

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

Report of the Inter-laboratory Comparison Project 2015

18th Inter-laboratory Comparison Project on Wet Deposition

11th Inter-laboratory Comparison Project on Dry Deposition

17th Inter-laboratory Comparison Project on Soil

16th Inter-laboratory Comparison Project

on Inland Aquatic Environment

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Network Center for EANET

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1. INTRODUCTION

The Inter-laboratory Comparison Project was conducted among the analytical laboratories in participating countries of the Acid Deposition Monitoring Network in East Asia (EANET), based on the Quality Assurance / Quality Control (QA/QC) Program 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 of EANET (NC) annually for the following items:

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

This report presented the results of the 18th Inter-laboratory Comparison Project on wet deposition, 11th Inter-laboratory Comparison Project on dry deposition, 17th Inter-laboratory Comparison Project on soil, and 16th Inter-laboratory Comparison Project on inland aquatic environment.

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

Table 1.1 listed the name and code of participating laboratories and data submission status. The check-mark mean the analytical results were submitted by individual laboratories.

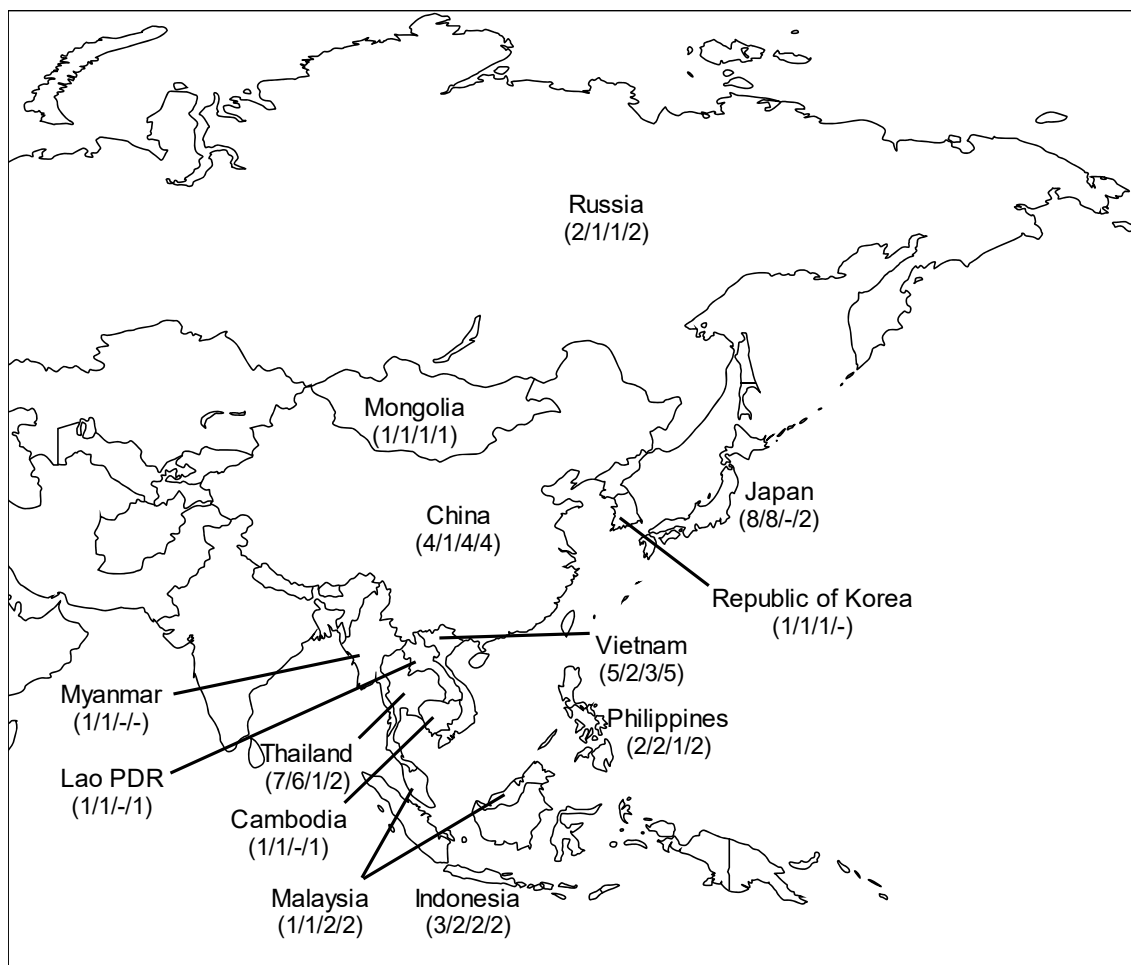


Figure 1.1 Number of participating laboratories in 2015

* 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
<u>Cambodia</u> Department of Environment Pollution Control, Ministry of Environment	KH01	✓	✓		✓
<u>China</u> Zhuhai Environmental Monitoring Center Station Xiamen Environmental Monitoring Station Xi'an Environmental Monitoring Center Station Chongqing Institute of Environmental Science	CN01 CN02 CN03 CN04	✓ ✓ ✓ ✓	 ✓ 	✓ ✓ ✓ ✓	✓ ✓ ✓ ✓
<u>Indonesia</u> Environmental Management Center (EMC), Environmental Impact Management Agency (BAPEDAL) 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	✓ ✓ ✓ ✓	✓ ✓ 	✓ ✓ 	✓ ✓
<u>Japan</u> 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 Shimane Prefectural Institute of Public Health and Environmental Science Kochi Prefectural Environmental Research Center Okinawa Prefectural Institute of Health and Environment Asia Center for Air Pollution Research (ACAP) Japan Environmental Sanitation Center (JESC)	JP01 JP02 JP03 JP04 JP05 JP07 JP08 JP09 JP10	✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓	 	 ✓ ✓
<u>Lao PDR</u> Environment Quality Monitoring Center (EQMC), Natural Resources and Environment Institute (NREI), Ministry of Natural Resources and Environment (MONRE)	LA01	✓	✓		✓
<u>Malaysia</u> Division of Environmental Health, Department of Chemistry (DOC) Faculty of Applied Science, University Technology Mara (UiTM) Universiti Putra Malaysia, Bintulu Sarawak Kampus (UPMKB) Soil Laboratory, Forest Research Institute Malaysia	MY01 MY03 MY04 MY05	✓ 	✓ 	 	✓
<u>Mongolia</u> Central Laboratory of Environment and Metrology	MN01	✓	✓	✓	✓
<u>Myanmar</u> Department of Meteorology and Hydrology (DMH)	MM01	✓	✓		
<u>Philippines</u> Environmental Management Bureau - Central Office (EMB-CO) Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR) University of the Philippines Los Baños (UPLB)	PH01 PH02 PH03	✓ ✓ 	✓ ✓ 	 	✓ ✓
<u>Republic of Korea</u> National Institute of Environment Research (NIER)	KR01	✓	✓	✓	
<u>Russia</u> Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB) Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	RU01 RU02	✓ ✓	✓ 	✓ 	✓ ✓
<u>Thailand</u> Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MONRE) Environmental Research and Training Centre (ERTC), Department of Research and Environmental Quality Promotion Chemistry Department, Science Faculty, Chiangmai University (CMU) Khon Kaen University (KKU) King Mongkut's University of Technology Thonburi (KMUTT) Kasetsart University Songkla University	TH01 TH02 TH04 TH05 TH06 TH07 TH08	✓ ✓ ✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓ 	✓ 	✓ ✓
<u>Vietnam</u> 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 Hydro Meteorology and Environment of South Vietnam (SIHYMETE) 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 :		36	27	13	23

2. 18th INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

2.1 Introduction

In the 18th 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 on beginning October 2015. Their analytical results were required to be submitted to the NC by 29 February 2016.

2.2 Procedures

2.2.1 Participating laboratories

The NC distributed the artificial rainwater samples to 37 laboratories in charge of chemical analysis in 13 countries of EANET. 36 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 in Chapter 1.

2.2.2 Description of samples

Two kinds of artificial rainwater samples were distributed to the laboratories. A description of the samples was 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. 151w No. 152w	100mL each	Polypropylene bottle 100mL	One bottle each	- Fixed quantity of reagents are dissolved in deionized water - Samples do not include other ions than shown in Table 2.2

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

Table 2.2 Prepared values/concentrations of analytical parameters*

	pH -	EC mS m ⁻¹	SO ₄ ²⁻ μmol L ⁻¹	NO ₃ ⁻ μmol L ⁻¹	Cl ⁻ μmol L ⁻¹	NH ₄ ⁺ μmol L ⁻¹	Na ⁺ μmol L ⁻¹	K ⁺ μmol L ⁻¹	Ca ²⁺ μmol L ⁻¹	Mg ²⁺ μmol L ⁻¹
No. 151w	4.74	3.05	44.1	38.9	56.8	43.9	48.8	7.8	22.2	10.5
No. 152w	5.15	0.94	11.9	10.7	19.8	9.8	12.8	3.2	7.0	3.7

* 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 the “Technical Manual for Wet Deposition Monitoring in East Asia -2010” and “Quality Assurance/Quality Control (QA/QC) Program for Wet Deposition Monitoring in East Asia”. Analytical methods specified in the Technical Manual were 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 [μeq L⁻¹]) was calculated by summing the concentrations of all anions (c [μmol 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 [μmol L⁻¹] of anion “i”.

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

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

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

- (3) Calculation of ion balance (R₁)

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

- (4) R₁ calculated by the above equation was compared with allowable ranges specified in the Technical Manual which were 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 [μeq L ⁻¹]	R ₁ [%]
< 50	± 30
50 – 100	± 15
> 100	± 8

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

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

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

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

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

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

Λ meas : measured conductivity

(3) R₂ calculated by the above equation was compared with allowable ranges specified in the Technical Manual which were 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 36 laboratories in the participating countries of EANET. The original data submitted by the laboratories were shown in Appendix 2.2.

Basic statistics of submitted data summarized in Table 2.6 were 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 which are apart from the average greater than a factor of 3 of S.D. were not included for the statistics calculation. As shown in Table 2.6, Difference of Va from prepared value (Vp) was slightly large. The range of $\Delta V/Vp$ was between -4.5% to 9.9% for the sample No. 151w, and -3.6% to 10.4% for the sample No. 152w.

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

Sample No. 151w

Constituents	Prepared (Vp)	Average (Va)	$\Delta V/Vp^{*1}$ %	S.D.	N	Min.	Max.
pH	4.74	4.80	1.3	0.11	35	4.56	5.22
EC [mS m ⁻¹]	3.05	2.95	-3.1	0.09	34	2.80	3.30
SO ₄ ²⁻ [μmol L ⁻¹]	44.1	43.6	-1.0	4.89	34	30.6	65.8
NO ₃ ⁻ [μmol L ⁻¹]	38.9	38.0	-2.2	2.61	34	31.3	47.3
Cl ⁻ [μmol L ⁻¹]	56.8	54.2	-4.5	3.15	32	43.2	57.3
NH ₄ ⁺ [μmol L ⁻¹]	43.9	45.0	2.4	2.80	33	39.9	55.0
Na ⁺ [μmol L ⁻¹]	48.8	49.6	1.7	4.34	33	44.2	67.1
K ⁺ [μmol L ⁻¹]	7.8	8.6	9.9	2.01	34	6.8	14.1
Ca ²⁺ [μmol L ⁻¹]	22.2	23.3	5.1	1.83	33	21.0	30.6
Mg ²⁺ [μmol L ⁻¹]	10.5	10.4	-0.7	0.95	33	8.6	14.2

Sample No. 152w

Constituents	Prepared (Vp)	Average (Va)	$\Delta V/Vp^{*1}$ %	S.D.	N	Min.	Max.
pH	5.15	5.19	0.8	0.13	35	4.89	5.46
EC [mS m ⁻¹]	0.94	0.94	0.0	0.07	35	0.75	1.11
SO ₄ ²⁻ [μmol L ⁻¹]	11.9	11.7	-1.6	1.33	34	8.0	17.1
NO ₃ ⁻ [μmol L ⁻¹]	10.7	10.3	-3.6	0.78	34	8.2	13.0
Cl ⁻ [μmol L ⁻¹]	19.8	19.3	-2.4	1.44	32	14.5	24.3
NH ₄ ⁺ [μmol L ⁻¹]	9.8	10.5	7.6	1.22	33	8.5	14.3
Na ⁺ [μmol L ⁻¹]	12.8	12.9	0.9	1.23	32	10.9	16.9
K ⁺ [μmol L ⁻¹]	3.2	3.4	6.4	0.70	33	2.5	5.5
Ca ²⁺ [μmol L ⁻¹]	7.0	7.7	10.4	1.06	32	5.8	9.7
Mg ²⁺ [μmol L ⁻¹]	3.7	3.9	5.5	0.53	33	3.0	5.8

Note: *1, (Va-Vp)/Vp x 100

The Data Quality Objective for accuracy (hereafter referred to as DQO) was specified in the QA/QC program of the 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. Flag “E” was put to the data exceed DQO within a factor of 2 ($\pm 15\%$ to $\pm 30\%$), and flag “X” was put to the data exceed DQO more than a factor of 2 (over $\pm 30\%$).

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. 151w and No. 152w,
- ii) Comparison of individual parameters,
- iii) Comparison of circumstances of chemical analysis in each participating laboratory.

Evaluation of analytical data on both the sample No. 151w and No. 152w was presented in “2.3.1 Evaluation of laboratories’ performance (by sample)”, evaluation of analytical data for each constituent was 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 were presented in “2.3.4 Information on laboratories”.

2.3.1 Evaluation of laboratories' performance (by sample)

1) Sample No. 151w

The number and percentage of flagged data for the sample No. 151w were shown in Table 2.7. 18 analytical data out of 346 exceeded DQO within a factor of 2 and were flagged by "E". 16 analytical data out of 346 exceeded DQO more than a factor of 2 and were flagged by "X". Data flagged by "E" and "X" shared 9.8 percent of all the submitted data for sample No. 151w. The data normalized by prepared value in each parameter were shown in Figure 2.1.

Table 2.7 Number of flagged data for the Sample No. 151w

Characterization of data	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total
Data within DQO	36	34	32	32	30	32	30	25	30	31	312
Data with flag E ^{*1}	0	2	0	2	2	2	2	5	2	1	18
Data with flag X ^{*2}	0	0	3	1	2	0	2	4	2	2	16
Flagged data [%]	0.0	5.6	8.6	8.6	11.8	5.9	11.8	26.5	11.8	8.8	9.8

(Total data = 346)

Note: *1, Data exceeded DQO within a factor of 2; *2, Data exceeded DQO more than a factor of 2

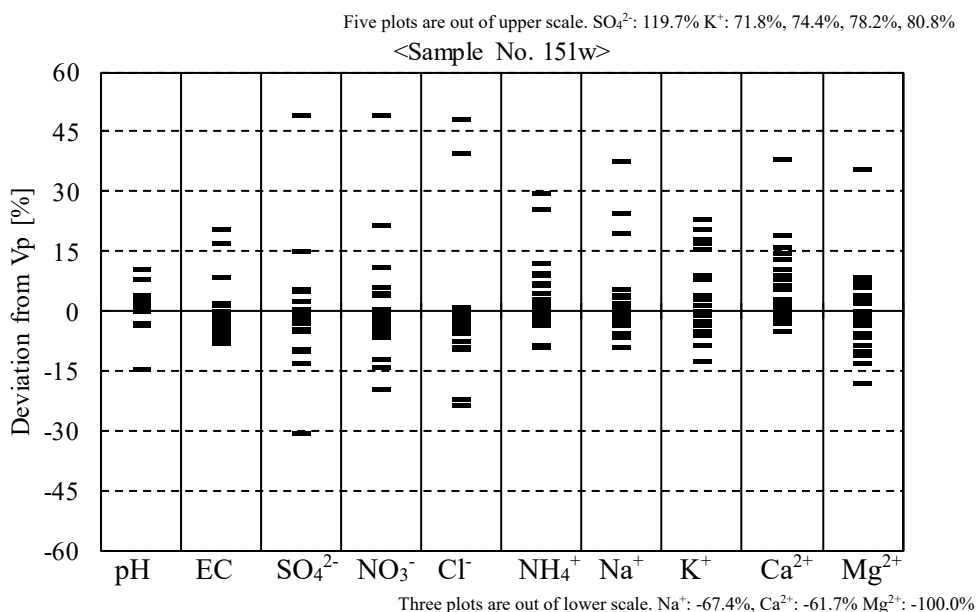


Figure 2.1 Distribution of the data normalized by prepared value in each parameter for sample No. 151w

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

Table 2.8 Analytical Results of Sample No. 151w

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 %
KH01	4.81	2.82	39.6	40.4	44.1 E	46.6	50.6	8.4	24.5	11.4	8.2 I	0.9
CN01	4.74	2.97	43.5	38.4	53.9	49.0	50.6	7.9	22.4	10.4	3.2	1.6
CN02	4.80	2.98	42.8	37.8	56.0	44.6	47.7	7.1	22.7	11.3	1.1	-0.6
CN03	4.78	2.97	44.0	37.5	54.5	44.4	47.8	7.7	22.5	10.5	0.7	0.0
CN04	4.82	3.00	43.5	36.2	51.2	47.9	49.2	7.4	24.0	10.9	4.1	-1.2
ID01	4.93	2.87	44.0	43.1	51.5	44.5	47.6	9.2 E	25.0	11.2	0.8	-0.1
ID02	4.73	2.81	50.6	47.3 E	57.1	40.1	47.1	6.8	24.2	11.4	-5.6	6.9
ID03	4.72	3.01	43.7	38.4	54.0	44.1	48.4	8.0	22.5	10.7	1.7	0.8
JP01	4.75	3.02	43.0	38.3	55.8	42.8	47.9	7.4	21.9	10.7	0.3	-0.5
JP03	4.79	2.99	44.2	38.7	56.0	44.4	48.9	7.9	21.6	9.9	-0.7	-0.3
JP04	4.78	2.92	43.8	38.5	56.2	44.3	48.3	7.6	22.6	10.4	0.1	1.1
JP05	4.77	2.97	42.6	38.6	57.3	44.8	47.4	7.6	21.5	10.3	-0.2	0.1
JP07	4.81	3.11	43.9	37.4	55.1	44.1	48.0	7.5	21.8	9.9	-0.5	-3.2
JP08	4.87	2.95	43.9	38.4	56.2	43.6	48.7	7.6	22.3	10.3	-1.1	-1.3
JP09	4.85	2.94	44.2	39.0	56.2	44.1	48.7	7.9	22.2	10.4	-1.0	-0.5
JP10	4.78	3.02	44.2	38.8	55.7	42.5	47.3	7.6	22.0	10.2	-1.2	-0.9
LA01	4.75	2.87	46.4	37.4	56.2	45.1	51.5	8.5	22.8	10.1	0.6	3.7
MY01	4.78	3.02	45.2	37.9	55.7	44.3	48.1	7.3	21.7	9.4	-1.5	-0.7
MN01	4.56	2.98	38.2	31.3 E	43.2 E	---	---	---	---	---	---	---
MM01	4.74	3.67 E	30.6 X	34.1	79.1 X	48.0	15.9 X	9.0 E	8.5 X	0.0 X	-23.5 I	-17.6 C
PH01	4.72	3.30	39.7	33.4	51.6	39.9	48.0	7.4	22.6	10.3	4.6	-6.5
PH02	4.86	3.57 E	96.9 X	41.1	55.9	56.9 E	60.6 E	9.6 E	30.6 X	14.2 X	-11.6 I	6.4
KR01	4.82	2.90	43.1	36.8	53.5	55.0 E	47.7	7.6	21.8	10.3	3.6	1.0
RU01	4.79	3.00	42.8	38.4	53.9	42.8	49.6	7.9	23.6	10.5	1.9	-0.8
RU02	4.78	2.96	43.3	37.6	55.7	42.3	50.4	8.1	26.4 E	11.1	3.4	1.0
TH01	4.84	2.99	41.7	36.5	53.6	46.8	45.4	7.1	21.0	9.6	0.4	-3.0
TH02	4.80	2.96	43.7	38.2	55.7	43.9	48.4	7.7	24.2	10.8	1.2	0.3
TH04	4.59	2.90	65.8 X	58.0 X	84.0 X	42.2	47.8	7.3	23.4	10.2	-18.0 I	15.9 C
TH05	4.74	2.95	45.2	38.3	54.8	47.7	44.2	6.8	22.2	9.1	-1.1	1.4
TH06	4.73	3.09	46.3	40.5	52.4	43.8	46.1	9.1 E	22.7	11.3	0.0	0.0
TH08	4.04	2.80	---	---	---	---	---	---	---	---	16.4 I*2	33.6 C*2
VN01	4.75	2.85	41.8	37.7	55.4	43.2	49.2	9.4 E	23.9	9.9	2.9	2.6
VN02	4.87	2.87	41.9	36.8	55.5	48.0	50.5	13.6 X	24.0	9.6	4.5	0.9
VN03	4.80	2.89	42.6	36.6	---	45.9	67.1 X	14.1 X	25.7 E	8.6 E	---	---
VN04	5.12	2.87	42.0	36.8	55.2	48.1	50.7	13.4 X	24.1	9.8	3.2	-2.7
VN05	5.22	2.89	42.1	37.3	56.7	44.7	58.3 E	13.9 X	25.4	9.3	3.8	-3.3
Vp	4.74	3.05	44.1	38.9	56.8	43.9	48.8	7.8	22.2	10.5	0.1	0.0
N of data	36	36	35	35	34	34	34	34	34	34		
Within DQO	36	34	32	32	30	32	30	25	30	31		
Flag E	0	2	0	2	2	2	2	5	2	1		
Flag X	0	0	3	1	2	0	2	4	2	2		

Note: "E", Value exceeded the DQO (Accuracy, ±15); "X", Value exceeded the DQO (Accuracy, ±15) more than a factor of 2;

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

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

*2: R₁ and R₂ for TH08 were calculated with results of ion concentration from TH06.

2) Sample No. 152w

The number and percentage of flagged data for the sample No. 152w were shown in Table 2.9. 44 analytical data out of 346 exceeded the DQO within a factor of 2 and were flagged by "E". 25 analytical data out of 346 exceeded the DQO more than a factor of 2 and were flagged by "X". Data marked with flags shared up to 19.9 percent of all the submitted data for sample No. 152w.

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

Table 2.9 Number of flagged data for the sample No. 152w

Characterization of data	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total
Data within DQO	36	33	30	31	30	23	29	23	18	24	277
Data with flag E ^{*1}	0	2	2	3	2	8	2	5	12	8	44
Data with flag X ^{*2}	0	1	3	1	2	3	3	6	4	2	25
Flagged data [%]	0.0	8.3	14.3	11.4	11.8	32.4	14.7	32.4	47.1	29.4	19.9

(Total data = 346)

Note: *1, Data exceeded DQO within a factor of 2; *2, Data exceeded DQO more than a factor of 2

Seven plots are out of upper scale. EC: 66.0%, SO₄²⁻: 115.1%, Na⁺: 82.8%, K⁺: 65.6%, 71.9%, 109.4%, Ca²⁺: 91.4%

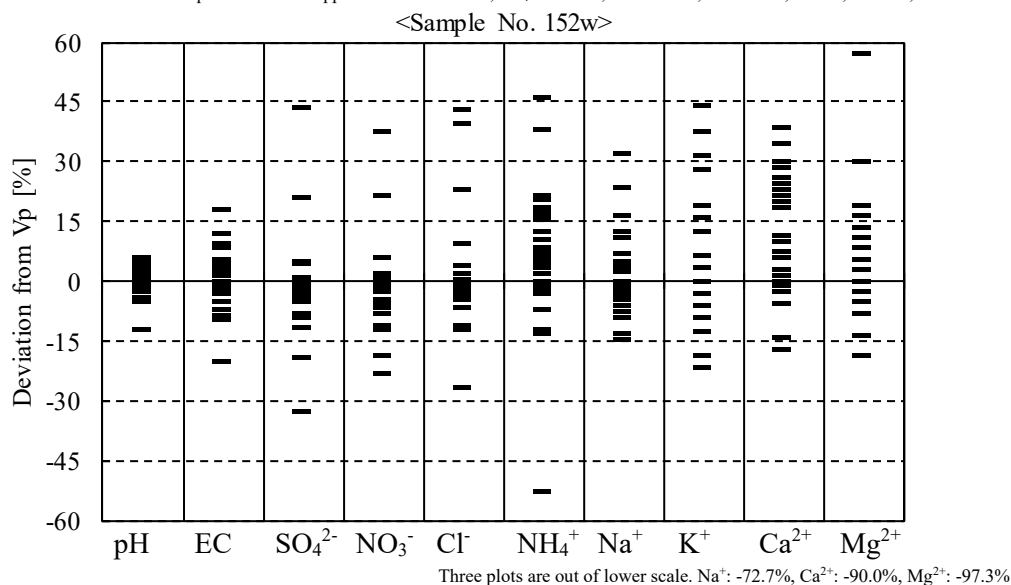


Figure 2.2 Distribution of the data normalized by prepared value for each parameter for sample No. 152w

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

Table 2.10 Analytical Results of Sample No. 152w

Lab. ID*1	pH	EC mS/m	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 %
KH01	5.21	0.92	10.9	10.9	18.9	11.0	11.8	3.3	8.6 E	4.3 E	5.9	0.2
CN01	5.13	0.91	11.8	9.5	19.7	10.1	13.3	3.2	7.1	3.7	2.6	2.4
CN02	5.08	0.97	11.7	10.0	19.9	8.5	12.6	2.6 E	7.0	3.8	0.3	0.0
CN03	5.18	0.97	11.7	10.0	19.3	9.1	12.2	3.1	7.2	4.2	1.0	-2.8
CN04	5.21	0.96	12.4	10.1	19.1	8.6	12.3	2.9	7.7	4.3 E	0.0	-2.4
ID01	5.41	0.86	11.5	10.6	20.2	9.6	10.9	4.6 X	9.1 E	4.4 E	2.0	0.2
ID02	4.93	0.89	14.4 E	13.0 E	20.6	9.8	12.3	3.1	9.1 E	4.4 E	1.2	14.9 C
ID03	5.44	0.75 E	11.5	10.8	18.5	11.8 E	13.7	3.6	8.3 E	4.2	4.9	6.5
JP01	5.13	0.99	11.4	10.5	19.7	10.8	14.4	3.1	6.0	3.6	1.8	-2.0
JP03	5.19	0.97	11.9	10.8	19.1	9.5	12.6	3.1	6.6	3.6	-1.6	-3.1
JP04	5.16	0.94	11.8	10.5	19.7	9.8	12.4	2.9	7.1	3.6	-0.4	-0.3
JP05	5.14	0.94	11.7	10.5	19.3	9.6	11.6	3.2	6.0	3.5	-2.5	-0.9
JP07	5.27	1.02	11.5	10.5	19.8	10.0	12.7	2.9	7.0	3.5	-1.3	-7.6
JP08	5.14	0.97	12.0	10.6	19.6	11.3 E	13.2	3.0	7.4	3.7	2.5	0.0
JP09	5.31	0.93	11.7	10.2	19.5	10.2	13.2	3.2	7.2	3.8	0.4	-3.3
JP10	5.16	0.98	11.9	10.5	19.3	9.5	12.5	3.1	6.8	3.6	-0.7	-2.7
LA01	5.07	0.92	12.5	10.2	19.4	11.4 E	14.9 E	4.1 E	7.8	3.4	5.8	5.9
MY01	5.15	0.99	10.8	9.8	19.2	10.3	12.4	2.9	6.6	3.0 E	1.2	-4.4
MN01	4.89	0.99	10.5	8.7 E	14.5 E	---	---	---	---	---	---	---
MM01	5.25	1.11 E	8.0 X	9.4	27.6 X	10.0	3.5 X	4.4 X	0.7 X	0.1 X	-35.7 I	-20.3 C
PH01	5.00	1.05	10.9	10.9	19.0	4.6 X	12.0	2.5 E	7.4	3.7	-0.4	-3.1
PH02	5.25	1.56 X	25.6 X	10.4	19.8	13.5 X	16.9 X	4.2 X	13.4 X	5.8 X	-1.7	-10.4
KR01	5.08	0.98	11.7	10.4	18.5	14.3 X	12.4	3.1	6.9	4.1	7.0	1.5
RU01	5.16	0.97	11.6	10.4	18.9	11.5 E	13.1	3.1	7.5	3.7	4.1	-1.2
RU02	5.12	0.97	12.0	10.8	21.6	10.4	13.4	3.4	8.4 E	3.2	1.4	1.6
TH01	5.40	0.95	9.6 E	8.2 E	17.4	11.6 E	12.2	2.9	6.9	3.5	6.9	-10.4
TH02	5.14	0.95	11.6	10.1	19.0	10.5	12.8	3.3	9.4 X	4.3 E	7.9	1.5
TH04	5.00	0.89	17.1 X	14.7 X	28.3 X	10.2	12.3	2.9	8.8 E	3.8	-12.0 I	16.7 C
TH05	5.22	0.93	11.6	10.4	17.6	11.3 E	11.1	2.8	5.8 E	4.8 E	1.2	-2.5
TH06	5.16	1.03	12.4	11.3	24.3 E	9.7	13.2	3.6	8.7 E	4.8 E	0.0	-0.3
TH08	4.51	0.85	---	---	---	---	---	---	---	---	16.6 *2	37.3 C*2
VN01	5.20	0.89	11.6	10.5	19.5	9.6	14.2	5.3 X	8.5 E	3.5	5.5	3.2
VN02	5.35	0.85	11.5	10.0	19.0	10.8	12.5	3.8 E	9.0 E	3.6	4.4	1.3
VN03	5.20	0.89	12.0	9.5	---	11.9 E	23.4 X	6.7 X	9.7 X	4.0	---	---
VN04	5.42	0.87	11.3	9.8	18.9	10.6	12.2	3.7 E	8.8 E	3.5	3.4	-2.0
VN05	5.46	0.85	11.6	10.9	19.6	11.3 E	15.8 E	5.5 X	9.0 E	3.9	7.1	2.0
Vp	5.15	0.94	11.9	10.7	19.8	9.8	12.8	3.2	7.0	3.7	0.0	0.4
N of data	36	36	35	35	34	34	34	34	34	34		
Within DQO	36	33	30	31	30	23	29	23	18	24		
Flag E	0	2	2	3	2	8	2	5	12	8		
Flag X	0	1	3	1	2	3	3	6	4	2		

Note: "E", Value exceeded the DQO (Accuracy, ±15); "X", Value exceeded the DQO (Accuracy, ±15) more than a factor of 2;

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

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

*2: R₁ and R₂ for TH08 were calculated with results of ion concentration from TH06.

3) Comparison of high and low concentration sample

The percentage of flagged data for Sample No. 151w and 152w were shown in Figure 2.3. The percentage of the data within the DQO for the sample No. 151w and 152w were 90.2% and 80.1% respectively. The difference between both samples was 10.1%. In this project, the total number of flagged data was 103 (E: 62, X: 41) among the whole set of 692 data.

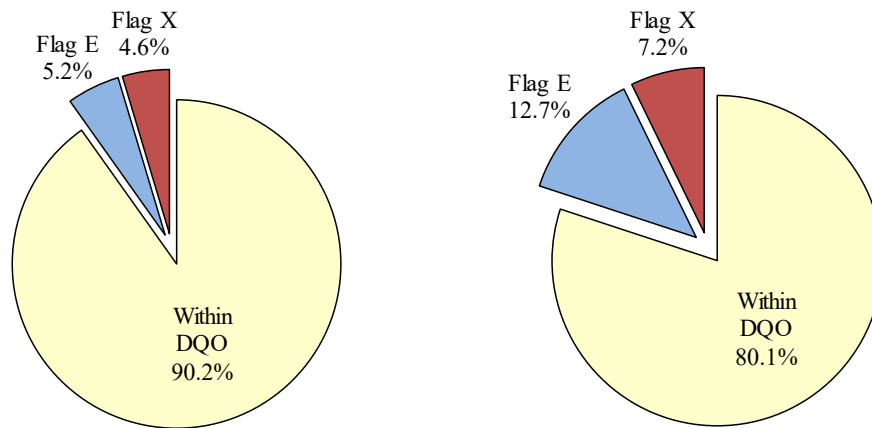


Figure 2.3 Percentage of flagged data for sample No. 151w and No. 152w (Left: No. 151w, Right: No. 152w)

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

The number of laboratory by number of flags was shown in Figure 2.4. The number of laboratory without flagged data was 10, which corresponds to 28.6% of all the participating laboratories.

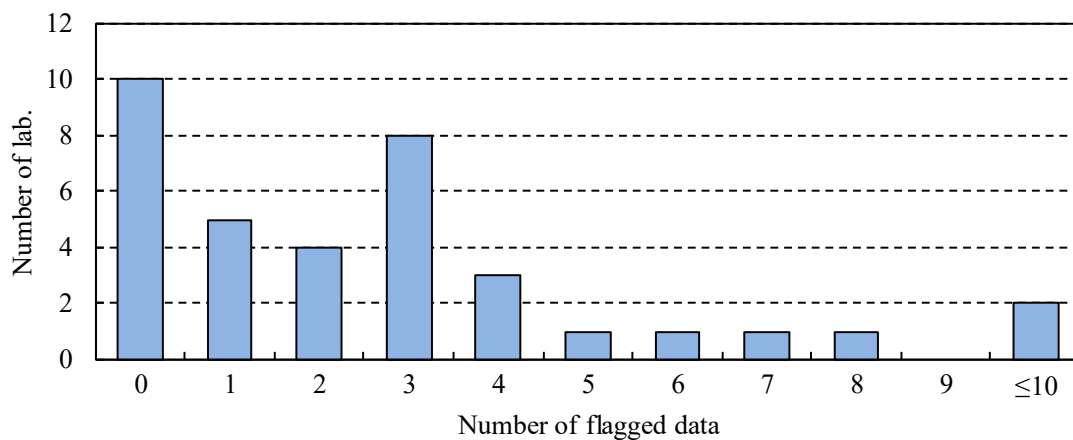


Figure 2.4 Distribution of the number of laboratory (by number of flags)

2.3.2 Evaluation of laboratories' performance (by analytical parameter)

The data normalized by Vp were 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. 151w and 152w, broken lines and dotted lines showed the values of $V_p \pm 15\%$ and $V_p \pm 30\%$ respectively.

1) pH

All participating laboratories used pH meter with glass electrode method for the measurement of pH. All the obtained data satisfied the DQO of the QA/QC program of EANET.

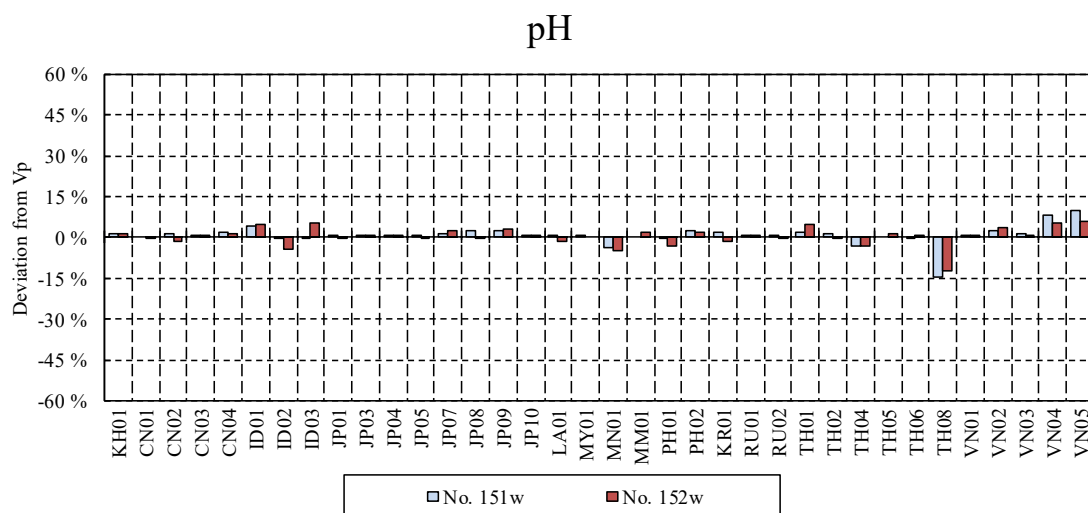


Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)

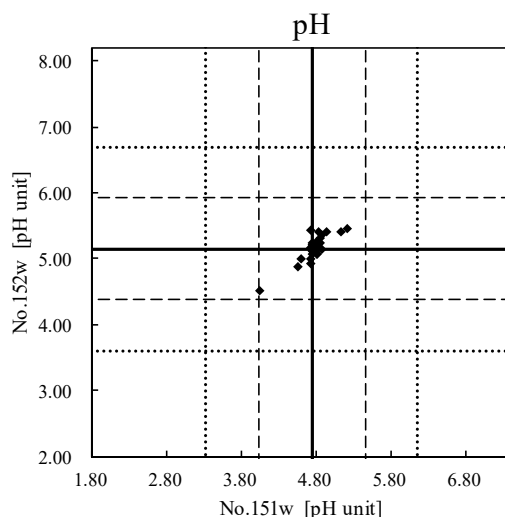


Figure 2.6 Scatter diagram for pH

2) EC

All participating laboratories used conductivity cell method for the measurement of EC. The data of sample No.151w from 2 laboratories (MM01 and PH02) and the data of sample No.152w from 2 laboratories (ID03 and MM01) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No.152w from PH02 the DQO more than a factor of 2 and were marked with flag “X”.

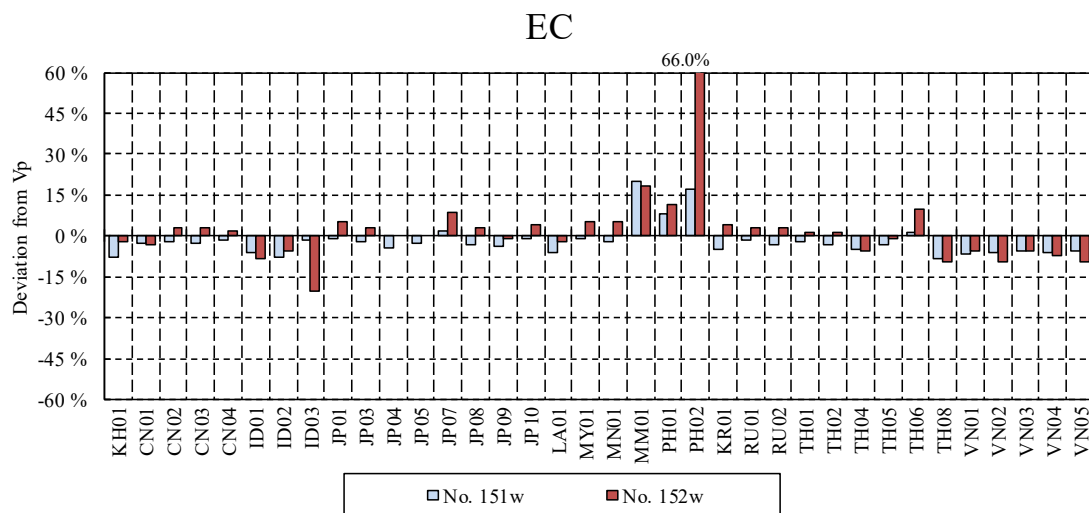


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)

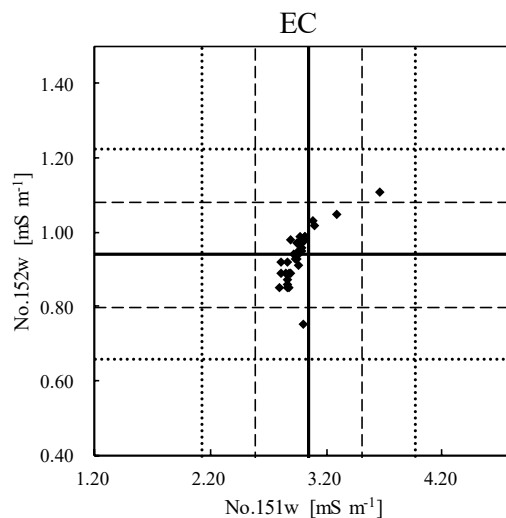


Figure 2.8 Scatter diagram for EC

3) SO_4^{2-}

The data of sample No. 152w from 2 laboratories (ID02 and TH01) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No.151w from 3 laboratories (MM01, PH02 and TH04) and the data of sample No.152w from 3 laboratories (MM01, PH02 and TH04) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

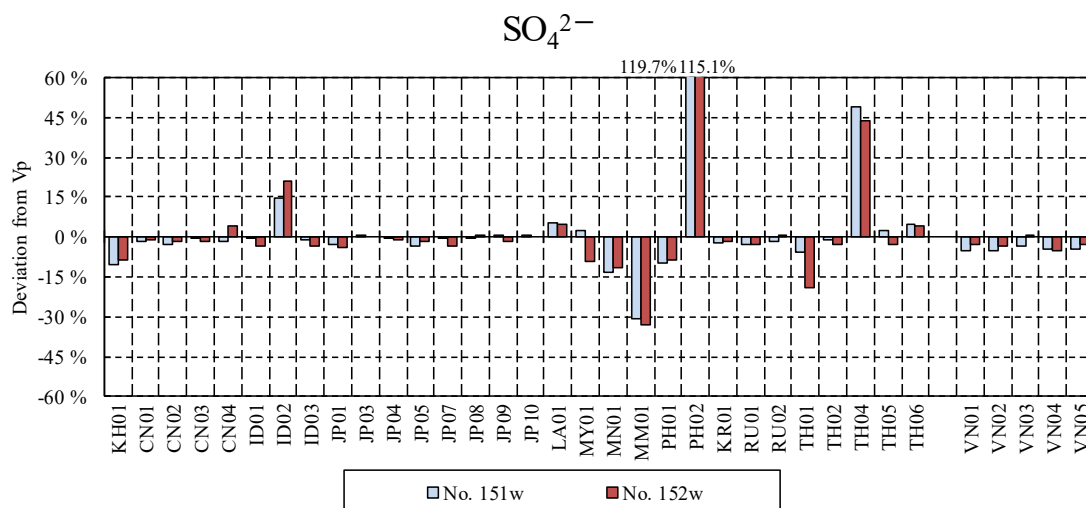


Figure 2.9 Deviation from prepared value for SO_4^{2-} (normalized by prepared value)

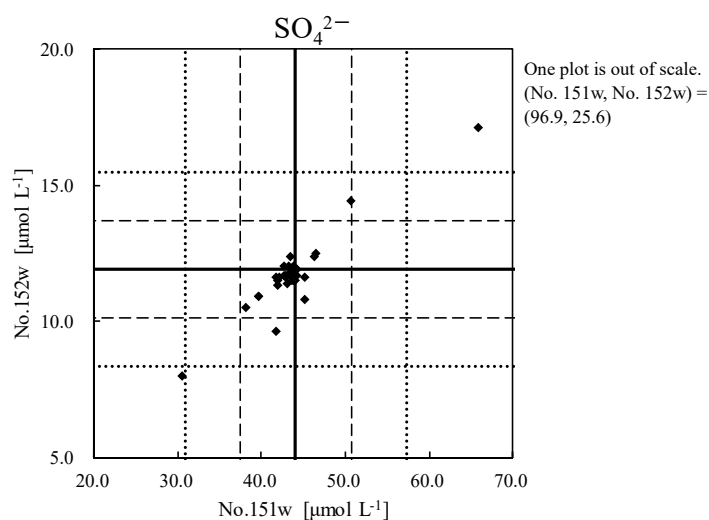


Figure 2.10 Scatter diagram for SO_4^{2-}

4) NO_3^-

The data of sample No. 151w from 2 laboratories (ID02 and MN01) and the data of sample No. 152w from 3 laboratories (ID02, MN01 and TH01) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No. 151w from TH04 and the data of sample No. 152w from TH04 exceeded the DQO more than a factor of 2 and were marked with flag “X”.

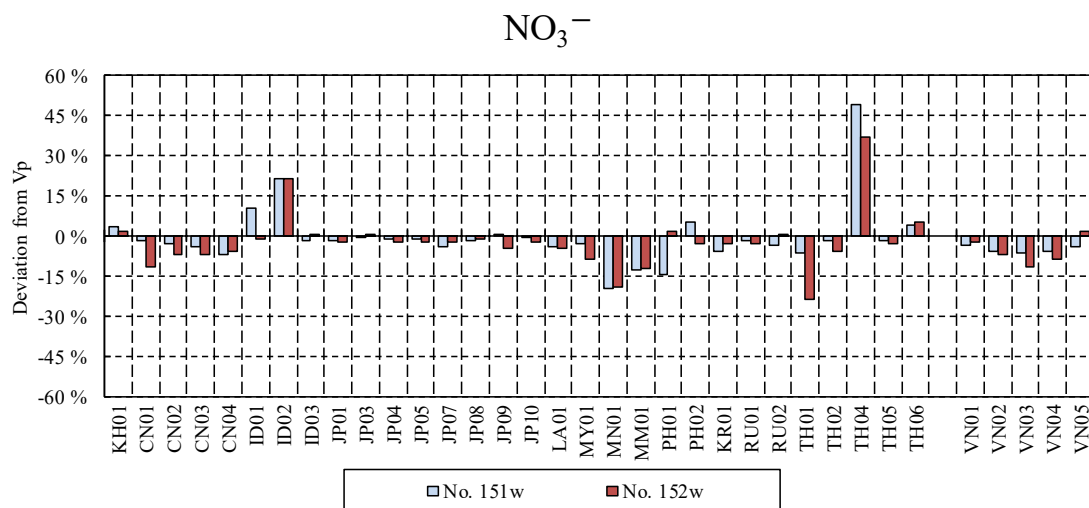


Figure 2.11 Deviation from prepared value for NO_3^- (normalized by prepared value)

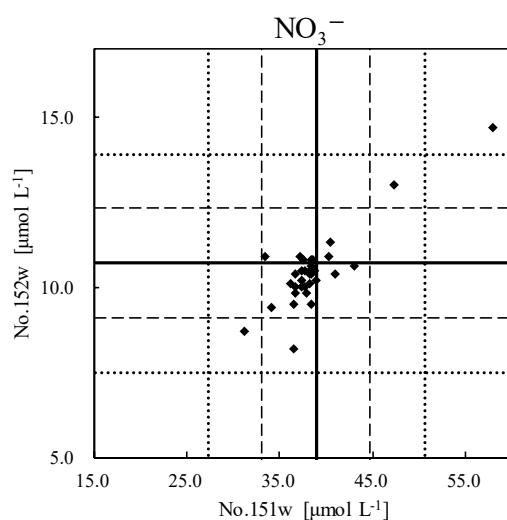


Figure 2.12 Scatter diagram for NO_3^-

5) Cl^-

The data of sample No.151w from 2 laboratories (KH01 and MN01) and the data of sample No.152w from 2 laboratories (MN01 and TH06) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No.151w from 2 laboratories (MM01 and TH04) and the data of sample No.152w from 2 laboratories (MM01 and TH04) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

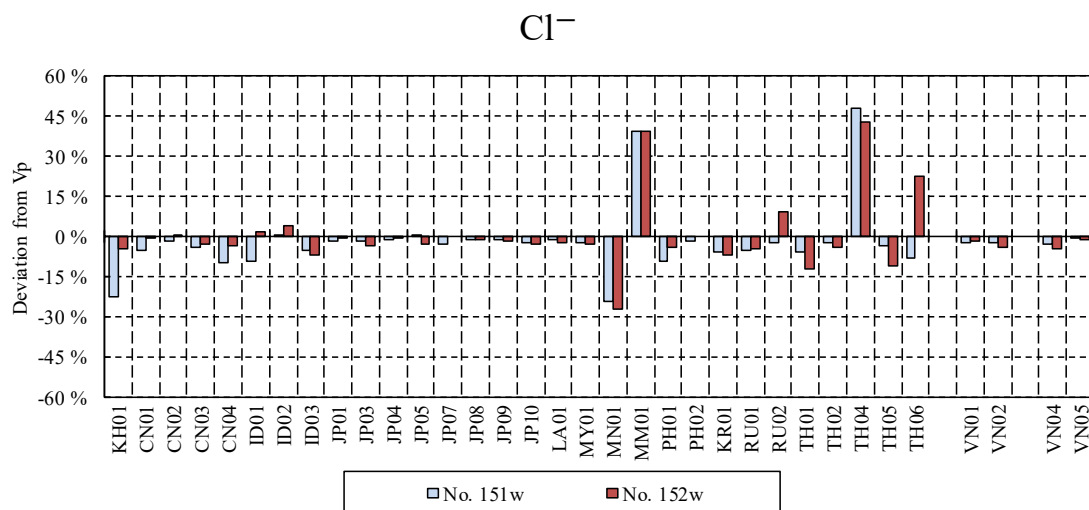


Figure 2.13 Deviation from prepared value for Cl^- (normalized by prepared value)

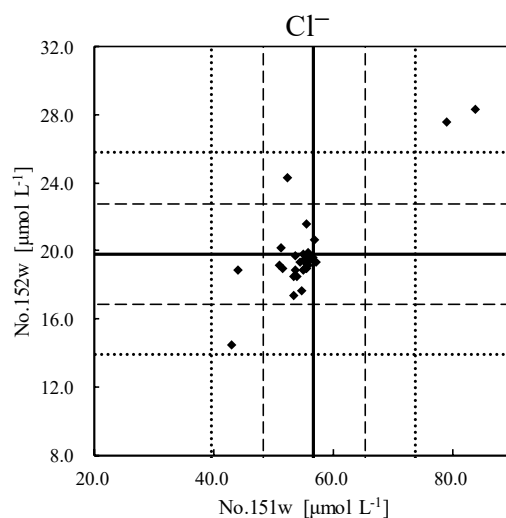


Figure 2.14 Scatter diagram for Cl^-

6) NH_4^+

The data of sample No. 151w from 2 laboratories (PH02 and KR01) and the data of sample No.152w from 8 laboratories (ID03, JP08, LA01, RU01, TH01, TH05, VN03 and VN05) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No. 152w from 3 laboratories (PH01, PH02 and KR01) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

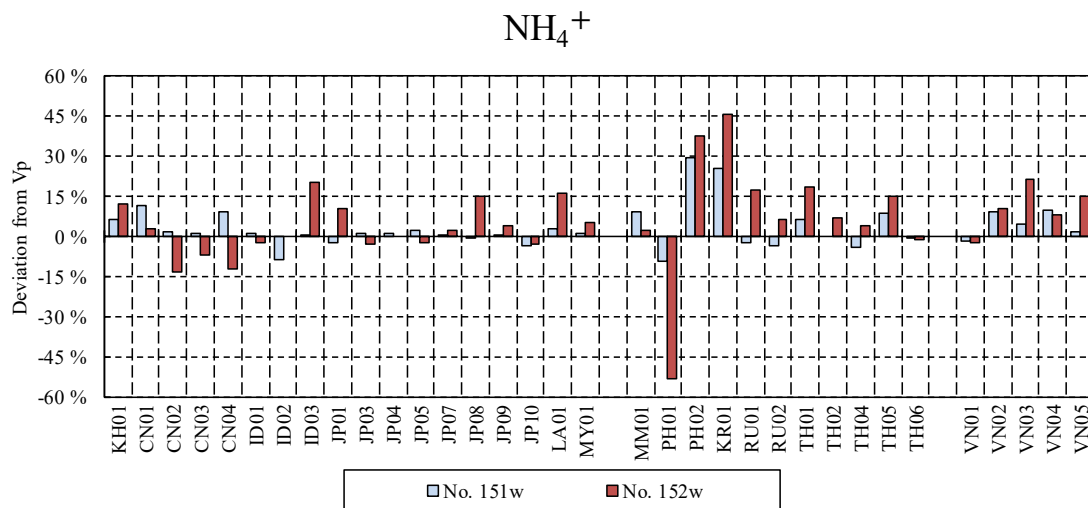


Figure 2.15 Deviation from prepared value for NH_4^+ (normalized by prepared value)

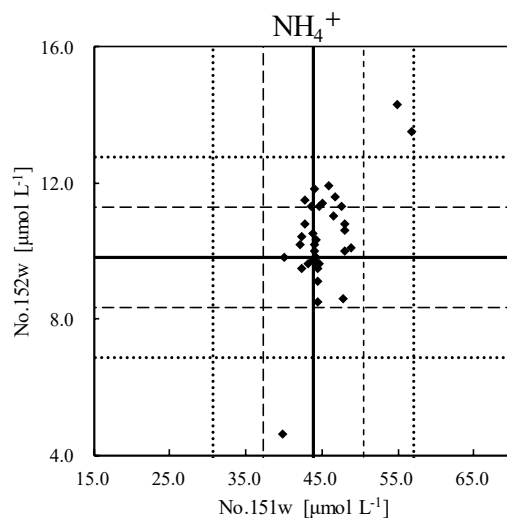


Figure 2.16 Scatter diagram for NH_4^+

7) Na⁺

The data of sample No. 151w from 2 laboratories (PH02 and VN05) and the data of sample No. 152w from 2 laboratories (LA01 and VN05) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No. 151w from 2 laboratories (MM01 and VN03) and the data of sample No. 152w from 3 laboratories (MM01, PH02 and VN03) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

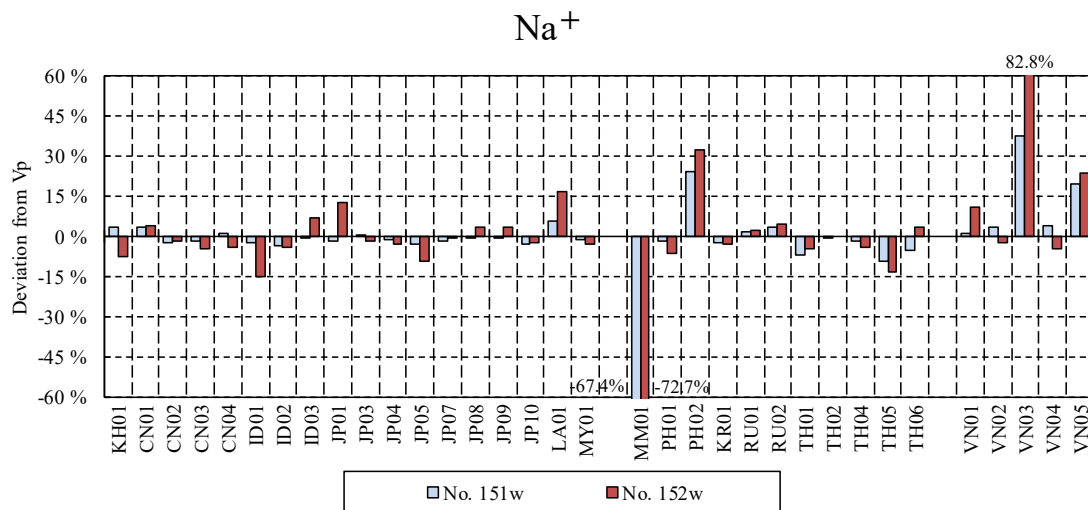


Figure 2.17 Deviation from prepared value for Na⁺ (normalized by prepared value)

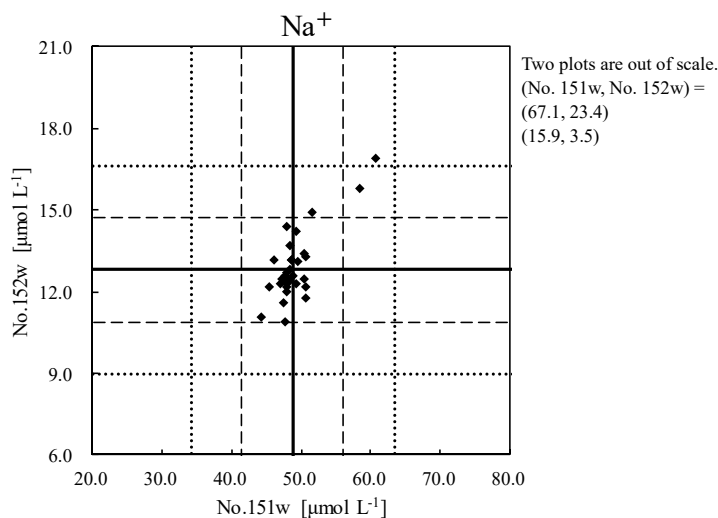


Figure 2.18 Scatter diagram for Na⁺

8) K^+

The data of sample No. 151w from 5 laboratories (ID01, MM01, PH02, TH06 and VN01) and the data of sample No. 152w from 5 laboratories (CN02, LA01, PH01, VN02 and VN04) exceeded the QO and were marked with flag “E”. Additionally, the data of sample No. 151w from 4 laboratories (VN02, VN03, VN04 and VN05) and the data of sample No. 152w from 6 laboratories (ID01, MM01, PH02, VN01, VN03 and VN05) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

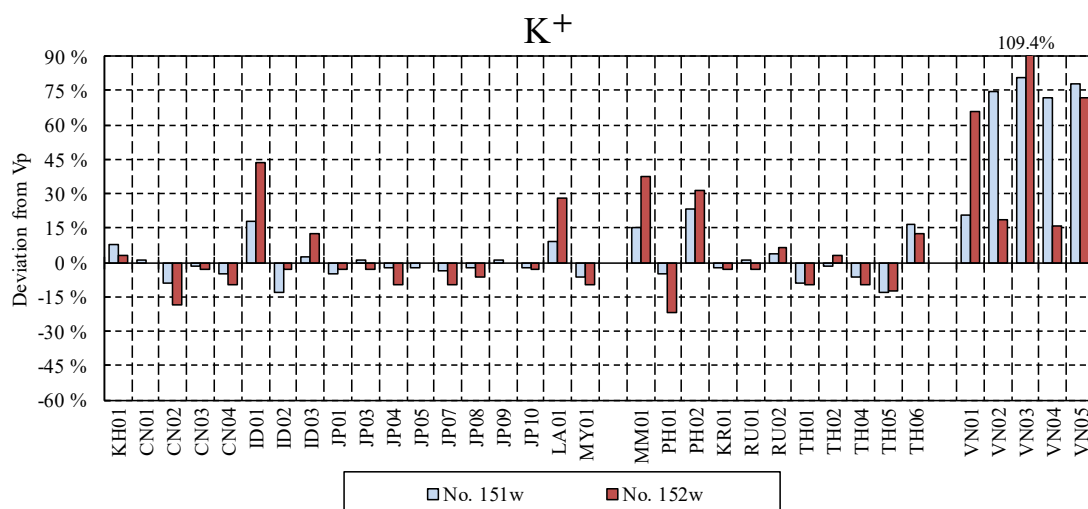


Figure 2.19 Deviation from prepared value for K^+ (normalized by prepared value)

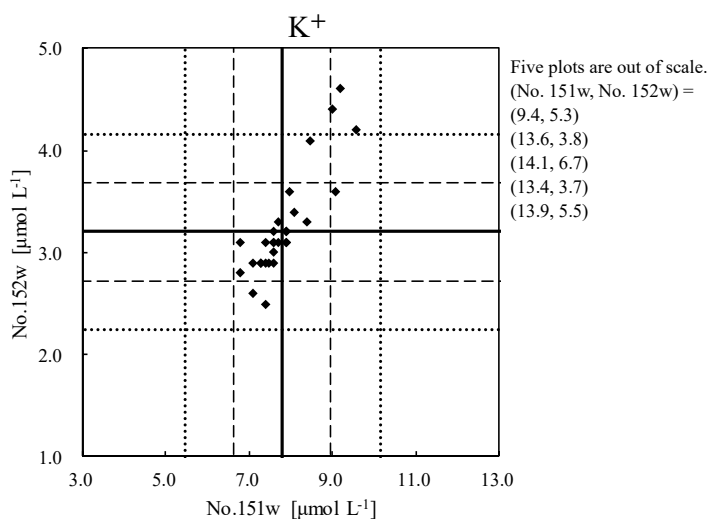


Figure 2.20 Scatter diagram for K^+

9) Ca^{2+}

The data of sample No. 151w from 2 laboratories (RU02 and VN03) and the data of sample No. 152w from 12 laboratories (KH01, ID01, ID02, ID03, RU02, TH04, TH05, TH06, VN01, VN02, VN04 and VN05) exceeded the DQO and were marked with flag “E”. Additionally the data of sample No.151w from 2 laboratories (MM01 and PH02) and the data of sample No. 152w from 4 laboratories (MM01, PH02, TH02 and VN03) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

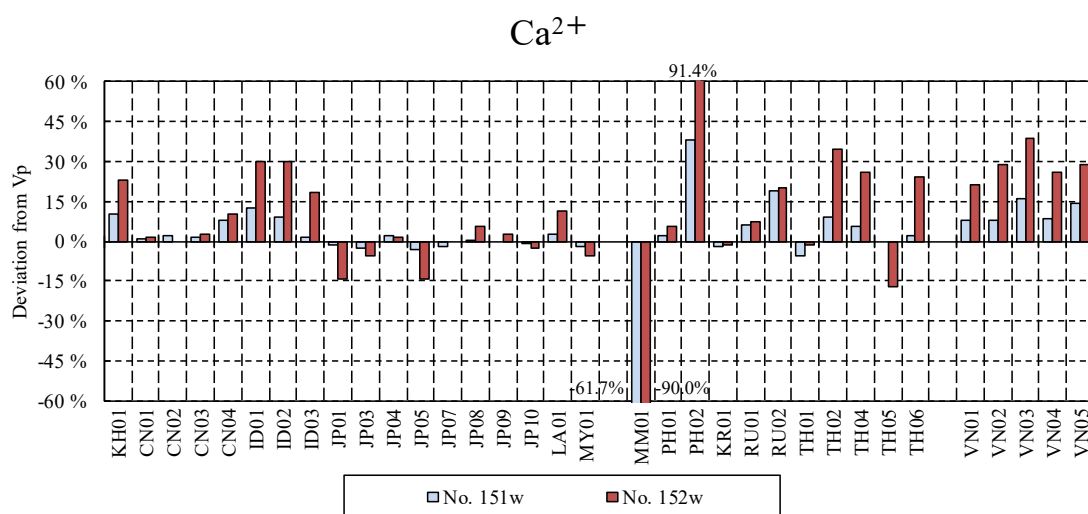


Figure 2.21 Deviation from prepared value for Ca^{2+} (normalized by prepared value)

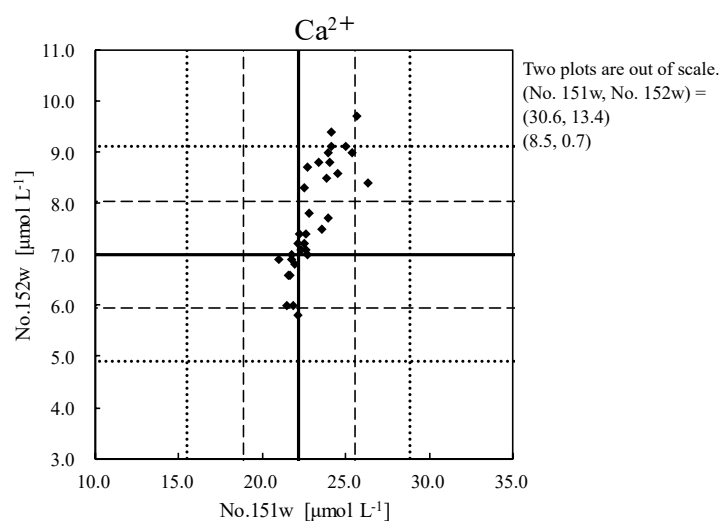


Figure 2.22 Scatter diagram for Ca^{2+}

10) Mg^{2+}

The data of sample No. 151w from VN03 and the data of sample No. 152w from 8 laboratories (KH01, CN04, ID01, ID02, MY01, TH02, TH05 and TH06) exceeded the DQO and marked with flag “E”. Additionally, the data of sample No. 151w from 2 laboratories (MM01 and PH02) and the data of sample No. 152w from 2 laboratories (MM01 and PH02) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

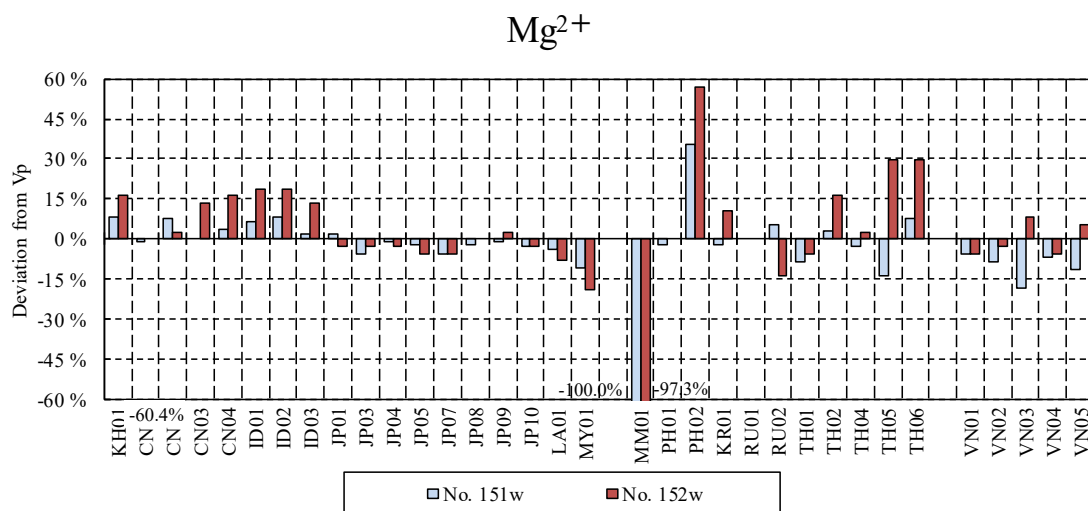


Figure 2.23 Deviation from prepared value for Mg^{2+} (normalized by prepared value)

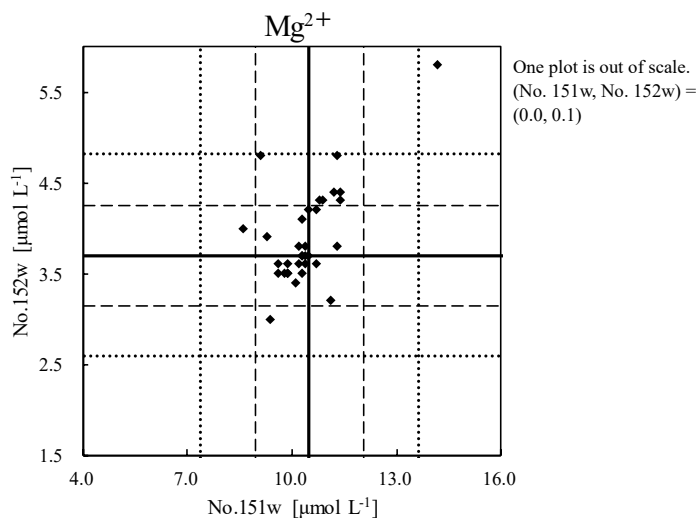


Figure 2.24 Scatter diagram for Mg^{2+}

11) Scatter diagrams

Most of constituents showed positive correlation between the submitted pairs of results of sample No. 151w and 152w. It suggested that systematic deviation could be the reason for the deviation of results in many of laboratories.

2.3.3 Sample and analysis evaluation

The concentrations of the analytical parameters in the samples for this survey were fixed on the basis of the reference to monitoring data on wet deposition in EANET. Two samples were not distinguished as high or low concentration samples when they were distributed to participating laboratories. Ions (including pH as H^+) concentrations of sample No. 151w were higher than those of No. 152w.

The relative standard deviations (R.S.D.) of each parameter for the sample No. 151w and No. 152w were shown in the Figure 2.25. The R.S.D. values for sample No. 152w were same or higher than those for sample No. 151w except K^+ . Especially, the difference between the R.S.D. values for sample No.151w and sample No. 152w were high in K^+ , Ca^{2+} and Mg^{2+} . The R.S.D. of K^+ for sample No. 151w was the highest in this survey.

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

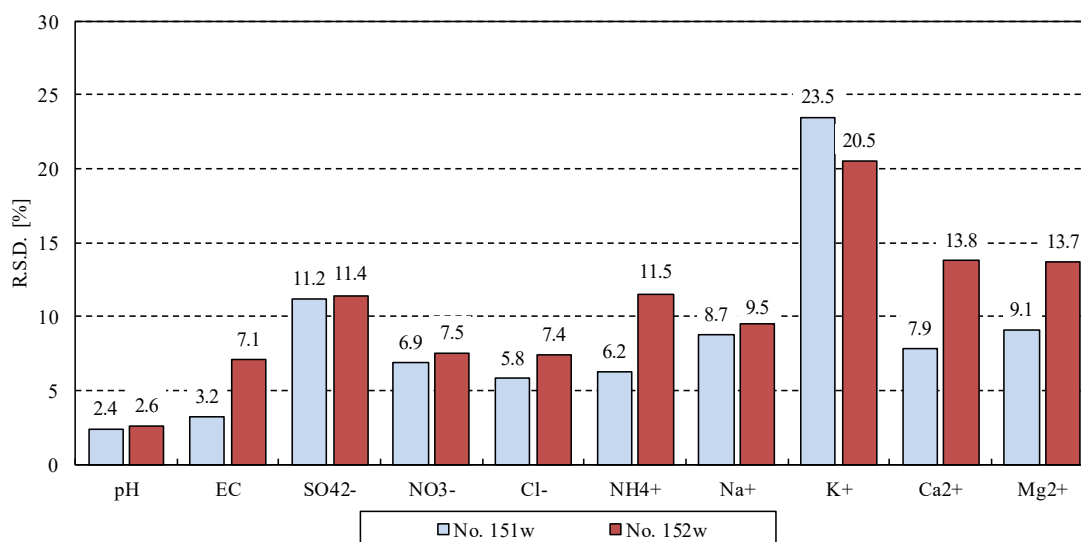


Figure 2.25 Relative standard deviations (R.S.D.) of each constituent

2.3.4 Information on laboratories

1) Number of analysts and their experience

Number of analysts and years of their experience were shown in Table 2.11 and Table 2.12 respectively. In the 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⁺
KH01	1	A	A	A	A	A	A	A	A	A	A
CN01	1	A	A	A	A	A	A	A	A	A	A
CN02	2	A	A	B	B	B	B	B	B	B	B
CN03	2	A	A	B	B	B	B	B	B	B	B
CN04	1	A	A	A	A	A	A	A	A	A	A
ID01	2	A	A	B	B	B	B	B	B	B	B
ID02	2	A	A	B	B	B	B	B	B	B	B
ID03	2	A	B	A	A	A	B	B	B	B	B
JP01	1	A	A	A	A	A	A	A	A	A	A
JP03	1	A	A	A	A	A	A	A	A	A	A
JP04	1	A	A	A	A	A	A	A	A	A	A
JP05	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
LA01	1	A	A	A	A	A	A	A	A	A	A
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	2	A	A	B	B	B	---	---	---	---	---
MM01	1	A	A	A	A	A	A	A	A	A	A
PH01	1	A	A	A	A	A	A	A	A	A	A
PH02	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	2	A	A	A	A	A	A	B	B	B	B
TH01	1	A	A	A	A	A	A	A	A	A	A
TH02	2	A	B	B	B	B	A	A	A	A	A
TH04	2	A	A	B	B	B	B	B	B	B	B
TH05	2	A	A	B	B	B	B	B	B	B	B
TH06	1	A	A	A	A	A	A	A	A	A	A
TH08	1	A	A	---	---	---	---	---	---	---	---
VN01	2	A	A	B	B	B	B	B	B	B	B
VN02	2	A	A	B	B	B	B	B	B	B	B
VN03	3	A	A	B	A	---	B	C	C	A	C
VN04	2	A	A	B	B	B	B	B	B	B	B
VN05	2	A	A	B	B	B	B	B	B	B	B

Note: Light mesh, Analytic data of sample No. 151w or No. 152w was marked with flag "E" or "X";

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

"---", Not measured

*: For TH08, ions were analyzed by TH06.

Total of 167 data out of 346 were analyzed by the analysts whose experience was less than 5 years. The number corresponds to 48.3% 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⁺
KH01	6	6	6	6	6	6	6	6	6	6
CN01	1	1	1	1	1	1	1	1	1	1
CN02	3	3	7	7	7	7	7	7	7	7
CN03	17	17	5	5	5	5	5	5	5	5
CN04	7	7	7	7	7	7	7	7	7	7
ID01	2	2	4	4	4	4	4	4	4	4
ID02	2	2	15	15	15	15	15	15	15	15
ID03	5	8	5	5	5	8	8	8	8	8
JP01	12	12	12	12	12	12	12	12	12	12
JP03	2	2	2	2	2	2	2	2	2	2
JP04	1	1	1	1	1	1	1	1	1	1
JP05	1	1	1	1	1	1	1	1	1	1
JP07	1	1	1	1	1	1	1	1	1	1
JP08	2	2	2	2	2	2	2	2	2	2
JP09	9	9	9	9	9	9	9	9	9	9
JP10	4	4	4	4	4	4	4	4	4	4
LA01	3	3	3	3	3	3	3	3	3	3
MY01	2	2	5	5	5	9	9	9	9	9
MN01	8	8	12	12	12	---	---	---	---	---
MM01	10	10	10	10	10	10	10	10	10	10
PH01	2	2	2	2	2	2	2	2	2	2
PH02	0	0	0	0	0	0	0	0	0	0
KR01	4	4	4	4	4	4	4	4	4	4
RU01	16	16	17	17	17	16	17	17	17	17
RU02	1	1	1	1	1	1	24	24	24	24
TH01	6	6	6	6	6	6	6	6	6	6
TH02	18	12	12	12	12	18	18	18	18	18
TH04	12	12	4	4	4	4	4	4	4	4
TH05	14	14	1	1	1	1	1	1	1	1
TH06	10	10	10	10	10	10	10	10	10	10
TH08	5	5	---	---	---	---	---	---	---	---
VN01	2	2	22	22	22	22	22	22	22	22
VN02	6	6	2	2	2	2	2	2	2	2
VN03	1	1	7	1	---	7	3	3	1	3
VN04	9	9	11	11	11	11	11	11	11	11
VN05	2	2	9	9	9	9	9	9	9	9

Note: Light mesh, Analytic data of sample No. 151w or No. 152w was marked with flag "E" or "X";

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

"---", Not measured

*: For TH08, ions were analyzed by TH06.

2) Analytical instruments

As shown in Figure 2.26, most of the participating laboratories used the specified methods described in the “*Technical Manual for Wet Deposition Monitoring in East Asia -2010*”. RU02 did not use the specified methods for the analyses of NH_4^+ (Spectrophotometry without Indophenol) and did not use the specified methods for the analyses of Cl^- (Titrimetry). The specified methods were shown in Table 2.3.

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

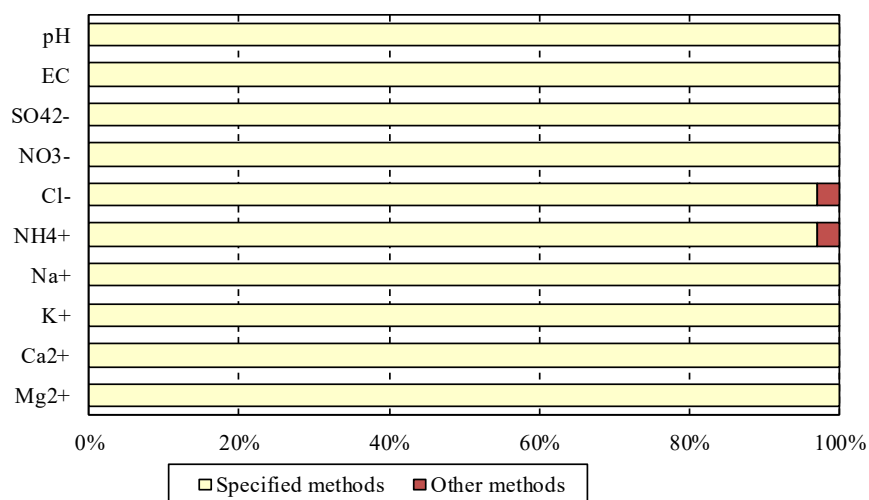


Figure 2.26 Percentage of laboratories that use the specified methods

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

Lab. ID	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
KH01	IC	IC	IC	IC	IC	IC	IC	IC
CN01	IC	IC	IC	IC	IC	IC	IC	IC
CN02	IC	IC	IC	IC	IC	IC	IC	IC
CN03	IC	IC	IC	IC	IC	IC	IC	IC
CN04	IC	IC	IC	IC	IC	IC	IC	IC
ID01	IC	IC	IC	IC	IC	IC	IC	IC
ID02	IC	IC	IC	IC	IC	IC	IC	IC
ID03	IC	IC	IC	IC	IC	IC	IC	IC
JP01	IC	IC	IC	IC	IC	IC	IC	IC
JP03	IC	IC	IC	IC	IC	IC	IC	IC
JP04	IC	IC	IC	IC	IC	IC	IC	IC
JP05	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
LA01	IC	IC	IC	IC	IC	IC	IC	IC
MY01	IC	IC	IC	IC	IC	IC	IC	IC
MN01	IC	IC	IC	---	---	---	---	---
MM01	IC	IC	IC	IC	IC	IC	IC	IC
PH01	IC	IC	IC	IC	IC	IC	IC	IC
PH02	IC	IC	IC	IC	IC	IC	IC	IC
KR01	IC	IC	IC	IC	IC	IC	IC	IC
RU01	IC	IC	IC	SP-IP	AES	AES	AAS	AAS
RU02	SP	SP	TI	SP-other	AES	AES	AAS	AAS
TH01	IC	IC	IC	IC	IC	IC	IC	IC
TH02	IC	IC	IC	IC	IC	IC	IC	IC
TH04	IC	IC	IC	IC	IC	IC	IC	IC
TH05	IC	IC	IC	IC	IC	IC	IC	IC
TH06	IC	IC	IC	IC	IC	IC	IC	IC
TH08	---	---	---	---	---	---	---	---
VN01	IC	IC	IC	IC	IC	IC	IC	IC
VN02	IC	IC	IC	IC	IC	IC	IC	IC
VN03	SP	SP	---	SP-IP	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 *: For TH08, ions were analyzed by TH06.

IC: Ion Chromatography

AAS: Atomic Absorption Spectrometry

AES: Atomic Emission Spectrometry

SP: Spectrophotometry

SP-IP: Spectrophotometry (Indophenol)

SP-other: Spectrophotometry (Other)

TI: Titrimetry

3) Date of analysis

Figure 2.27 shows the distribution of “Start date” and “Finish date” of analysis in the participating laboratories. In total, 61% of all the submitted data was determined within the year of 2015, and 3% was finished after the deadline of data submission in this project.

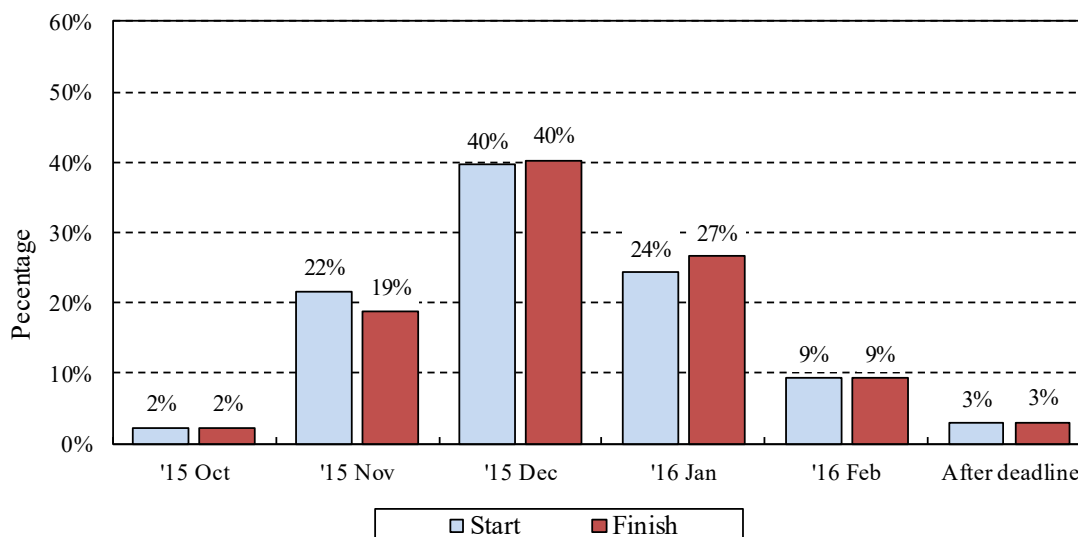


Figure 2.27 Distribution of start date and finish date of analysis

Figure 2.28 shows how many days were needed to determine the analytical data in the participating laboratories. Most analytical data were obtained within less than 3 days.

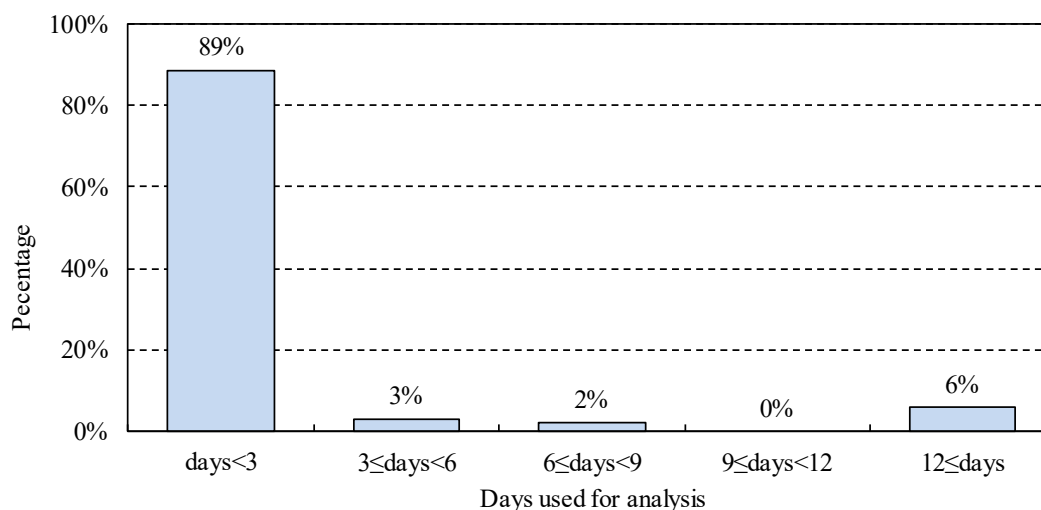


Figure 2.28 Distribution of days used for analysis

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

2.4 Comparison with past surveys

Since the beginning of EANET, inter-laboratory comparison on wet deposition reached the 18th survey. The results showing the percentages of flagged data and percentage of data that satisfied the DQO were shown in Figure 2.29. Hereafter, sample No. 151w and sample No. 152w were treated as high and low concentration samples respectively.

The percentages of data within DQO for the sample No. 151w and No. 152w were 90.2% and 80.1% respectively. Compared to previous survey, the percentage of data within DQO was slightly increase in high concentration samples and decrease in low concentration samples.

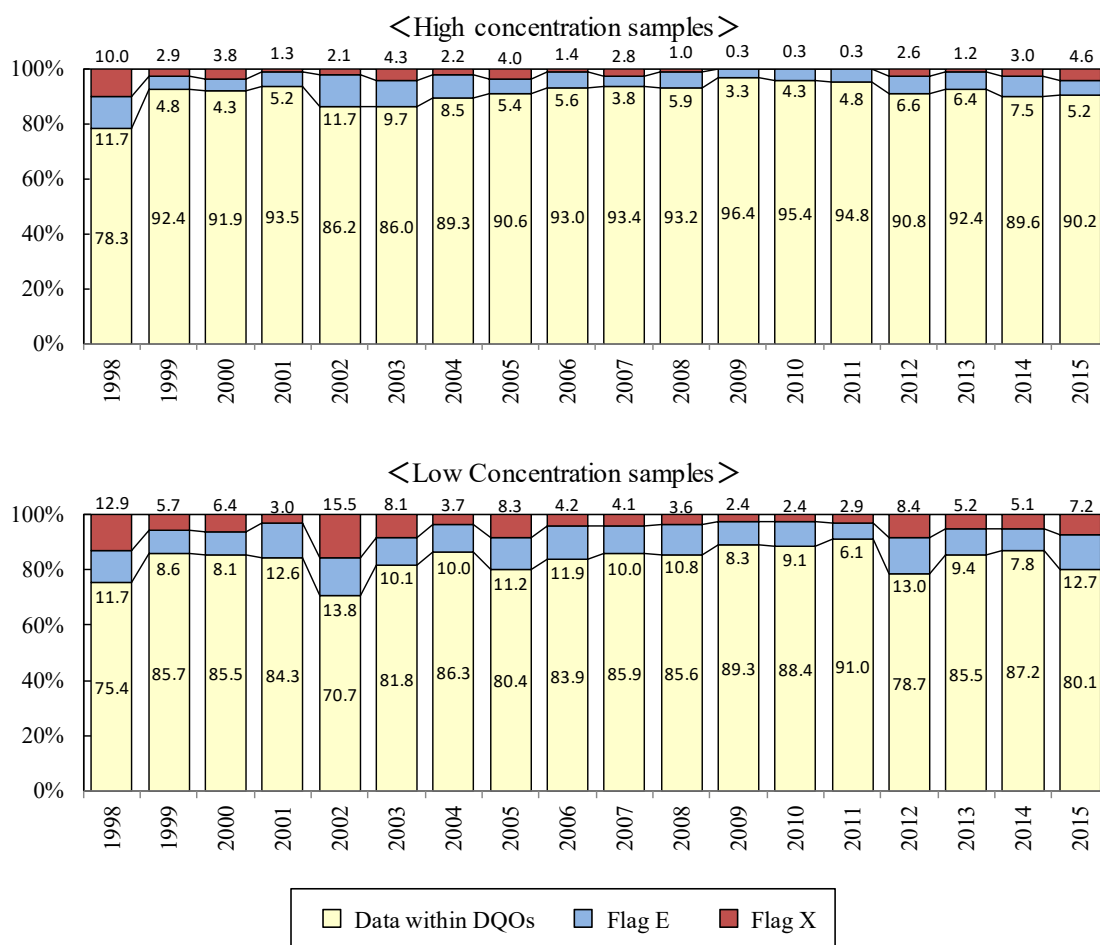


Figure 2.29 Comparison of results from the inter-laboratory comparison projects

Figure 2.30 showed the trend of the prepared values and the percentage of flagged data. The percentages of flagged data were relatively high in cations than anions through the series of surveys. It is suggested that the concentration of ions affect to the percentage of flagged data. In 2015, the percentage of flagged data were increased from 2014. This trends are in inverse proportion to the concentration of ions.

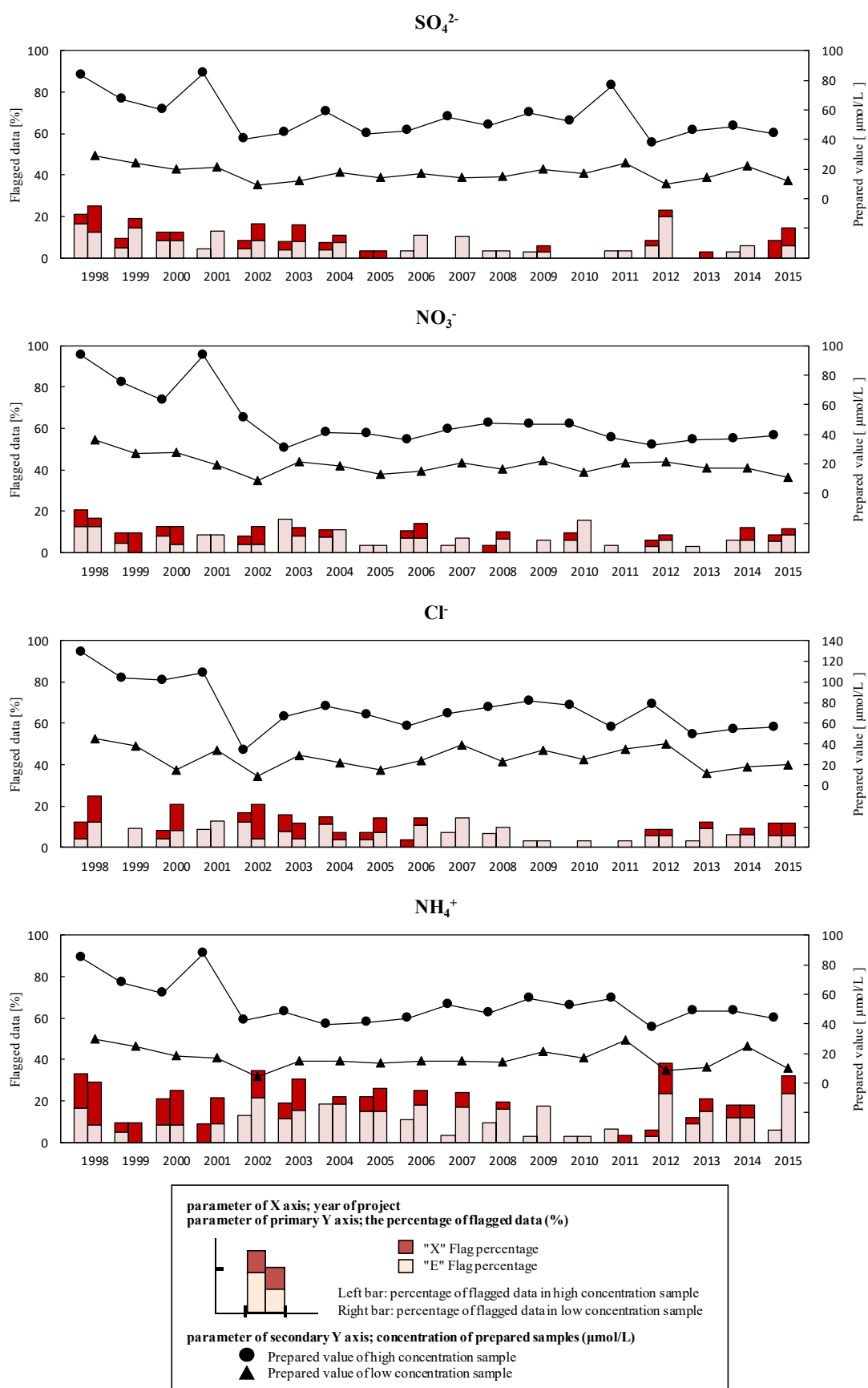


Figure 2.30 Comparison for each parameter in inter-laboratory comparison (ILC) project

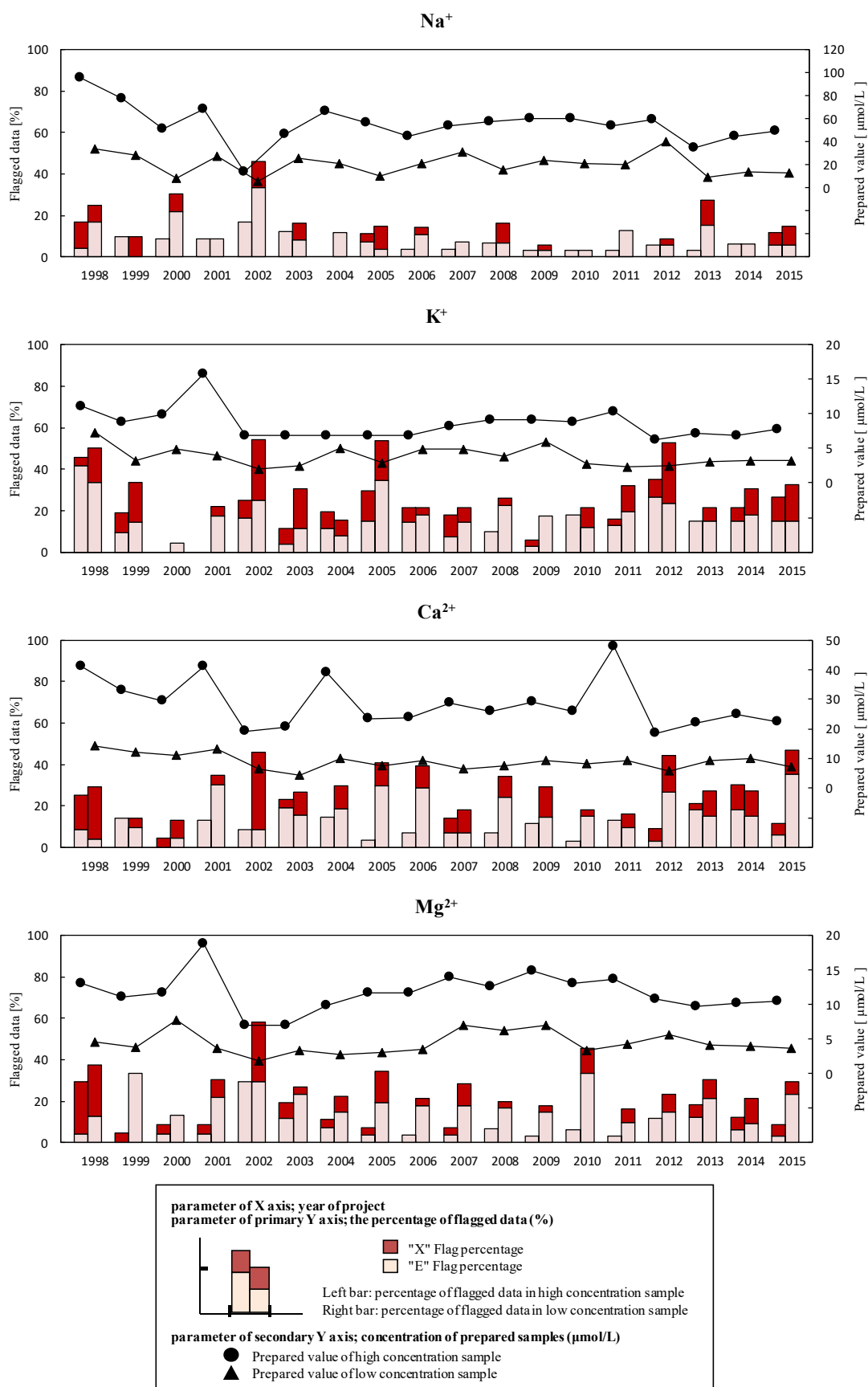


Figure 2.30 Comparison for each parameter in ILC project (continued)

As shown in the figure 2.31, the total number of data in this survey was 692.

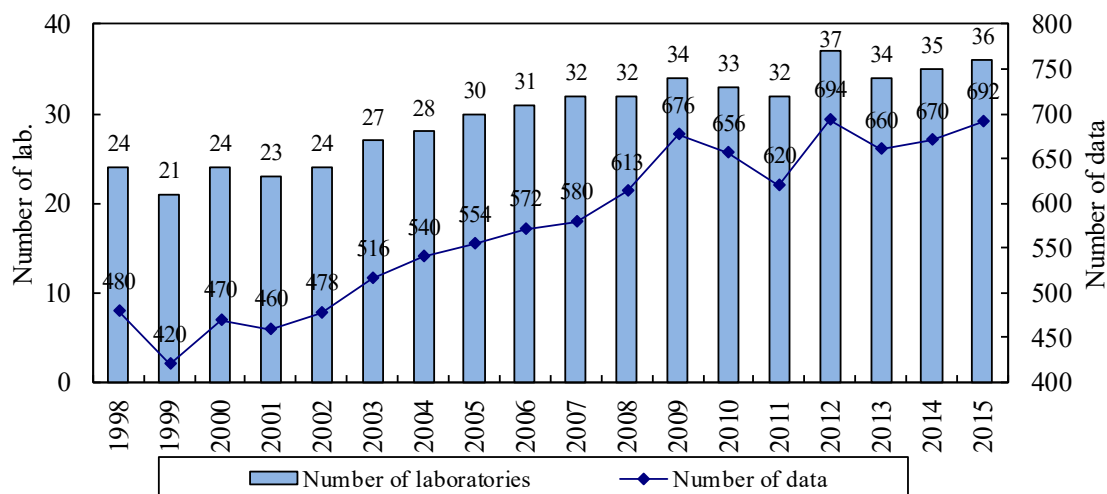


Figure 2.31 The number of participating laboratories and data in the inter-laboratory comparison projects on wet deposition

2.5 Recommendations for improvement

The fundamental matters for QA/QC on measurements and analyses of samples are described on the page 22 through 29 of the “Quality Assurance/Quality Control (QA/QC) Program for Wet Deposition Monitoring in East Asia”.

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, 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 the “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 (2000). *Guidelines for Acid Deposition Monitoring in East Asia*. Acid Deposition and Oxidant Research Center, Niigata, Japan, 25p.
- EANET (2000). *Technical Manual for Wet Deposition Monitoring in East Asia*. Acid Deposition and Oxidant Research Center, Niigata, Japan, 68p.
- EANET (2000). *Quality Assurance/Quality Control (QA/QC) Program for Wet Deposition Monitoring in East Asia*, Acid Deposition and Oxidant Research Center, Niigata, Japan, 29p.
- EANET (2010). *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. Asia Center for Air Pollution Research, Niigata, Japan, 113p.

Appendix 2.1 Data precision of submitted data

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

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

σ : standard deviation of result

V_a : average of result

In appendix table 2.1.1 and appendix table 2.1.2, data precisions calculated from the submitted results were shown. Sample No. 151w of higher concentration had a tendency to show better R.S.D. than sample No. 152w 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. 151w

Lab. ID	pH as H ⁺ %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	NH ₄ ⁺ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %
KH01	8.2	0.7	15.2	13.6	21.8	0.1	0.7	0.6	1.7	1.5
CN01	3.0	0.3	0.2	0.3	0.3	0.2	0.3	0.9	0.2	0.7
CN02	1.5	0.4	0.2	0.2	0.2	0.1	0.1	0.0	0.3	0.6
CN03	0.8	0.0	0.2	0.2	0.1	0.2	0.2	1.0	0.3	0.7
CN04	4.5	0.5	0.6	0.6	0.7	0.5	0.9	1.2	0.4	2.7
ID01	4.3	1.5	1.2	3.7	1.6	0.8	1.6	2.5	3.2	2.0
ID02	1.4	0.1	0.5	0.4	0.1	0.2	0.1	1.3	0.3	0.4
ID03	10.4	5.4	0.4	0.5	0.7	0.3	0.6	1.2	0.8	0.6
JP01	2.7	0.9	1.2	1.1	1.3	0.9	1.2	2.7	0.7	0.8
JP03	1.2	0.2	0.2	0.3	0.4	0.8	0.3	0.4	0.6	0.4
JP04	5.0	3.3	0.1	0.2	0.1	0.5	0.8	3.2	1.2	1.5
JP05	2.1	0.6	0.2	0.1	0.1	0.3	0.2	0.6	0.0	0.5
JP07	11.5	0.7	0.6	0.7	0.5	1.5	0.4	0.8	3.5	0.9
JP08	13.4	2.5	0.4	0.4	0.2	0.6	0.3	1.1	0.3	1.2
JP09	3.8	0.2	1.0	0.8	1.0	0.6	0.6	3.6	0.7	0.7
JP10	2.7	0.2	0.1	0.3	0.2	0.2	0.1	0.0	0.2	0.5
LA01	14.0	0.5	2.7	1.1	1.3	1.9	0.6	2.6	5.6	2.7
MY01	2.4	0.2	0.2	0.3	0.7	0.5	0.6	0.7	1.1	1.4
MN01	7.9	1.6	0.7	2.9	3.1	--	--	--	--	--
MM01	18.8	1.7	2.3	4.5	2.7	2.4	1.8	6.1	147.8	198.4
PH01	9.1	0.5	0.9	2.1	0.5	1.4	0.4	2.2	0.7	2.6
PH02	2.0	0.3	1.0	0.9	3.0	2.8	0.9	6.1	2.1	1.8
KR01	1.8	0.2	0.4	0.3	0.2	0.3	0.5	1.7	0.3	0.4
RU01	1.2	0.3	0.8	0.7	0.9	0.5	0.1	0.4	0.8	0.4
RU02	5.3	3.3	1.3	1.1	1.4	0.6	0.4	2.8	1.3	12.3
TH01	2.5	0.7	3.1	5.4	1.0	8.1	8.8	9.5	9.0	8.9
TH02	2.4	0.2	0.4	0.4	0.3	1.0	0.6	2.2	0.8	0.7
TH04	10.3	0.3	0.9	0.9	0.4	2.2	1.7	3.2	4.3	2.3
TH05	5.7	0.4	0.5	0.6	0.9	0.8	0.9	8.2	1.2	6.4
TH06	1.2	0.2	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
TH08	13.0	0.6	--	--	--	--	--	--	--	--
VN01	7.0	0.5	0.1	0.2	0.1	0.7	0.9	2.7	0.6	0.5
VN02	3.1	0.8	2.1	1.1	0.4	0.8	0.8	6.7	3.1	2.0
VN03	1.6	0.3	0.6	0.3	--	0.3	0.3	0.7	0.2	0.4
VN04	2.1	0.3	0.4	0.6	0.5	0.3	1.0	0.9	0.8	1.3
VN05	23.5	0.3	3.0	2.3	2.7	5.1	2.4	18.9	3.2	6.5
Number of data	36	36	35	35	34	34	34	34	34	34
Minimum	0.8	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
25% value	2.0	0.3	0.2	0.3	0.2	0.3	0.3	0.7	0.3	0.5
Median	3.5	0.5	0.6	0.6	0.5	0.6	0.6	1.5	0.8	1.1
75% value	8.4	0.8	1.1	1.1	1.2	1.0	0.9	3.1	2.0	2.3
Maximum	23.5	5.4	15.2	13.6	21.8	8.1	8.8	18.9	147.8	198.4

Note: 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. 152w

Lab. ID	pH as H ⁺ %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	NH ₄ ⁺ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %
KH01	16.4	0.5	14.5	7.8	10.0	16.1	7.9	3.0	11.1	8.2
CN01	5.4	1.0	0.9	0.4	0.6	1.0	0.9	1.6	0.7	1.3
CN02	1.7	0.3	0.7	0.3	0.3	0.6	0.5	0.0	0.0	0.0
CN03	0.0	0.0	0.6	0.7	0.4	0.7	0.6	1.7	1.1	1.6
CN04	4.7	1.6	1.3	1.0	0.7	3.1	1.4	5.4	1.9	4.9
ID01	16.9	0.5	2.8	4.3	1.3	2.6	2.7	5.3	3.5	4.5
ID02	7.2	0.0	0.6	0.6	0.2	0.5	0.4	1.4	1.0	0.0
ID03	5.4	0.9	1.9	1.2	1.3	1.6	1.3	7.3	1.8	2.0
JP01	2.4	1.7	0.9	1.0	0.8	0.8	0.8	1.9	0.9	0.9
JP03	1.6	0.5	0.9	1.7	0.6	0.6	0.6	1.6	2.2	0.9
JP04	7.2	1.2	0.0	0.0	0.2	1.2	3.6	13.6	1.4	4.4
JP05	2.9	1.4	0.0	0.3	0.0	0.7	0.7	1.0	0.8	0.0
JP07	20.8	0.7	1.3	1.1	1.3	0.8	1.3	1.5	1.0	0.9
JP08	2.4	2.0	0.3	0.0	0.3	2.5	0.5	0.0	1.0	1.2
JP09	7.8	0.8	0.6	0.7	1.5	0.6	0.7	1.6	1.9	2.6
JP10	2.0	0.3	0.4	0.0	0.3	0.4	0.4	1.4	0.6	0.0
LA01	15.4	3.4	2.5	2.8	3.0	7.0	5.4	13.8	5.5	3.9
MY01	6.1	0.5	0.3	2.8	1.1	0.4	1.3	2.7	4.3	4.6
MN01	6.0	2.0	2.3	0.6	3.7	--	--	--	--	--
MM01	14.3	1.3	6.7	10.8	2.0	37.2	4.4	6.9	81.0	131.3
PH01	33.8	0.0	3.0	6.2	2.7	9.0	0.9	8.1	3.3	4.2
PH02	6.3	0.9	3.8	0.5	1.8	1.3	3.5	10.2	17.7	3.4
KR01	4.3	0.9	0.3	0.5	0.4	0.5	0.6	0.0	0.7	1.3
RU01	1.7	0.5	0.7	0.7	0.5	0.5	0.7	1.4	1.6	0.0
RU02	3.5	4.4	2.6	3.2	1.9	2.0	2.0	4.0	2.9	4.4
TH01	8.9	0.8	3.5	7.6	0.7	1.3	1.0	1.7	2.7	1.0
TH02	1.2	0.5	0.4	0.5	0.3	1.1	0.6	4.0	0.5	0.8
TH04	12.6	0.9	1.9	2.6	1.1	5.3	6.9	2.3	5.6	4.6
TH05	12.3	2.0	3.1	2.3	6.2	3.3	4.8	24.4	6.6	4.5
TH06	1.4	0.0	0.0	0.0	0.0	0.5	0.3	0.0	0.0	0.0
TH08	11.6	2.2	--	--	--	--	--	--	--	--
VN01	2.9	2.8	0.5	1.2	0.7	3.2	0.8	3.1	2.3	1.7
VN02	2.7	1.5	1.8	1.5	1.1	2.0	3.1	3.8	2.3	4.1
VN03	0.8	1.2	0.6	0.7	--	0.9	0.7	1.8	0.5	1.8
VN04	2.3	0.8	1.9	1.0	1.3	1.5	1.5	2.7	1.3	2.9
VN05	5.6	2.4	2.3	1.9	3.4	2.2	1.9	4.8	5.4	7.7
Number of data	36	36	35	35	34	34	34	34	34	34
Minimum	0.0	0.0	0.0	0.0	0.0	0.4	0.3	0.0	0.0	0.0
25% value	2.3	0.5	0.5	0.5	0.4	0.6	0.6	1.5	0.9	0.9
Median	5.4	0.9	0.9	1.0	1.0	1.3	1.0	2.5	1.8	1.9
75% value	9.6	1.7	2.4	2.5	1.7	2.6	2.6	5.2	3.4	4.4
Maximum	33.8	4.4	14.5	10.8	10.0	37.2	7.9	24.4	81.0	131.3

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

"--", Not measured

Appendix 2.2 Analytical results submitted by the laboratories

Appendix Table 2.2.1 Analytical data concerning sample No. 151w

Lab. ID	pH	EC mS/m	SO ₄ ²⁻ μmol/L	NO ₃ ⁻ μmol/L	Cl ⁻ μmol/L	NH ₄ ⁺ μmol/L	Na ⁺ μmol/L	K ⁺ μmol/L	Ca ²⁺ μmol/L	Mg ²⁺ μmol/L
KH01	4.81	2.82	39.6	40.4	44.1	46.6	50.6	8.4	24.5	11.4
CN01	4.74	2.97	43.5	38.4	53.9	49.0	50.6	7.9	22.4	10.4
CN02	4.80	2.98	42.8	37.8	56.0	44.6	47.7	7.1	22.7	11.3
CN03	4.78	2.97	44.0	37.5	54.5	44.4	47.8	7.7	22.5	10.5
CN04	4.82	3.00	43.5	36.2	51.2	47.9	49.2	7.4	24.0	10.9
ID01	4.93	2.87	44.0	43.1	51.5	44.5	47.6	9.2	25.0	11.2
ID02	4.73	2.81	50.6	47.3	57.1	40.1	47.1	6.8	24.2	11.4
ID03	4.72	3.01	43.7	38.4	54.0	44.1	48.4	8.0	22.5	10.7
JP01	4.75	3.02	43.0	38.3	55.8	42.8	47.9	7.4	21.9	10.7
JP03	4.79	2.99	44.2	38.7	56.0	44.4	48.9	7.9	21.6	9.9
JP04	4.78	2.92	43.8	38.5	56.2	44.3	48.3	7.6	22.6	10.4
JP05	4.77	2.97	42.6	38.6	57.3	44.8	47.4	7.6	21.5	10.3
JP07	4.81	3.11	43.9	37.4	55.1	44.1	48.0	7.5	21.8	9.9
JP08	4.87	2.95	43.9	38.4	56.2	43.6	48.7	7.6	22.3	10.3
JP09	4.85	2.94	44.2	39.0	56.2	44.1	48.7	7.9	22.2	10.4
JP10	4.78	3.02	44.2	38.8	55.7	42.5	47.3	7.6	22.0	10.2
LA01	4.75	2.87	46.4	37.4	56.2	45.1	51.5	8.5	22.8	10.1
MY01	4.78	3.02	45.2	37.9	55.7	44.3	48.1	7.3	21.7	9.4
MN01	4.56	2.98	38.2	31.3	43.2	---	---	---	---	---
MM01	4.74	3.67	30.6	34.1	79.1	48.0	15.9	9.0	8.5	0.0
PH01	4.72	3.30	39.7	33.4	51.6	39.9	48.0	7.4	22.6	10.3
PH02	4.86	3.57	96.9	41.1	55.9	56.9	60.6	9.6	30.6	14.2
KR01	4.82	2.90	43.1	36.8	53.5	55.0	47.7	7.6	21.8	10.3
RU01	4.79	3.00	42.8	38.4	53.9	42.8	49.6	7.9	23.6	10.5
RU02	4.78	2.96	43.3	37.6	55.7	42.3	50.4	8.1	26.4	11.1
TH01	4.84	2.99	41.7	36.5	53.6	46.8	45.4	7.1	21.0	9.6
TH02	4.80	2.96	43.7	38.2	55.7	43.9	48.4	7.7	24.2	10.8
TH04	4.59	2.90	65.8	58.0	84.0	42.2	47.8	7.3	23.4	10.2
TH05	4.74	2.95	45.2	38.3	54.8	47.7	44.2	6.8	22.2	9.1
TH06	4.73	3.09	46.3	40.5	52.4	43.8	46.1	9.1	22.7	11.3
TH08	4.04	2.80	---	---	---	---	---	---	---	---
VN01	4.75	2.85	41.8	37.7	55.4	43.2	49.2	9.4	23.9	9.9
VN02	4.87	2.87	41.9	36.8	55.5	48.0	50.5	13.6	24.0	9.6
VN03	4.80	2.89	42.6	36.6	---	45.9	67.1	14.1	25.7	8.6
VN04	5.12	2.87	42.0	36.8	55.2	48.1	50.7	13.4	24.1	9.8
VN05	5.22	2.89	42.1	37.3	56.7	44.7	58.3	13.9	25.4	9.3
Prepared value	4.74	3.05	44.1	38.9	56.8	43.9	48.8	7.8	22.2	10.5
Number of data	35	34	34	34	32	33	33	34	33	33
Average	4.80	2.95	43.6	38.0	54.2	45.0	49.6	8.6	23.3	10.4
Minimum	4.56	2.80	30.6	31.3	43.2	39.9	44.2	6.8	21.0	8.6
Maximum	5.22	3.30	65.8	47.3	57.3	55.0	67.1	14.1	30.6	14.2
Standard deviation	0.11	0.09	4.89	2.61	3.15	2.80	4.34	2.01	1.83	0.95

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

"---", Not measured

Appendix Table 2.2.2 Analytical data concerning sample No. 152w

Lab. ID	pH	EC mS/m	SO ₄ ²⁻ μmol/L	NO ₃ ⁻ μmol/L	Cl ⁻ μmol/L	NH ₄ ⁺ μmol/L	Na ⁺ μmol/L	K ⁺ μmol/L	Ca ²⁺ μmol/L	Mg ²⁺ μmol/L
KH01	5.21	0.92	10.9	10.9	18.9	11.0	11.8	3.3	8.6	4.3
CN01	5.13	0.91	11.8	9.5	19.7	10.1	13.3	3.2	7.1	3.7
CN02	5.08	0.97	11.7	10.0	19.9	8.5	12.6	2.6	7.0	3.8
CN03	5.18	0.97	11.7	10.0	19.3	9.1	12.2	3.1	7.2	4.2
CN04	5.21	0.96	12.4	10.1	19.1	8.6	12.3	2.9	7.7	4.3
ID01	5.41	0.86	11.5	10.6	20.2	9.6	10.9	4.6	9.1	4.4
ID02	4.93	0.89	14.4	13.0	20.6	9.8	12.3	3.1	9.1	4.4
ID03	5.44	0.75	11.5	10.8	18.5	11.8	13.7	3.6	8.3	4.2
JP01	5.13	0.99	11.4	10.5	19.7	10.8	14.4	3.1	6.0	3.6
JP03	5.19	0.97	11.9	10.8	19.1	9.5	12.6	3.1	6.6	3.6
JP04	5.16	0.94	11.8	10.5	19.7	9.8	12.4	2.9	7.1	3.6
JP05	5.14	0.94	11.7	10.5	19.3	9.6	11.6	3.2	6.0	3.5
JP07	5.27	1.02	11.5	10.5	19.8	10.0	12.7	2.9	7.0	3.5
JP08	5.14	0.97	12.0	10.6	19.6	11.3	13.2	3.0	7.4	3.7
JP09	5.31	0.93	11.7	10.2	19.5	10.2	13.2	3.2	7.2	3.8
JP10	5.16	0.98	11.9	10.5	19.3	9.5	12.5	3.1	6.8	3.6
LA01	5.07	0.92	12.5	10.2	19.4	11.4	14.9	4.1	7.8	3.4
MY01	5.15	0.99	10.8	9.8	19.2	10.3	12.4	2.9	6.6	3.0
MN01	4.89	0.99	10.5	8.7	14.5	---	---	---	---	---
MM01	5.25	1.11	8.0	9.4	27.6	10.0	3.5	4.4	0.7	0.1
PH01	5.00	1.05	10.9	10.9	19.0	4.6	12.0	2.5	7.4	3.7
PH02	5.25	1.56	25.6	10.4	19.8	13.5	16.9	4.2	13.4	5.8
KR01	5.08	0.98	11.7	10.4	18.5	14.3	12.4	3.1	6.9	4.1
RU01	5.16	0.97	11.6	10.4	18.9	11.5	13.1	3.1	7.5	3.7
RU02	5.12	0.97	12.0	10.8	21.6	10.4	13.4	3.4	8.4	3.2
TH01	5.40	0.95	9.6	8.2	17.4	11.6	12.2	2.9	6.9	3.5
TH02	5.14	0.95	11.6	10.1	19.0	10.5	12.8	3.3	9.4	4.3
TH04	5.00	0.89	17.1	14.7	28.3	10.2	12.3	2.9	8.8	3.8
TH05	5.22	0.93	11.6	10.4	17.6	11.3	11.1	2.8	5.8	4.8
TH06	5.16	1.03	12.4	11.3	24.3	9.7	13.2	3.6	8.7	4.8
TH08	4.51	0.85	---	---	---	---	---	---	---	---
VN01	5.20	0.89	11.6	10.5	19.5	9.6	14.2	5.3	8.5	3.5
VN02	5.35	0.85	11.5	10.0	19.0	10.8	12.5	3.8	9.0	3.6
VN03	5.20	0.89	12.0	9.5	---	11.9	23.4	6.7	9.7	4.0
VN04	5.42	0.87	11.3	9.8	18.9	10.6	12.2	3.7	8.8	3.5
VN05	5.46	0.85	11.6	10.9	19.6	11.3	15.8	5.5	9.0	3.9
Prepared value	5.15	0.94	11.9	10.7	19.8	9.8	12.8	3.2	7.0	3.7
Number of data	35	35	34	34	32	33	32	33	32	33
Average	5.19	0.94	11.7	10.3	19.3	10.5	12.9	3.4	7.7	3.9
Minimum	4.89	0.75	8.0	8.2	14.5	8.5	10.9	2.5	5.8	3.0
Maximum	5.46	1.11	17.1	13.0	24.3	14.3	16.9	5.5	9.7	5.8
Standard deviation	0.13	0.07	1.33	0.78	1.44	1.22	1.23	0.70	1.06	0.53

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

"---", Not measured

Appendix 2.3 Normalized data

Appendix Table 2.3.1 Deviation% from prepared values of sample No. 151w

Lab. ID	pH %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	NH ₄ ⁺ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %
KH01	1.5	-7.5	-10.2	3.9	-22.4	6.2	3.7	7.7	10.4	8.6
CN01	0.0	-2.6	-1.4	-1.3	-5.1	11.6	3.7	1.3	0.9	-1.0
CN02	1.3	-2.3	-2.9	-2.8	-1.4	1.6	-2.3	-9.0	2.3	7.6
CN03	0.8	-2.6	-0.2	-3.6	-4.0	1.1	-2.0	-1.3	1.4	0.0
CN04	1.7	-1.6	-1.4	-6.9	-9.9	9.1	0.8	-5.1	8.1	3.8
ID01	4.0	-5.9	-0.2	10.8	-9.3	1.4	-2.5	17.9	12.6	6.7
ID02	-0.2	-7.9	14.7	21.6	0.5	-8.7	-3.5	-12.8	9.0	8.6
ID03	-0.4	-1.3	-0.9	-1.3	-4.9	0.5	-0.8	2.6	1.4	1.9
JP01	0.2	-1.0	-2.5	-1.5	-1.8	-2.5	-1.8	-5.1	-1.4	1.9
JP03	1.1	-2.0	0.2	-0.5	-1.4	1.1	0.2	1.3	-2.7	-5.7
JP04	0.8	-4.3	-0.7	-1.0	-1.1	0.9	-1.0	-2.6	1.8	-1.0
JP05	0.6	-2.6	-3.4	-0.8	0.9	2.1	-2.9	-2.6	-3.2	-1.9
JP07	1.5	2.0	-0.5	-3.9	-3.0	0.5	-1.6	-3.8	-1.8	-5.7
JP08	2.7	-3.3	-0.5	-1.3	-1.1	-0.7	-0.2	-2.6	0.5	-1.9
JP09	2.3	-3.6	0.2	0.3	-1.1	0.5	-0.2	1.3	0.0	-1.0
JP10	0.8	-1.0	0.2	-0.3	-1.9	-3.2	-3.1	-2.6	-0.9	-2.9
LA01	0.2	-5.9	5.2	-3.9	-1.1	2.7	5.5	9.0	2.7	-3.8
MY01	0.8	-1.0	2.5	-2.6	-1.9	0.9	-1.4	-6.4	-2.3	-10.5
MN01	-3.8	-2.3	-13.4	-19.5	-23.9	---	---	---	---	---
MM01	0.0	20.3	-30.6	-12.3	39.3	9.3	-67.4	15.4	-61.7	-100.0
PH01	-0.4	8.2	-10.0	-14.1	-9.2	-9.1	-1.6	-5.1	1.8	-1.9
PH02	2.5	17.0	119.7	5.7	-1.6	29.6	24.2	23.1	37.8	35.2
KR01	1.7	-4.9	-2.3	-5.4	-5.8	25.3	-2.3	-2.6	-1.8	-1.9
RU01	1.1	-1.6	-2.9	-1.3	-5.1	-2.5	1.6	1.3	6.3	0.0
RU02	0.8	-3.0	-1.8	-3.3	-1.9	-3.6	3.3	3.8	18.9	5.7
TH01	2.1	-2.0	-5.4	-6.2	-5.6	6.6	-7.0	-9.0	-5.4	-8.6
TH02	1.3	-3.0	-0.9	-1.8	-1.9	0.0	-0.8	-1.3	9.0	2.9
TH04	-3.2	-4.9	49.2	49.1	47.9	-3.9	-2.0	-6.4	5.4	-2.9
TH05	0.0	-3.3	2.5	-1.5	-3.5	8.7	-9.4	-12.8	0.0	-13.3
TH06	-0.2	1.3	5.0	4.1	-7.7	-0.2	-5.5	16.7	2.3	7.6
TH08	-14.8	-8.2	---	---	---	---	---	---	---	---
VN01	0.2	-6.6	-5.2	-3.1	-2.5	-1.6	0.8	20.5	7.7	-5.7
VN02	2.7	-5.9	-5.0	-5.4	-2.3	9.3	3.5	74.4	8.1	-8.6
VN03	1.3	-5.2	-3.4	-5.9	---	4.6	37.5	80.8	15.8	-18.1
VN04	8.0	-5.9	-4.8	-5.4	-2.8	9.6	3.9	71.8	8.6	-6.7
VN05	10.1	-5.2	-4.5	-4.1	-0.2	1.8	19.5	78.2	14.4	-11.4
Number of data	36	36	35	35	34	34	34	34	34	34
Average	0.8	-1.9	2.4	-0.7	-1.7	3.2	-0.3	9.9	3.1	-3.6
Minimum	-14.8	-8.2	-30.6	-19.5	-23.9	-9.1	-67.4	-12.8	-61.7	-100.0
Maximum	10.1	20.3	119.7	49.1	47.9	29.6	37.5	80.8	37.8	35.2

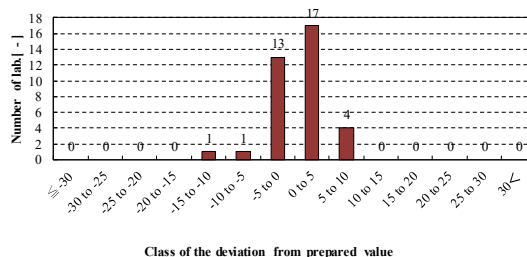
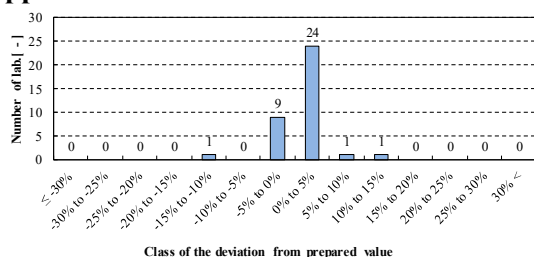
Note: "---", Not measured

Appendix Table 2.3.2 Deviation% from prepared values of sample No. 152w

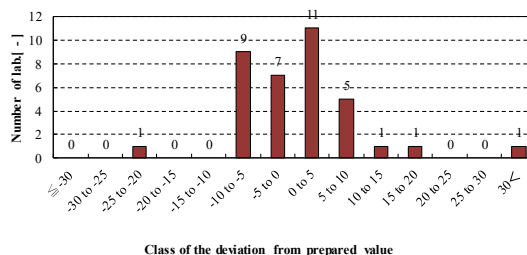
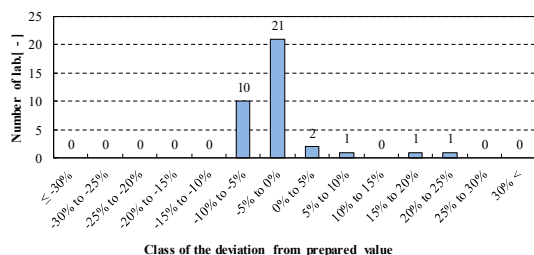
Lab. ID	pH %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	NH ₄ ⁺ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %
KH01	1.2	-2.1	-8.4	1.9	-4.5	12.2	-7.8	3.1	22.9	16.2
CN01	-0.4	-3.2	-0.8	-11.2	-0.5	3.1	3.9	0.0	1.4	0.0
CN02	-1.4	3.2	-1.7	-6.5	0.5	-13.3	-1.6	-18.8	0.0	2.7
CN03	0.6	3.2	-1.7	-6.5	-2.5	-7.1	-4.7	-3.1	2.9	13.5
CN04	1.2	2.1	4.2	-5.6	-3.5	-12.2	-3.9	-9.4	10.0	16.2
ID01	5.0	-8.5	-3.4	-0.9	2.0	-2.0	-14.8	43.8	30.0	18.9
ID02	-4.3	-5.3	21.0	21.5	4.0	0.0	-3.9	-3.1	30.0	18.9
ID03	5.6	-20.2	-3.4	0.9	-6.6	20.4	7.0	12.5	18.6	13.5
JP01	-0.4	5.3	-4.2	-1.9	-0.5	10.2	12.5	-3.1	-14.3	-2.7
JP03	0.8	3.2	0.0	0.9	-3.5	-3.1	-1.6	-3.1	-5.7	-2.7
JP04	0.2	0.0	-0.8	-1.9	-0.5	0.0	-3.1	-9.4	1.4	-2.7
JP05	-0.2	0.0	-1.7	-1.9	-2.5	-2.0	-9.4	0.0	-14.3	-5.4
JP07	2.3	8.5	-3.4	-1.9	0.0	2.0	-0.8	-9.4	0.0	-5.4
JP08	-0.2	3.2	0.8	-0.9	-1.0	15.3	3.1	-6.3	5.7	0.0
JP09	3.1	-1.1	-1.7	-4.7	-1.5	4.1	3.1	0.0	2.9	2.7
JP10	0.2	4.3	0.0	-1.9	-2.5	-3.1	-2.3	-3.1	-2.9	-2.7
LA01	-1.6	-2.1	5.0	-4.7	-2.0	16.3	16.4	28.1	11.4	-8.1
MY01	0.0	5.3	-9.2	-8.4	-3.0	5.1	-3.1	-9.4	-5.7	-18.9
MN01	-5.0	5.3	-11.8	-18.7	-26.8	---	---	---	---	---
MM01	1.9	18.1	-32.8	-12.1	39.4	2.0	-72.7	37.5	-90.0	-97.3
PH01	-2.9	11.7	-8.4	1.9	-4.0	-53.1	-6.3	-21.9	5.7	0.0
PH02	1.9	66.0	115.1	-2.8	0.0	37.8	32.0	31.3	91.4	56.8
KR01	-1.4	4.3	-1.7	-2.8	-6.6	45.9	-3.1	-3.1	-1.4	10.8
RU01	0.2	3.2	-2.5	-2.8	-4.5	17.3	2.3	-3.1	7.1	0.0
RU02	-0.6	3.2	0.8	0.9	9.1	6.1	4.7	6.3	20.0	-13.5
TH01	4.9	1.1	-19.3	-23.4	-12.1	18.4	-4.7	-9.4	-1.4	-5.4
TH02	-0.2	1.1	-2.5	-5.6	-4.0	7.1	0.0	3.1	34.3	16.2
TH04	-2.9	-5.3	43.7	37.4	42.9	4.1	-3.9	-9.4	25.7	2.7
TH05	1.4	-1.1	-2.5	-2.8	-11.1	15.3	-13.3	-12.5	-17.1	29.7
TH06	0.2	9.6	4.2	5.6	22.7	-1.0	3.1	12.5	24.3	29.7
TH08	-12.4	-9.6	---	---	---	---	---	---	---	---
VN01	1.0	-5.3	-2.5	-1.9	-1.5	-2.0	10.9	65.6	21.4	-5.4
VN02	3.9	-9.6	-3.4	-6.5	-4.0	10.2	-2.3	18.8	28.6	-2.7
VN03	1.0	-5.3	0.8	-11.2	---	21.4	82.8	109.4	38.6	8.1
VN04	5.2	-7.4	-5.0	-8.4	-4.5	8.2	-4.7	15.6	25.7	-5.4
VN05	6.0	-9.6	-2.5	1.9	-1.0	15.3	23.4	71.9	28.6	5.4
Number of data	36	36	35	35	34	34	34	34	34	34
Average	0.4	1.8	1.7	-2.4	0.2	5.9	1.1	9.5	9.9	2.5
Minimum	-12.4	-20.2	-32.8	-23.4	-26.8	-53.1	-72.7	-21.9	-90.0	-97.3
Maximum	6.0	66.0	115.1	37.4	42.9	45.9	82.8	109.4	91.4	56.8

Note: "---", Not measured

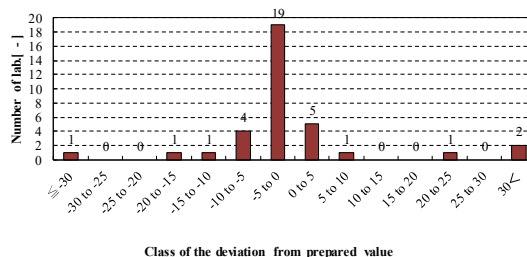
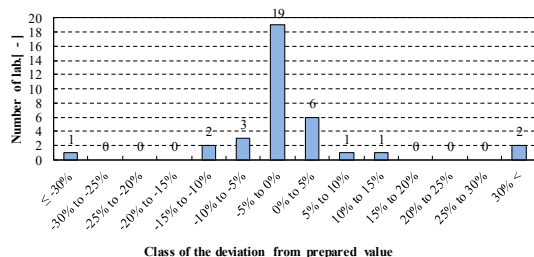
Appendix 2.4 Data distribution



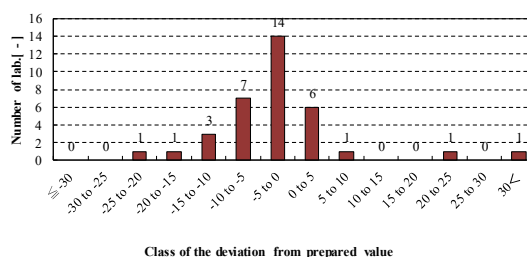
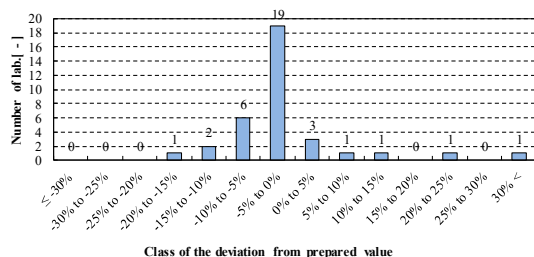
Appendix Figure 2.4.1 Data distribution for pH (Left: 151w, Right: 152w)



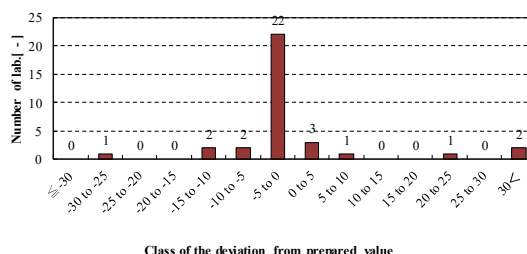
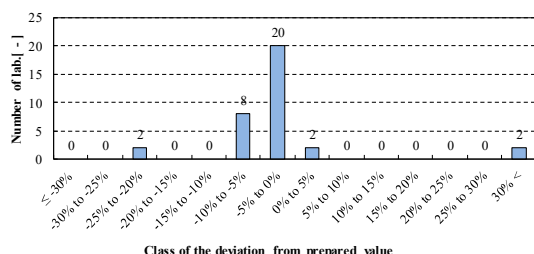
Appendix Figure 2.4.2 Data distribution for EC (Left: 151w, Right: 152w)



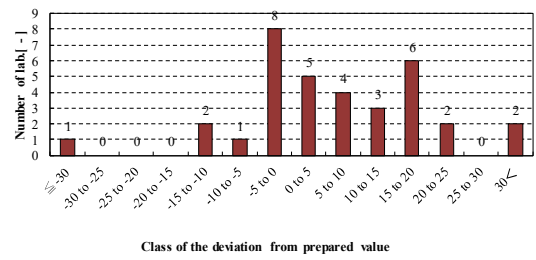
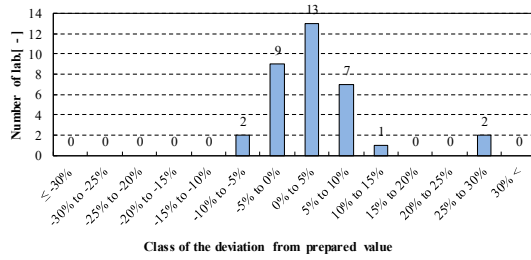
Appendix Figure 2.4.3 Data distribution for SO_4^{2-} (Left: 151w, Right: 152w)



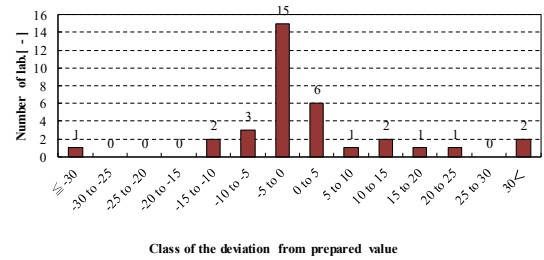
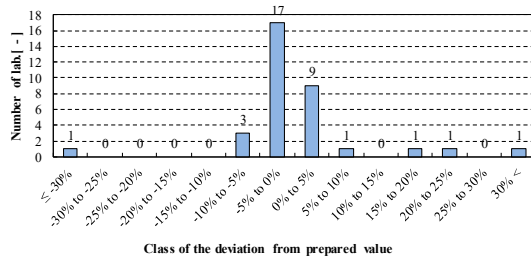
Appendix Figure 2.4.4 Data distribution for NO_3^- (Left: 151w, Right: 152w)



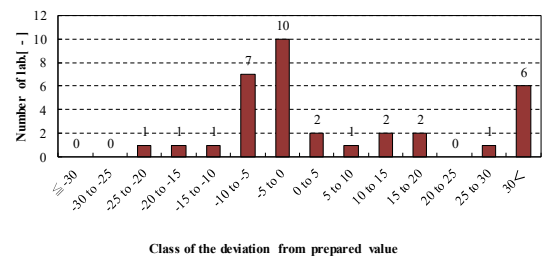
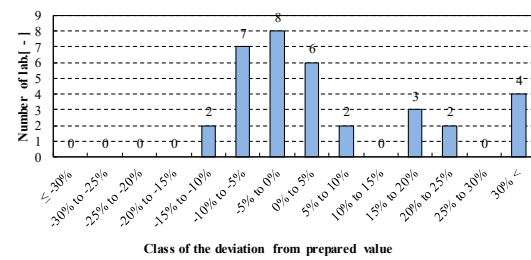
Appendix Figure 2.4.5 Data distribution for Cl^- (Left: 151w, Right: 152w)



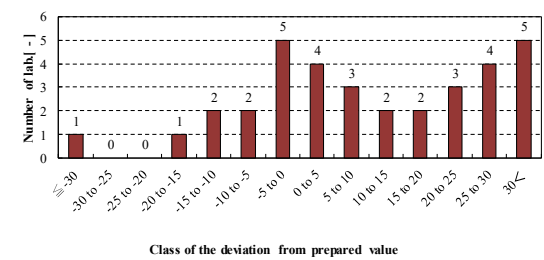
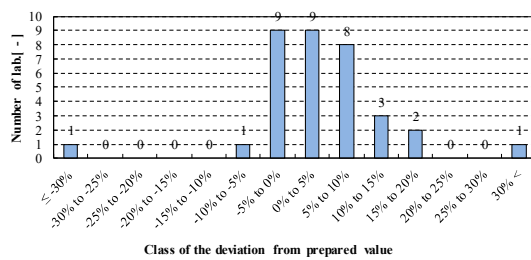
Appendix Figure 2.4.6 Data distribution for NH_4^+ (Left: 151w, Right: 152w)



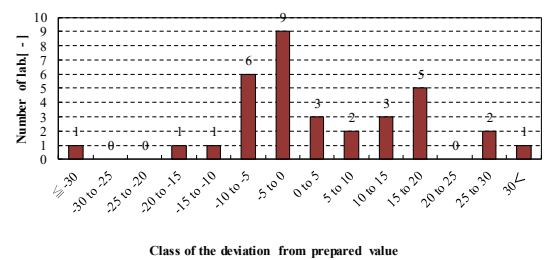
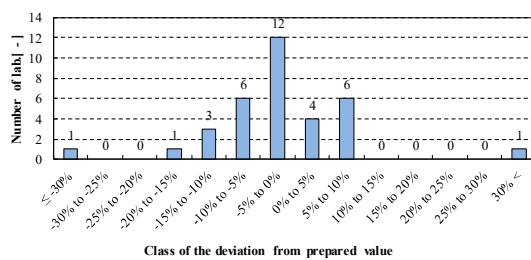
Appendix Figure 2.4.7 Data distribution for Na^+ (Left: 151w, Right: 152w)



Appendix Figure 2.4.8 Data distribution for K^+ (Left: 151w, Right: 152w)



Appendix Figure 2.4.9 Data distribution for Ca^{2+} (Left: 151w, Right: 152w)



Appendix Figure 2.4.10 Data distribution for Mg^{2+} (Left: 151w, Right: 152w)

3. 11th 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 2015. Most of the laboratories which monitor with the filter pack method in EANET joined this activity and submitted their analytical results to the NC. These results were compared with the corresponding prepared value and statistically analyzed.

3.2 Procedures

3.2.1 Participating Laboratories

A total of 28 laboratories in charge of EANET dry monitoring participated in this eleventh activity and 27 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 were 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.151d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Two kinds of the standard solutions which contained known concentration of sulfate or chloride ion were added.
No.151d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	One kind of the standard solution which contained known concentration of ammonium ion was added.
No.152d-1	Alkali (K_2CO_3)	Polyethylene	3	Two kinds of the standard solutions

	impregnated filter	centrifuge tube		which contained known concentration of sulfate or chloride ion were added.
No.152d-2	Acid (H ₃ PO ₄) impregnated filter	Polyethylene centrifuge tube	3	One kind of the standard solution which contained known concentration of ammonium ion was added.
No.153d-1	Alkali (K ₂ CO ₃) impregnated filter	Polyethylene centrifuge tube	3	Blank
No.153d-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 micrograms (μg).

3.2.4 Analytical Methodologies

The recommended procedure for sample analyses on the filter pack method is described in the document, "Technical Document for Filter Pack Method in East Asia" (EANET, 2003). 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.151d-1, No.152d-1, No.153d-1

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

(2) Sample No.151d-2, No.152d-2, No.153d-2

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

(3) Filtration

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

Note 1) Carry out the analyses immediately after extraction.

Note 2) In principle, it is strongly recommended that the filtrate be analyzed immediately after extraction, however, in the case that they need to be kept for certain reasons, store them in a refrigerator at 4°C.

The participating laboratories were expected to use the analytical methods specified in the Technical Manual (EANET, 2010) in Table 3.2.

Table 3.2 Analytical methods specified in the Technical Manual

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

3.2.5 Data Check Procedures

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

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

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

where M_{sol} : quantity of each component in the filtrate (μg);
 C_{sol} : concentration of each component in the filtrate ($\mu\text{mol L}^{-1}$);
 V_{sol} : volume of the solvent (20 mL);

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

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

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

$M_{\text{sol, Sample}}$: quantity (μg) of each component in the filtrate from sample No.151d-1, No.151d-2, No.152d-1 and No.152d-2;

$M_{\text{sol, Blank}}$: the average quantity (μg) in the filtrate from blank sample No.153d-1 and No.153d-2.

3.3 Results

The NC distributed the filter samples to 28 laboratories in the participating countries of EANET, and received their results from 27 laboratories. The results compared to the prepared values are summarized in Table 3.3. The average, minimum, maximum, standard deviation (S.D.) and number of data (N) were calculated from each analyzed ion quantity. Analytical results of Samples

No.151d and No.152d are shown in Table 3.5 and Table 3.7.

Outliers exceeding three times the standard deviation (S.D.) should be rejected before calculation and there are four rejected values this year.

As shown in Table 3.3, the deviations ($\Delta V/V_p$) for SO_4^{2-} in Sample No. 151d and Sample No.152d were -10.3% and -4.1%. The deviations for Cl^- in Sample No. 151d and Sample No.152d were -9.0% and -7.8%. The deviations for NH_4^+ in Sample No. 151d and Sample No.152d were 4.3% and 1.8%.

The Data Quality Objectives (DQOs) of EANET are specified on the QA/QC program of EANET that determined values are expected to fall within $\pm 15\%$ deviation from the prepared values. Each laboratory analyzed each sample 3 times, averaged the values, and these average values were compared with the corresponding prepared values for this report. The flag "E" indicates that the deviation exceeds $\pm 15\%$ but not $\pm 30\%$, and the flag "X" indicates that the 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.151d and No.152d 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)	Average (V _a)	$\Delta V/V_p^*$ (%)	S.D.	Number (N)	Minimum	Maximum
<u>Sample No. 151d</u>								
SO ₄ ²⁻	(µg)	18	16.1	-10.3	2.19	26	11.6	19.5
Cl ⁻	(µg)	3.5	3.19	-9.0	0.69	27	1.60	4.79
NH ₄ ⁺	(µg)	9.5	9.91	4.3	1.27	25	7.77	13.5
<u>Sample No. 152d</u>								
SO ₄ ²⁻	(µg)	74	71.0	-4.1	10.08	27	47.0	96.3
Cl ⁻	(µg)	14	12.9	-7.8	1.65	26	9.01	16.9
NH ₄ ⁺	(µg)	51	51.9	1.8	4.46	25	39.3	62.2

* Prepared: Prepared values

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

3.3.1 Evaluation of Laboratories' Performance (by sample)

Samples No. 151d-1, No.151d-2

For Sample No.151d , 19 analytical data in 80 results were flagged E, and 11 analytical data were flagged X. The total percentage of flagged samples was 37.5%. (Figure 3.1, Table 3.4 and 3.5).

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

	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	Total
Flag E *	8	7	4	19
Flag X *	3	5	3	11
Data within DQOs	16	15	19	50
Ratio of Flagged (%)	40.7	44.4	26.9	37.5

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

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

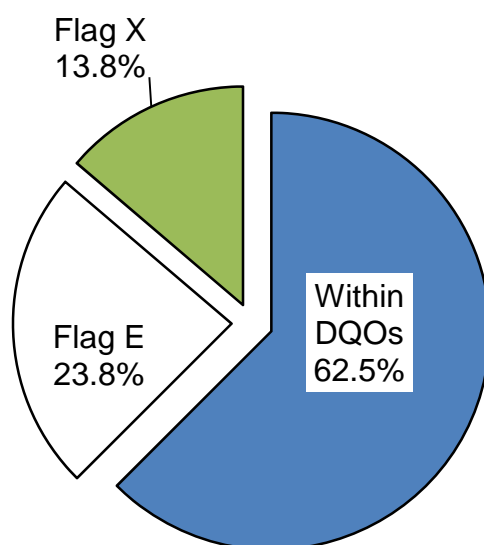


Figure 3.1 Percentage of flagged data for Sample No.151d

Table 3.5 Average analytical results of Sample No.151d

Lab. Code	SO ₄ ²⁻ (µg)		Cl ⁻ (µg)		NH ₄ ⁺ (µg)
KH01	16.4		3.08		9.39
CN02	35.9	X	2.84	E	9.73
ID01	17.7		4.22	E	8.80
ID03	18.5		4.79	X	9.08
JP01	16.2		3.23		9.07
JP02	18.5		3.32		9.48
JP03	18.5		3.10		9.97
JP04	18.1		3.28		9.70
JP05	18.7		3.43		9.40
JP08	17.8		3.19		9.41
JP09	19.2		3.42		9.50
JP10	15.3		3.06		9.35
LA01	14.9	E	3.29		19.9 X
MY01	13.9	E	3.03		9.45
MN01	15.0	E	2.20	X	--
MM01	11.6	X	4.02		7.77 E
PH01	14.0	E	3.08		10.1
PH02	13.9	E	1.60	X	13.0 X
KR01	14.8	E	3.16		13.5 X

RU01	17.7		3.18		10.3
TH01	12.4	X	2.42	X	11.4 E
TH02	16.3		2.92	E	9.89
TH04	19.5		4.04	E	8.05 E
TH05	13.5	E	2.11	X	11.5 E
TH06	17.8		2.86	E	10.3
VN01	15.6		4.54	E	10.3
VN02	13.8	E	2.61	E	9.35

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

“—” : Not measured

Samples No. 152d-1, No.152d-2

For Sample No.152d, 12 analytical data in 80 results were flagged E, and 6 analytical data were flagged X. The total percentage of flagged samples was 22.5%. (Figure 3.2, Table 3.6 and 3.7).

Table 3.6 Number of flagged data for Sample No.152d				
	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	Total
Flag E *	5	4	3	12
Flag X *	2	3	1	6
Data within DQOs	20	20	22	62
Ratio of Flagged (%)	25.9	25.9	15.4	22.5

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

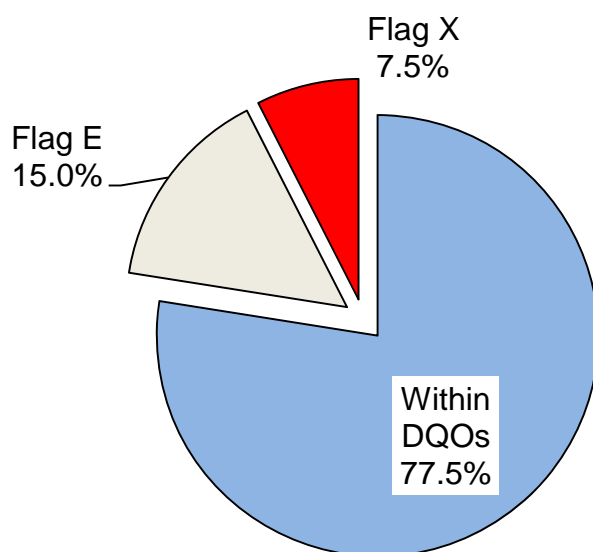


Figure 3.2 Percentage of flagged data for Sample No.152d

Table 3.7 Average analytical results of Sample No.152d

Lab. Code	SO ₄ ²⁻ (µg)	Cl ⁻ (µg)	NH ₄ ⁺ (µg)
KH01	68.6	12.5	58.2
CN02	91.5 E	12.6	50.6
ID01	74.0	13.8	39.3 E
ID03	74.1	14.5	54.7
JP01	75.1	13.9	51.8
JP02	74.3	13.3	52.0
JP03	72.6	13.2	55.6
JP04	75.7	13.9	52.4
JP05	75.4	14.1	51.2
JP08	73.8	13.5	51.0
JP09	89.9 E	15.6	51.1
JP10	68.0	13.1	49.8
LA01	71.0	12.9	74.8 X
MY01	68.9	13.3	50.4
MN01	63.8	10.5 E	--
MM01	47.0 X	16.9 E	51.8
PH01	66.4	12.1	50.8
PH02	58.3 E	9.01 X	62.2 E
KR01	69.6	12.7	56.7

RU01	70.8		13.2		46.1
TH01	65.2		11.5	E	54.7
TH02	70.1		12.8		52.3
TH04	96.3	X	19.4	X	43.3 E
TH05	58.9	E	9.7	X	55.0
TH06	72.8		12.2		52.1
VN01	67.4		14.0		54.5
VN02	56.9	E	10.9	E	50.0

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

“—” : Not measured

Blank Sample (No.153d)

Each quantity of SO_4^{2-} , Cl^- , and NH_4^+ was determined for blank sample No.153d-1 and No.153d-2. Their obtained values are shown in Table 3.8. Blank values were detected in a wide range, including 0 μg . Table 3.9 showed the ratio of the blank value to analytical results by laboratory. At some laboratories, results were not flagged even though some blank values were high.

Table 3.8 Analytical results of Sample No.153d (blank)			
Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
KH01	1.34	2.50	1.90
CN02	1.97	3.02	0.00
ID01	0.00	1.14	2.28
ID03	0.00	0.00	1.74
JP01	0.08	0.75	0.32
JP02	0.00	0.36	0.24
JP03	0.00	0.94	0.13
JP04	0.24	0.92	0.14
JP05	0.00	0.79	0.34
JP08	0.00	1.38	0.40
JP09	0.24	1.01	0.66
JP10	0.42	0.74	0.15
LA01	2.21	2.22	10.9
MY01	0.48	1.10	0.63
MN01	0.20	0.80	--
MM01	0.06	5.04	2.78

PH01	0.00	0.88	0.18
PH02	0.00	1.05	1.51
KR01	1.19	2.02	0.27
RU01	0.50	0.85	0.23
TH01	0.04	0.50	0.29
TH02	0.26	1.01	0.52
TH04	2.72	1.86	0.57
TH05	3.80	3.40	0.04
TH06	0.09	0.94	0.52
VN01	0.00	0.00	0.54
VN02	0.15	0.95	1.09
Average	0.59	1.34	1.09
Median	0.15	0.95	0.46
Minimum	0.00	0.00	0.00
Maximum	3.80	5.04	10.9
Standard deviation	0.97	1.08	2.09

“—” : Not measured

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

Lab. Code	Sample No.151d			Sample No.152d		
	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺
KH01	7.6	44.8	16.8	1.9	16.7	3.2
CN02	5.2	51.6	0.0	2.1	19.3	0.0
ID01	0.0	21.3	20.6	0.0	7.6	5.5
ID03	0.0	0.0	16.1	0.0	0.0	3.1
JP01	0.5	18.8	3.4	0.1	5.1	0.6
JP02	0.0	9.1	2.6	0.0	2.6	0.5
JP03	0.0	23.3	1.3	0.0	6.7	0.2
JP04	1.3	21.9	1.4	0.3	6.2	0.3
JP05	0.0	18.7	3.5	0.0	5.3	0.7
JP08	0.0	30.2	4.1	0.0	9.3	0.8
JP09	1.2	22.8	6.5	0.3	6.1	1.3
JP10	2.7	19.5	1.6	0.6	5.3	0.3
LA01	12.9	40.3	35.3	12.9	40.3	35.3
MY01	3.3	26.6	6.2	0.7	7.6	1.2
MN01	1.3	26.7	--	0.3	7.1	--

MM01	0.5	55.6	26.4	0.1	23.0	5.1
PH01	0.0	22.2	1.8	0.0	6.8	0.4
PH02	0.0	39.6	10.4	0.0	10.4	2.4
KR01	7.5	39.0	1.9	1.7	13.8	0.5
RU01	2.7	21.0	2.2	0.7	6.0	0.5
TH01	0.3	17.1	2.5	0.1	4.2	0.5
TH02	1.5	25.7	5.0	0.4	7.3	1.0
TH04	12.3	31.5	6.6	2.7	8.7	1.3
TH05	22.0	61.7	0.3	6.1	26.0	0.1
TH06	0.5	24.7	4.8	0.1	7.1	1.0
VN01	0.0	0.0	5.0	0.0	0.0	1.0
VN02	1.1	26.7	10.4	0.3	8.0	2.1

: Data Flagged E
 : Data Flagged X
 “—” : Not measured

3.3.2 Comparison of Laboratories' Performance (by Analyte)

The overview of the results is shown in the following figures and tables for each analyte (SO_4^{2-} , Cl^- and NH_4^+). The obtained values from each laboratory were evaluated for their deviations. The number of flagged data is shown in Table 3.4 and 3.6 for each analyte.

SO_4^{2-} (Sulfate)

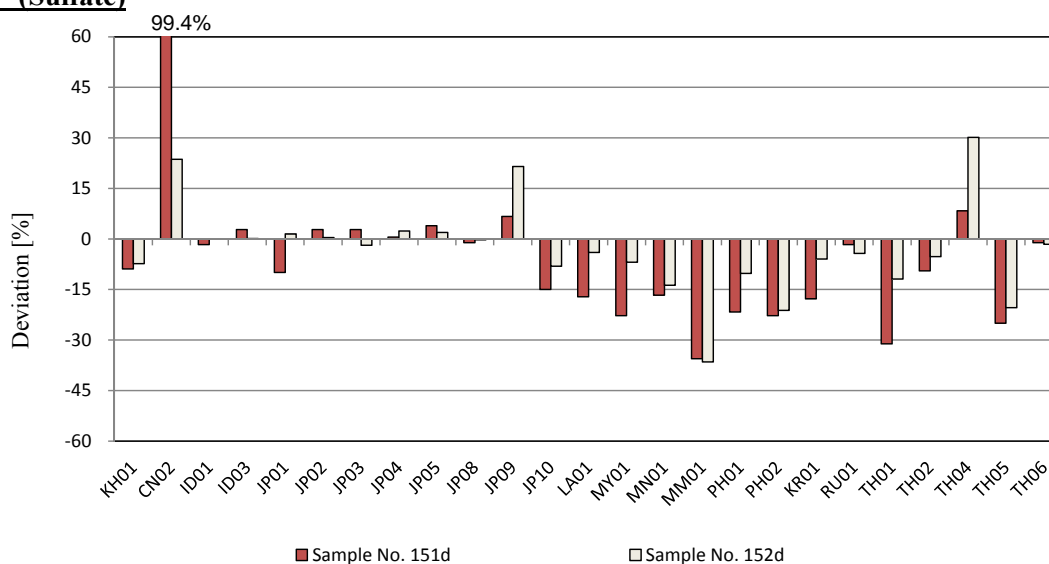


Figure 3.3 Deviation for SO_4^{2-}

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

Table 3.10.1 Analytical method of SO₄²⁻

<i>Analytical Method</i>	
Ion Chromatography	27/27

Table 3.10.2 Flagged data of SO₄²⁻

<i>Flagged Data</i>	Flag E	Flag X	Flagged (%)
Sample No.151d	8	3	40.7
Sample No.152d	5	2	25.9

All laboratories used Ion Chromatography for the determination of SO₄²⁻. E flag appeared at 13 laboratories for Sample No.151d and No. 152d. X flag appeared at 5 laboratories for Sample No.151d and No. 152d.

Cl⁻ (Chloride)

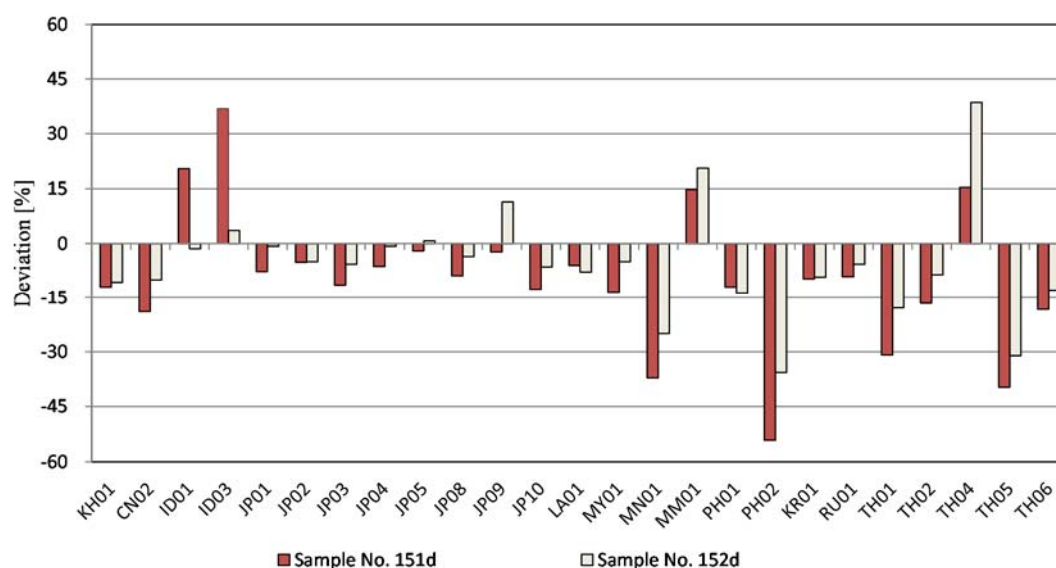
**Figure 3.4 Deviation for Cl⁻**

Table 3.11.1 Analytical method of Cl⁻

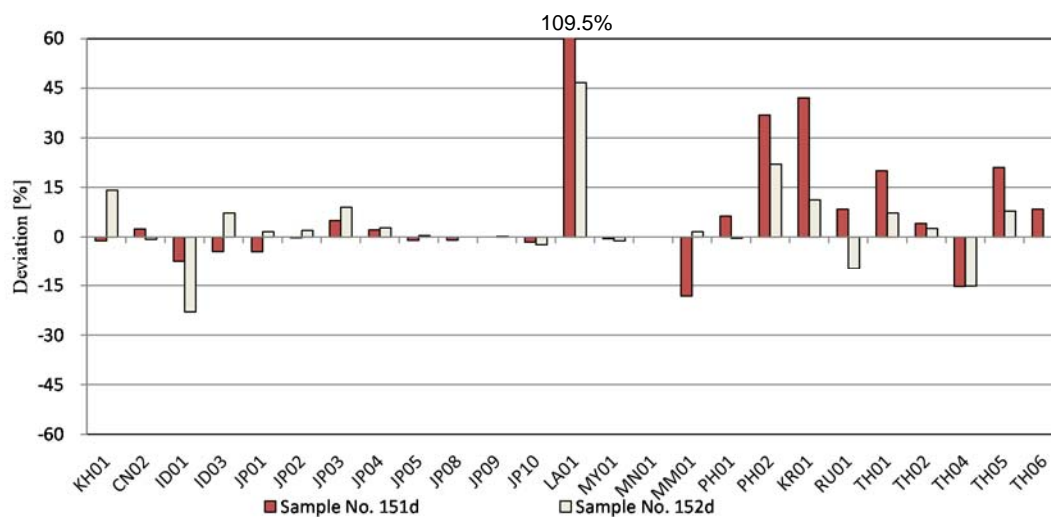
<u>Analytical Method</u>	
Ion Chromatography	27/27

Table 3.11.2 Flagged data of Cl⁻

<u>Flagged Data</u>	Flag E	Flag X	Flagged (%)
Sample No.151d	7	5	44.4
Sample No.152d	4	3	25.9

As with the analysis of Cl⁻, all laboratories used Ion Chromatography for the determination of Cl⁻. E flag appeared at 11 laboratories for Sample No.151d and No. 152d. X flag appeared at 8 laboratories for Sample No. 151d and No. 152d.

NH₄⁺ (Ammonium)

**Figure 3.5 Deviation for NH₄⁺****Table 3.12.1 Analytical method of NH₄⁺**

<u>Analytical Method</u>	
Ion Chromatography	26/26

Table 3.12.2 Flagged data of NH₄⁺			
<i>Flagged Data</i>	Flag E	Flag X	Flagged (%)
Sample No.151d	4	3	26.9
Sample No.152d	3	1	15.4

All laboratories used Ion Chromatography for the determination of NH₄⁺. E flag appeared at 7 laboratories for Sample No.151d and No.152d. X flag appeared at 4 laboratories.

3.3.3 Information on Laboratories

Methodologies used

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

Table 3.13 Analytical methods used for sample analysis		
Lab. Code	SO ₄ ²⁻ , Cl ⁻	NH ₄ ⁺
KH01	Ion Chromatography	Ion Chromatography
CN02		Ion Chromatography
ID01		Ion Chromatography
ID03		Ion Chromatography
JP01		Ion Chromatography
JP02		Ion Chromatography
JP03		Ion Chromatography
JP04		Ion Chromatography
JP05		Ion Chromatography
JP08		Ion Chromatography
JP09		Ion Chromatography
JP10		Ion Chromatography
LA01		Ion Chromatography
MY01		Ion Chromatography
MN01		Ion Chromatography
MM01		Ion Chromatography
PH01		Ion Chromatography
PH02		Ion Chromatography
KR01		Ion Chromatography

RU01	Ion Chromatography
TH01	Ion Chromatography
TH02	Ion Chromatography
TH04	Ion Chromatography
TH05	Ion Chromatography
TH06	Ion Chromatography
VN01	Ion Chromatography
VN02	Ion Chromatography

“—”: Not measured


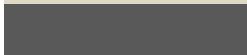
Years of staff experience

Years of staff experience are summarized in Table 3.14. Data in light gray color cells indicate that there is a flag for Sample No.151d or 152d. Data in dark gray color cells indicate flagged data in both Sample No.151d and No.152d.

Table 3.14 Years of staff experience (unit: year)

Lab. Code	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺
KH01	6	6	6
CN02	7	7	7
ID01	13	13	No information
ID03	5	5	5
JP01	31	31	31
JP02	2	2	2
JP03	1.5	1.5	1.5
JP04	1	1	1
JP05	2	2	2
JP08	2	2	2
JP09	9	9	9
JP10	4	4	4
LA01	3	3	3
MY01	5	5	9
MN01	12	12	--
MM01	4	4	4
PH01	10	10	10
PH02	1	1	1
KR01	3.5	3.5	3.5

RU01	15	15	34
TH01	6	6	6
TH02	12	12	12
TH04	4	4	4
TH05	15	15	15
TH06	10	10	10
VN01	22	22	22
VN02	2	2	2

 : One datum (either sample) is flagged.
 : Two data (both samples) are flagged.
 “—” : Not measured

Flagged Data

In the results of Sample No.151d and 152d, the total number of flagged data was 48 (E: 31, X: 17) in the whole values (160). The number of flagged data in each laboratory is shown in Figure 3.6. Nine laboratories met DQOs (33.3%).

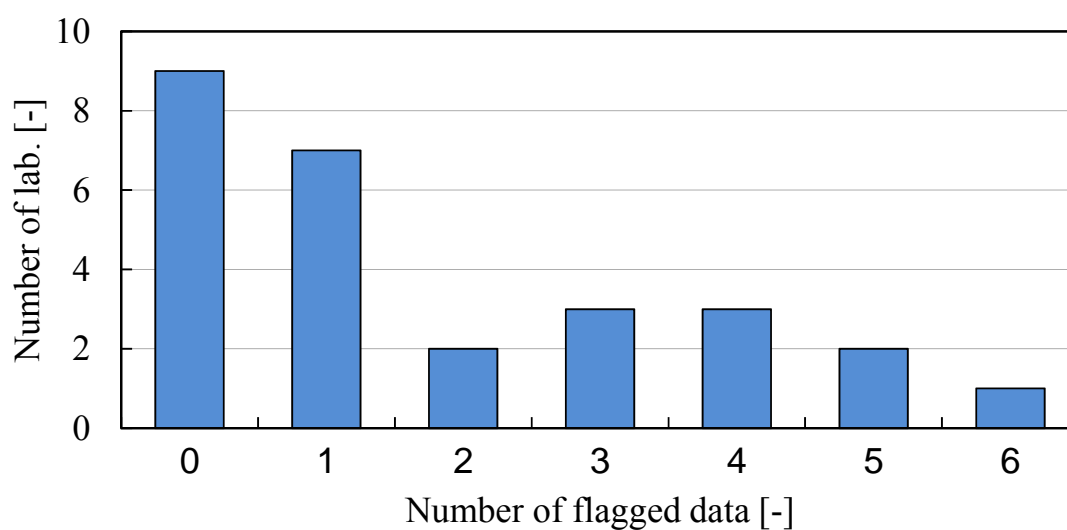


Figure 3.6 Number of flagged data and laboratories

Calibration standard solution

Table 3.15 shows the lowest and highest concentrations of their calibration standard solutions (SO_4^{2-} , Cl^- , NH_4^+) used in each laboratory, and also shows their concentrations of the prepared values in $\mu\text{mol L}^{-1}$. The concentrations of the standard solutions in some laboratories were not in the appropriate range. A gray highlighted value in Table 3.15 indicates that the concentration value of standard solution is lower than that of the prepared value. In contrast, some laboratories used extremely high concentration standards comparing with samples concentrations.

Each concentration of the prepared values was expected within the range of both concentrations of lowest and highest standard solutions. However, some laboratories used inappropriate solution ranges. If the concentrations of their obtained values were not in the range of the calibration standard, laboratories should have analyzed again with the appropriate concentration range of standard solution.

Table 3.15 Ranges of the calibration standard solution in each laboratory

Lab Code.	SO_4^{2-} ($\mu\text{mol L}^{-1}$)		Cl^- ($\mu\text{mol L}^{-1}$)		NH_4^+ ($\mu\text{mol L}^{-1}$)	
	Lowest	Highest	Lowest	Highest	Lowest	Highest
KH01	0.0	52.0	0.0	141.3	0.0	277.2
CN02	0.0	81.6	0.0	225.4	0.0	111.1
ID01	0.0	31.2	0.0	87.4	0.0	64.7
ID03	0.0	104.2	0.0	112.7	0.0	110.9
JP01	0.0	104.2	0.0	282.1	0.0	277.2
JP02	0.0	104.1	0.0	282.1	0.0	554.3
JP03	0.0	104.1	0.0	56.4	0.0	166.3
JP04	0.0	104.2	0.0	140.8	0.0	294.1
JP05	0.0	520.5	0.0	705.2	0.0	1385.8
JP08	0.0	104.1	0.0	282.1	0.0	277.2
JP09	0.3	62.5	0.8	169.3	1.7	332.6
JP10	0.0	52.1	0.0	70.5	0.0	277.2
LA01	0.9	52.2	3.0	141.7	5.1	277.5
MY01	0.0	104.0	0.0	281.9	0.0	166.4
MN01	--	--	--	--	--	--
MM01	0.0	73.2	0.0	40.9	0.0	161.0
PH01	0.0	104.1	0.0	282.1	0.0	554.0

PH02	8.8	155.8	5.3	72.1	0.7	550.2
KR01	0.0	104.3	0.0	282.2	0.0	563.8
RU01	0.0	285.6	0.0	285.6	0.0	277.8
TH01	0.0	104.3	0.0	284.6	0.0	556.7
TH02	0.2	62.5	0.6	169.3	1.1	277.2
TH04	0.0	19.8	0.0	54.8	0.0	111.0
TH05	0.0	62.5	0.0	112.8	0.0	221.7
TH06	0.0	72.9	0.0	197.5	0.0	166.3
VN01	0.0	104.1	0.0	141.0	0.0	277.2
VN02	0.0	83.3	0.0	112.8	0.0	110.9
*Sample No. 151d		9.37		4.94		26.3
*Sample No. 152d		38.5		19.7		141.4

Gray Cell : The measured value was out of the calibration range.

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

“—“ : No information

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

MW: molecular weight

3.4 Comparison with past surveys

This Inter-laboratory Comparison on dry deposition has been implemented since 2005. The results showing the percentages of flagged data and percentages of data that were satisfied the DQOs were shown in Figure 3.7.

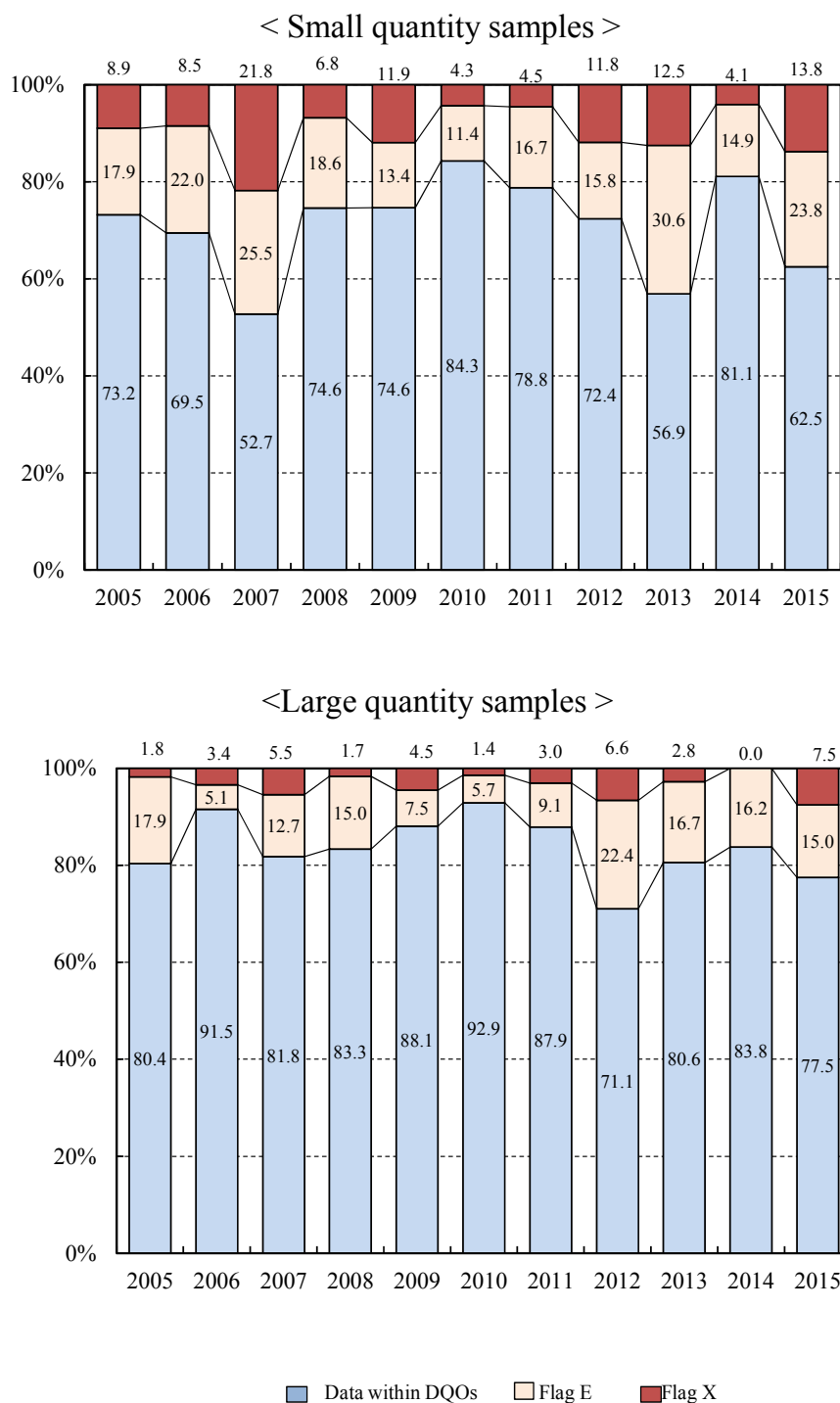


Figure 3.7 Comparison of DQOs' results for the past years

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

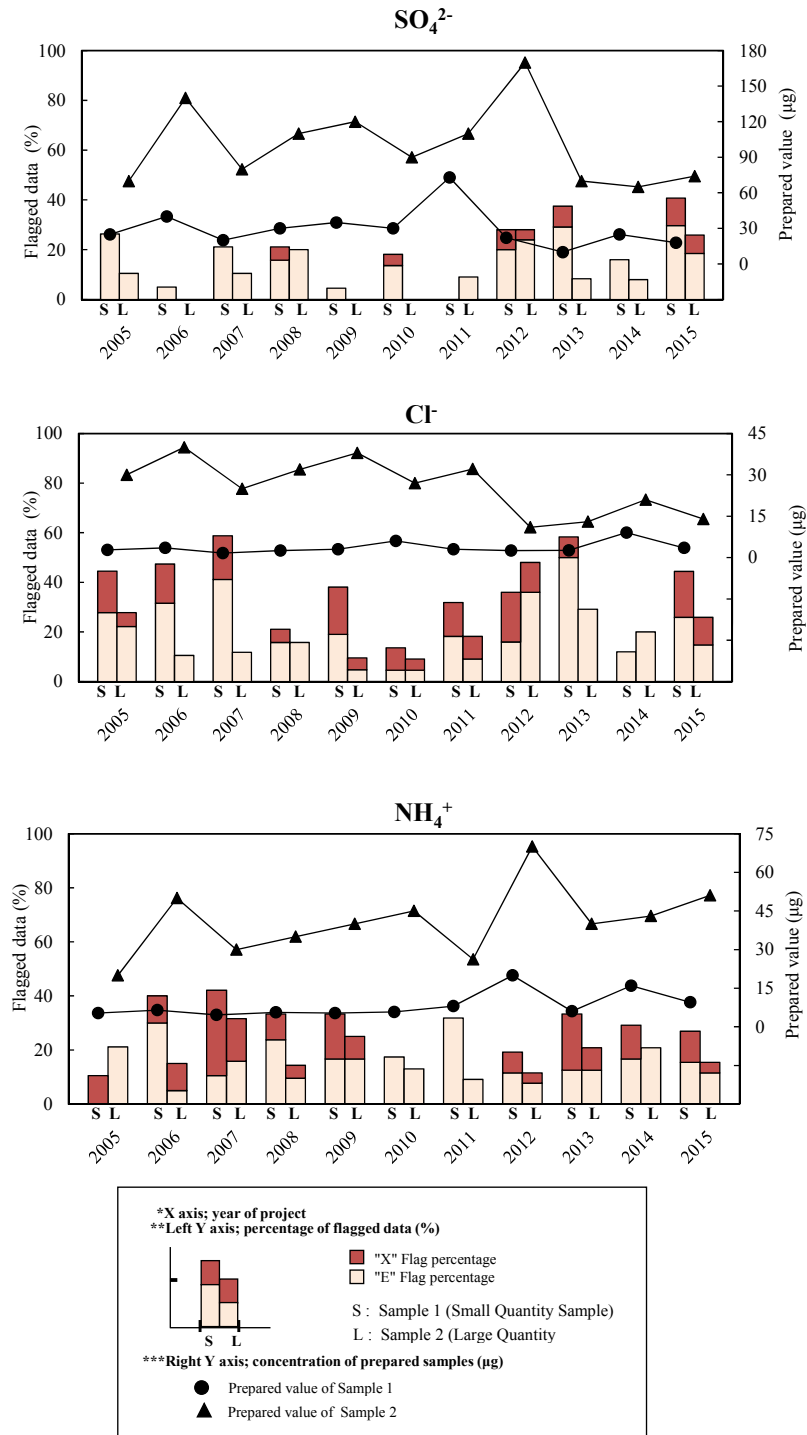


Figure 3.8 Comparison for each parameter in inter-laboratory comparison project

References

EANET (2000a). *Guidelines for Acid Deposition Monitoring in East Asia*. Acid Deposition and Oxidant Research Center, Niigata, Japan, 25p.

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

4. 17th 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 17th project, Network Center (NC) provided two soil samples (No.151s and No.152s) 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 7 countries participated in the 17th project. The results from 13 laboratories of those have been submitted to the network center and analyzed statistically. Names of the participating laboratories are listed in Table 1.1.

4.2.2 Description of Samples

The characteristics of the soil samples were as follows:

Sample No.151s: Acrisols

Sample No.152s: Cambisols

Soils for Sample No.151s and No.152s were collected in *Cryptomeria japonica* plantation in Niigata Prefecture, Japan. Both soils were collected from B-horizon composed chiefly of soil minerals. The soils were air-dried, sieved to separate the fine earth fraction (< 2 mm) and mixed well by the following procedures; 1) the bulk sample was divided into two parts, 2) each part was mixed well, 3) the parts were joined and mixed well and 4) the sample was divided again. This procedure was repeated 15 times to ensure a completely homogeneous bulk sample. Finally, portions of 400 - 500 g were weighed out, packed in 500 ml plastic bottles, and then, sterilized using radioisotope (20 kGy) for distributing (exporting) to the participating countries.

4.2.3 Parameters Analyzed

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

Table 4.1 Parameters to be measured

Parameters	Unit	No.151s and 152s
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** 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 100g-Sr/L solution to be 1000mg-Sr/L 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 100g-Sr/L 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:

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

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

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

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

Where

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

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

mcf = Moisture correction factor (Measured value)

S = Weight of air-dry sample (g)

V = Volume of extract (mL)

4.2.4.3 Procedures for Ex-acidity

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

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

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

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

Where

A_{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 0.025M NaOH solution needed for blank (mL)

bl_{HCl} = Titration volume of 0.02M HCl solution needed for blank (mL)

M_{NaOH} = Molarity of NaOH solution (mol/L)

M_{HCl} = Molarity of HCl solution (mol/L)

S = Weight of air-dry sample (g)

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

4.2.4.4 Reporting

(1) Preparation of the report

Digital formats (Microsoft Excel) were provided to the participating laboratories. Chemical

properties of soil sample were calculated automatically by the formula written in the formats.

(2) Submission of the report

Entered data in digital formats and other information (e.g. calibration curve) were submitted by E-mail.

4.2.4.5 Data Checking Procedures

We statistically evaluated the data according to the following procedures described in the “Technical Manual for Soil and Vegetation Monitoring in East Asia” (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 13 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 was shown in Table 4.2. On the 17th inter-laboratory project, pH(H₂O), pH(KCl), Ex-base cations, and Ex-acidity were largely different between both samples. pH(H₂O) and Ex-base cations were higher in No.151s than in No.152s, whereas pH(KCl) and Ex-acidity were higher in No.152s than in No.151s. We observed the large variations in the analyzed data (CVs) of Ex-Ca, Ex-Mg, Ex-K, Ex-acidity, Ex-Al and Ex-H in both samples (> 15%). Meanwhile, in both samples, CVs were relatively small for both pH(H₂O) and pH(KCl) (< 7%).

Table 4.2 Statistical summary

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. 151s									
Number of Laboratories	13	13	10	10	10	10	13	13	13
Total average	5.0	3.9	3.93	1.10	0.60	0.22	3.98	3.12	0.85
Median	5.0	3.9	3.98	1.12	0.64	0.22	4.00	3.25	0.51
Maximum	5.2	4.1	5.03	1.30	0.71	0.28	5.23	4.33	5.23
Minimum	4.2	3.8	2.27	0.67	0.36	0.19	2.93	0.00	0.32
Standard deviation	0.3	0.1	0.84	0.18	0.11	0.02	0.61	1.03	1.32
CV (%) ^{*1}	6.0	2.6	21.4	16.4	18.3	9.1	15.3	33.0	155.3
No. 152s									
Number of Laboratories	13	13	10	10	10	10	13	13	13
Total average	4.7	4.1	0.19	0.21	0.27	0.16	5.11	4.13	0.97
Median	4.8	4.1	0.17	0.22	0.26	0.15	4.88	4.21	0.43
Maximum	4.9	4.3	0.39	0.26	0.38	0.19	7.23	5.43	7.23
Minimum	3.9	4.0	0.08	0.14	0.21	0.14	3.73	0.00	0.12
Standard deviation	0.3	0.1	0.09	0.04	0.04	0.01	0.97	1.39	1.90
CV (%) ^{*1}	6.4	2.4	47.4	19.0	14.8	6.3	19.0	33.7	195.9

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

We also have an overview of the data by box-and-whisker plot (Figure 4.1) of No.151s and 152s 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 because the values were 5-20 times higher or lower than average. Therefore, in following section, we removed these outliers by parametrically statistical method to calculate the good reference more close to true value.

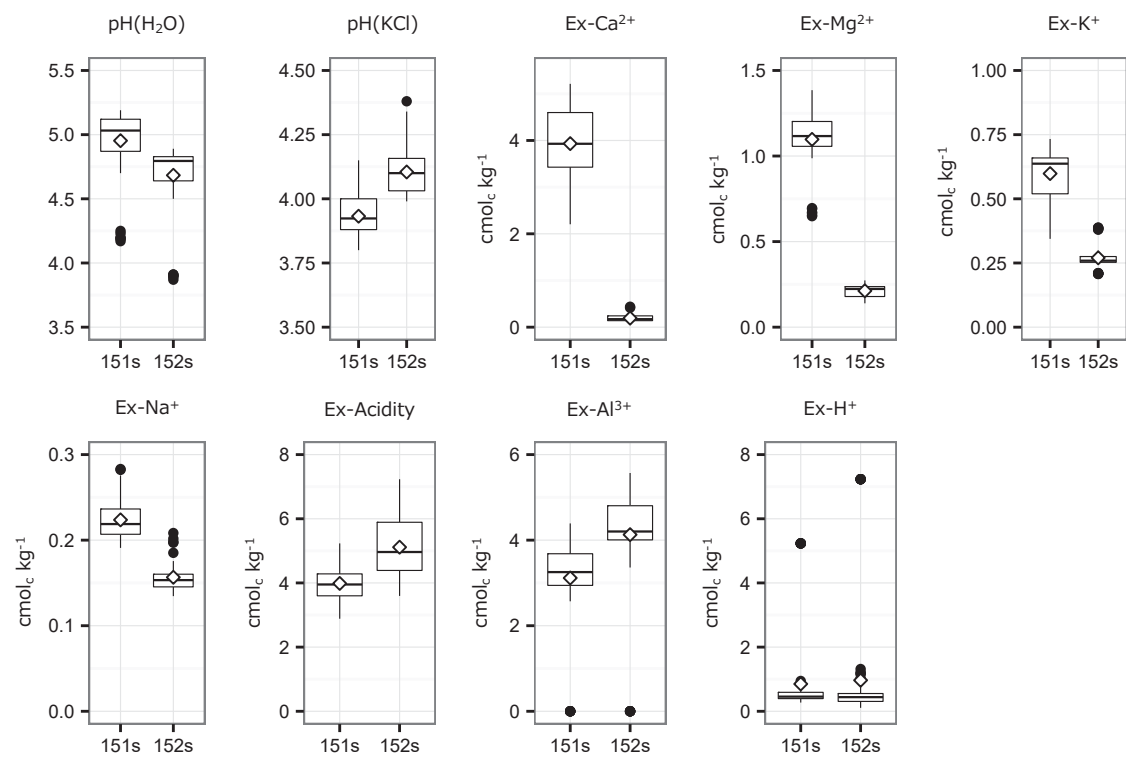


Fig. 4.1 Data variability of No. 151s and 152s

Table 4.3 Data verification by Cochran-Grubbs methods

No. 151s

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 kg ⁻¹						
China	CN01	1st	4.9	3.8	4.56	1.00	0.65	0.21	3.57	3.18	0.39
		2nd	4.9	3.8	4.55	1.00	0.66	0.21	3.56	3.18	0.38
	CN02	1st	5.1	4.0	3.52	1.06	0.52	0.21	4.27	3.66	0.61
		2nd	5.1	4.0	3.55	1.06	0.52	0.21	4.30	3.75	0.63
	CN03	1st	5.0	4.0	2.26	0.68 g	0.36 g	0.19	4.74	4.36	0.38
		2nd	5.0	4.0	2.27	0.66 g	0.35 g	0.20	4.67	4.29	0.38
	CN04	1st	5.1	3.9	3.43	1.05	0.49	0.23	3.98 c	3.30	0.68 c
		2nd	5.1	3.9	3.40	1.08	0.50	0.25	4.13 c	3.27	0.86 c
Indonesia	ID01	1st	5.2	3.9	5.09	1.22	0.68	0.24	3.95	3.42	0.53
		2nd	5.2	3.9	4.96	1.14	0.71	0.23	3.98	3.45	0.54
	ID04	1st	4.8	4.0	4.38	1.16	0.65	0.28 g	2.94	2.59	0.35 c
		2nd	4.8	4.0	4.48	1.19	0.64	0.28 g	2.93	2.64	0.29 c
Mongolia	MN01	1st	4.2 g	4.1	NA	NA	NA	NA	5.23	0.00 g	5.23 g
		2nd	4.2 g	4.1	NA	NA	NA	NA	5.23	0.00 g	5.23 g
Korea	KR01	1st	5.1	4.0	3.44	1.10	0.64	0.21	3.64	3.25	0.39
		2nd	5.2	4.0	3.39	1.10	0.64	0.21	3.64	3.25	0.40
Russia	RU01	1st	5.0	3.9	4.22 c	1.24	0.63	0.24	3.57	3.19	0.43
		2nd	5.0	3.9	4.63 c	1.36	0.63	0.24	3.65	3.31	0.40
Thailand	TH01	1st	5.1	3.9	3.41	1.13	0.62	0.20	3.86 c	2.87 c	0.59
		2nd	5.1	3.9	3.61	1.17	0.66	0.21	4.14 c	3.36 c	0.57
Vietnam	VN01	1st	5.1	3.9	4.75	1.28	0.71	0.23	3.25	2.83	0.42
		2nd	5.1	3.9	4.74	1.28	0.71	0.23	3.26	2.84	0.42
	VN02	1st	4.9	3.9	NA	NA	NA	NA	4.28	3.74	0.50
		2nd	4.9	3.9	NA	NA	NA	NA	4.28	3.74	0.54
	VN04	1st	4.9	3.9	NA	NA	NA	NA	4.26	3.76	0.51
		2nd	4.9	3.9	NA	NA	NA	NA	4.26	3.76	0.51

No. 152s

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 kg ⁻¹						
China	CN01	1st	4.6	4.0	0.24	0.19	0.26	0.15	4.12	4.00	0.12
		2nd	4.6	4.0	0.25	0.19	0.26	0.15	4.17	4.06	0.11
	CN02	1st	4.8	4.2	0.14	0.18	0.21 g	0.15	5.25	4.74	0.50
		2nd	4.8	4.2	0.14	0.18	0.21 g	0.15	5.35	4.80	0.55
	CN03	1st	4.8	4.1	0.15	0.15	0.29	0.16	5.90	5.48	0.42
		2nd	4.8	4.1	0.15	0.14	0.28	0.16	5.82	5.38	0.45
	CN04	1st	4.9	4.0	0.17	0.22	0.25	0.15	5.64	4.51	1.24 g
		2nd	4.9	4.0	0.18	0.23	0.26	0.14	5.53	4.52	1.02 g
Indonesia	ID01	1st	4.9	4.1	0.19	0.25	0.26	0.16	4.62	4.20	0.42
		2nd	4.9	4.1	0.20	0.23	0.25	0.15	4.62	4.23	0.39
	ID04	1st	4.5	4.2 c	0.27	0.26	0.38 g	0.19 g	3.67	3.40	0.28
		2nd	4.5	4.1 c	0.26	0.26	0.39 g	0.19 g	3.79	3.40	0.39
Mongolia	MN01	1st	3.9 g	4.3 g	NA	NA	NA	NA	7.23	0.00 g	7.23 g
		2nd	3.9 g	4.3 g	NA	NA	NA	NA	7.23	0.00 g	7.23 g
Korea	KR01	1st	4.8	4.2	0.12	0.18	0.25	0.14	4.39	4.17	0.21
		2nd	4.8	4.2	0.12	0.18	0.25	0.14	4.39	4.17	0.22
Russia	RU01	1st	4.8	4.1	0.40 g	0.27 c	0.28	0.17	4.79	4.35	0.46
		2nd	4.8	4.1	0.39 g	0.24 c	0.28	0.17	4.53	4.31	0.24
Thailand	TH01	1st	4.8	4.0	0.16	0.22	0.27	0.15	4.80	4.21	0.30
		2nd	4.8	4.0	0.16	0.22	0.27	0.15	4.97	4.13	0.56
Vietnam	VN01	1st	4.8	4.1	0.08	0.23	0.26	0.15	4.22	3.86	0.36
		2nd	4.8	4.1	0.08	0.23	0.26	0.15	4.21	3.88	0.36
	VN02	1st	4.7	4.1	NA	NA	NA	NA	5.93	5.43	0.48
		2nd	4.7	4.1	NA	NA	NA	NA	5.91	5.43	0.48
	VN04	1st	4.6	4.0	NA	NA	NA	NA	5.95	5.35	0.55
		2nd	4.6	4.0	NA	NA	NA	NA	5.94	5.35	0.55

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

4.3.2 Detection of outliers

Detection of outliers by Cochran-Grubbs methods were shown in Table 4.3. The laboratory which has a large difference in repeat analyses was judged as outlier by Cochran method (examination of the evenness of within-laboratory precision); e.g. “RU01” in Ex-Ca, “CN04” in Ex-acidity of No.151s. Then, the rest of data were tested by Grubbs method (examination of the average value of each laboratory). In this method, the laboratory which has remarkably large or small average was judged as outliers. Cochran-Grubbs method detected the several outliers for each parameter. As a result of removing outliers, the “verified” dataset consisting of 11-13 laboratories in pH(H₂O) and pH(KCl), 8-9 laboratories in Ex-base cations and 10-13 laboratories in Ex-acidity, Al and H were used for further analysis in the following section.

4.3.3 Statistical summary for verified data

The statistical summary for verified datasets in No.151s and No.152s were shown in Table 4.4. Although the chemical properties in both soils were not largely changed by verification, the data variability of almost all items decreased from the entire dataset. However, these variations were still too large to compare the regular monitoring data among the participating countries, accurately. The variation may include an error produced by same person (repetition), different person (within-laboratory) or different laboratories (inter-laboratory). We separated this variation in next section to detect the source of it.

Table 4.4 Statistical summary of the “verified” dataset^{*2}

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. 151s									
Number of Laboratories	12	13	9	9	9	9	11	11	10
Total average	5.0	3.9	3.88	1.14	0.63	0.22	3.98	3.40	0.48
Median	5.1	3.9	3.54	1.15	0.64	0.21	3.97	3.28	0.46
Maximum	5.2	4.1	5.03	1.30	0.71	0.24	5.23	4.33	0.62
Minimum	4.8	3.8	2.27	1.00	0.49	0.19	2.93	2.62	0.38
Standard deviation	0.1	0.1	0.87	0.10	0.07	0.02	0.66	0.47	0.09
CV (%) ^{*1}	2.0	2.6	22.4	8.8	11.1	9.1	16.6	13.8	18.8
No. 152s									
Number of Laboratories	12	11	9	9	8	9	13	12	11
Total average	4.7	4.1	0.17	0.21	0.26	0.15	5.11	4.47	0.38
Median	4.8	4.1	0.16	0.22	0.26	0.15	4.88	4.27	0.41
Maximum	4.9	4.2	0.27	0.26	0.28	0.17	7.23	5.43	0.55
Minimum	4.5	4.0	0.08	0.14	0.25	0.14	3.73	3.40	0.12
Standard deviation	0.1	0.1	0.06	0.04	0.01	0.01	0.97	0.65	0.13
CV (%) ^{*1}	2.1	2.4	35.3	19.0	3.8	6.7	19.0	14.5	34.2

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

^{*2}: Dataset is verified removing outliers determined by Cochran-Grubbs methods.

4.3.4 Analysis of variance for verified data

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

1) Repeatability-precision

Repeatability-precision was enough high for all properties. The CVs were less than 1% in both pH(H₂O) and pH(KCl), < 5% in Ex-base cations, Ex-acidity and Ex-Al, while it was almost 15% in Ex-H. The result suggests that triplicate analyses were carried out under the same condition. In general, the participating laboratories could analyze the parameters with their own standard procedures and stable instruments.

2) Within-laboratory precision

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

3) Inter-laboratories precision

The CVs in the inter-laboratories precision were less than 3% in pH (H₂O) and pH (KCl). However, the CVs of the rest of the items ranged from 5 to 35%. Thus, in this inter-laboratory comparison, almost all error in each parameter was produced by different laboratories. We discussed the possible factor of the relatively high CVs in inter-laboratory precision, in the following section.

4) Calculation of permissible tolerance

The repeatability limit and within-laboratory reproducibility limit might be enough small to use as a reference value for the repeat analysis on the instrumental analysis in the respective laboratories. For assessment of temporal pH change of monitoring data at each site, participating laboratories can detect the significant change more than 0.1 pH units. Meanwhile, the result about reproducibility limit (inter-laboratories reproducibility limit) suggested that participating laboratories can detect the significant difference between the monitoring sites if the differences are more than about 0.4 for pH(H₂O), 0.2 for pH(KCl), 0.03-2.4 cmol_c kg⁻¹ for Ex-base cations, 1-3 cmol_c kg⁻¹ for Ex-acidity and Ex-Al, and 0.3-0.4 cmol_c kg⁻¹ for Ex-H.

Table 4.5 Analysis of variance for “verified” dataset

Statistics	No. 151s								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	12	13	9	9	9	9	11	11	10
Total sum of square	130000	94000	44000	3800	1100	140	69000	50000	810
ST/lmd	1800	1200	810	71	21	2.6	1000	760	14
Number of Laboratories	12	13	9	9	9	9	11	11	10
Number of Data	72	78	54	54	54	54	66	66	60
Total sum	360	310	210	62	34	12	260	220	29
Total average	5.0	3.9	3.88	1.14	0.63	0.22	3.98	3.40	0.48
Sum of square inter-laboratories (S _R)	1.2	0.4	36.64	0.48	0.25	0.01	26.41	13.45	0.42
Sum of square within-laboratory (S _{RW})	0.0	0.0	0.11	0.04	0.00	0.00	0.02	0.05	0.00
Sum of square repeatability (S _r)	0.0	0.0	0.16	0.01	0.01	0.00	0.07	0.15	0.19
Total sum of square (S _T)	1.2	0.4	36.91	0.53	0.26	0.02	26.51	13.66	0.61
Inter-laboratories degree of freedom (φ _R)	11	12	8	8	8	8	10	10	9
Within-laboratory degree of freedom (φ _{RW})	12	13	9	9	9	9	11	11	10
Repeatability degree of freedom (φ _r)	48	52	36	36	36	36	44	44	40
Total degree of freedom (φ _T)	71	77	53	53	53	53	65	65	59
Inter-laboratories variance (V _R = S _R /φ _R)	0.1	0.0	4.58	0.06	0.03	0.00	2.64	1.35	0.05
Within-laboratory variance (V _{RW} = S _{RW} /φ _{RW})	0.0	0.0	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability variance (V _r = S _r /φ _r)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Laboratory component of variance (s _b ² = (V _R -V _{RW})/(2*3))	0.0	0.0	0.76	0.01	0.01	0.00	0.44	0.22	0.01
Within-laboratory component of variance (s _c ² = (V _{RW} -V _r)/3)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability component of variance (s _r ² = V _r)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Inter-laboratories standard deviation (s _R = SQRT(s _b ² /(2*3) + s _c ² /2 + s _r ²))	0.1	0.1	0.87	0.10	0.07	0.02	0.66	0.47	0.09
Within-laboratory standard deviation (s _{RW} = SQRT(s _r ² /3 + s _c ²))	0.0	0.0	0.06	0.04	0.01	0.00	0.03	0.04	0.01
Repeatability standard deviation (s _r = SQRT(s _r ²))	0.0	0.0	0.07	0.02	0.01	0.01	0.04	0.06	0.07
Inter-laboratories precision CV (%)	2.6	1.9	22.53	8.75	11.51	7.56	16.68	13.93	18.44
Within-laboratory precision CV (%)	0.2	0.2	1.64	3.18	1.96	2.25	0.67	1.14	2.58
Repeatability precision CV (%)	0.6	0.4	1.74	1.48	1.94	3.02	1.04	1.74	14.54
Reproducibility limit (R = D(2, 0.95)*s _R)	0.4	0.2	2.45	0.28	0.20	0.05	1.86	1.33	0.25
Within-laboratory-reproducibility limit (R _W = D(2, 0.95)*s _{RW})	0.0	0.0	0.18	0.10	0.03	0.01	0.07	0.11	0.03
Repeatability limit (r = D(3, 0.95)*s _r)	0.1	0.1	0.22	0.06	0.04	0.02	0.14	0.19	0.23
Statistics	No. 152s								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	12	11	9	9	8	9	13	12	11
Total sum of square	120000	73000	85	130	160	68	160000	100000	640
ST/lmd	1600	1100	1.6	2.3	3.3	1.3	2000	1400	9.6
Number of Laboratories	12	11	9	9	8	9	13	12	11
Number of Data	72	66	54	54	48	54	78	72	66
Total sum	340	270	9.2	11	13	8.2	400	320	25
Total average	4.7	4.1	0.17	0.21	0.26	0.15	5.11	4.47	0.38
Sum of square inter-laboratories (S _R)	0.9	0.2	0.17	0.07	0.01	0.00	67.87	27.95	0.99
Sum of square within-laboratory (S _{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.21	0.04	0.21
Sum of square repeatability (S _r)	0.0	0.0	0.00	0.00	0.00	0.00	0.49	0.49	0.11
Total sum of square (S _T)	0.9	0.2	0.17	0.07	0.01	0.01	68.58	28.48	1.31
Inter-laboratories degree of freedom (φ _R)	11	10	8	8	7	8	12	11	10
Within-laboratory degree of freedom (φ _{RW})	12	11	9	9	8	9	13	12	11
Repeatability degree of freedom (φ _r)	48	44	36	36	32	36	52	48	44
Total degree of freedom (φ _T)	71	65	53	53	47	53	77	71	65
Inter-laboratories variance (V _R = S _R /φ _R)	0.1	0.0	0.02	0.01	0.00	0.00	5.66	2.54	0.10
Within-laboratory variance (V _{RW} = S _{RW} /φ _{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.02	0.00	0.02
Repeatability variance (V _r = S _r /φ _r)	0.0	0.0	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Laboratory component of variance (s _b ² = (V _R -V _{RW})/(2*3))	0.0	0.0	0.00	0.00	0.00	0.00	0.94	0.42	0.01
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	0.01
Repeatability component of variance (s _r ² = V _r)	0.0	0.0	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Inter-laboratories standard deviation (s _R = SQRT(s _b ² /(2*3) + s _c ² /2 + s _r ²))	0.1	0.1	0.06	0.04	0.01	0.01	0.97	0.65	0.13
Within-laboratory standard deviation (s _{RW} = SQRT(s _r ² /3 + s _c ²))	0.0	0.0	0.00	0.00	0.01	0.00	0.07	0.03	0.08
Repeatability standard deviation (s _r = SQRT(s _r ²))	0.0	0.0	0.01	0.00	0.01	0.01	0.10	0.10	0.05
Inter-laboratories precision CV (%)	2.4	1.5	34.57	17.93	4.48	5.82	18.98	14.55	33.66
Within-laboratory precision CV (%)	0.3	0.2	1.67	1.87	1.99	2.41	1.45	0.75	20.73
Repeatability precision CV (%)	0.3	0.2	3.47	2.40	2.79	3.86	1.90	2.26	13.15
Reproducibility limit (R = D(2, 0.95)*s _R)	0.3	0.2	0.17	0.10	0.03	0.02	2.72	1.82	0.36
Within-laboratory-reproducibility limit (R _W = D(2, 0.95)*s _{RW})	0.0	0.0	0.01	0.01	0.01	0.01	0.21	0.09	0.22
Repeatability limit (r = D(3, 0.95)*s _r)	0.1	0.0	0.02	0.02	0.02	0.02	0.32	0.33	0.17

4.3.5 Inter-laboratory variations in each parameter

To assess the precision in each laboratories and properties, we showed scatter plots between No.151s and No.152s with its “verified” mean indicated by solid line (Figure 4.2). As a guide for comparison, mean \pm standard deviation was added by dotted lines. The plot did not include extreme outliers for eye-friendly.

1) pH

Linear correlation between No.151s and No.152s indicated 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 to the stabilization of value may lead to the variation because a carbon dioxide pressure, leakage of KCl solution from the electrode or settling the clay particles in the sample tube change the ion balance in soil suspension. Meanwhile, most laboratories were included within the range of mean \pm S.D. for No.151s and No.152s.

2) Base cations

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

3) Acidity

The plots of Ex-acidity and Ex-Al indicated 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. Participating laboratories should check the standard of procedure based on the Technical Manual for Soil and Vegetation Monitoring (EANET, 2000).

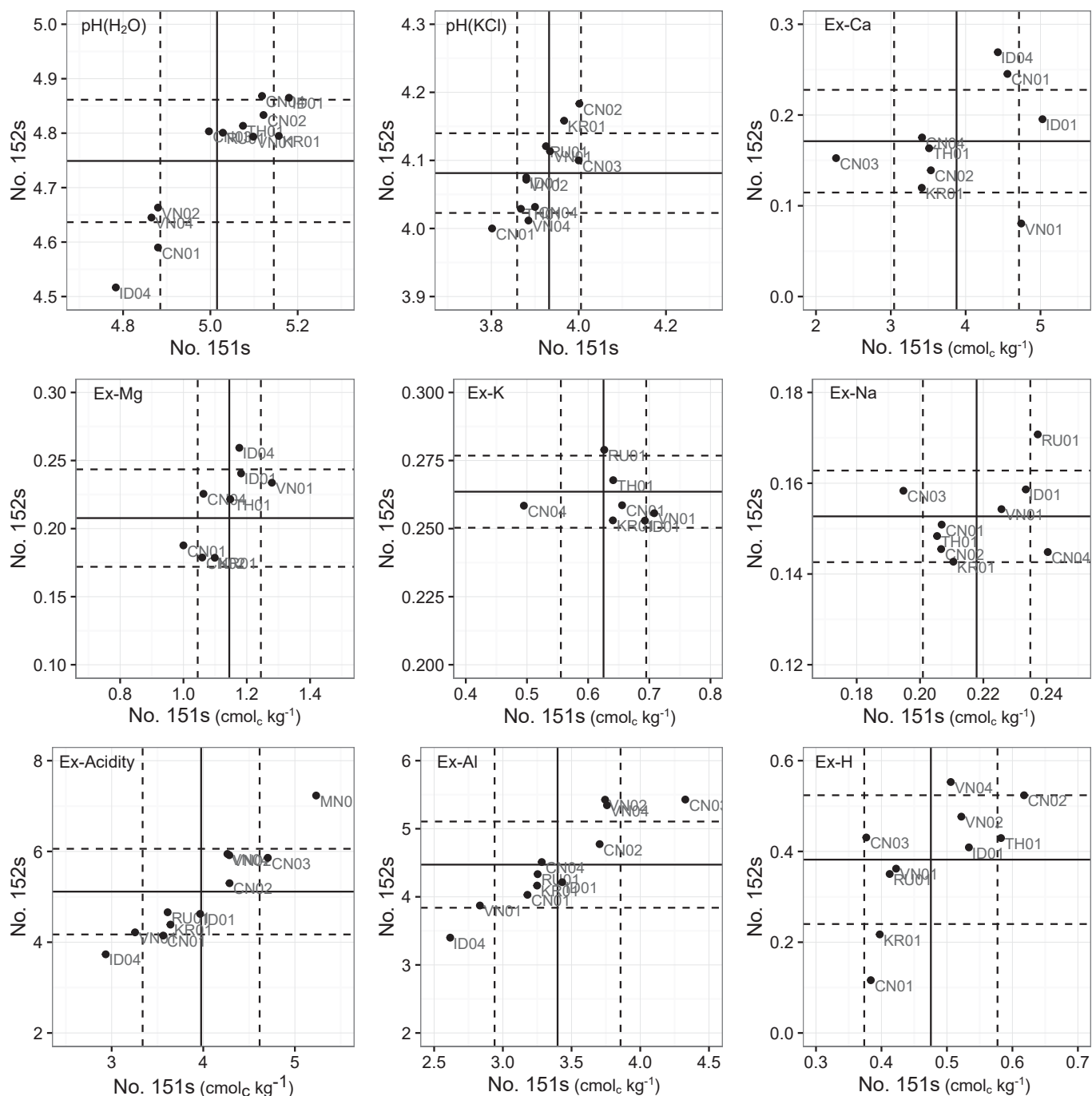


Fig. 4.2 Scatter plots of each soil chemical property between 151s and 152s
Solid and dotted lines indicate mean and mean \pm SD of verified dataset, respectively.
Raw data reported from laboratories are used in these plots.

4.3.6 Comparison with information on Laboratories

1) Number of analysts and their experience

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

2) Analytical instruments and condition of instruments

Analytical instruments used for the measurement, procedures for extraction of base cations, and size of burette used for the titration method in Ex-acidity were shown in Table 4.7. Ex-base cations were analyzed either ICP-AES, ICP-OES or AAS. FEP was not used in the 17th inter-laboratory comparison. Years in use of instruments ranged from 1 to 30.

Four laboratories used percolation tube procedures for extraction of exchangeable base cations, while Buchner funnel procedures, centrifuge procedures and automatic extractor procedures were used in 2, 3 and 1 laboratories, respectively. No clear difference was observed among data by different procedures. As for the size of burette for titration of Ex-acidity, the capacities were varied from 5 to 50 ml while minimum graduates were 0.00125 to 0.1.

3) Date of analysis

Dates of analysis in the respective laboratories and days used for the analysis were shown in Table 4.8. There was no significant implication between date of analysis and the data. Days used for the analysis were only one or two days in most laboratories. Interval between the first and second analyses of the repeat analyses was varied from 0 (in a same day) to 35 days. It was suggested that repeat analyses would be carried out with several-day interval (three days or more) in order to estimate actual within-laboratory reproducibility, as a supplementary instruction for the project, based on the discussion at SAC3 (The third session of the Scientific Advisory Committee on EANET). Mostly half of the laboratories followed the recommendation, although a few laboratories might conduct the instrumental analysis of both samples in a same day.

Table 4.6 Number and experience of analyst

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience		Number of analyst	Years of experience		
		Chemical	Soil		Chemical	Soil	
CN01	3	8	8	3	8	8	s
CN02	1	13	2	1	10	10	d
CN03	1	5	5	1	20	17	d
CN04	1	9	7	1	9	7	s
ID01	1	11	8	1	11	8	s
ID04	1	33	31	1	17	15	d
MN01	-	-	-	1	14	14	-
KR01	1	10	7	1	10	7	s
RU01	1	15	12	1	15	12	s
TH01	1	12	12	1	22	5	d
VN01	1	23	18	1	23	18	s
VN02	-	-	-	1	11	7	-
VN04	-	-	-	1	12	11	-

-, not analyzed; n, no information; s, same analysts; d, different analysts.

Table 4.7 Analytical instruments and their conditions for exchangeable cations

Lab.	Sample	Ex-Ca		Ex-Mg		Interference depressant for Ca and Mg	Ex-K		Ex-Na		Interference depressant for K and Na	Procedures for extraction of Ex-base cations	method	Ex-Acidity, Al and H	
		Instrument	Years ^{*1}	Instrument	Years		Instrument	Years	Instrument	Years				Size of burette (ml)	
														Capacity	Minimum graduate
CN01	No.151	AAS	8	AAS	8	La	AAS	8	AAS	8	La	Centrifuge	Titration	10	0.1
	No.152	AAS	8	AAS	8	La	AAS	8	AAS	8	La			10	0.1
CN02	No.151	AAS	5	AAS	5	Sr	AAS	5	AAS	5	Sr	Percolation tube	Titration	25	0.1
	No.152	AAS	5	AAS	5	Sr	AAS	5	AAS	5	Sr			25	0.1
CN03	No.151	AAS	6	AAS	6	Sr	AAS	6	AAS	6	La	Automatic extractor	Titration	5	0.00125
	No.152	AAS	6	AAS	6	Sr	AAS	6	AAS	6	La			5	0.00125
CN04	No.151	ICP	3	ICP	3	+	ICP	3	ICP	3	+	Percolation tube	Titration	25	0.1
	No.152	ICP	3	ICP	3	+	ICP	3	ICP	3	+			25	0.1
ID01	No.151	AAS	11	AAS	11	La	AAS	11	AAS	11	La	Centrifuge	Titration	50	0.05
	No.152	AAS	11	AAS	11	La	AAS	11	AAS	11	La			50	0.05
ID04	No.151	AAS	1	AAS	1	+	AAS	1	AAS	1	+	Percolation tube	Titration	50	0.02
	No.152	AAS	1	AAS	1	+	AAS	1	AAS	1	+			50	0.02
MN01	No.151						-						Titration	25	0.1
	No.152													25	0.1
KR01	No.151	ICP-AES	2	ICP-AES	2	Sr	ICP-AES	2	ICP-AES	2	Sr	Centrifuge	Titration	5	0.01
	No.152	ICP-AES	2	ICP-AES	2	Sr	ICP-AES	2	ICP-AES	2	Sr			5	0.01
RU01	No.151	AAS	30	AAS	30	+	AAS	30	AAS	30	na	Percolation tube	Titration	5	0.05
	No.152	AAS	30	AAS	30	+	AAS	30	AAS	30	na			5	0.05
TH01	No.151	ICP-OES	2	ICP-OES	2	na	ICP-OES	2	ICP-OES	2	na	Buchner funnel	Titration	25	0.05
	No.152	ICP-OES	2	ICP-OES	2	na	ICP-OES	2	ICP-OES	2	na			25	0.05
VN01	No.151	AAS	9	AAS	9	+	AAS	9	AAS	9	+	Buchner funnel	Titration	10	0.05
	No.152	AAS	9	AAS	9	+	AAS	9	AAS	9	+			10	0.05
VN02	No.151						-						Titration	10	0.05
	No.152													10	0.05
VN04	No.151						-						Titration	10	0.05
	No.152													10	0.05

Table 4.8 Date of analysis and days used for the analysis

Lab.	Repeat	pH			Ex-Ca and Mg			Ex-K and Na			Ex-acidity, Al and H				
		Date ^{*1}	Analysis ^{*2}		Interval ^{*3}	Date ^{*1}	Analysis ^{*2}		Interval ^{*3}	Date ^{*1}	Analysis ^{*2}		Interval ^{*3}		
			Days				Days				Days			Days	
CN01	1st	2015/11/28	1	1	2015/12/2	1	9	2015/12/2	1	9	2015/12/12	1	1		
	2nd	2015/11/29	1		2015/12/11	1		2015/12/11	1		2015/12/13	1			
CN02	1st	2016/2/23	1	1	2016/2/24	2	1	2016/2/24	2	1	2016/2/23	1	2		
	2nd	2016/2/24	1		2016/2/25	2		2016/2/25	2		2016/2/25	1			
CN03	1st	2016/1/12	2	15	2016/1/13	3	15	2016/1/28	3	0	2016/1/14	2	14		
	2nd	2016/1/27	2		2016/1/28	3		2016/1/28	3		2016/1/28	3			
CN04	1st	2015/12/3	2	3	2016/1/13	8	2	2016/1/13	8	2	2016/1/12	3	11		
	2nd	2015/12/6	2		2016/1/15	8		2016/1/15	8		2016/1/23	2			
ID01	1st	2016/1/4	1	7	2016/1/17	3	8	2016/1/17	3	8	2016/1/6	2	6		
	2nd	2016/1/11	1		2016/1/25	4		2016/1/25	4		2016/1/12	2			
ID04	1st	2016/1/14	4	7	2016/1/14	4	7	2016/1/14	4	7	2016/1/14	4	7		
	2nd	2016/1/21	4		2016/1/21	4		2016/1/21	4		2016/1/21	4			
MN01	1st	2016/1/29	5	0		-			-		2016/1/29	5	0		
	2nd	2016/1/29	5								2016/1/29	5			
KR01	1st	2016/7/11	1	1	2016/7/21	1	1	2016/7/21	1	1	2016/7/18	1	1		
	2nd	2016/7/12	1		2016/7/22	1		2016/7/22	1		2016/7/19	1			
RU01	1st	2016/2/2	1	8	2016/2/4	2	8	2016/2/4	2	8	2016/2/1	1	7		
	2nd	2016/2/10	1		2016/2/12	2		2016/2/12	2		2016/2/8	1			
TH01	1st	2016/1/29	1	4	2016/1/27	3	35	2016/1/27	3	35	2016/1/12	2	8		
	2nd	2016/2/2	1		2016/3/2	61		2016/3/2	61		2016/1/20	2			
VN01	1st	2015/12/16	1	7	2015/12/16	1	7	2015/12/16	1	7	2015/12/16	1	7		
	2nd	2015/12/23	1		2015/12/23	1		2015/12/23	1		2015/12/23	1			
VN02	1st	2015/12/22	1	0		-			-		2015/12/24	2	0		
	2nd	2015/12/22	1								2015/12/24	2			
VN04	1st	2015/12/18	5	0		-			-		2015/12/18	5	0		
	2nd	2015/12/18	5								2015/12/18	5			

^{*1}, Finish date of 1st and 2nd analyses; ^{*2}, Days used for analysis; ^{*3}, Interval between the repeat analyses; +, not reported.

4.4 Needs for improvement of soil analysis

Figure 4.3 shows the change of outlier ratio in all properties and laboratories from 2002 to 2015 (the ratio is calculated by $\{(N \text{ of entire dataset}) - (N \text{ of verified dataset})\} / (N \text{ of entire dataset})$). Although the ratio decreased from first experiment in 2002, this is still high (10-20% from 2003 to 2015).

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 liquid, dilution rate and calculation should be checked to reduce the extremely wrong value which is considered as outlier.

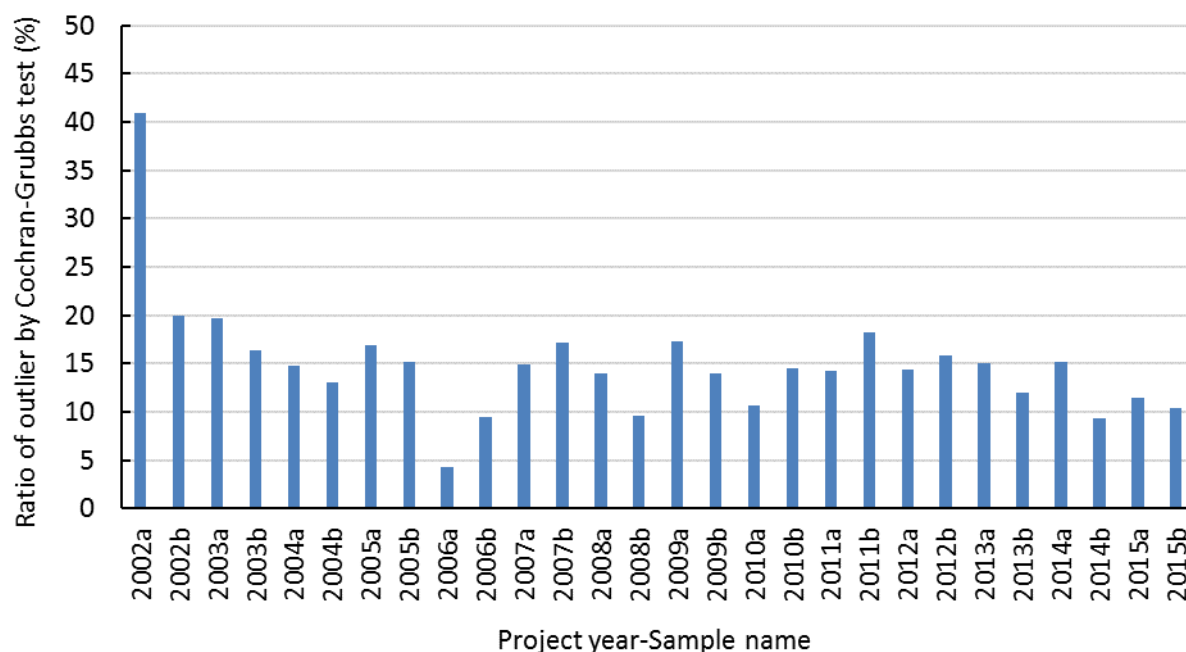


Figure 4.3 Change of the outlier ratio in all properties and laboratories from 2002 to 2015 calculated by $\{(N \text{ of entire dataset}) - (N \text{ of verified dataset})\} / (N \text{ of entire dataset})$. "a" and "b" show the 2 kinds of the samples in each year (e.g. 151s and 152s). The ratios from 2002 to 2014 were from *Report of Inter-Laboratory Comparison Project 2000-2014* (<http://www.eanet.asia/product/index.html>).

4.5 Recommendations

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

References

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

Appendix Table 4.1 Results submitted by the laboratories (sample No. 151s)

Appendix Table 4.2 Results submitted by the laboratories (sample No. 152s)

Lab	pH(H ₂ O)			pH(KCl)			Ex-Ca			Ex-Mg			Ex-K			Ex-Na			Ex-Acidity			Ex-Al			Ex-H		
	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 (0.0)	4.6 (0.0)	4.6 (0.0)	4.0 (0.0)	4.0 (0.0)	4.0 (0.0)	0.25 (0.01)	0.24 (0.01)	0.26 (0.01)	0.19 (0.01)	0.19 (0.01)	0.20 (0.01)	0.26 (0.01)	0.26 (0.01)	0.27 (0.01)	0.15 (0.01)	0.15 (0.01)	0.15 (0.01)	4.15 (0.14)	4.12 (0.20)	4.32 (0.15)	4.03 (0.22)	4.00 (0.22)	3.77 (0.01)	0.12 (0.01)	0.12 (0.02)	0.14 (0.11)
	4.6 (0.0)	4.6 (0.0)	4.6 (0.0)	4.0 (0.0)	4.0 (0.0)	4.0 (0.0)	0.25 (0.01)	0.24 (0.01)	0.26 (0.01)	0.19 (0.01)	0.19 (0.01)	0.17 (0.01)	0.26 (0.00)	0.26 (0.00)	0.26 (0.00)	0.15 (0.01)	0.15 (0.01)	0.15 (0.01)	4.17 (0.05)	4.17 (0.05)	4.12 (0.05)	4.06 (0.06)	4.06 (0.06)	4.06 (0.06)	0.11 (0.01)	0.11 (0.01)	0.12 (0.11)
CN02	4.8 (0.0)	4.8 (0.0)	4.8 (0.0)	4.2 (0.0)	4.2 (0.0)	4.2 (0.0)	0.14 (0.00)	0.14 (0.00)	0.14 (0.00)	0.18 (0.00)	0.18 (0.00)	0.18 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.15 (0.00)	0.15 (0.00)	0.15 (0.00)	5.30 (0.08)	5.25 (0.06)	5.17 (0.06)	4.74 (0.05)	4.74 (0.05)	4.71 (0.05)	0.52 (0.06)	0.50 (0.06)	0.46 (0.48)
	4.8 (0.0)	4.8 (0.0)	4.8 (0.0)	4.2 (0.0)	4.2 (0.0)	4.2 (0.0)	0.14 (0.00)	0.14 (0.00)	0.14 (0.00)	0.18 (0.00)	0.18 (0.00)	0.18 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.15 (0.00)	0.15 (0.00)	0.15 (0.00)	5.35 (0.06)	5.39 (0.06)	5.39 (0.06)	4.80 (0.00)	4.80 (0.00)	4.80 (0.00)	0.55 (0.06)	0.55 (0.06)	0.58 (0.58)
CN03	4.8 (0.0)	4.8 (0.0)	4.8 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	0.15 (0.00)	0.15 (0.00)	0.15 (0.00)	0.14 (0.01)	0.15 (0.01)	0.15 (0.01)	0.28 (0.01)	0.29 (0.01)	0.29 (0.01)	0.16 (0.00)	0.16 (0.00)	0.16 (0.00)	5.86 (0.12)	5.90 (0.13)	5.97 (0.13)	5.43 (0.12)	5.48 (0.12)	5.53 (0.12)	0.43 (0.02)	0.42 (0.03)	0.45 (0.40)
	4.8 (0.0)	4.8 (0.0)	4.8 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	0.15 (0.00)	0.15 (0.00)	0.15 (0.00)	0.14 (0.01)	0.15 (0.01)	0.15 (0.01)	0.28 (0.01)	0.28 (0.01)	0.28 (0.01)	0.16 (0.00)	0.16 (0.00)	0.16 (0.00)	5.82 (0.13)	5.82 (0.13)	5.75 (0.13)	5.38 (0.13)	5.38 (0.13)	5.30 (0.13)	0.45 (0.00)	0.45 (0.00)	0.45 (0.45)
CN04	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.0 (0.0)	4.0 (0.0)	4.0 (0.0)	0.18 (0.00)	0.17 (0.00)	0.18 (0.00)	0.22 (0.00)	0.22 (0.00)	0.22 (0.00)	0.26 (0.01)	0.25 (0.01)	0.25 (0.01)	0.14 (0.01)	0.15 (0.01)	0.14 (0.01)	5.59 (0.10)	5.64 (0.08)	5.55 (0.08)	4.51 (0.04)	4.51 (0.04)	4.55 (0.04)	1.13 (0.16)	1.24 (0.07)	1.32 (1.18)
	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.0 (0.0)	4.0 (0.0)	4.0 (0.0)	0.18 (0.00)	0.17 (0.00)	0.17 (0.00)	0.23 (0.00)	0.23 (0.00)	0.23 (0.00)	0.26 (0.01)	0.26 (0.01)	0.26 (0.01)	0.14 (0.01)	0.14 (0.01)	0.13 (0.01)	5.53 (0.10)	5.57 (0.10)	5.62 (0.10)	4.52 (0.05)	4.52 (0.05)	4.46 (0.05)	1.02 (0.14)	1.02 (0.14)	1.16 (0.87)
ID01	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	0.20 (0.01)	0.19 (0.01)	0.19 (0.01)	0.24 (0.01)	0.25 (0.01)	0.25 (0.01)	0.26 (0.01)	0.26 (0.01)	0.26 (0.01)	0.16 (0.01)	0.16 (0.01)	0.15 (0.01)	4.62 (0.06)	4.62 (0.06)	4.59 (0.06)	4.21 (0.04)	4.20 (0.04)	4.20 (0.04)	0.41 (0.08)	0.42 (0.06)	0.39 (0.39)
	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	0.20 (0.01)	0.19 (0.01)	0.19 (0.01)	0.24 (0.01)	0.25 (0.01)	0.25 (0.01)	0.26 (0.01)	0.26 (0.01)	0.26 (0.01)	0.16 (0.01)	0.16 (0.01)	0.15 (0.01)	4.62 (0.06)	4.62 (0.06)	4.70 (0.06)	4.23 (0.05)	4.23 (0.05)	4.20 (0.05)	0.39 (0.10)	0.39 (0.10)	0.30 (0.30)
ID04	4.5 (0.0)	4.5 (0.0)	4.5 (0.0)	4.2 (0.0)	4.2 (0.0)	4.2 (0.0)	0.27 (0.01)	0.27 (0.01)	0.27 (0.01)	0.26 (0.01)	0.26 (0.01)	0.26 (0.01)	0.38 (0.00)	0.38 (0.00)	0.38 (0.00)	0.19 (0.02)	0.19 (0.02)	0.21 (0.02)	3.73 (0.08)	3.67 (0.07)	3.73 (0.07)	3.40 (0.04)	3.40 (0.04)	3.38 (0.04)	0.33 (0.07)	0.28 (0.07)	0.34 (0.28)
	4.5 (0.0)	4.5 (0.0)	4.5 (0.0)	4.2 (0.0)	4.2 (0.0)	4.2 (0.0)	0.27 (0.01)	0.27 (0.01)	0.27 (0.01)	0.26 (0.01)	0.26 (0.01)	0.26 (0.01)	0.39 (0.00)	0.39 (0.00)	0.39 (0.00)	0.19 (0.02)	0.19 (0.02)	0.17 (0.02)	3.79 (0.04)	3.79 (0.04)	3.75 (0.04)	3.40 (0.06)	3.40 (0.06)	3.36 (0.06)	0.39 (0.02)	0.39 (0.02)	0.41 (0.41)
MN01	3.9 (0.0)	3.9 (0.0)	3.9 (0.0)	4.3 (0.0)	4.3 (0.0)	4.3 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	7.23 (0.00)	7.23 (0.00)	7.23 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	7.23 (0.00)	7.23 (0.00)	7.23 (7.23)
	3.9 (0.0)	3.9 (0.0)	3.9 (0.0)	4.3 (0.0)	4.3 (0.0)	4.3 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	7.23 (0.00)	7.23 (0.00)	7.23 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	7.23 (0.00)	7.23 (0.00)	7.23 (7.23)
	3.9 (0.0)	3.9 (0.0)	3.9 (0.0)	4.3 (0.0)	4.3 (0.0)	4.3 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	7.23 (0.00)	7.23 (0.00)	7.23 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	7.23 (0.00)	7.23 (0.00)	7.23 (7.23)
	3.9 (0.0)	3.9 (0.0)	3.9 (0.0)	4.3 (0.0)	4.3 (0.0)	4.3 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	7.23 (0.00)	7.23 (0.00)	7.23 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	7.23 (0.00)	7.23 (0.00)	7.23 (7.23)

Appendix Table 4.2 continued

Lab	pH(H ₂ O)			pH(KCl)			Ex-Ca (emol kg^{-1})			Ex-Mg (emol kg^{-1})			Ex-K (emol kg^{-1})			Ex-Na (emol kg^{-1})			Ex-Acidity (emol kg^{-1})			Ex-Al (emol kg^{-1})			Ex-H (emol 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
KR01	4.8 (0.0)	4.8 (0.0)	4.8 (0.0)	4.2 (0.0)	4.2 (0.0)	4.1 (0.0)	0.12 (0.00)	0.12 (0.00)	0.12 (0.00)	0.18 (0.00)	0.18 (0.00)	0.18 (0.00)	0.25 (0.00)	0.25 (0.00)	0.25 (0.00)	0.14 (0.00)	0.14 (0.00)	0.14 (0.00)	4.39 (0.01)	4.39 (0.01)	4.39 (0.01)	4.17 (0.00)	4.17 (0.00)	4.17 (0.00)	0.22 (0.00)	0.21 (0.00)	0.21 (0.00)
RU01	4.8 (0.0)	4.8 (0.0)	4.8 (0.0)	4.2 (0.0)	4.2 (0.0)	4.2 (0.0)	0.12 (0.00)	0.12 (0.00)	0.12 (0.00)	0.18 (0.00)	0.18 (0.00)	0.18 (0.00)	0.25 (0.00)	0.25 (0.00)	0.25 (0.00)	0.14 (0.00)	0.14 (0.00)	0.14 (0.00)	4.39 (0.00)	4.39 (0.00)	4.39 (0.00)	4.17 (0.00)	4.17 (0.00)	4.17 (0.00)	0.22 (0.01)	0.21 (0.01)	0.21 (0.01)
TH01	4.8 (0.0)	4.8 (0.0)	4.8 (0.0)	4.0 (0.0)	4.0 (0.0)	4.0 (0.0)	0.16 (0.01)	0.16 (0.01)	0.16 (0.01)	0.22 (0.00)	0.22 (0.00)	0.22 (0.00)	0.27 (0.00)	0.27 (0.00)	0.27 (0.00)	0.15 (0.00)	0.15 (0.00)	0.15 (0.00)	4.88 (0.22)	4.88 (0.22)	4.88 (0.22)	4.21 (0.18)	4.21 (0.18)	4.21 (0.18)	0.43 (0.14)	0.30 (0.01)	0.29 (0.01)
VN01	4.8 (0.0)	4.8 (0.0)	4.8 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	0.08 (0.00)	0.08 (0.00)	0.08 (0.00)	0.23 (0.00)	0.23 (0.00)	0.23 (0.00)	0.26 (0.00)	0.26 (0.00)	0.26 (0.00)	0.15 (0.00)	0.15 (0.00)	0.15 (0.00)	4.22 (0.01)	4.22 (0.01)	4.22 (0.01)	3.86 (0.02)	3.86 (0.02)	3.86 (0.02)	0.36 (0.01)	0.37 (0.01)	0.37 (0.01)
VN02	4.7 (0.0)	4.7 (0.0)	4.7 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	5.92 (0.03)	5.92 (0.03)	5.92 (0.03)	5.43 (0.06)	5.43 (0.06)	5.43 (0.06)	0.48 (0.06)	0.55 (0.06)	0.55 (0.06)
VN04	4.6 (0.0)	4.6 (0.0)	4.6 (0.0)	4.0 (0.0)	4.0 (0.0)	4.0 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	5.94 (0.03)	5.94 (0.03)	5.94 (0.03)	5.35 (0.06)	5.35 (0.06)	5.35 (0.06)	0.55 (0.00)	0.55 (0.00)	0.55 (0.00)

5. 16th INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENT

5.1 Introduction

In the Inter-laboratory Comparison Project on inland aquatic environment, an artificial inland water sample containing known concentrations of major ions was prepared and sent to the EANET participating countries by the Network Center (NC). The measured results of pH, EC, alkalinity and concentrations of SO_4^{2-} , NO_3^- , Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+ in the participating laboratories were compared with the prepared values and the results were statistically analyzed.

5.2 Procedures

5.2.1 Participating Laboratories

In the 16th Project, the NC shipped an artificial inland water sample on October 9, 2015 to 24 laboratories involved in the EANET activities, and most of them submitted their analytical data to the NC by February 29, 2016. Participating laboratories and their identification codes are listed in Table 1.1. For this attempt, the laboratory MN01 submitted the data of 6 parameters, namely pH, EC, alkalinity, SO_4^{2-} , NO_3^- and Cl^- .

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 ⁻	0.5 – 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 the “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 for Inland Aquatic Environment Monitoring in East Asia (2010)

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⁻	Ion Chromatography or Spectrophotometry
NO ₃ ⁻	
Cl ⁻	Ion Chromatography or Titration
Na ⁺	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
K ⁺	
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 (A) equivalent concentration ($\mu\text{eq L}^{-1}$) is calculated by sum up the concentration of anions (C: $\mu\text{mol L}^{-1}$) and alkalinity (ALK: $\mu\text{eq L}^{-1}$). Alkalinity considered to be corresponded to bicarbonate ions (HCO₃⁻).

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

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

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

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

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

- (3) Calculation of ion balance (R_1)

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

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

Table 5.5 Allowable ranges for R_1 in different concentration ranges

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

Reference: “Technical Manual for Inland Aquatic Environment Monitoring in East Asia (2010)”

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

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

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

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

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

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

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

Table 5.6 Allowable ranges for R_2 in different concentration ranges

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

Reference: “Technical Manual for Inland Aquatic Environment Monitoring in East Asia (2010)”

5.3 Results

5.3.1 Outline of Results

Original data from the laboratories are shown in APPENDIX5-2 and APPENDIX5-3. Table 5.7 shows summary of the analytical results. Outlying data that deviated from the average three times greater than standard deviation (S.D.) is not included for the calculation in Table 5.7. Average of submitted data agreed well with the prepared value/concentration within a range of $\pm 15\%$.

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	6.88	0.21	23	6.52	7.32
EC (mS m^{-1})	5.22	5.00	0.11	22	4.80	5.20
Alkalinity (meq L^{-1})	0.161	0.166	0.02	23	0.120	0.229
SO_4^{2-} (mg L^{-1})	5.94	5.78	0.37	23	4.80	6.34
NO_3^- (mg L^{-1})	0.67	0.64	0.05	23	0.52	0.76
Cl^- (mg L^{-1})	4.90	4.73	0.29	23	3.89	5.35
Na^+ (mg L^{-1})	4.96	5.14	0.36	22	4.73	5.95
K^+ (mg L^{-1})	0.70	0.69	0.07	22	0.51	0.84
Ca^{2+} (mg L^{-1})	2.16	2.21	0.27	22	1.79	2.98
Mg^{2+} (mg L^{-1})	0.92	0.84	0.17	22	0.54	1.21
NH_4^+ (mg L^{-1})	0.29	0.30	0.05	22	0.19	0.41

(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 is specified as $\pm 15\%$ for every constituent by the QA/QC program of the EANET. In this report, analytical data on artificial inland aquatic environmental samples is compared with the prepared value/concentration and evaluated by the DQO criteria: the flag "E" is put to the data that exceed DQO within a factor of 2 ($\pm 15\% - \pm 30\%$) and the flag "X" is put to the data that exceed DQO more than a factor of 2 ($< -30\%$ or $> 30\%$). Data set for each laboratory was evaluated by the data checking procedures described in chapter 5.2.4 of this report. The results were evaluated following the two aspects: i) comparison of individual parameters, and ii) comparison of conditions in each participating laboratory. Evaluation of data for each constituent is presented in "5.3.2 Evaluation of laboratories' performance (by analytical parameters)", and evaluation of data by laboratory conditions such as analytical methods used for the project, experience of personnel, and other analytical

conditions is described in “5.3.4 Information on laboratories”.

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

Table 5.8 Number of flagged data

Flag [*]	pH	EC	Alkalinity	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total	Ratio
E	0	0	1	1	2	1	3	3	4	0	4	19	7.7%
X	0	0	2	0	0	0	0	0	1	6	4	13	5.2%
Data within DQOs	23	23	20	22	21	22	19	19	17	16	14	216	87.1%
Flagged(%)	0.0	0.0	13.0	4.3	8.7	4.3	13.6	13.6	22.7	27.3	36.4	12.9	

*E: Value exceeded the DQO within a factor of 2 ($\pm 15\%$ – $\pm 30\%$)

*X: Value exceeded the DQO more than a factor of 2 ($< -30\%$ or $> 30\%$)

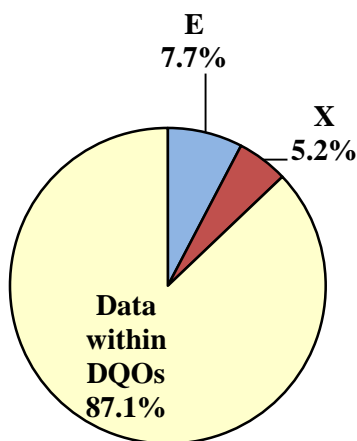


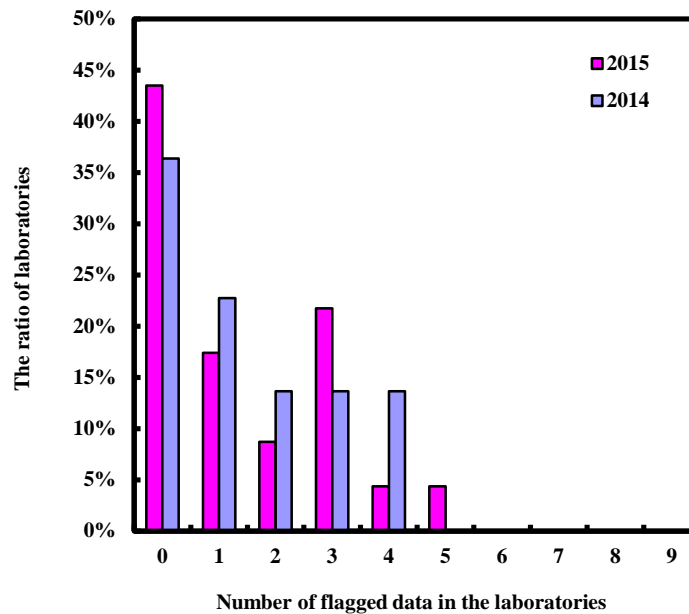
Figure 5.1 Percentage of flagged data

The data flagged by "E", which exceeded the DQOs within a factor of 2, shared 7.7% of all the reported data of samples. Furthermore, the data flagged by "X", which exceeded the DQOs more than a factor of 2, shared 5.2% of all the reported data of samples. Concerning the respective parameters, the percentage of flagged NH₄⁺ was highest, 36.4%.

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	10	43%
1	4	17%
2	2	9%
3	5	22%
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 43% in this attempt, while that in the last attempt (2014) was 36%. The maximum number of flagged data was five, which was submitted by one laboratory.

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

Table 5.10 Analytical Results of Sample No.141i (artificial inland aquatic environment sample : EANET in 2015)

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
KH01	6.85	4.86	0.180	4.80 E	0.60	4.25	5.08	0.68	2.28	0.91	0.27	3.82	1.57
CN01	6.74	4.98	0.146	5.93	0.59	4.71	4.92	0.66	2.22	0.91	0.31	2.61	1.25
CN02	6.95	4.95	0.148	5.94	0.64	4.76	4.87	0.65	2.09	0.86	0.27	0.26	0.92
CN03	6.92	4.90	0.150	6.00	0.62	4.74	4.92	0.65	2.09	0.88	0.30	0.64	1.85
CN04	6.94	5.05	0.170	5.67	0.66	4.58	4.80	0.67	2.29	0.91	0.28	0.32	0.79
ID01	7.12	4.88	0.177	6.04	0.76	4.52	4.95	0.74	2.51 E	0.98	0.29	1.57	4.81
ID05	6.99	5.20	0.220 X	5.10	0.52 E	5.10	4.90	0.70	2.20	0.86	0.31	-5.44	1.43
JP04	7.12	5.04	0.168	5.93	0.62	4.86	4.75	0.66	1.95	0.83	0.29	-4.04	0.34
JP05	7.01	4.98	0.173	5.89	0.66	4.68	4.73	0.68	2.23	0.85	0.30	-2.06	1.78
LA01	6.78	4.89	0.229 X	6.11	0.62	4.94	5.13	0.73	2.27	0.89	0.19 X	-7.00	6.59
MY01	6.84	5.02	0.179	5.92	0.64	4.84	4.95	0.66	2.27	0.89	0.28	-1.69	2.62
MN01	6.91	4.96	0.120 E	5.09	0.56 E	3.89 E						-	-
PH01	6.69	5.63	0.162	5.49	0.67	4.58	4.94	0.64	2.45	0.94	0.19 X	2.94	-4.69
PH02	7.32	5.03	0.160	6.27	0.66	4.87	5.95 E	0.83 E	2.98 X	1.21 X	0.21 E	10.33 I	7.41
RU01	7.02	5.11	0.146	6.34	0.66	5.35	4.98	0.71	2.22	0.93	0.32	0.06	2.38
RU02	6.96	5.18	0.146	6.16	0.67	5.15	5.00	0.70	2.05	0.91	0.29	-0.15	0.34
TH01	7.27	5.11	0.171	5.74	0.59	4.56	5.03	0.64	2.21	0.92	0.28	0.83	0.47
TH02	6.64	4.96	0.163	5.93	0.63	4.77	4.98	0.67	2.61 E	0.98	0.28	3.23	3.85
VN01	6.52	4.94	0.160	5.72	0.64	4.75	5.44	0.51 E	2.07	0.58 X	0.35 E	-0.38	1.23
VN02	6.63	4.92	0.145	5.70	0.65	4.70	5.75 E	0.69	2.00	0.56 X	0.38 X	3.28	1.44
VN03	6.70	4.80	0.172	5.60	0.67	4.68	5.60	0.84 E	1.79 E	0.54 X	0.34 E	-1.59	2.78
VN04	6.63	4.93	0.150	5.78	0.66	4.73	5.73 E	0.68	2.00	0.60 X	0.41 X	2.85	2.02
VN05	6.65	4.93	0.173	5.74	0.64	4.72	5.60	0.75	1.82 E	0.58 X	0.36 E	-1.76	1.97
Expected value	7.06	5.22	0.161	5.94	0.67	4.90	4.96	0.70	2.16	0.92	0.29	-	-

E: Value exceeded the DQO within a factor of 2 ($\pm 15\%$ – $\pm 30\%$)

X: Value exceeded the DQO more than a factor of 2 ($< -30\%$ or $> 30\%$)

I: Poor ion balance (R1)

C: Rich Conductivity agreement (R2)

5.3.2 Evaluation of laboratories' performance (by analytical parameters)

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

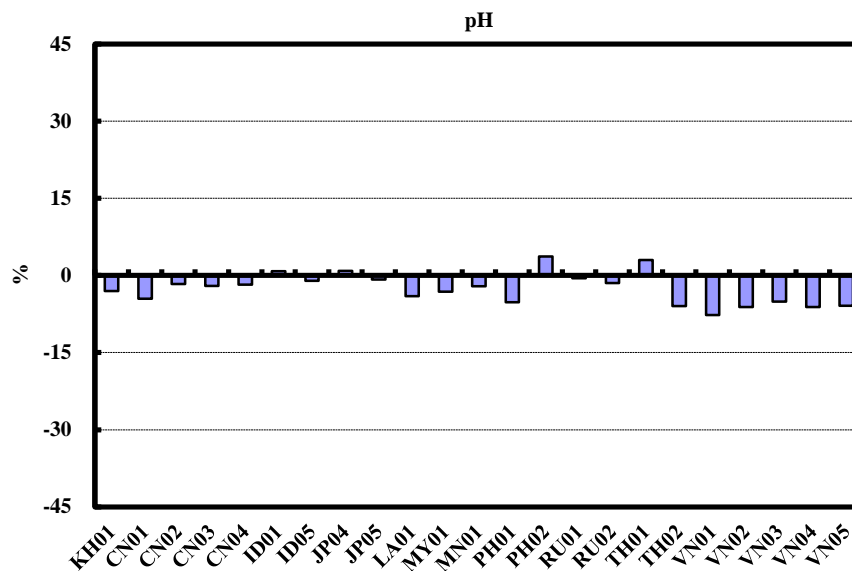


Figure 5.3 Distribution of results for pH (normalized by the prepared value)

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

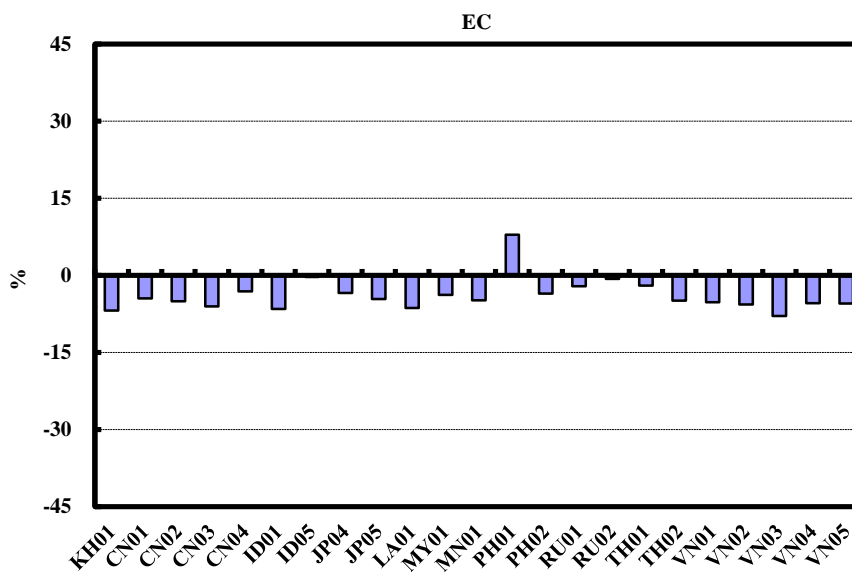


Figure 5.4 Distribution of results for EC (normalized by the prepared value)

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

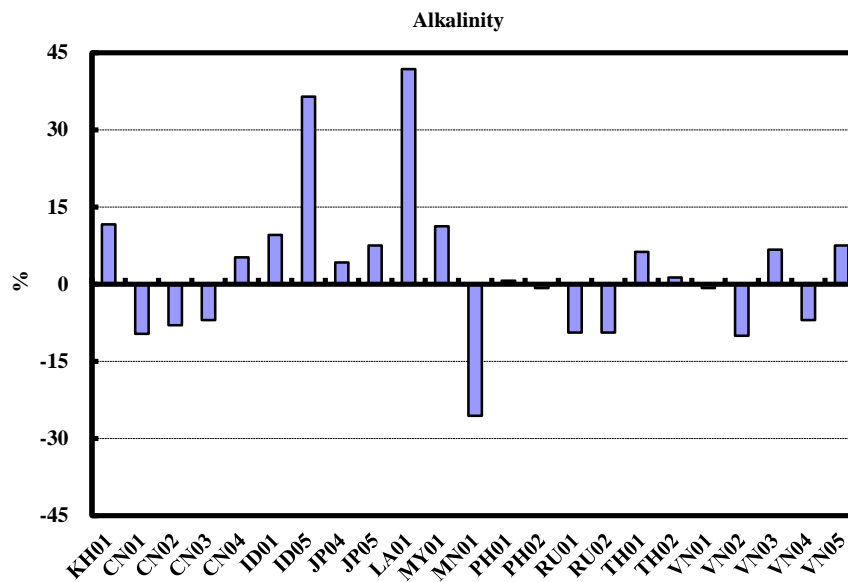


Figure 5.5 Distribution of results for alkalinity (normalized by prepared concentration)

Except for ID05, LA01 and MN01, all the submitted data of alkalinity were within DQO, 15%. The number of flagged data of alkalinity was eight in last attempt. The flagged data decreased dramatically.

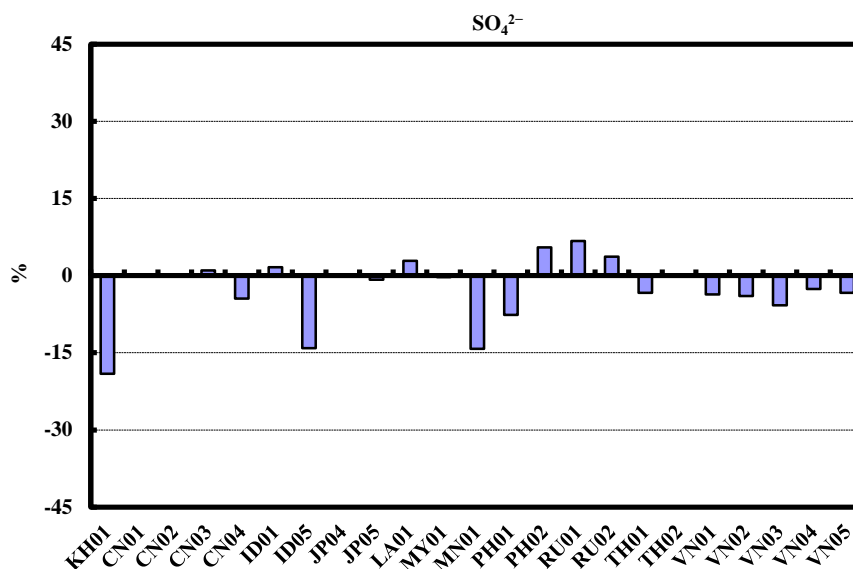


Figure 5.6 Distribution of results for SO₄²⁻ (normalized by prepared concentration)

Except for KH01, all the submitted data of SO₄²⁻ were within DQO, 15%. Almost all of them

were lower than the prepared value.

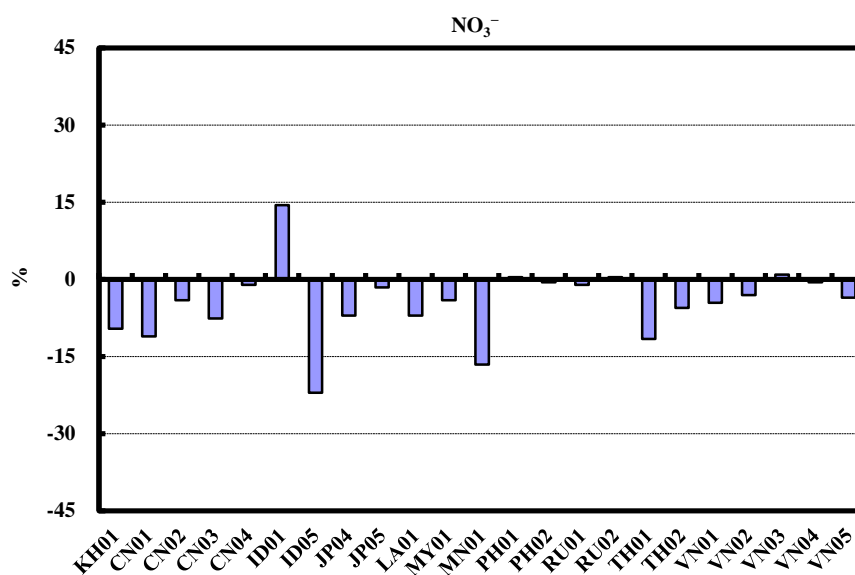


Figure 5.7 Distribution of results for NO₃⁻ (normalized by prepared concentration)

Except for ID05 and MN01, all the submitted data of NO₃⁻ were within DQO, 15%. The number of flagged data of alkalinity was seven in last attempt. The flagged data decreased dramatically.

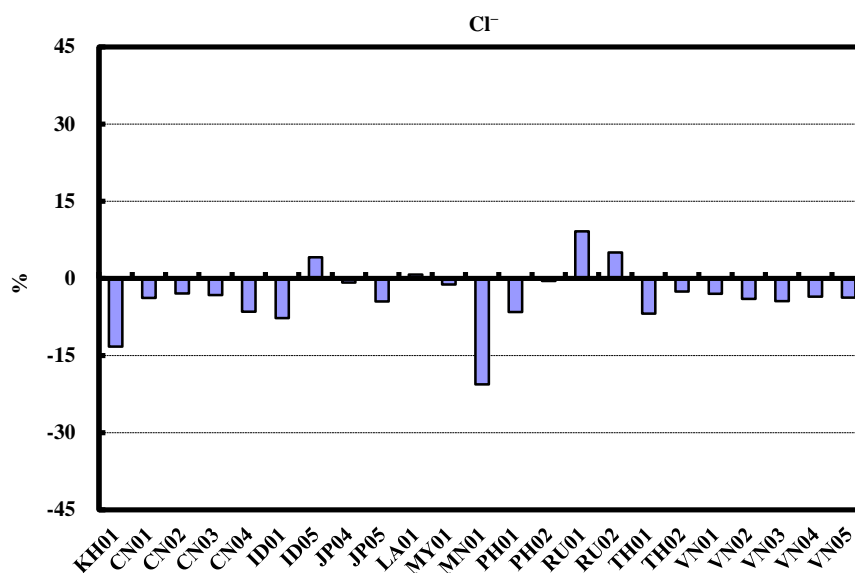


Figure 5.8 Distribution of results for Cl⁻ (normalized by prepared concentration)

Except for MN01, all the submitted data of Cl⁻ were within DQOs. Almost all of them were lower than the prepared value.

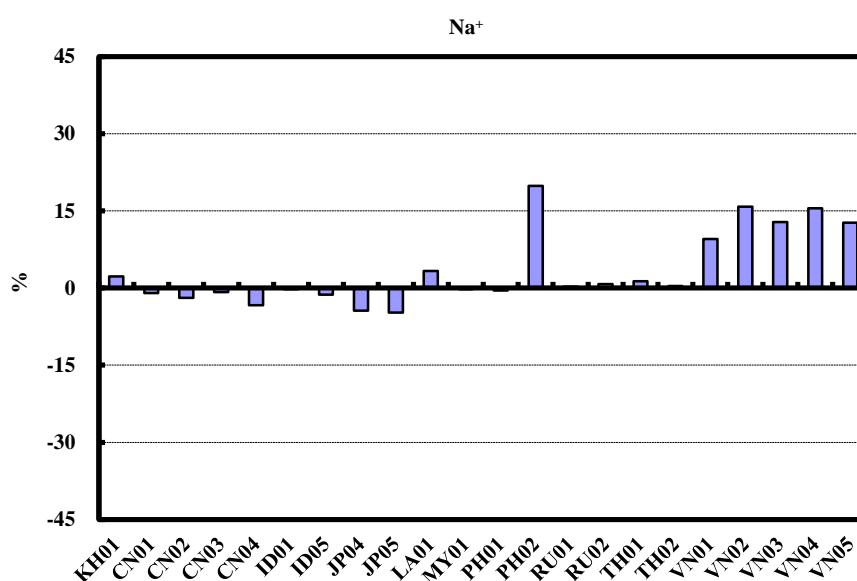


Figure 5.9 Distribution of results for Na⁺ (normalized by prepared concentration)

Except for PH02, VN02 and VN04, all the submitted data of Na⁺ were within DQOs.

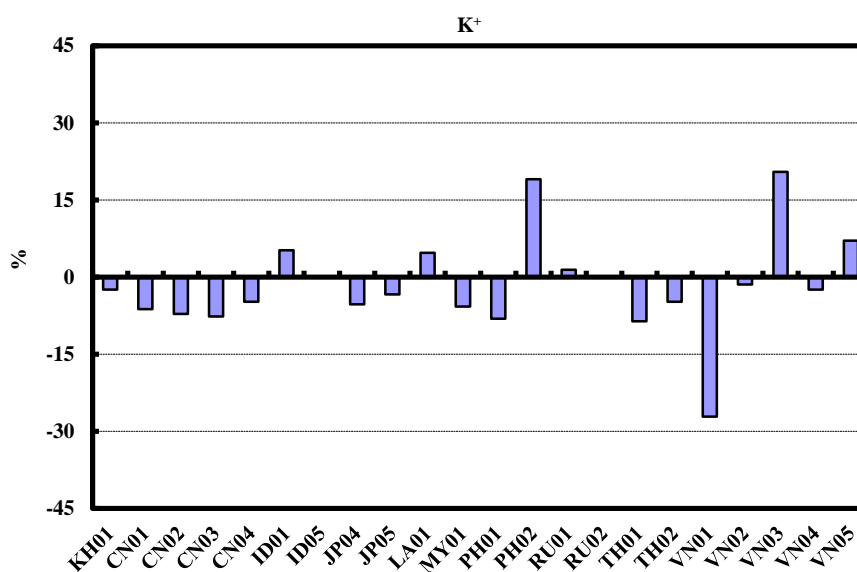


Figure 5.10 Distribution of results for K⁺ (normalized by prepared concentration)

Except for PH02, VN01 and VN03, all the submitted data of K⁺ were within DQOs. Almost all of them were lower than the prepared value.

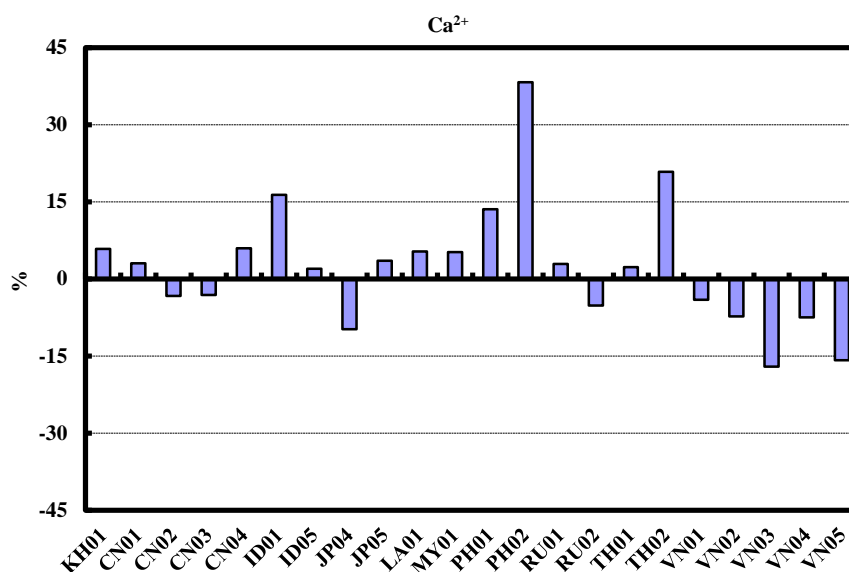


Figure 5.11 Distribution of results for Ca^{2+} (normalized by prepared concentration)

Data from five laboratories were flagged. Four of them used ion chromatography for the determination, and another one used flame (emission) photometry.

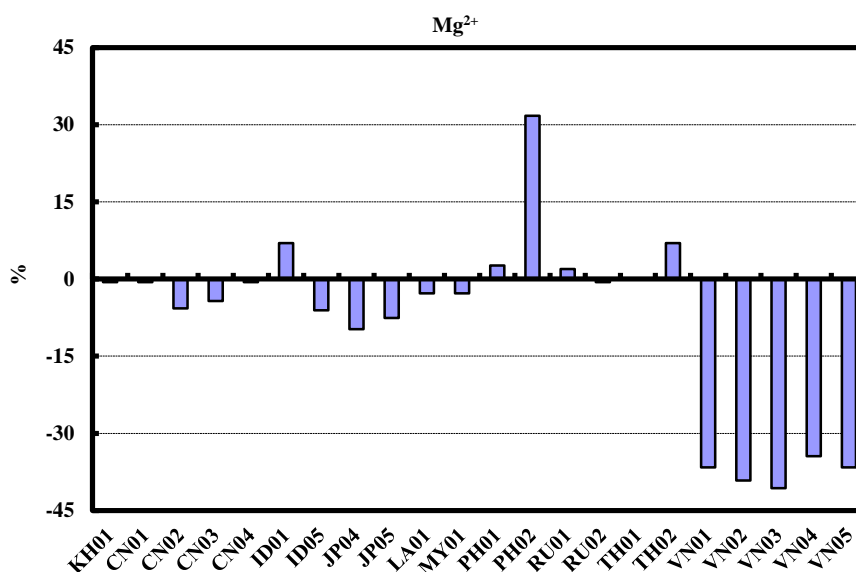


Figure 5.12 Distribution of results for Mg^{2+} (normalized by prepared concentration)

Data from six laboratories were flagged, and all of them were deviated more than 30%. Five of them used ion chromatography for the determination, and another one used flame (emission) photometry.

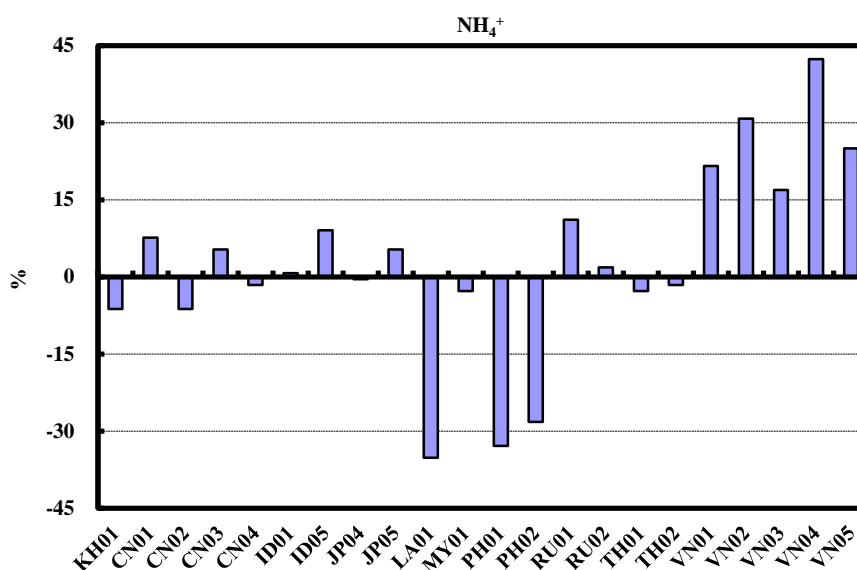


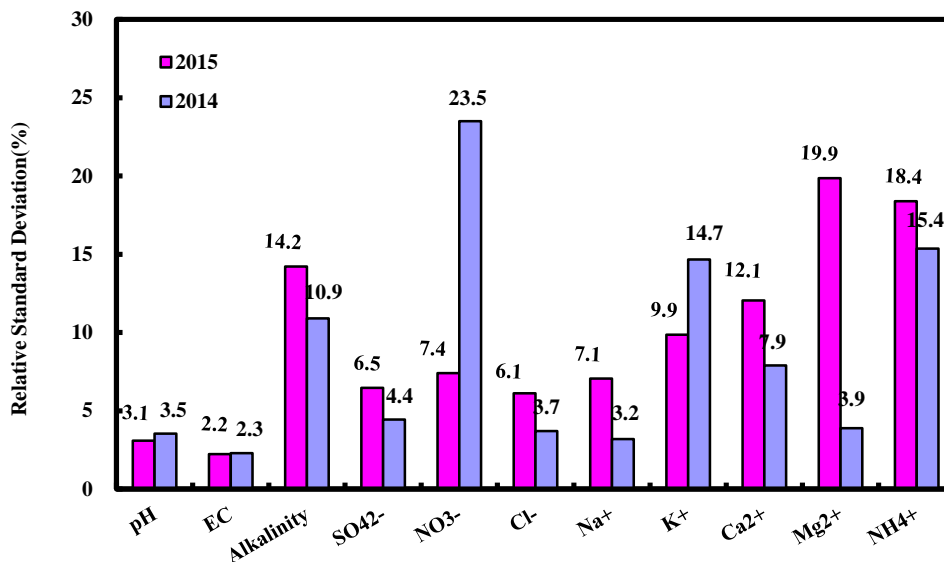
Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

Data from eight laboratories were flagged, and four of them were deviated more than 30%. Among 22 participating laboratories, 17 laboratories used ion chromatography, 4 laboratories used spectrophotometry (Indophenol) and 1 laboratory used spectrophotometry (other method) for the determination of NH_4^+ . Six laboratories with flagged data used ion chromatography, and another one laboratory used spectrophotometry (Indophenol) methods.

NH_4^+ was the parameter that has the highest flagged percentage in this attempt. Other cations had also high-level flagged percentages, too. In particular, flagged percentages of Ca^{2+} and Mg^{2+} became higher than last attempt.

5.3.3 Overall Evaluation

Calculated relative standard deviation of the whole sets of analytical data is presented in Figure 5.14 with comparison to last attempt (2014).



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

Figure 5.14 Relative standard deviation of each constituent

The relative standard deviation (RSD) of NO₃⁻ in 2015 became lower than the last attempt. On the other hand, almost all RSDs of major ions became higher, especially Mg²⁺.

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.

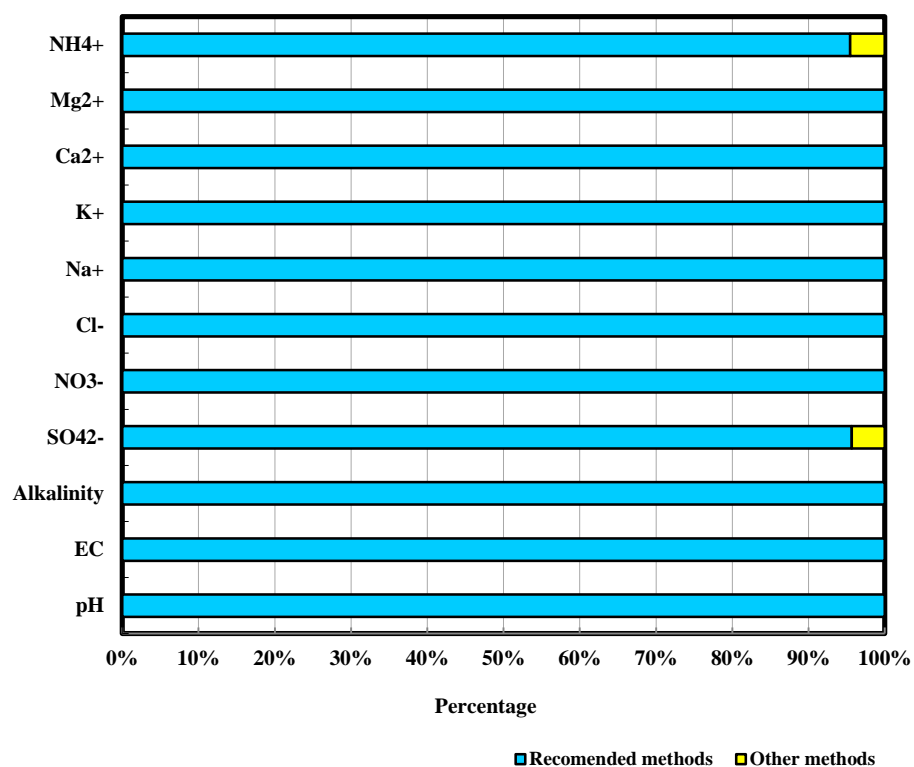


Figure 5.15 Percentage of laboratories using the recommended methods

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	23										
1		23									
2			23(3)			3					
3							5	5(1)	5(1)	5(1)	
4				20(1)	19(1)	20(1)	17(3)	17(2)	17(4)	17(5)	17(7)
5											
6											
7				2	4(1)						1
8											4(1)
9											
10											
11				1							
Flagged E	0	0	1	1	2	1	3	3	4	0	4
Flagged X	0	0	2	0	0	0	0	0	1	6	4

Reverse mesh is a recommended method of EANET

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

The participating laboratories used recommended methods of the EANET except for measurement of SO₄²⁻ and NH₄⁺.

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 ⁺
KH01	1	A	A	A	A	A	A	A	A	A	A	A
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	2	A	A	A	B	B	B	B	B	B	B	B
CN04	1	A	A	A	A	A	A	A	A	A	A	A
ID01	2	A	A	A	B	B	B	B	B	B	B	B
ID05	7	A	A	B	C	D	E	E	F	F	F	G
JP04	1	A	A	A	A	A	A	A	A	A	A	A
JP05	3	A	A	B	A	A	A	C	C	C	C	A
LA01	1	A	A	A	A	A	A	A	A	A	A	A
MY01	4	A	A	B	C	C	C	D	D	D	D	D
MN01	3	A	A	B	B	B	B					
PH01	4	A	A	B	A	A	A	A	A	A	A	A
PH02	2	A	A	A	B	B	B	B	B	B	B	B
RU01	4	A	A	A	B	B	B	C	C	C	C	A
RU02	3	A	B	A	C	B	A	D	D	D	D	C
TH01	1	A	A	A	A	A	A	A	A	A	A	A
TH02	2	A	B	A	B	B	B	A	A	A	A	A
VN01	2	A	A	B	B	B	B	B	B	B	B	B
VN02	3	A	A	B	C	C	C	C	C	C	C	C
VN03	3	A	A	B	B	A	A	C	C	A	C	B
VN04	3	A	A	B	C	C	C	C	C	C	C	C
VN05	3	A	A	B	C	C	C	C	C	C	C	C

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

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

-: no information

blank: not analyzed

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

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

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

Table 5.14 Years of experience

Lab.ID	pH	EC	Alkalinity	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Unit : year	
KH01	8	8	8	8	8	8	8	8	8	8	8		
CN01	1	1	1	1	1	1	1	1	1	1	1		
CN02	18	18	10	10	10	10	10	10	10	10	10		
CN03	20	20	20	5	5	5	5	5	5	5	5		
CN04	9	9	9	9	9	9	9	9	9	9	9		
ID01	4	4	4	5	5	5	5	5	5	5	5		
ID05	3	3	33	4	7	5	5	7	7	7	7		
JP04	7	7	7	7	7	7	7	7	7	7	7		
JP05	3	3	1	3	3	3	15	15	15	15	15		
LA01	3	3	3	3	3	3	3	3	3	3	3		
MY01	2	2	3	5	5	5	9	9	9	9	9		
MN01	14	14	17	17	17	17							
PH01	2	2	7	2	2	2	2	2	2	2	2		
PH02	1	1	1	5	5	5	5	5	5	5	5		
RU01	22	22	22	20	20	20	30	30	30	30	30		
RU02	55	37	55	30	37	55	24	24	24	24	24		
TH01	18	18	18	18	18	18	18	18	18	18	18		
TH02	18	12	18	12	12	12	18	18	18	18	18		
VN01	2	2	23	23	23	23	23	23	23	23	23		
VN02	9	9	11	11	11	11	11	11	11	11	11		
VN03	1	1	7	7	1	7	3	3	1	3	7		
VN04	10	10	12	12	12	12	12	12	12	12	12		
VN05	3	3	11	12	12	12	12	12	12	12	12		

Reverse mesh: Data were Flagged by “E” or “X” in sample

1 year means experienced with one year or less.

-: no information

blank: not analyzed

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

5.4. Comparison with past surveys

The inter-laboratory comparison projects of the EANET have been carried out 16 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.

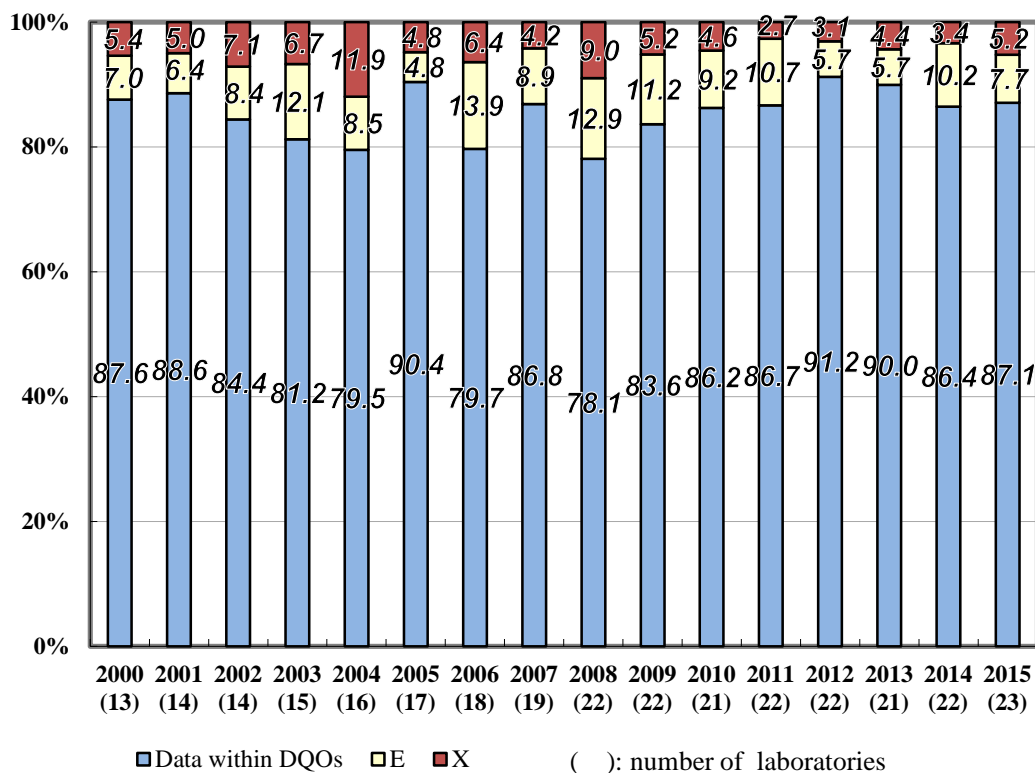


Figure 5. 16 Comparison of the results from the inter-laboratory comparison projects

The percentage of data satisfied the DQOs kept on decreasing since 2012 to 2014, but it increased slightly in this attempt. The percentage of each data in this attempt were almost same as the last attempt.

The values/concentrations for each parameter from the 1st to 16th project were compared with the percentage of flagged data in Figure 5.17.

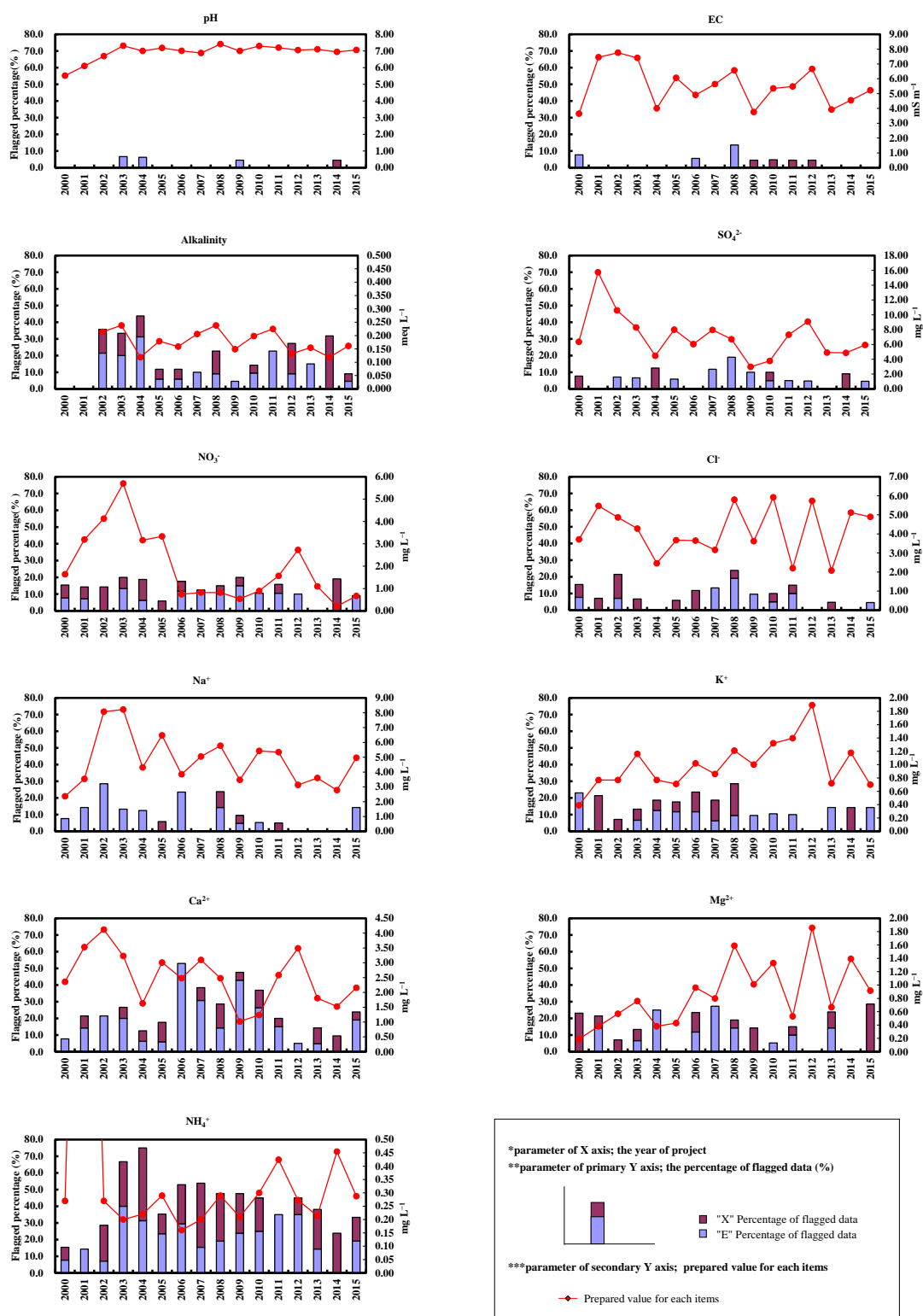


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects

There was no flagged data in pH and EC in this attempt. The analyses of pH, alkalinity, SO_4^{2-} and NO_3^- were improved, but flagged data appeared in Cl^- , Na^+ and Mg^{2+} . In this attempt, flagged percentages of almost all cations 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 NH_4^+ than for other parameters in every survey except for the 1st- 3rd project. The percentage of flagged Ca^{2+} in the 7th - 11th project was also comparatively high. Therefore, in the inland water analysis, it is necessary to pay more attention to NH_4^+ and Ca^{2+} .

5.5. Recommendations for improvement

The following fundamental matters should be taken into account in measurement, analysis, and data control processes for improvement of precision.

5.5.1 Measurement and Analysis

1) General

- ▶ Clearance from contamination of the apparatus, materials and reagents used for measurement and analysis must be confirmed beforehand.
- ▶ Blank values of target substances should be as low as possible.
- ▶ Measurement and analysis should be conducted by persons who are well trained.
- ▶ To maintain high analytical quality, SOP (Standard Operating Procedures) must be prepared for the management of apparatus, reagents, and procedure of operation.

2) Deionized water

- ▶ Water with conductivity less than 0.15mS 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, 124p.

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)
KH01	6.85	4.86	0.180	4.80	0.60	4.25	5.08	0.68	2.28	0.91	0.27
CN01	6.74	4.98	0.146	5.93	0.59	4.71	4.92	0.66	2.22	0.91	0.31
CN02	6.95	4.95	0.148	5.94	0.64	4.76	4.87	0.65	2.09	0.86	0.27
CN03	6.92	4.90	0.150	6.00	0.62	4.74	4.92	0.65	2.09	0.88	0.30
CN04	6.94	5.05	0.170	5.67	0.66	4.58	4.80	0.67	2.29	0.91	0.28
ID01	7.12	4.88	0.177	6.04	0.76	4.52	4.95	0.74	2.51	0.98	0.29
ID05	6.99	5.20	0.220	5.10	0.52	5.10	4.90	0.70	2.20	0.86	0.31
JP04	7.12	5.04	0.168	5.93	0.62	4.86	4.75	0.66	1.95	0.83	0.29
JP05	7.01	4.98	0.173	5.89	0.66	4.68	4.73	0.68	2.23	0.85	0.30
LA01	6.78	4.89	0.229	6.11	0.62	4.94	5.13	0.73	2.27	0.89	0.19
MY01	6.84	5.02	0.179	5.92	0.64	4.84	4.95	0.66	2.27	0.89	0.28
MN01	6.91	4.96	0.120	5.09	0.56	3.89					
PH01	6.69	5.63	0.162	5.49	0.67	4.58	4.94	0.64	2.45	0.94	0.19
PH02	7.32	5.03	0.160	6.27	0.66	4.87	5.95	0.83	2.98	1.21	0.21
RU01	7.02	5.11	0.146	6.34	0.66	5.35	4.98	0.71	2.22	0.93	0.32
RU02	6.96	5.18	0.146	6.16	0.67	5.15	5.00	0.70	2.05	0.91	0.29
TH01	7.27	5.11	0.171	5.74	0.59	4.56	5.03	0.64	2.21	0.92	0.28
TH02	6.64	5.0	0.163	5.93	0.63	4.77	4.98	0.67	2.61	0.98	0.28
VN01	6.52	4.9	0.160	5.72	0.64	4.75	5.44	0.51	2.07	0.58	0.35
VN02	6.63	4.9	0.145	5.70	0.65	4.70	5.75	0.69	2.00	0.56	0.38
VN03	6.70	4.8	0.172	5.60	0.67	4.68	5.60	0.84	1.79	0.54	0.34
VN04	6.63	4.9	0.150	5.78	0.66	4.73	5.73	0.68	2.00	0.60	0.41
VN05	7.06	5.2	0.161	5.94	0.67	4.90	4.96	0.70	2.16	0.92	0.29
Expected value	7.06	5.22	0.161	5.94	0.67	4.90	4.96	0.70	2.16	0.92	0.29
Number of data	23	23	23	23	23	23	22	22	22	22	22
Average	6.88	5.01	0.17	5.78	0.64	4.73	5.14	0.69	2.21	0.84	0.30
Minimum	6.52	4.80	0.12	4.80	0.52	3.89	4.73	0.51	1.79	0.54	0.19
Maximum	7.32	5.63	0.23	6.34	0.76	5.35	5.95	0.84	2.98	1.21	0.41

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 ⁺ (%)
KH01	-3.0	-6.8	11.7	-19.1	-9.6	-13.3	2.3	-2.4	5.8	-0.6	-6.2
CN01	-4.5	-4.5	-9.6	-0.1	-11.1	-3.8	-0.9	-6.2	3.1	-0.6	7.7
CN02	-1.6	-5.0	-8.0	0.0	-4.1	-2.9	-1.9	-7.2	-3.3	-5.7	-6.2
CN03	-2.0	-6.0	-6.9	1.0	-7.6	-3.3	-0.8	-7.6	-3.1	-4.3	5.4
CN04	-1.8	-3.1	5.3	-4.5	-1.1	-6.4	-3.4	-4.8	6.0	-0.6	-1.6
ID01	0.8	-6.5	9.6	1.7	14.4	-7.7	-0.2	5.2	16.3	7.0	0.7
ID05	-1.0	-0.3	36.5	-14.1	-22.1	4.1	-1.3	0.0	2.0	-6.1	9.1
JP04	0.9	-3.4	4.2	-0.1	-7.1	-0.8	-4.4	-5.2	-9.8	-9.7	-0.4
JP05	-0.8	-4.6	7.5	-0.8	-1.6	-4.5	-4.8	-3.3	3.5	-7.5	5.4
LA01	-4.0	-6.3	41.9	2.9	-7.1	0.8	3.4	4.8	5.4	-2.8	-35.2
MY01	-3.1	-3.8	11.2	-0.3	-4.1	-1.2	-0.2	-5.7	5.2	-2.8	-2.7
MN01	-2.1	-4.9	-25.6	-14.2	-16.6	-20.6					
PH01	-5.2	7.9	0.7	-7.6	0.4	-6.5	-0.5	-8.1	13.6	2.7	-32.8
PH02	3.7	-3.5	-0.7	5.5	-0.6	-0.5	19.9	19.0	38.3	31.8	-28.2
RU01	-0.5	-2.1	-9.4	6.8	-1.1	9.1	0.3	1.4	2.9	1.9	11.1
RU02	-1.4	-0.7	-9.4	3.7	0.4	5.0	0.8	0.0	-5.1	-0.6	1.9
TH01	3.0	-2.0	6.3	-3.3	-11.6	-6.9	1.3	-8.6	2.3	0.1	-2.7
TH02	-6.0	-4.9	1.3	-0.1	-5.6	-2.6	0.4	-4.8	20.8	7.0	-1.6
VN01	-7.7	-5.2	-0.7	-3.7	-4.6	-3.0	9.5	-27.1	-4.1	-36.7	21.6
VN02	-6.1	-5.6	-10.1	-4.0	-3.1	-4.0	15.8	-1.4	-7.3	-39.2	30.8
VN03	-5.1	-7.9	6.7	-5.7	0.9	-4.4	12.8	20.5	-17.0	-40.7	16.9
VN04	-6.2	-5.4	-6.9	-2.6	-0.6	-3.5	15.5	-2.4	-7.5	-34.5	42.4
VN05	-5.9	-5.5	7.5	-3.3	-3.6	-3.7	12.8	7.1	-15.8	-36.7	25.0
Minimum	-7.7	-7.9	-25.6	-19.1	-22.1	-20.6	-4.8	-27.1	-17.0	-40.7	-35.2
Maximum	3.7	7.9	41.9	6.8	14.4	9.1	19.9	20.5	38.3	31.8	42.4
Average	-2.6	-3.9	2.7	-2.7	-4.6	-3.5	3.5	-1.7	2.4	-8.1	2.7
blank: not analyzed											

blank: not analyzed

6. ACKNOWLEDGEMENT

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

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