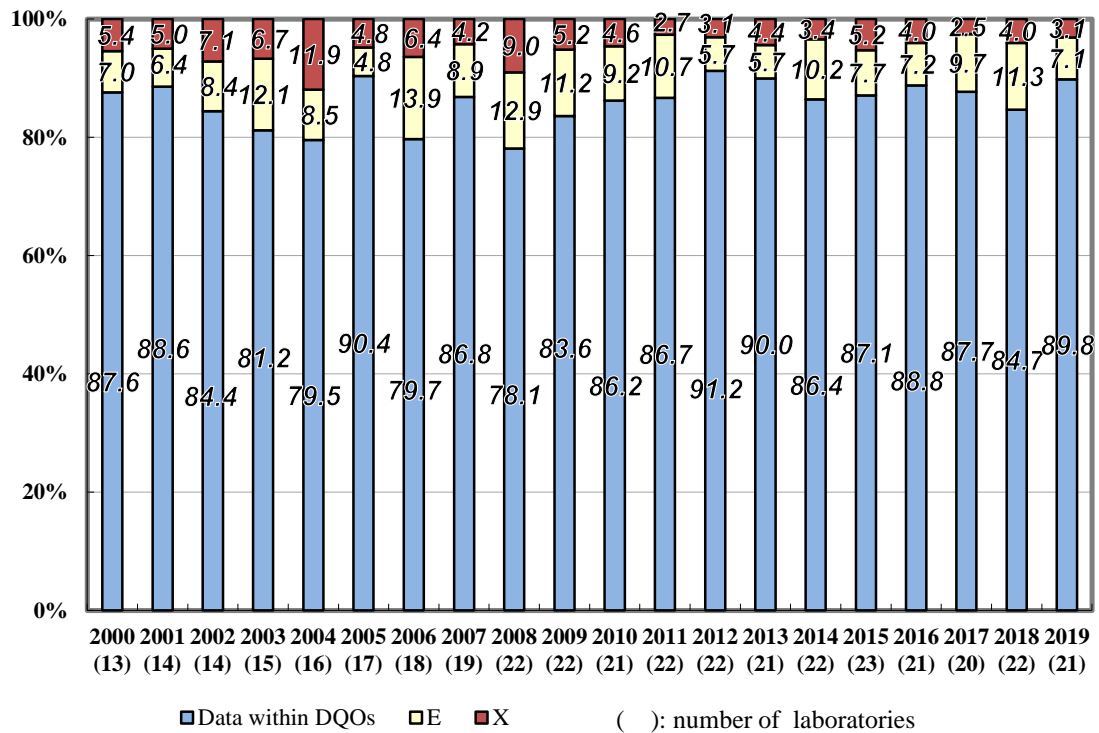


Figure 5.16 Comparison of the results from the inter-laboratory comparison projects

The percentage of data satisfied the DQOs increased from the last attempt (2018).

The values/concentrations for each parameter from the 1st to 20th projects were compared with the percentage of flagged data in Figure 5.17.

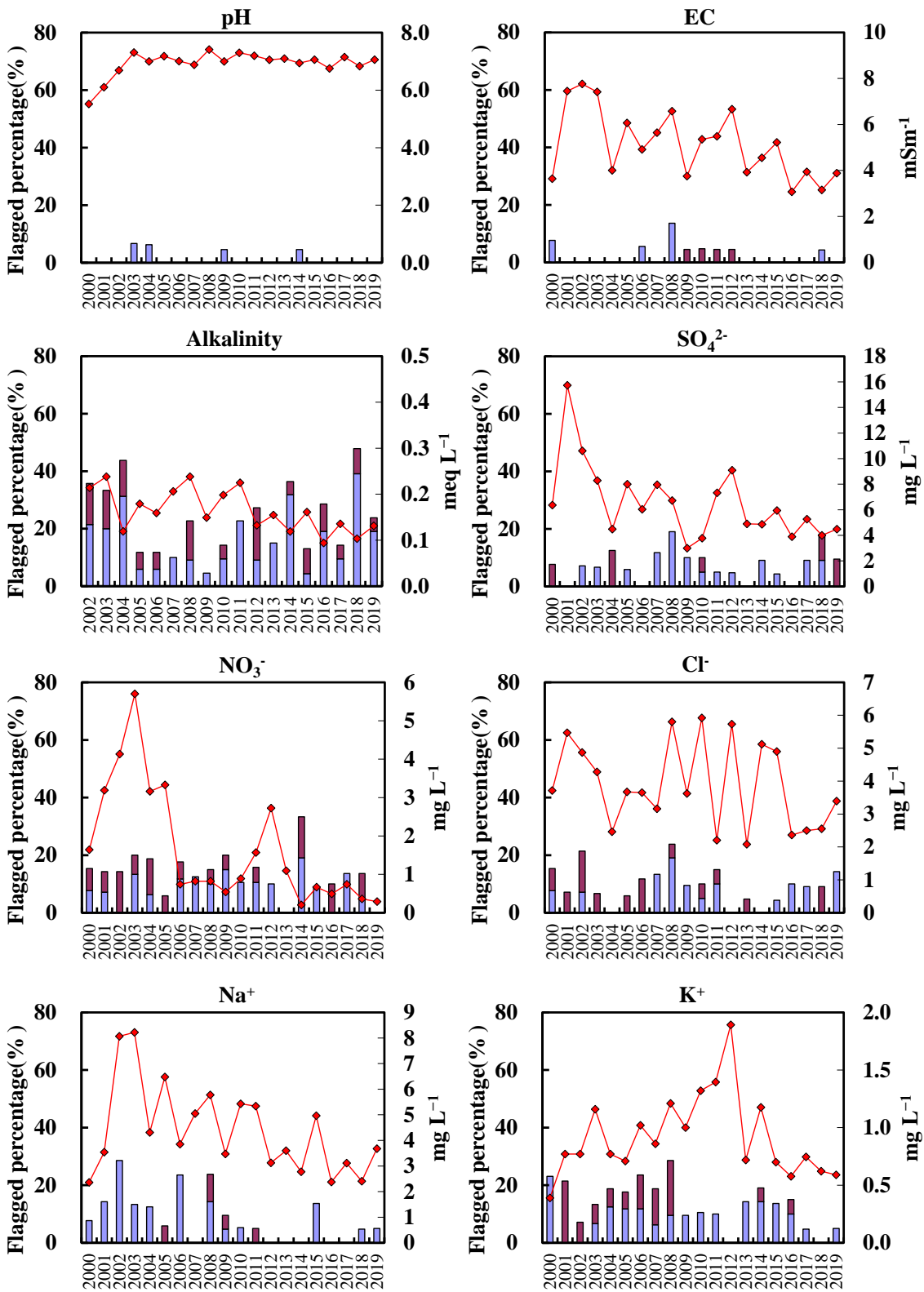


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects

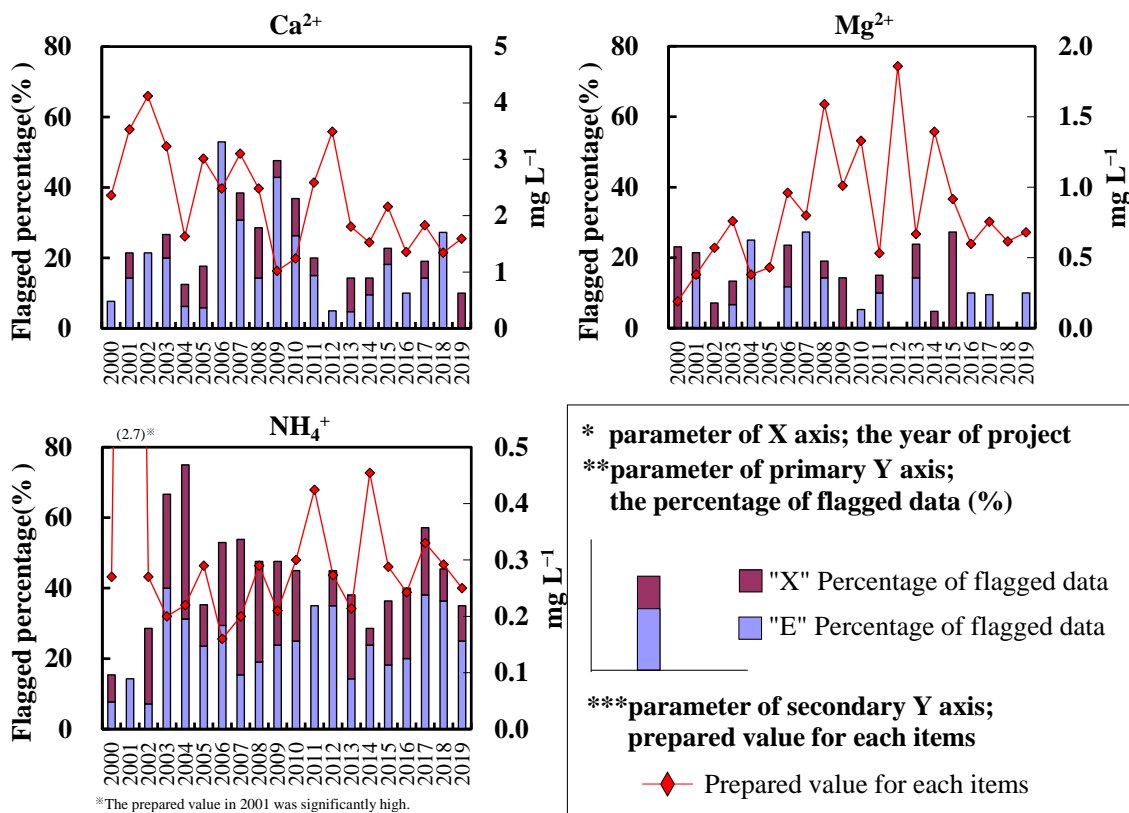


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects (Continued)

There was no flagged data in pH, EC and NO₃⁻ in this attempt. The analyses of Alkalinity, SO₄²⁻ Ca²⁺ and NH₄⁺ were improved. In this attempt, flagged percentages of Cl⁻, Na⁺, K⁺ and Mg²⁺ became higher than the last attempt. It may be caused by condition of instrument, especially ion chromatography column.

Furthermore, the percentage of flagged data was larger in NH₄⁺ than for other parameters in every survey except for the 1st- 3rd project. The percentage of flagged Ca²⁺ in the 7th - 11th project was also comparatively high. Therefore, in the inland water analysis, it is necessary to pay more attention to NH₄⁺ and Ca²⁺.

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	3.81	0.143	4.44	0.30	3.35	3.66	0.59	1.58	0.71	0.29
CN02	6.99	3.80	0.125	4.46	0.30	3.34	3.57	0.57	1.58	0.68	0.24
CN03	6.99	3.87	0.130	4.44	0.30	3.34	3.63	0.54	1.57	0.67	0.24
CN04	6.98	3.88	0.135	4.44	0.26	3.32	3.63	0.56	1.57	0.69	0.24
ID01	6.89	3.87	0.163	4.33	0.29	2.99	3.64	0.57	1.65	0.61	0.19
ID05	7.22	3.60	0.157	2.39	0.26	3.97	3.58	0.55	0.90	0.62	0.49
JP03	7.08	3.77	0.143	4.59	0.31	3.29	3.63	0.57	1.63	0.66	0.22
JP04	7.19	3.77	0.141	4.48	0.29	3.34	3.60	0.59	1.62	0.67	0.24
LA01	6.75	3.77	0.090	0.31	0.25	3.23					
MY01	6.86	3.92	0.143	4.54	0.29	3.39	3.75	0.56	1.58	0.64	0.22
MN01	6.46	3.64	0.140	4.65	0.28	3.42	3.69	0.50	1.58	0.61	0.26
PH01	6.91	3.79	0.139	4.33	0.27	3.45	3.43	0.55	1.61	0.69	0.04
RU01	6.96	3.81	0.120	4.23	0.27	3.57	3.51	0.55	1.50	0.65	0.22
RU02	6.79	3.87	0.110	3.94	0.26	3.91	3.50	0.63	1.53	0.65	0.24
TH01	7.13	3.86	0.133	4.30	0.25	3.16	3.64	0.51	1.75	0.68	0.22
TH02	6.69	3.73	0.092	4.55	0.27	3.35	3.64	0.57	1.09	0.50	0.21
VN01	6.65	3.63	0.134	4.40	0.29	3.37	4.11	0.54	1.62	0.67	0.22
VN02	6.70	3.64	0.133	4.39	0.30	3.37	3.92	0.54	1.65	0.69	0.23
VN03	6.96	3.96	0.130	4.43	0.31	2.84	3.37	0.54	1.56	0.67	0.22
VN04	6.69	3.64	0.133	4.43	0.27	3.37	4.37	0.53	1.53	0.66	0.21
VN05	6.98	3.93	0.140	4.39	0.31	2.94	3.24	0.50	1.45	0.58	0.19
Expected value	7.06	3.88	0.131	4.48	0.29	3.39	3.68	0.59	1.59	0.68	0.25
Number of data	21	21	21	21	21	21	20	20	20	20	20
Average	6.90	3.79	0.13	4.12	0.28	3.35	3.66	0.55	1.53	0.65	0.23
Minimum	6.46	3.60	0.09	0.31	0.25	2.84	3.24	0.50	0.90	0.50	0.04
Maximum	7.22	3.96	0.16	4.65	0.31	3.97	4.37	0.63	1.75	0.71	0.49

blank: not analyzed

Appendix Table 5.2 Data normalized by the prepared value

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

Lab. ID	pH (%)	EC (%)	Alkalinity (%)	SO ₄ ²⁻ (%)	NO ₃ ⁻ (%)	Cl ⁻ (%)	Na ⁺ (%)	K ⁺ (%)	Ca ²⁺ (%)	Mg ²⁺ (%)	NH ₄ ⁺ (%)
CN01	-0.8	-1.9	9.0	-0.9	2.6	-1.0	-0.4	0.3	-0.3	4.2	16.0
CN02	-1.1	-2.1	-4.5	-0.4	3.8	-1.3	-3.0	-3.1	-0.5	-0.2	-4.0
CN03	-1.0	-0.3	-0.4	-0.9	3.8	-1.2	-1.3	-8.2	-1.1	-1.2	-4.0
CN04	-1.2	0.0	2.9	-0.9	-10.1	-1.9	-1.3	-5.4	-1.1	1.8	-4.0
ID01	-2.4	-0.3	24.8	-3.3	-0.8	-11.7	-1.0	-3.7	3.7	-10.0	-24.0
ID05	2.2	-7.2	19.7	-46.6	-8.9	17.3	-2.6	-6.5	-43.3	-8.5	96.0
JP03	0.2	-2.8	9.5	2.6	7.2	-2.7	-1.3	-3.1	2.4	-2.6	-10.7
JP04	1.8	-2.7	8.0	0.0	0.3	-1.3	-2.0	0.3	2.0	-1.2	-4.0
LA01	-4.4	-2.8	-31.2	-93.0	-14.7	-4.7					
MY01	-2.8	1.0	9.3	1.4	0.3	0.2	1.9	-4.8	-0.5	-6.0	-12.0
MN01	-8.5	-6.3	7.0	3.9	-2.0	0.9	0.5	-15.0	-0.5	-10.0	2.7
PH01	-2.1	-2.3	6.2	-3.2	-6.6	1.9	-6.8	-5.9	1.2	0.8	-84.0
RU01	-1.5	-1.7	-8.3	-5.5	-5.4	5.6	-4.6	-6.5	-5.3	-4.1	-13.3
RU02	-3.9	-0.3	-15.9	-12.0	-8.9	15.6	-4.7	6.5	-3.7	-4.1	-2.7
TH01	1.0	-0.6	1.6	-3.9	-14.7	-6.7	-1.0	-13.3	10.0	-0.2	-12.0
TH02	-5.2	-3.9	-29.4	1.6	-5.4	-0.9	-1.0	-3.1	-31.4	-26.1	-16.0
VN01	-5.9	-6.5	2.4	-1.7	-0.8	-0.6	11.8	-8.8	1.8	-1.6	-12.0
VN02	-5.2	-6.2	1.4	-2.0	2.6	-0.5	6.5	-8.8	3.7	1.3	-6.7
VN03	-1.5	2.1	-0.7	-1.1	6.1	-16.0	-8.2	-8.2	-2.0	-1.6	-12.0
VN04	-5.3	-6.3	1.6	-1.0	-6.6	-0.6	19.0	-10.5	-3.9	-3.6	-17.3
VN05	-1.2	1.2	7.0	-2.0	8.4	-13.2	-11.8	-15.6	-8.9	-15.3	-24.0
Minimum	-8.5	-7.2	-31.2	-93.0	-14.7	-16.0	-11.8	-15.6	-43.3	-26.1	-84.0
Maximum	2.2	2.1	24.8	3.9	8.4	17.3	19.0	6.5	10.0	4.2	96.0
Average	-2.3	-2.4	1.0	-8.0	-2.4	-1.1	-0.6	-6.2	-3.9	-4.4	-7.4

blank: not analyzed

6. ACKNOWLEDGEMENT

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

7. CONTACT INFORMATION

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