

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

Report of the Inter-laboratory Comparison Project 2011

14th Inter-laboratory Comparison Project on Wet Deposition

7th Inter-laboratory Comparison Project on Dry Deposition

13th Inter-laboratory Comparison Project on Soil

12th Inter-laboratory Comparison Project

on Inland Aquatic Environment

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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 14th Inter-laboratory Comparison Project on wet deposition, 7th Inter-laboratory Comparison Project on dry deposition, 13th Inter-laboratory Comparison Project on soil, and 12th Inter-laboratory Comparison Project on inland aquatic environment.

The number of participating laboratories from each country by project was shown in Figure 1.1, and all participating laboratories and their codes were listed in Table 1.1.

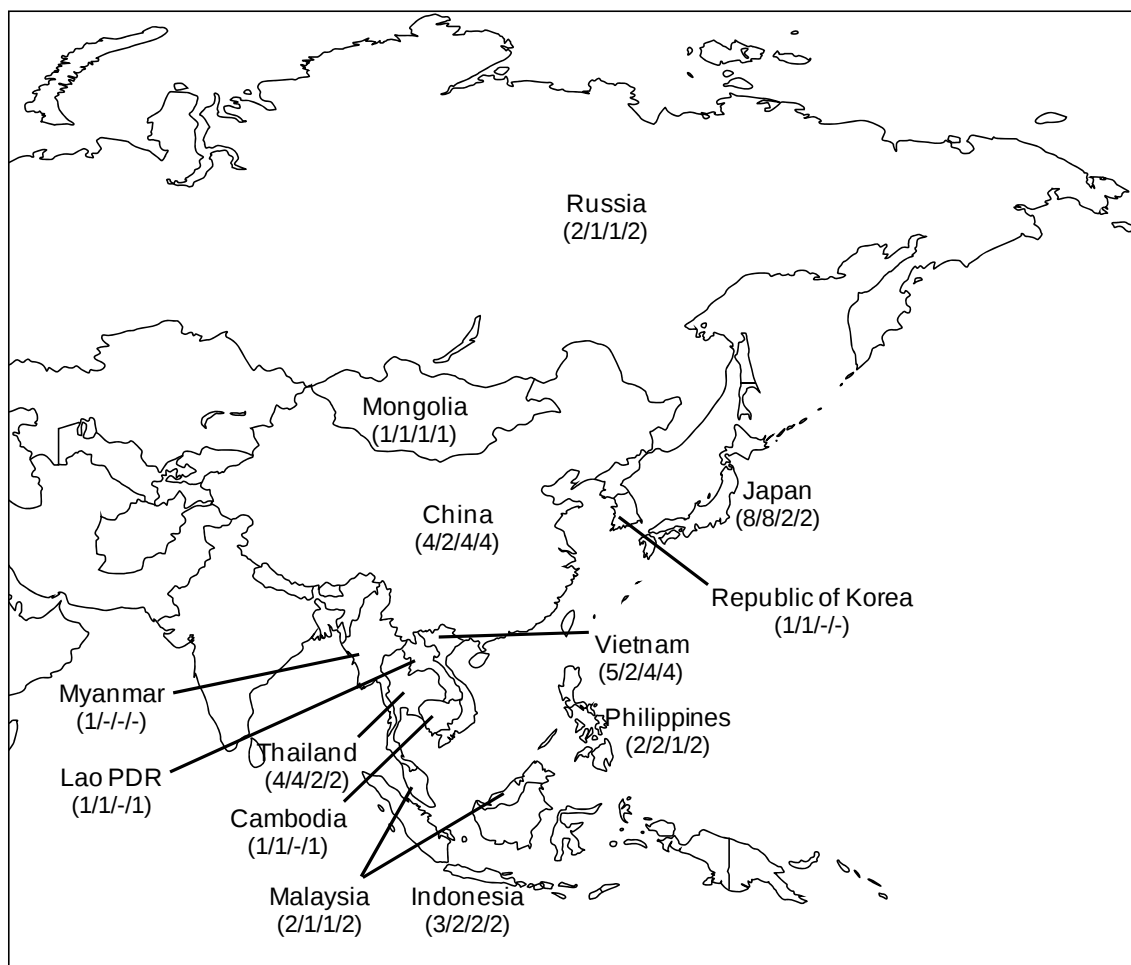


Figure 1.1 Number of participating laboratories in 2011

* The values in parentheses show the number of participating laboratories from each country.
(Wet/Dry/Soil/Inland aquatic environment)

Table 1.1 Participating laboratories

Laboratories	Code	Wet	Dry	Soil	IAE
Cambodia Department of Environment Pollution Control, Ministry of Environment	KH01	✓	✓		✓
China Zhuhai Environmental Monitoring Center Station Xiamen Environmental Monitoring Station Xi'an Environmental Monitoring Center Station Chongqing Institute of Environmental Science	CN01 CN02 CN03 CN04	✓ ✓ ✓ ✓	 ✓ ✓	✓ ✓ ✓ ✓	✓ ✓ ✓ ✓
Indonesia 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	ID01 ID02 ID03 ID04 ID05	✓ ✓ ✓ ✓	✓ ✓ 	✓ ✓ 	✓ ✓
Japan Institute of Environmental Sciences, Hokkaido Research Organization Niigata Prefectural Institute of Public Health and Environmental Sciences Nagano Environmental Conservation Research Institute Gifu Prefectural Research Institute for Health and Environmental Sciences Shimane Prefectural Institute of Public Health and Environmental Science Shimane Agricultural Technology Center 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 JP06 JP07 JP08 JP09 JP10	✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓	 ✓ ✓ 	 ✓ ✓
Lao PDR Environment Quality Monitoring Center, Environment Research Institute, Science technology and Environment	LA01	✓	✓		✓
Malaysia Division of Environmental Health, Department of Chemistry (DOC) Faculty of Applied Science, University Technology Mara (UiTM) Universiti Putra Malaysia, Bintulu Sarawak Campus (UPMKB)	MY01 MY03 MY04	✓ ✓ ✓	✓ 	 ✓	✓ ✓
Mongolia Central Laboratory of of Environment and Metrology	MN01	✓	✓	✓	✓
Myanmar Department of Meteorology and Hydrology (DMH)	MM01	✓			
Philippines Environmental Management Bureau - Central Office (EMB-CO) Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR) University of the Philippines Los Baños (UPLB)	PH01 PH02 PH03	✓ ✓ ✓	✓ ✓ 	 ✓	✓ ✓
Republic of Korea National Institute of Environment Research (NIER)	KR01	✓	✓		
Russia Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB) Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	RU01 RU02	✓ ✓	✓ 	✓ 	✓ ✓
Thailand Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MONRE) Environmental Research and Training Centre (ERTC), Department of Research and Environmental Quality Chemistry Department, Science Faculty, Chiangmai University (CMU) Khon Kaen University (KKU) King Mongkut's University of Technology Thonburi (KMUTT)	TH01 TH02 TH04 TH05 TH06	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ 	✓ ✓	✓ ✓
Vietnam Environmental Laboratory - Center for Environmental Research - Vietnam Institute of Meteorology, Hydrology and Environment (IMHEN)- MoNRE Mid- Central Regional Hydro Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE Sub-Institute of HydroMeteorology and 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)	VN01 VN02 VN03 VN04 VN05	✓ ✓ ✓ ✓ ✓	✓ ✓ 	✓ ✓ ✓ ✓ 	✓ ✓ ✓ ✓
Total :		35	26	18	23

2. 14th INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

2.1 Introduction

In the 14th 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 3 October 2011. Their analytical results were required to be submitted to the NC by 28 February 2012.

2.2 Procedures

2.2.1 Participating Laboratories

The NC distributed the artificial rainwater samples to 35 laboratories in charge of chemical analysis in 13 countries of EANET. 32 of the participating laboratories submitted their analytical results to the NC. A list of the participating laboratories and their codes were shown 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. 111w No. 112w	100mL each	Plastic bottle 100mL	One bottle each	Fixed quantity of reagents are dissolved in deionized water

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	SO ₄ ²⁻ μmol/L	NO ₃ ⁻ μmol/L	Cl ⁻ μmol/L	Na ⁺ μmol/L	K ⁺ μmol/L	Ca ²⁺ μmol/L	Mg ²⁺ μmol/L	NH ₄ ⁺ μmol/L
No. 111w	5.52	3.52	76.4	37.8	56.7	53.7	10.4	47.6	13.7	57.5
No. 112w	4.60	2.16	23.7	20.8	35.4	20.4	2.3	9.1	4.3	29.2

* For 100 times diluted samples.

2.2.3 Analytical Methods and Data Checking Procedures

Before the measurement, the samples have to be diluted 100 times accurately with deionized 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⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺ and NH₄⁺.

The laboratories were required to apply the analytic methods and data checking procedures that were specified in the “Technical Manual for Wet Deposition Monitoring in East Asia” and “Quality Assurance/Quality Control (QA/QC) Program for Wet Deposition Monitoring in East Asia”. Analytical methods specified in the manual were listed in Table 2.3.

Table 2.3 Analytical methods specified in the 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
Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺	Ion Chromatography Atomic Absorption Spectrometry Atomic Emission Spectrometry
NH ₄ ⁺	Ion Chromatography Spectrophotometry (Indophenol Blue Method)

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

Calculation of ion balance (R_1)

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

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

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

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

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

n , C_{Ci} : electric charge 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 calculated by the above equation was compared with allowable ranges in Table 2.4. If R_1 was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

Table 2.4 Allowable ranges for R_1 in different concentration ranges

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

Reference: Technical Documents for Wet Deposition Monitoring in East Asia (2000)

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

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

$$\begin{aligned}\Lambda \text{ calc } [\text{mS m}^{-1}] = & \{349.7 \times 10 (6\text{-pH}) + 80.0 \times 2c (\text{SO}_4^{2-}) + 71.5 \times c (\text{NO}_3^-) \\ & + 76.3 \times c (\text{Cl}^-) + 73.5 \times c (\text{NH}_4^+) + 50.1 \times c (\text{Na}^+) + 73.5 \times c (\text{K}^+) \\ & + 59.8 \times 2c (\text{Ca}^{2+}) + 53.3 \times 2c (\text{Mg}^{2+})\} / 10000\end{aligned}$$

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 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

Reference: Technical Documents for Wet Deposition Monitoring in East Asia (2000)

2.3 Results

The NC received the analytical results from 32 laboratories in the participating countries of EANET. The original data submitted by the laboratories were shown in Appendix 2.1 and 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, Va agreed with prepared value (Vp) fairly well. The range of $\Delta V/Vp$ was between -2.9% to 3.4% for the sample No. 111w, and -3.6% to 6.2% for the sample No. 112w.

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

Sample No. 111w

Constituents	Prepared (Vp)	Average (Va)	$\Delta V/Vp^{*1}$ %	S.D.	N	Min.	Max.
pH	5.52	5.36	-2.9	0.18	32	4.83	5.71
EC [mS m ⁻¹]	3.52	3.47	-1.5	0.08	30	3.27	3.67
SO ₄ ²⁻ [μmol L ⁻¹]	76.4	76.8	0.5	2.47	30	70.1	81.1
NO ₃ ⁻ [μmol L ⁻¹]	37.8	38.0	0.6	1.38	29	35.0	42.1
Cl ⁻ [μmol L ⁻¹]	56.7	57.1	0.8	1.96	30	54.3	62.5
Na ⁺ [μmol L ⁻¹]	53.7	52.8	-1.7	2.02	30	48.2	59.6
K ⁺ [μmol L ⁻¹]	10.4	10.4	0.2	0.86	30	9.3	12.5
Ca ²⁺ [μmol L ⁻¹]	47.6	49.2	3.4	4.24	31	41.3	59.9
Mg ²⁺ [μmol L ⁻¹]	13.7	13.6	-0.6	0.77	30	11.8	15.1
NH ₄ ⁺ [μmol L ⁻¹]	57.5	56.9	-1.1	3.11	30	50.0	66.2

Sample No. 112w

Constituents	Prepared (Vp)	Average (Va)	$\Delta V/Vp^{*1}$ %	S.D.	N	Min.	Max.
pH	4.60	4.63	0.7	0.06	31	4.43	4.73
EC [mS m ⁻¹]	2.16	2.08	-3.6	0.09	31	1.93	2.36
SO ₄ ²⁻ [μmol L ⁻¹]	23.7	23.4	-1.4	1.29	31	19.5	26.5
NO ₃ ⁻ [μmol L ⁻¹]	20.8	20.6	-0.8	0.82	30	18.9	22.4
Cl ⁻ [μmol L ⁻¹]	35.4	35.3	-0.3	1.24	29	33.5	38.2
Na ⁺ [μmol L ⁻¹]	20.4	20.3	-0.5	1.71	31	16.8	24.5
K ⁺ [μmol L ⁻¹]	2.3	2.4	6.2	0.40	31	1.7	3.4
Ca ²⁺ [μmol L ⁻¹]	9.1	9.1	-0.5	1.00	30	7.4	11.9
Mg ²⁺ [μmol L ⁻¹]	4.3	4.2	-3.1	0.43	30	3.0	4.8
NH ₄ ⁺ [μmol L ⁻¹]	29.2	29.1	-0.2	1.53	30	25.8	31.7

Note: *1, $(Va-Vp)/Vp \times 100$

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 chapter 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. 111w and No. 112w,
- 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. 111w and No. 112w 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 parameters)”, 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. 111w

The number and percentage of flagged data for the sample No. 111w were shown in Table 2.7. Fifteen analytical data out of 310 exceeded DQO within a factor of 2 and were flagged by "E". One analytical data out of 310 exceeded DQO more than a factor of 2 flagged by "X". Data flagged by "E" and "X" shared about 5.2 percent of all the submitted data for sample No. 111w. 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. 111w

Table for report No. 111w

Characterization of data	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total
Data within DQO	32	31	30	29	30	30	26	27	30	29	294
Data with flag E ^{*1}	0	1	1	1	0	1	4	4	1	2	15
Data with flag X ^{*2}	0	0	0	0	0	0	1	0	0	0	1
Flagged data [%]	0.0	3.1	3.2	3.3	0.0	3.2	16.1	12.9	3.2	6.5	5.2

(Total data = 310)

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

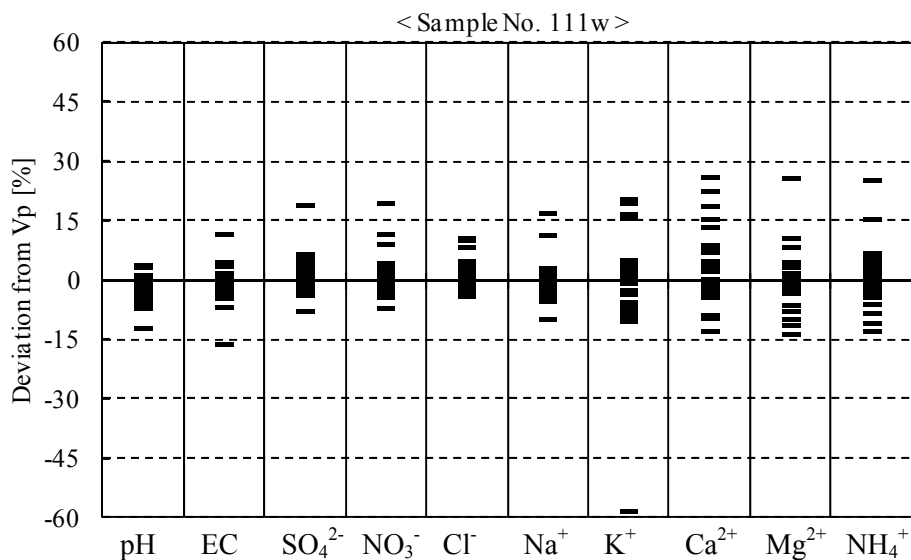


Figure 2.1 Distribution of the data normalized by prepared value in each parameter for sample No. 111w

The parameter which had 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. 111w

Lab. ID*1	pH	EC mS/m	SO ₄ ²⁻ μmol/L	NO ₃ ⁻ μmol/L	Cl ⁻ μmol/L	Na ⁺ μmol/L	K ⁺ μmol/L	Ca ²⁺ μmol/L	Mg ²⁺ μmol/L	NH ₄ ⁺ μmol/L	R ₁ %	R ₂ %
KH01	5.22	3.67	90.7 E	42.1	62.2	55.1	9.6	47.0	13.5	59.1	-6.5	3.4
CN01	5.40	3.45	78.1	38.9	62.5	52.6	9.7	51.2	13.8	61.1	0.0	3.3
CN02	5.31	3.56	77.2	38.5	57.2	53.0	10.0	49.7	13.7	57.8	0.5	0.9
CN03	5.33	3.42	74.5	37.2	59.2	55.2	9.5	51.3	13.9	55.6	2.0	2.4
CN04	5.29	3.55	77.3	37.6	57.2	50.9	9.7	53.8	14.8	55.4	1.8	1.5
ID01	5.43	3.48	80.2	38.3	57.0	52.2	10.7	45.4	12.1	53.9	-4.1	0.7
ID02	5.57	2.94 E	70.1	35.0	57.0	52.8	10.9	49.0	14.3	52.6	2.8	6.8
ID03	5.70	3.36	74.6	37.6	55.8	50.8	10.9	41.3	13.3	56.0	-2.9	-0.3
JP01	5.41	3.57	76.2	37.6	55.5	54.6	9.7	43.2	12.8	58.3	-1.4	-1.4
JP03	5.38	3.56	76.3	36.4	55.6	52.9	10.3	48.8	13.7	56.5	0.9	-0.3
JP04	5.48	3.43	76.4	37.9	56.7	50.7	10.5	49.5	13.9	56.8	0.1	1.4
JP05	5.37	3.37	73.2	37.4	56.2	51.8	10.9	45.7	13.4	55.4	0.1	1.2
JP07	5.39	3.40	75.6	38.9	57.4	50.8	9.6	49.2	13.7	60.5	0.7	2.5
JP08	5.46	3.35	76.7	38.4	56.6	54.2	10.1	51.2	14.1	57.9	1.6	3.4
JP09	5.51	3.50	76.4	37.1	56.1	52.5	10.4	45.9	13.2	56.4	-1.1	-0.5
JP10	5.47	3.42	73.7	36.1	54.4	51.5	9.8	46.5	13.2	54.8	0.2	-0.3
MY01	5.45	3.48	75.3	37.2	56.4	53.5	9.4	47.5	11.8	58.8	-0.1	0.1
MN01	5.43	3.44	---	---	---	---	---	---	---	---	---	---
MM01	5.68	3.49	79.1	36.8	57.7	54.4	9.8	47.5	13.4	55.4	-1.9	0.2
PH01	5.38	3.92	77.8	39.3	57.1	52.4	10.8	51.7	14.3	56.9	0.8	-3.7
PH02	5.71	3.42	76.6	38.0	54.3	51.2	10.7	56.3 E	17.2 E	50.0	3.0	1.7
KR01												
RU01	5.17	3.44	75.4	39.2	58.6	55.1	10.0	43.1	13.4	59.1	-0.9	2.4
RU02	5.24	3.53	79.8	41.1	61.3	59.6	10.1	42.9	14.8	61.2	-1.9	2.8
TH01	5.37	3.49	74.8	36.3	55.1	54.1	10.1	48.8	12.3	59.8	1.9	0.5
TH02	5.36	3.51	81.1	38.7	58.1	62.7 E	12.0 E	59.9 E	15.1	66.2 E	6.5	5.7
TH04	5.19	3.41	75.1	37.9	55.4	51.4	12.1 E	48.5	13.6	55.2	1.2	2.7
TH05	5.25	3.44	78.4	38.4	56.6	54.3	9.3	58.1 E	14.8	71.8 E	6.5	6.0
VN01	5.25	3.63	74.7	45.0 E	56.7	51.5	12.5 E	47.4	13.7	55.8	-0.7	-0.1
VN02	5.13	3.44	81.1	37.9	56.6	52.1	10.6	50.8	13.6	57.1	-0.1	4.6
VN03	5.12	3.40	77.9	---	---	52.5	12.4 E	49.1	14.3	55.3	---	---
VN04	5.15	3.54	80.6	37.8	55.8	52.5	10.4	51.0	13.3	56.8	0.1	2.8
VN05	4.83	3.27	78.8	38.7	57.6	48.2	4.3 X	54.8 E	12.6	51.1	-0.1	9.2 C
Vp	5.52	3.52	76.4	37.8	56.7	53.7	10.4	47.6	13.7	57.5	0.0	-0.1
N of data	32	32	31	30	30	31	31	31	31	31		
Within DQO	32	31	30	29	30	30	26	27	30	29		
Flag E	0	1	1	1	0	1	4	4	1	2		
Flag X	0	0	0	0	0	0	1	0	0	0		

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) Sample No. 112w

The number and percentage of flagged data for the sample No. 112w were shown in Table 2.9. Nineteen analytical data out of 310 exceeded the DQO within a factor of 2 and were flagged by "E". Nine analytical data out of 310 exceeded the DQO more than a factor of 2 and were flagged by "X". Data marked with flags shared up to 9.0 percent of all the submitted data for sample No. 112w.

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. 112w

Charactarization of data	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total
Data within DQO	32	31	30	30	29	27	21	26	26	30	282
Data with flag E ^{*1}	0	1	1	0	1	4	6	3	3	0	19
Data with flag X ^{*2}	0	0	0	0	0	0	4	2	2	1	9
Flagged data [%]	0.0	3.1	3.2	0.0	3.3	12.9	32.3	16.1	16.1	3.2	9.0

(Total data = 310)

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

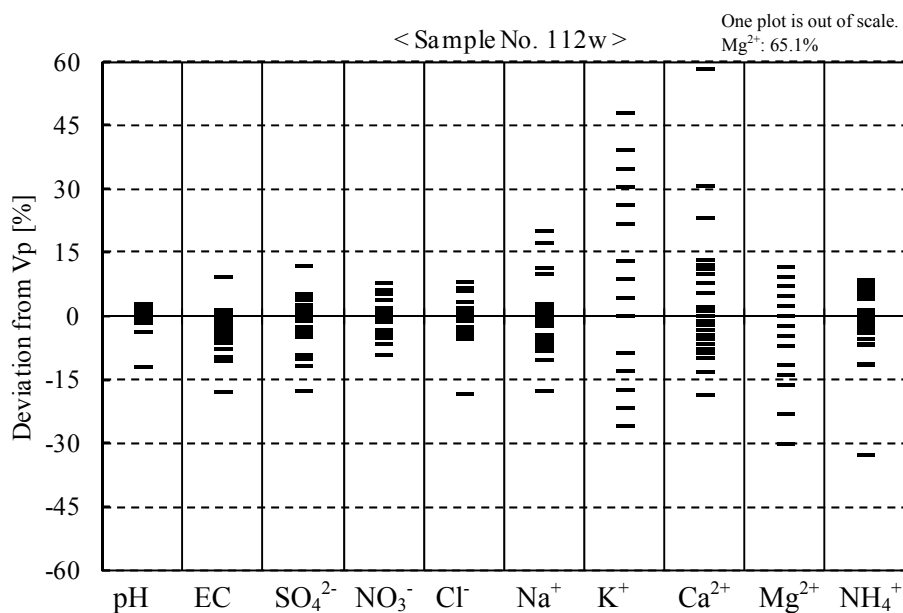


Figure 2.2 Distribution of the data normalized by prepared value for each parameter for sample No. 112w

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. 112w

Lab. ID* ¹	pH	EC mS/m	SO ₄ ²⁻ μmol/L	NO ₃ ⁻ μmol/L	Cl ⁻ μmol/L	Na ⁺ μmol/L	K ⁺ μmol/L	Ca ²⁺ μmol/L	Mg ²⁺ μmol/L	NH ₄ ⁺ μmol/L	R ₁ %	R ₂ %
KH01	4.58	1.95	26.5	22.4	37.5	20.0	1.7 E	8.3	4.2	29.5	-4.8	7.4
CN01	4.64	2.15	24.9	21.6	37.6	20.2	2.6	10.1	4.5	27.3	-3.2	-0.5
CN02	4.62	2.11	23.9	21.1	36.1	20.7	2.3	9.8	4.6	27.2	-1.0	0.6
CN03	4.58	2.08	24.1	20.9	34.2	20.8	2.9 E	8.9	3.6 E	25.8	-1.2	2.3
CN04	4.59	2.15	23.7	20.6	34.1	20.4	2.0	11.9 X	4.8	28.3	3.6	1.2
ID01	4.62	2.05	24.1	20.8	35.2	19.5	2.8 E	8.3	3.3 E	29.2	-2.7	1.4
ID02	4.68	1.77 E	19.5 E	20.0	28.9 E	19.9	2.8 E	10.3	4.8	28.6	7.6	3.8
ID03	4.61	1.93	22.9	20.7	34.2	20.0	2.4	9.3	4.4	30.5	2.0	5.0
JP01	4.66	2.19	23.0	19.7	34.0	21.0	2.5	8.4	4.5	30.9	1.2	-3.7
JP03	4.65	2.15	23.1	20.5	35.1	19.9	2.3	9.2	4.2	29.0	-0.7	-2.3
JP04	4.65	2.11	23.4	20.6	35.2	19.4	2.0	9.0	4.0	28.5	-2.1	-1.6
JP05	4.70	2.02	23.5	20.8	35.2	18.9	2.4	8.4	4.1	29.6	-3.6	-1.4
JP07	4.64	2.09	24.2	21.1	35.0	18.7	2.6	8.7	4.1	28.8	-2.9	-0.3
JP08	4.71	1.94	23.7	21.0	35.2	20.6	2.4	9.6	4.3	30.5	-1.4	1.2
JP09	4.70	2.10	23.4	20.5	34.0	20.1	2.4	8.4	4.1	28.5	-2.7	-3.7
JP10	4.65	2.10	21.3	18.9	33.5	19.4	2.1	8.6	4.0	28.0	1.1	-3.0
MY01	4.64	2.17	22.7	20.0	35.5	19.2	1.8 E	7.4 E	3.0 X	31.2	-2.5	-3.2
MN01	4.69	2.09	---	---	---	---	---	---	---	---	---	---
MM01	4.70	2.02	24.8	19.9	35.2	20.0	2.1	8.9	4.1	30.9	-2.8	-0.5
PH01	4.67	2.36	24.2	18.9	36.6	18.7	2.3	10.2	4.2	28.7	-2.0	-7.3
PH02	4.73	2.04	23.8	21.0	34.1	19.3	2.6	7.4 E	7.1 X	30.4	-1.4	-2.4
KR01												
RU01	4.55	2.12	23.6	21.2	35.9	20.6	2.3	9.1	4.2	29.1	1.2	3.6
RU02	4.59	1.95	22.5	22.1	38.2	24.5 E	2.4	9.3	4.4	31.0	2.6	6.8
TH01	4.61	2.09	20.9	19.4	34.3	20.3	2.1	8.2	3.3 E	31.7	3.1	-0.3
TH02	4.66	2.14	23.1	20.0	34.5	23.9 E	3.0 X	11.2 E	4.7	31.5	5.3	-1.0
TH04	4.43	2.09	22.7	20.1	33.7	19.5	2.5	10.0	4.3	27.6	7.5	9.9
TH05	4.52	2.07	24.3	21.2	34.5	18.3	1.9 E	7.9	3.8	30.7	0.1	5.8
VN01	4.62	1.99	24.6	20.5	36.1	19.0	2.5	8.8	4.3	28.3	-2.8	3.3
VN02	4.67	2.04	23.8	20.9	35.7	22.7	3.2 X	8.3	4.5	28.4	-1.4	0.1
VN03	4.54	2.03	21.5	---	---	24.5 E	3.1 X	9.3	4.4	25.9	---	---
VN04	4.64	2.15	23.6	21.0	35.2	22.4	3.4 X	8.5	4.6	28.8	0.1	-1.2
VN05	4.05	2.10	22.8	21.9	37.7	16.8 E	2.3	14.4 X	3.7	19.6 X	21.8 I	35.2 C
Vp	4.60	2.16	23.7	20.8	35.4	20.4	2.3	9.1	4.3	29.2	0.1	0.1
N of data	32	32	31	30	30	31	31	31	31	31		
Within DQO	32	31	30	30	29	27	21	26	26	30		
Flag E	0	1	1	0	1	4	6	3	3	0		
Flag X	0	0	0	0	0	0	4	2	2	1		

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

3) Comparison of High and Low Concentration Sample

The percentage of flagged data for Sample No. 111w and 112w were shown in Figure 2.3.

The percentage of the data within the DQO for the sample No. 111w and 112w were 94.8% and 91.0% respectively. The difference between both samples was 3.8%. In this project, the total number of flagged data was 44 (E: 34, X: 10) among the whole set of 620 data.

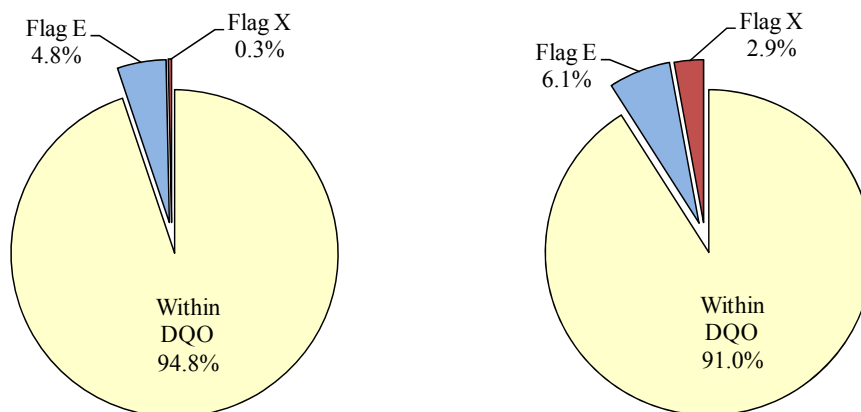


Figure 2.3 Percentage of flagged data for Sample No. 111w and No. 112w (Left: No. 111w, Right: No. 112w)

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 15, which corresponds to 46.9% of all the participating laboratories.

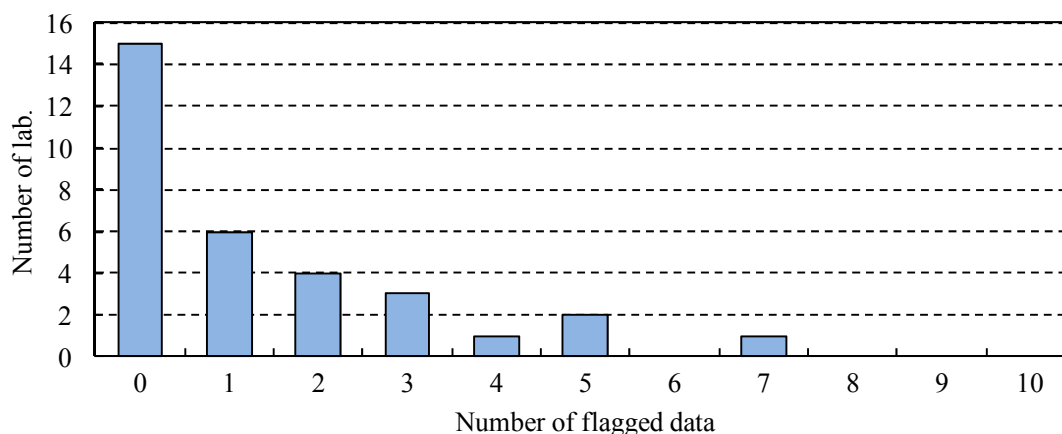


Figure 2.4 Distribution of the number of laboratory (by number of flags)

2.3.2 Evaluation of laboratories' performance (by analytical parameter)

The data normalized by V_p 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. 111w and 112w, 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.

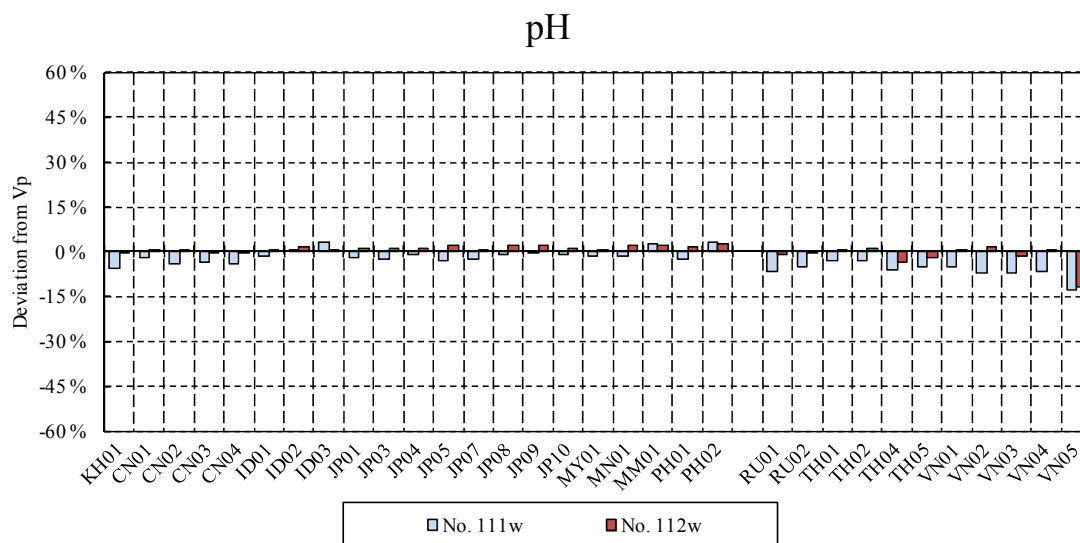


Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)

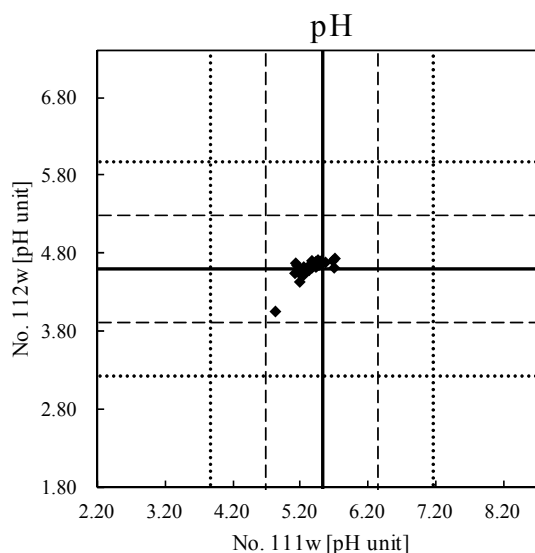


Figure 2.6 Scatter diagram for pH

2) EC

All participating laboratories used conductivity cell method for the measurement of EC. The data of sample No. 111w and the data of sample No. 112w from ID02 exceeded the DQO and were marked with flag “E”.

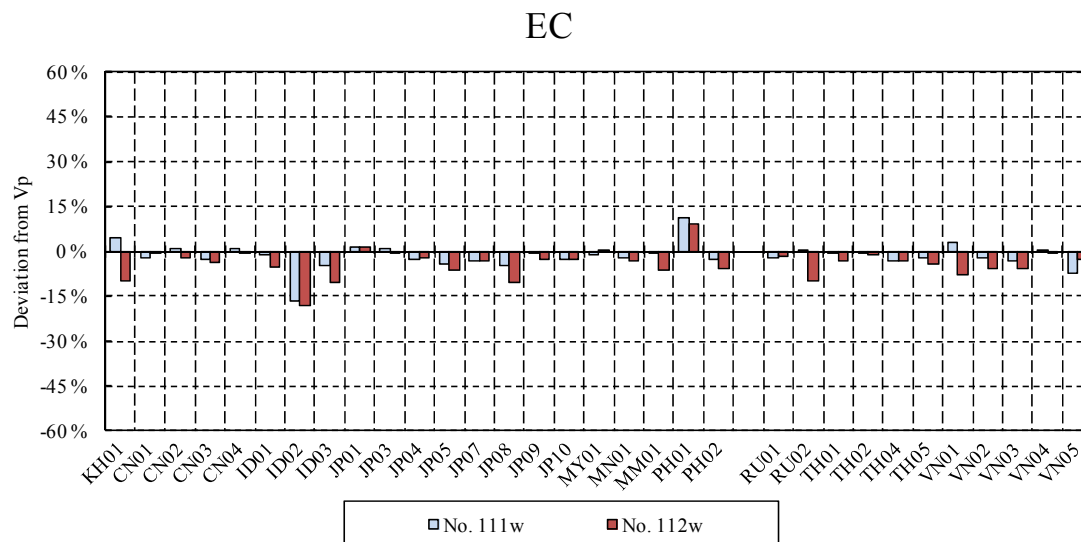


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)

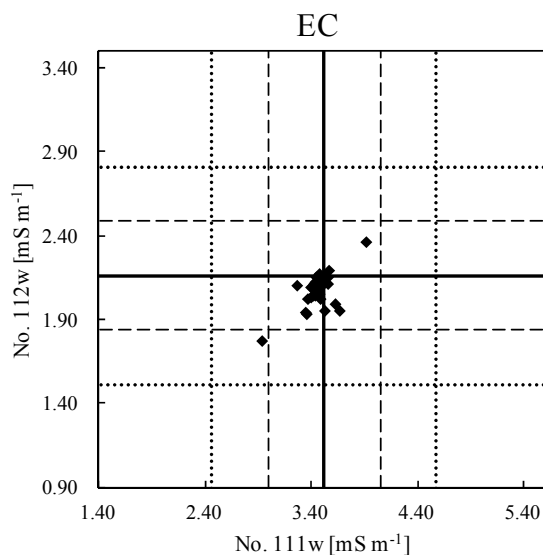


Figure 2.8 Scatter diagram for EC

3) SO_4^{2-}

The data of sample No. 111w from KH01 and the data of sample No. 112w from ID02 exceeded the DQO and were marked with flag “E”.

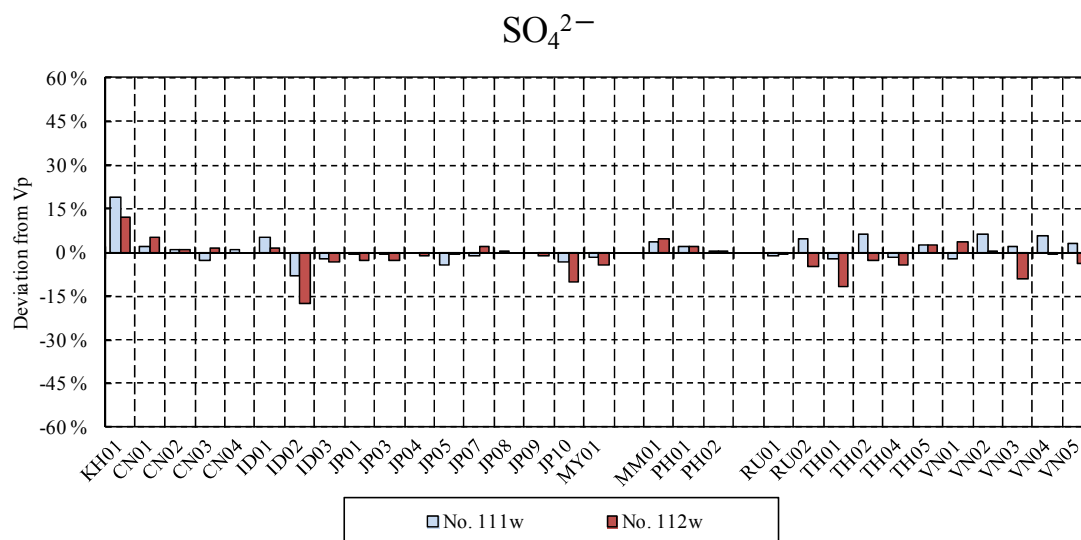


Figure 2.9 Deviation from prepared value for SO_4^{2-} (normalized by prepared value)

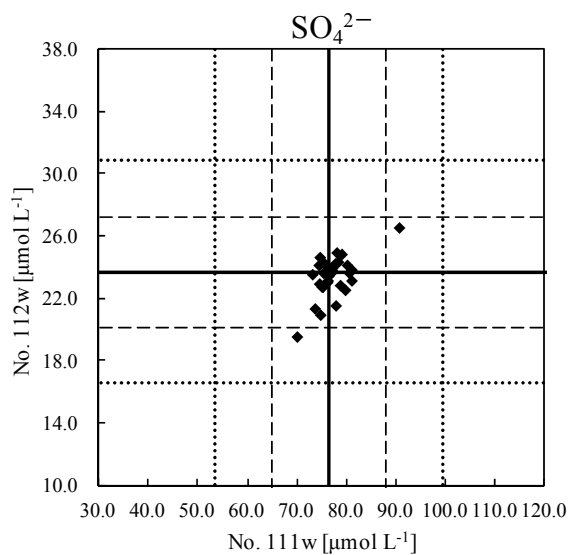


Figure 2.10 Scatter diagram for SO_4^{2-}

4) NO_3^-

The data of sample No. 111w from VN01 exceeded the DQO and was marked with flag “E”.

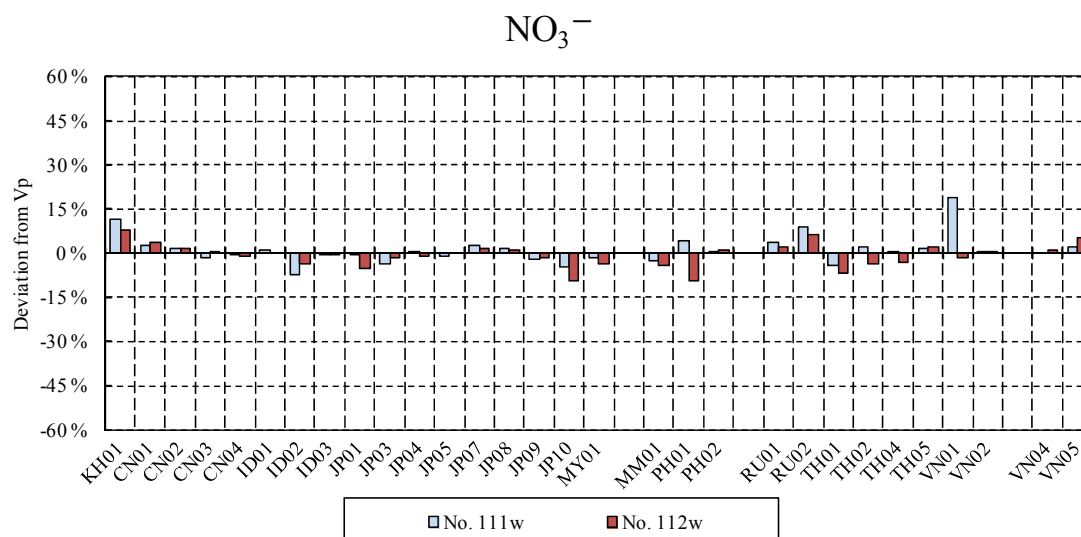


Figure 2.11 Deviation from prepared value for NO_3^- (normalized by prepared value)

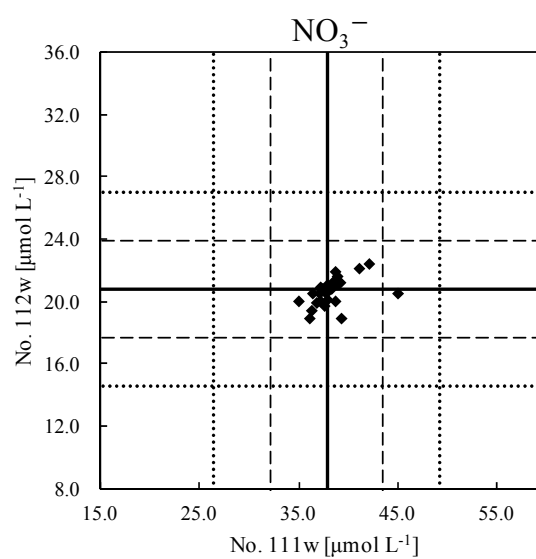


Figure 2.12 Scatter diagram for NO_3^-

5) Cl^-

All data of sample No. 111w satisfied the DQO. The data of sample No. 112w from ID02 exceeded the DQO and was marked with flag “E”.

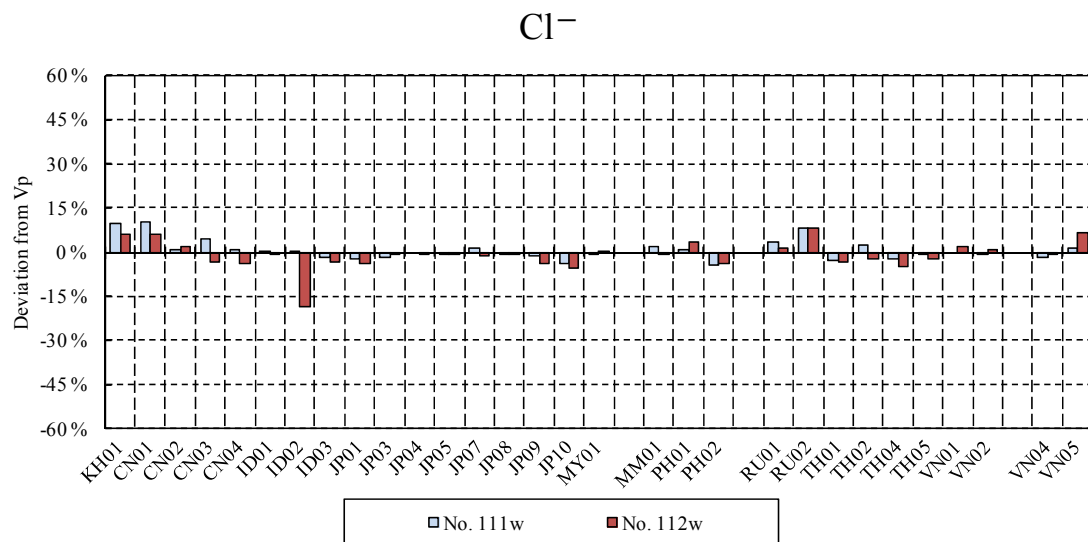


Figure 2.13 Deviation from prepared value for Cl^- (normalized by prepared value)

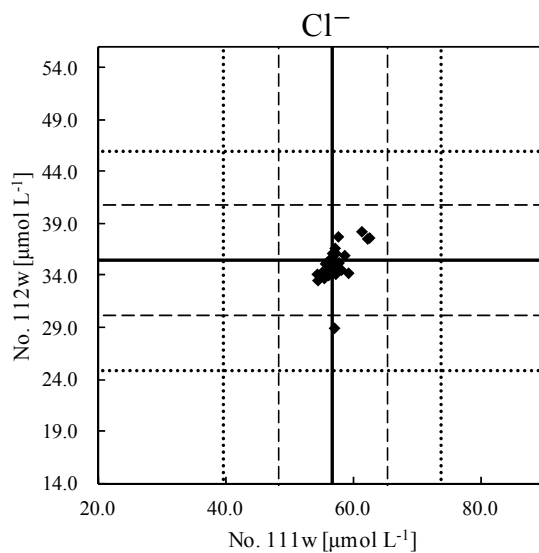


Figure 2.14 Scatter diagram for Cl^-

6) Na^+

The data of sample No. 111w from TH02 and the data of sample No. 112w from 4 laboratories (RU02, TH02, VN03 and VN05) exceeded the DQO and were marked with flag “E”.

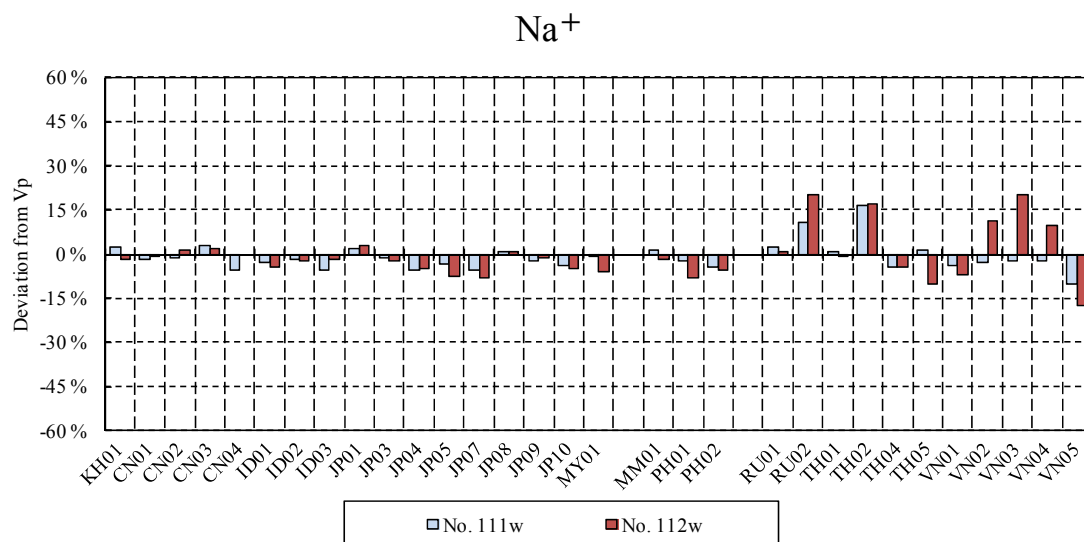


Figure 2.15 Deviation from prepared value for Na^+ (normalized by prepared value)

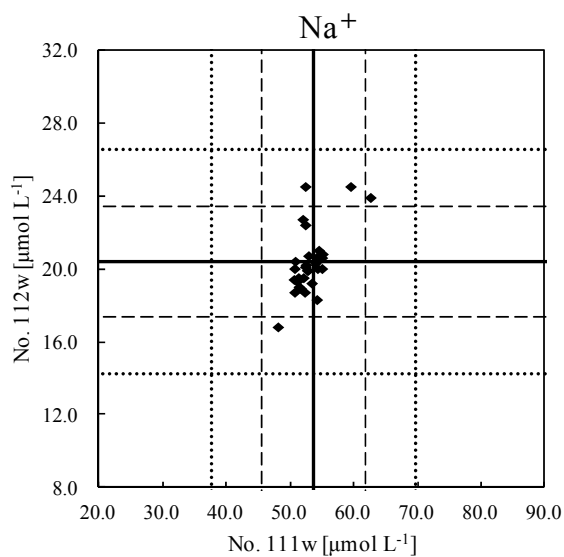


Figure 2.16 Scatter diagram for Na^+

7) K^+

The data of sample No. 111w from 4 laboratories (TH02, TH04, VN01 and VN03) and the data of sample No. 112w from 6 laboratories (KH01, CN03, ID01, ID02, MY01 and TH05) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No. 111w from VN05 and the data of sample No. 112w from 4 laboratories (TH02, VN02, VN03 and VN04) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

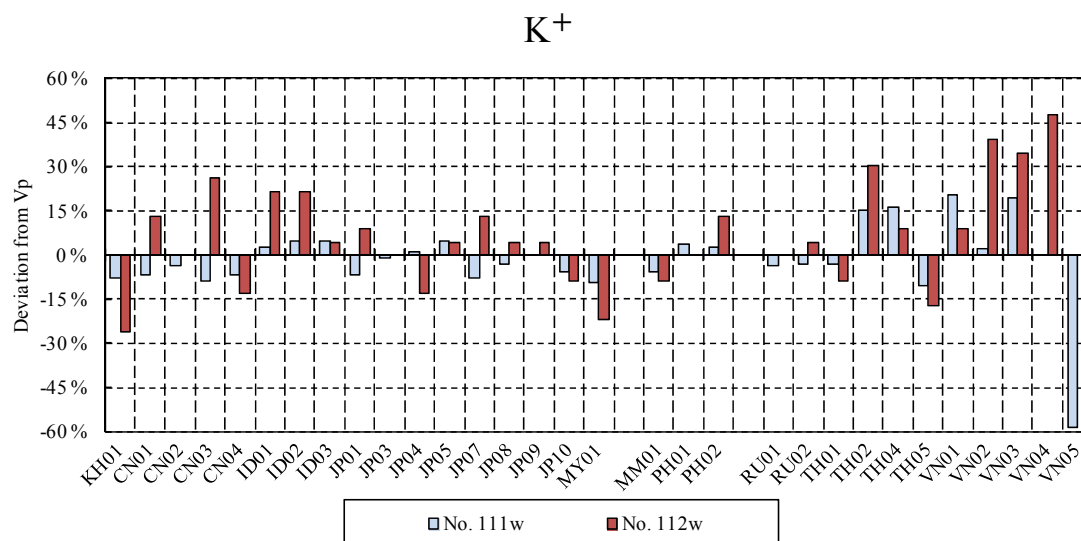


Figure 2.17 Deviation from prepared value for K^+ (normalized by prepared value)

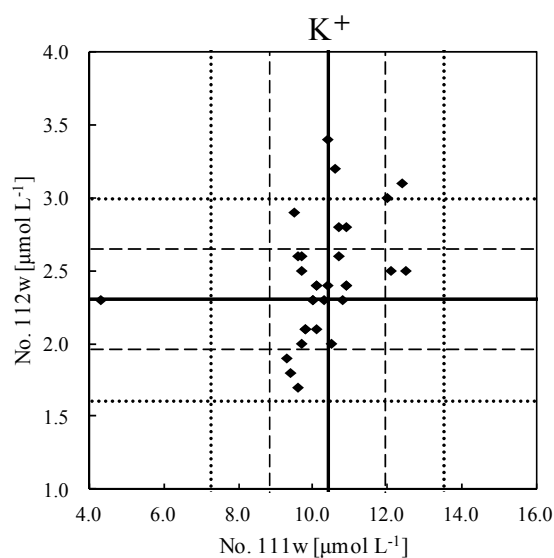


Figure 2.18 Scatter diagram for K^+

8) Ca^{2+}

The data of sample No. 111w from 4 laboratories (PH02, TH02, TH05 and VN05) and the data of sample No. 112w from 3 laboratories (MY01, PH02 and TH02) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No. 112w from 2 laboratories (CN04 and VN05) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

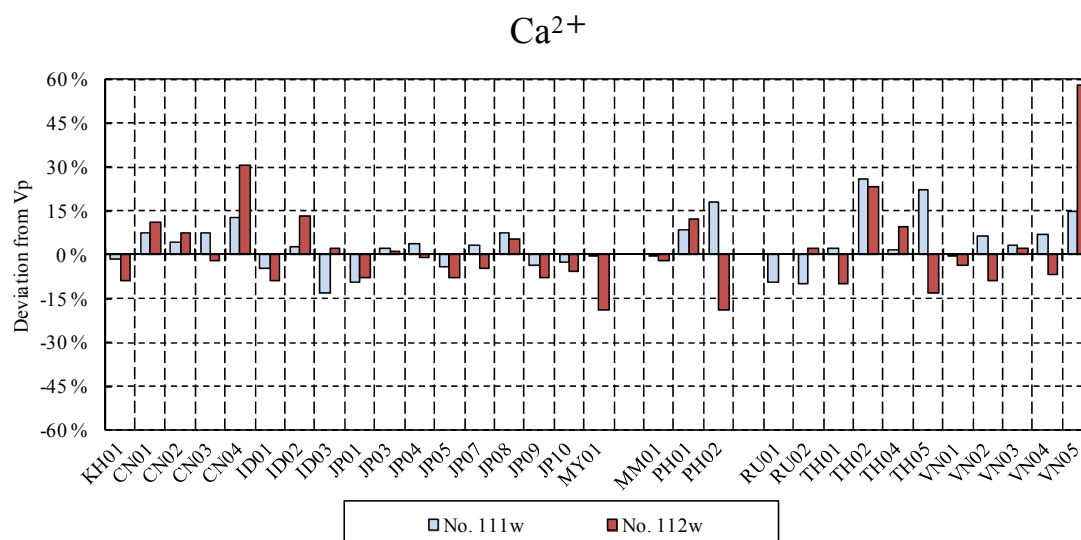


Figure 2.19 Deviation from prepared value for Ca^{2+} (normalized by prepared value)

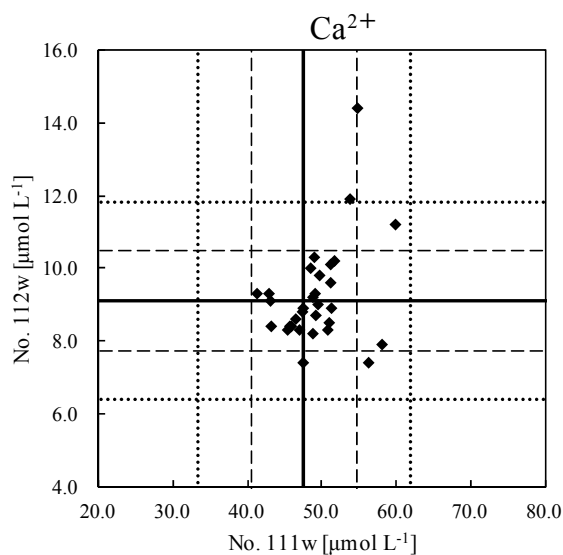


Figure 2.20 Scatter diagram for Ca^{2+}

9) Mg^{2+}

The data of sample No. 111w from PH02 and the data of sample No. 112w from 3 laboratories (CN03, ID01 and TH01) exceeded the DQO and marked with flag “E”. Additionally, the data of sample No. 112w from 2 laboratories (MY01 and PH02) exceeded the DQO more than a factor of 2 and were marked with flag “X”.

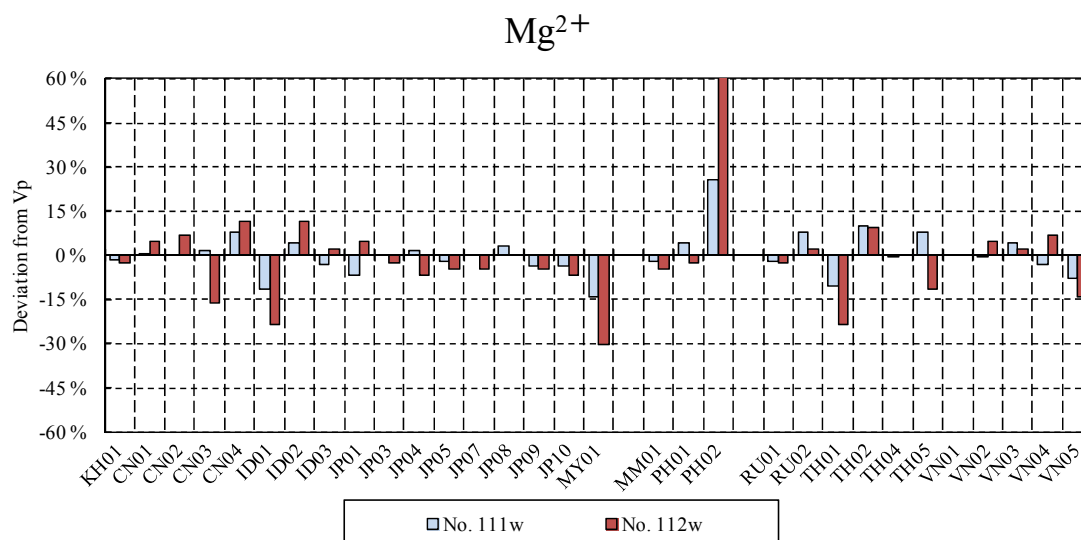


Figure 2.21 Deviation from prepared value for Mg^{2+} (normalized by prepared value)

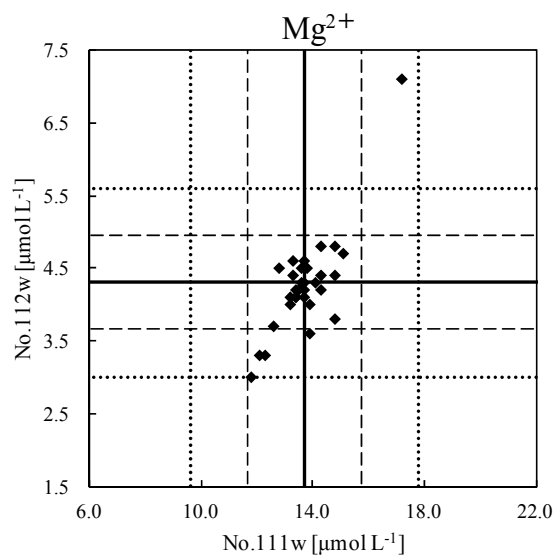


Figure 2.22 Scatter diagram for Mg^{2+}

10) NH_4^+

The data of sample No. 111w from 2 laboratories (TH02 and TH05) exceeded the DQO and marked with flag “E”. Additionally, the data of sample No. 112w from VN05 exceeded the DQO more than a factor of 2 and was marked with flag “X”.

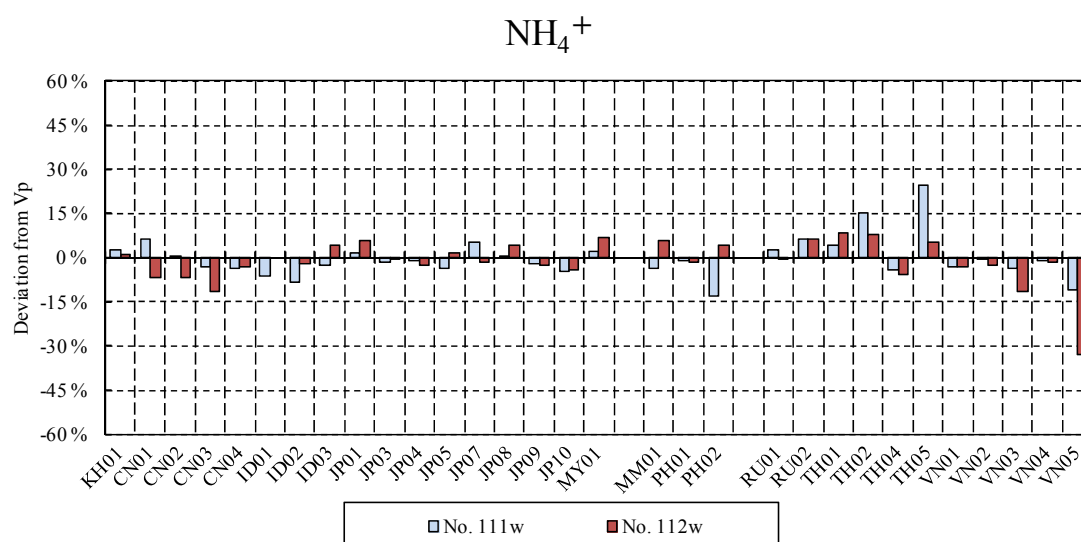


Figure 2.23 Deviation from prepared value for NH_4^+ (normalized by prepared value)

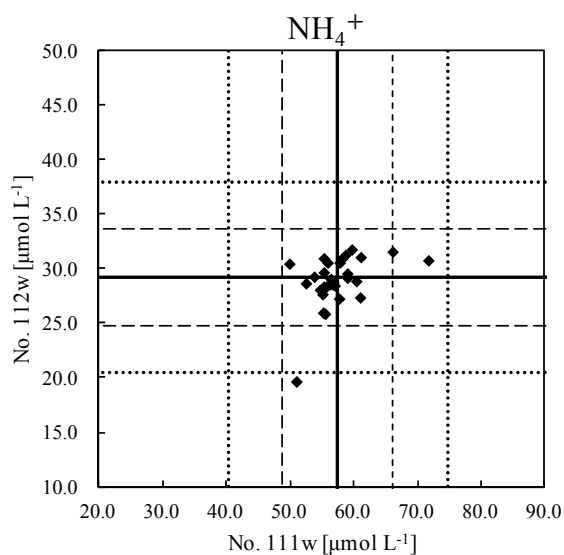


Figure 2.24 Scatter diagram for NH_4^+

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. From this year's survey, two samples are not distinguished as high or low concentration samples when they were distributed to participating laboratories. Ions except for H^+ concentrations of sample No. 111w were higher than those of No. 112w, whereas H^+ concentration of sample No. 111w was lower than that of No. 112w.

The relative standard deviations (R.S.D.) of each parameter for the sample No. 111w and No. 112w were shown in the Figure 2.25. The R.S.D. of K^+ for sample No. 112w was the highest in this survey. The R.S.D. values for sample No. 112w were higher than those for sample No. 111w except for pH and NH_4^+ .

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

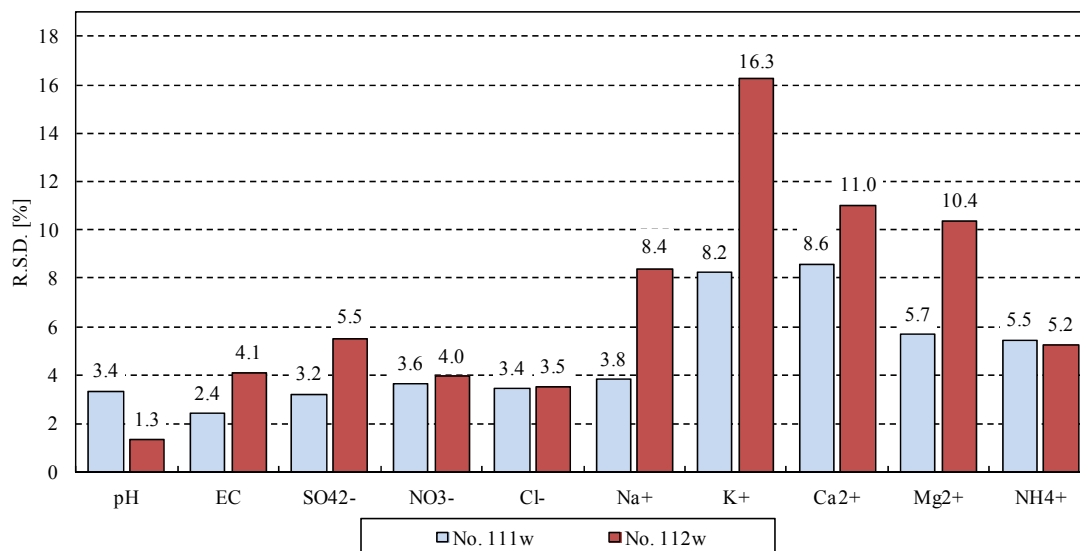


Figure 2.25 Relative standard deviations (R.S.D.) of each constituent

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”, “C” and “D” mean individuals of analysts in each laboratory who carried out analyses. In 14 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 ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
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	3	A	A	B	B	B	C	C	C	C	B
CN03	2	A	A	B	B	B	B	B	B	B	B
CN04	2	A	A	B	B	B	B	B	B	B	B
ID01	1	A	A	A	A	A	A	A	A	A	A
ID02	4	A	B	C	C	C	D	D	D	D	C
ID03	2	A	A	B	B	B	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	2	A	B	B	B	B	B	B	B	B	B
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	1	A	A	--	--	--	--	--	--	--	--
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	3	A	A	B	B	B	C	C	C	C	C
KR01											
RU01	3	A	A	B	B	B	C	C	C	C	A
RU02	2	A	A	A	A	A	B	B	B	B	A
TH01	1	A	A	A	A	A	A	A	A	A	A
TH02	3	A	B	B	B	B	C	C	C	C	C
TH04	2	A	A	B	B	B	B	B	B	B	B
TH05	2	A	A	B	B	B	B	B	B	B	B
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	B	B	--	--	C	C	C	C	B
VN04	2	A	A	B	B	B	B	B	B	B	B
VN05	2	A	A	B	B	B	B	B	B	B	B

Note: Light mesh, Analytic data of sample No. 111w or No. 112w was marked with flag "E" or "X";

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

"--", Not measured

Total of 160 data out of 310 were analyzed by the analysts whose experience was less than 5 years. The number corresponds to 51.6% 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 ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
KH01	3	3	3	3	3	3	3	3	3	3
CN01	20	20	20	20	20	20	20	20	20	20
CN02	13	13	3	3	3	6	6	6	6	3
CN03	1	1	1	1	1	1	1	1	1	1
CN04	3	3	16	16	16	16	16	16	16	16
ID01	10	10	10	10	10	10	10	10	10	10
ID02	6	6	12	12	12	5	5	5	5	12
ID03	2	2	3	3	3	3	3	3	3	3
JP01	8	8	8	8	8	8	8	8	8	8
JP03	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
JP04	2	2	2	2	2	2	2	2	2	2
JP05	2	2	2	2	2	2	2	2	2	2
JP07	2	2	2	2	2	2	2	2	2	2
JP08	1	1	1	1	1	1	1	1	1	1
JP09	3	3	3	3	3	3	3	3	3	3
JP10	0	0	0	0	0	0	0	0	0	0
MY01	5	5	2	2	2	1	1	1	1	1
MN01	<1	<1	--	--	--	--	--	--	--	--
MM01	6	6	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
PH01	2	2	4	4	4	14	14	14	14	4
PH02	8	8	4	4	4	4	4	4	4	4
KR01										
RU01	7	7	13	13	13	13	13	13	13	7
RU02	0.5	0.5	0.5	0.5	0.5	20	20	20	20	0.5
TH01	2	2	2	2	2	2	2	2	2	2
TH02	14	8	8	8	8	14	14	14	14	14
TH04	8	8	5	5	5	5	5	5	5	5
TH05	10	10	8	8	8	8	8	8	8	8
VN01	3	3	18	18	18	18	18	18	18	18
VN02	2	2	7	7	7	7	7	7	7	7
VN03	5	5	5	--	--	8	8	8	8	6
VN04	5	5	7	7	7	7	7	7	7	7
VN05	3	3	5	5	5	5	5	5	5	5

Note: Light mesh, Analytic data of sample No. 111w or No. 112w was marked with flag "E" or "X";

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

"--", Not measured

2) Analytical instruments

As shown in Figure 2.26, most of the participating laboratories used the specified methods described in the “Technical Manual for Wet Deposition Monitoring in East Asia”. Laboratory of CN02 did not use the specified methods for the analyses of NH_4^+ . (Spectrophotometry without Indophenol) Laboratory of RU02 did not use the specified methods for the analyses of Cl^- and NH_4^+ . (Cl^- : Titrimetry, NH_4^+ : Spectrophotometry without Indophenol) 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.

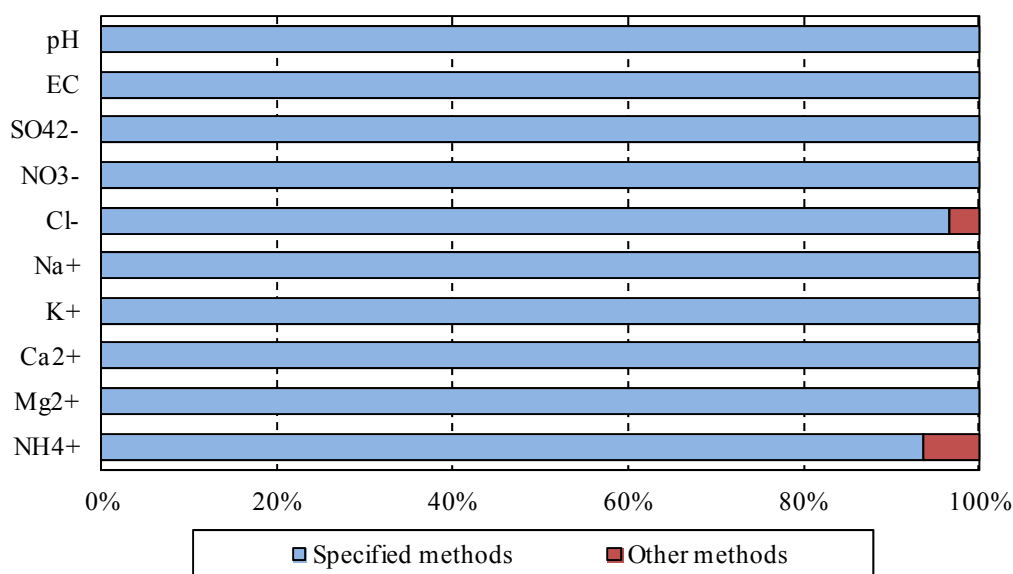


Figure 2.26 Percentage of laboratories that use the specified methods

3) Date of Analysis

Figure 2.27 shows the distribution of “Start date” and “Finish date” of analysis in the participating laboratories. In total, 58% of all the submitted data was determined within the year of 2011, and 3% was determined after the deadline of data submission in this project.

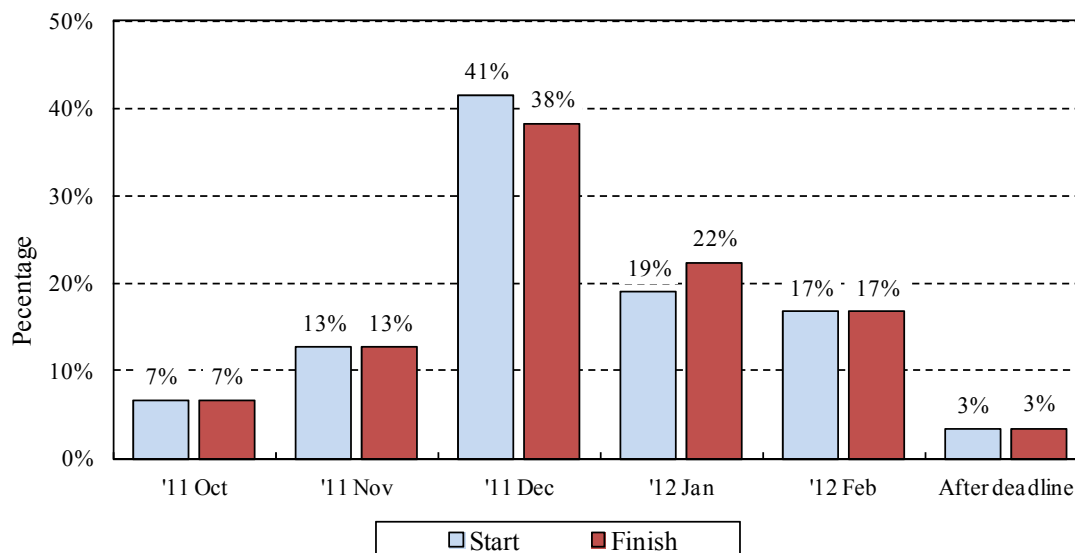


Figure 2.27 Distribution of Start date and Finish date of analysis

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.

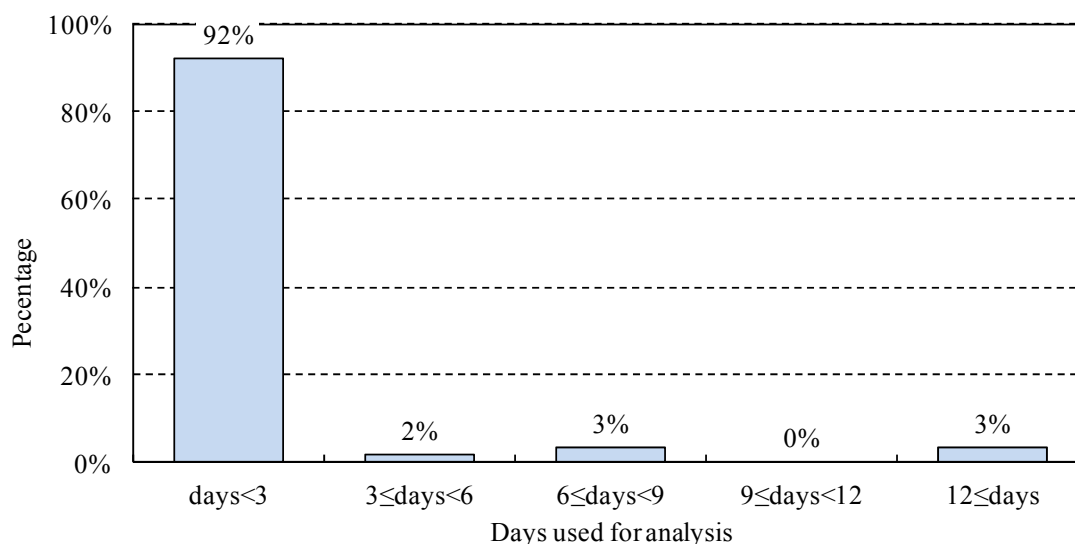


Figure 2.28 Distribution of Days used for analysis

2.4 Comparison with past surveys

Since the beginning of EANET, inter-laboratory comparison on wet deposition reached the 14th 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. 111w and sample No. 112w were treated as high and low concentration samples respectively, in consideration of the sum total of ionic equivalent.

The percentages of data within DQO for the sample No. 111w was 94.8%, which was a little lower than that of high concentration sample of previous survey. On the other hand, the percentage of data within DQO for the sample No. 112w was 91.0%, which was the highest among low concentration samples. The accuracy of the measurement on wet deposition monitoring might have improved due to the continuous efforts and experiences in participating laboratories.

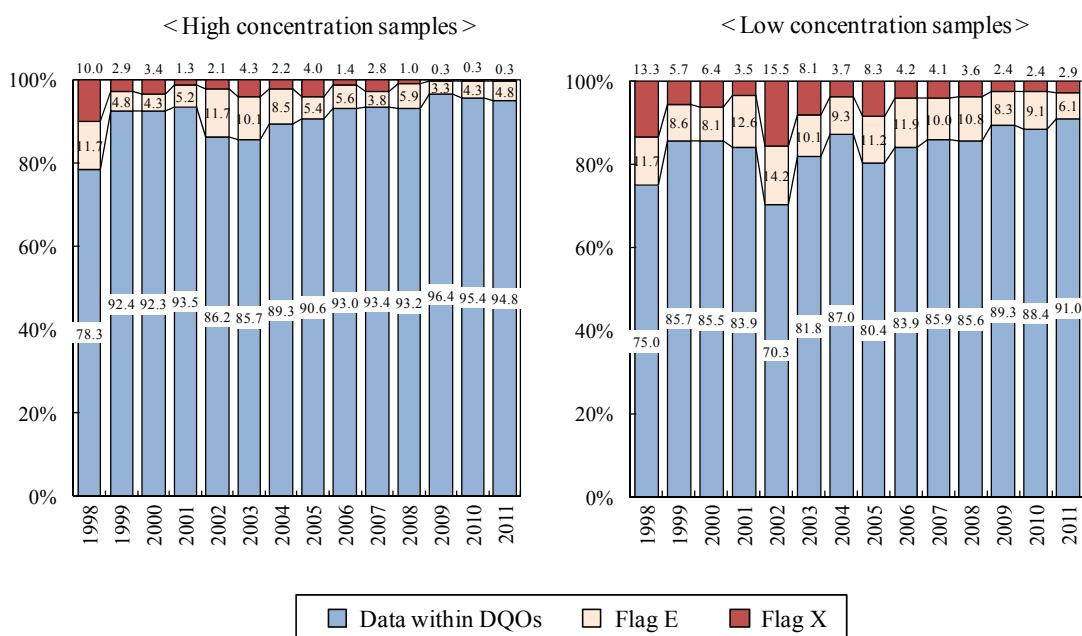


Figure 2.29 Comparison of results from the inter-laboratory comparison projects

Figure 2.30 showed the trend of the prepared values and the percentage of flagged data. Although the percentages of data marked with flags “E” and “X” decreased in most parameters compared with past surveys, the percentages were relatively high in cations as ever.

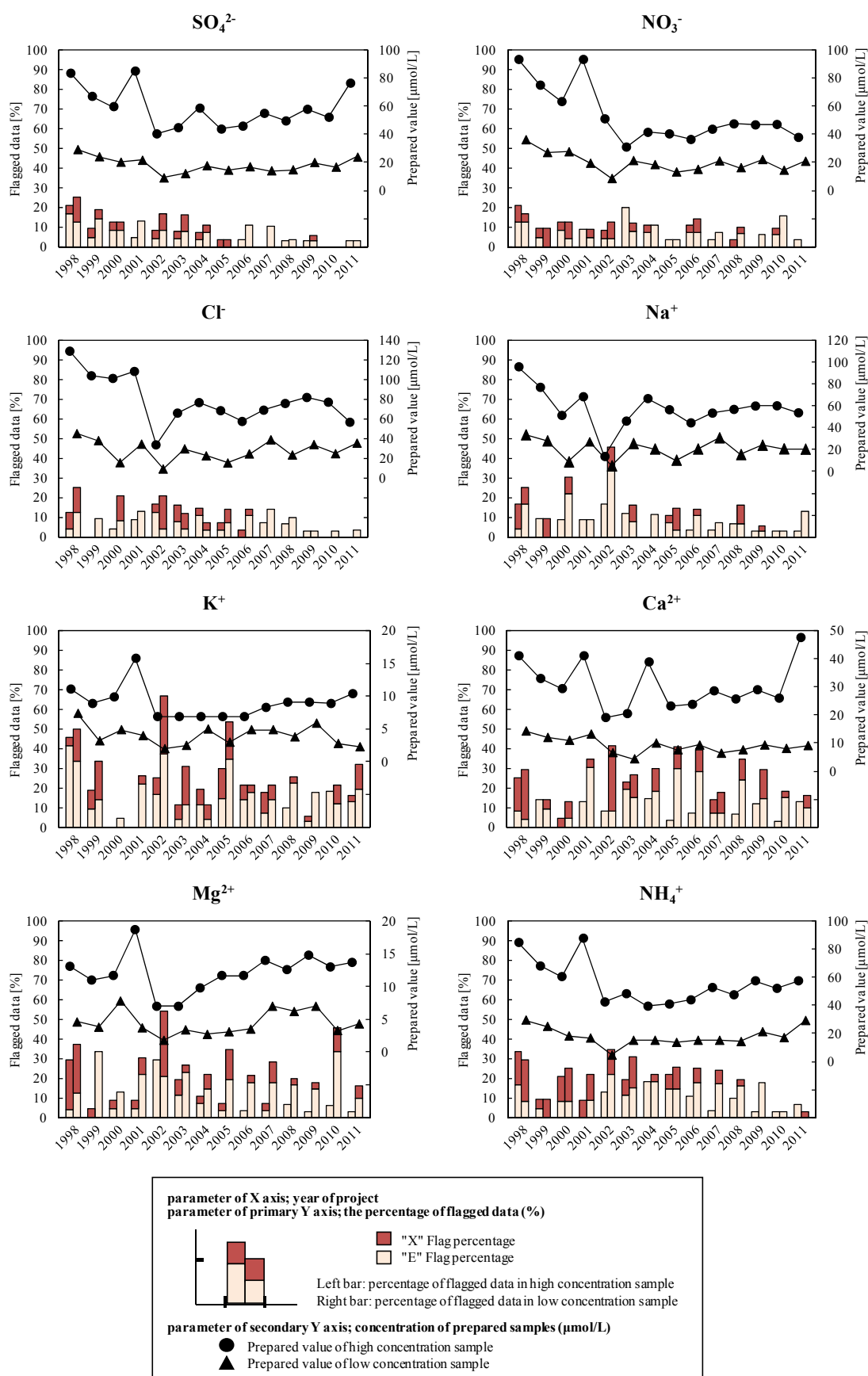


Figure 2.30 Comparison for each parameter in inter-laboratory comparison project

As shown in the figure 2.31, the number of data was decreased from the survey in last year. The total number of data was 620 in this survey because some participating laboratories did not submit analytical data.

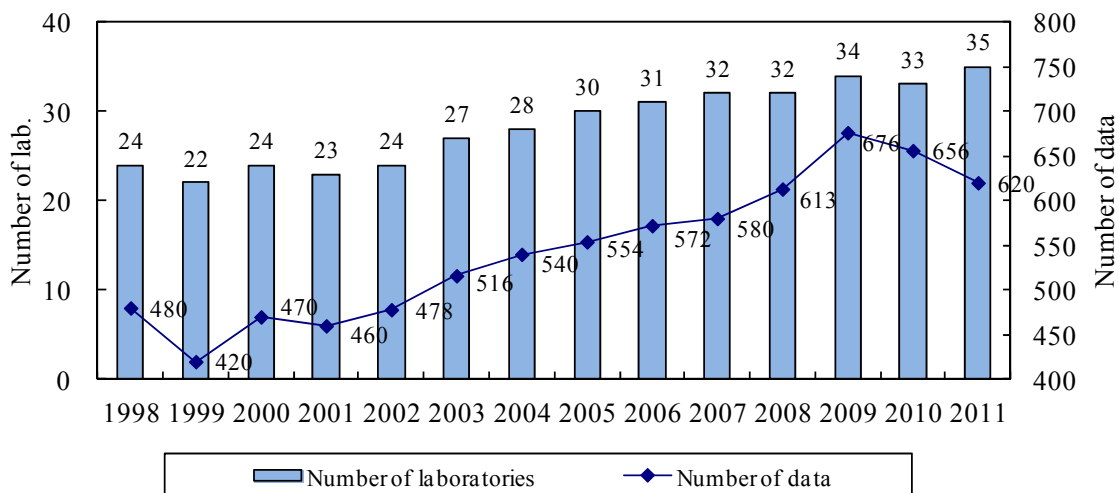


Figure 2.31 The number of participating laboratories and data in the inter-laboratory comparison projects on wet deposition

2.5 Recommendations for improvement

The fundamental matters for QA/QC on measurements and analyses of samples were 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

- After drawing calibration curves for the determination of ion concentrations, accuracy check by analyzing “Reference Materials” is recommended.
- Ranges of calibration curves need to cover the concentrations of the samples.

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 values of artificial samples used for this survey are theoretically zero because they don’t contain other extra ion species. 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.

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Appendix 2.1 Analytical Results submitted by the laboratories

Appendix Table 2.1.1 Analytical data concerning high conc. sample No. 111w

Sample No. 111w

Lab. ID	pH	EC mS/m	SO ₄ ²⁻ μmol/L	NO ₃ ⁻ μmol/L	Cl ⁻ μmol/L	Na ⁺ μmol/L	K ⁺ μmol/L	Ca ²⁺ μmol/L	Mg ²⁺ μmol/L	NH ₄ ⁺ μmol/L
KH01	5.22	3.67	90.7	42.1	62.2	55.1	9.6	47.0	13.5	59.1
CN01	5.40	3.45	78.1	38.9	62.5	52.6	9.7	51.2	13.8	61.1
CN02	5.31	3.56	77.2	38.5	57.2	53.0	10.0	49.7	13.7	57.8
CN03	5.33	3.42	74.5	37.2	59.2	55.2	9.5	51.3	13.9	55.6
CN04	5.29	3.55	77.3	37.6	57.2	50.9	9.7	53.8	14.8	55.4
ID01	5.43	3.48	80.2	38.3	57.0	52.2	10.7	45.4	12.1	53.9
ID02	5.57	2.94	70.1	35.0	57.0	52.8	10.9	49.0	14.3	52.6
ID03	5.70	3.36	74.6	37.6	55.8	50.8	10.9	41.3	13.3	56.0
JP01	5.41	3.57	76.2	37.6	55.5	54.6	9.7	43.2	12.8	58.3
JP03	5.38	3.56	76.3	36.4	55.6	52.9	10.3	48.8	13.7	56.5
JP04	5.48	3.43	76.4	37.9	56.7	50.7	10.5	49.5	13.9	56.8
JP05	5.37	3.37	73.2	37.4	56.2	51.8	10.9	45.7	13.4	55.4
JP07	5.39	3.40	75.6	38.9	57.4	50.8	9.6	49.2	13.7	60.5
JP08	5.46	3.35	76.7	38.4	56.6	54.2	10.1	51.2	14.1	57.9
JP09	5.51	3.50	76.4	37.1	56.1	52.5	10.4	45.9	13.2	56.4
JP10	5.47	3.42	73.7	36.1	54.4	51.5	9.8	46.5	13.2	54.8
MY01	5.45	3.48	75.3	37.2	56.4	53.5	9.4	47.5	11.8	58.8
MN01	5.43	3.44	---	---	---	---	---	---	---	---
MM01	5.68	3.49	79.1	36.8	57.7	54.4	9.8	47.5	13.4	55.4
PH01	5.38	3.92	77.8	39.3	57.1	52.4	10.8	51.7	14.3	56.9
PH02	5.71	3.42	76.6	38.0	54.3	51.2	10.7	56.3	17.2	50.0
KR01										
RU01	5.17	3.44	75.4	39.2	58.6	55.1	10.0	43.1	13.4	59.1
RU02	5.24	3.53	79.8	41.1	61.3	59.6	10.1	42.9	14.8	61.2
TH01	5.37	3.49	74.8	36.3	55.1	54.1	10.1	48.8	12.3	59.8
TH02	5.36	3.51	81.1	38.7	58.1	62.7	12.0	59.9	15.1	66.2
TH04	5.19	3.41	75.1	37.9	55.4	51.4	12.1	48.5	13.6	55.2
TH05	5.25	3.44	78.4	38.4	56.6	54.3	9.3	58.1	14.8	71.8
VN01	5.25	3.63	74.7	45.0	56.7	51.5	12.5	47.4	13.7	55.8
VN02	5.13	3.44	81.1	37.9	56.6	52.1	10.6	50.8	13.6	57.1
VN03	5.12	3.40	77.9	---	---	52.5	12.4	49.1	14.3	55.3
VN04	5.15	3.54	80.6	37.8	55.8	52.5	10.4	51.0	13.3	56.8
VN05	4.83	3.27	78.8	38.7	57.6	48.2	4.3	54.8	12.6	51.1
Prepared value	5.52	3.52	76.4	37.8	56.7	53.7	10.4	47.6	13.7	57.5
Number of data	32	30	30	29	30	30	30	31	30	30
Average	5.36	3.47	76.8	38.0	57.1	52.8	10.4	49.2	13.6	56.9
Minimum	4.83	3.27	70.1	35.0	54.3	48.2	9.3	41.3	11.8	50.0
Maximum	5.71	3.67	81.1	42.1	62.5	59.6	12.5	59.9	15.1	66.2
Standard deviation	0.18	0.08	2.47	1.38	1.96	2.02	0.86	4.24	0.77	3.11

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

"---", Not measured

Appendix Table 2.1.2 Analytical data concerning low conc. sample No. 112w

Sample No. 112w

Lab. ID	pH	EC mS/m	SO ₄ ²⁻ μmol/L	NO ₃ ⁻ μmol/L	Cl ⁻ μmol/L	Na ⁺ μmol/L	K ⁺ μmol/L	Ca ²⁺ μmol/L	Mg ²⁺ μmol/L	NH ₄ ⁺ μmol/L
KH01	4.58	1.95	26.5	22.4	37.5	20.0	1.7	8.3	4.2	29.5
CN01	4.64	2.15	24.9	21.6	37.6	20.2	2.6	10.1	4.5	27.3
CN02	4.62	2.11	23.9	21.1	36.1	20.7	2.3	9.8	4.6	27.2
CN03	4.58	2.08	24.1	20.9	34.2	20.8	2.9	8.9	3.6	25.8
CN04	4.59	2.15	23.7	20.6	34.1	20.4	2.0	11.9	4.8	28.3
ID01	4.62	2.05	24.1	20.8	35.2	19.5	2.8	8.3	3.3	29.2
ID02	4.68	1.77	19.5	20.0	28.9	19.9	2.8	10.3	4.8	28.6
ID03	4.61	1.93	22.9	20.7	34.2	20.0	2.4	9.3	4.4	30.5
JP01	4.66	2.19	23.0	19.7	34.0	21.0	2.5	8.4	4.5	30.9
JP03	4.65	2.15	23.1	20.5	35.1	19.9	2.3	9.2	4.2	29.0
JP04	4.65	2.11	23.4	20.6	35.2	19.4	2.0	9.0	4.0	28.5
JP05	4.70	2.02	23.5	20.8	35.2	18.9	2.4	8.4	4.1	29.6
JP07	4.64	2.09	24.2	21.1	35.0	18.7	2.6	8.7	4.1	28.8
JP08	4.71	1.94	23.7	21.0	35.2	20.6	2.4	9.6	4.3	30.5
JP09	4.70	2.10	23.4	20.5	34.0	20.1	2.4	8.4	4.1	28.5
JP10	4.65	2.10	21.3	18.9	33.5	19.4	2.1	8.6	4.0	28.0
MY01	4.64	2.17	22.7	20.0	35.5	19.2	1.8	7.4	3.0	31.2
MN01	4.69	2.09	---	---	---	---	---	---	---	---
MM01	4.70	2.02	24.8	19.9	35.2	20.0	2.1	8.9	4.1	30.9
PH01	4.67	2.36	24.2	18.9	36.6	18.7	2.3	10.2	4.2	28.7
PH02	4.73	2.04	23.8	21.0	34.1	19.3	2.6	7.4	7.1	30.4
KR01										
RU01	4.55	2.12	23.6	21.2	35.9	20.6	2.3	9.1	4.2	29.1
RU02	4.59	1.95	22.5	22.1	38.2	24.5	2.4	9.3	4.4	31.0
TH01	4.61	2.09	20.9	19.4	34.3	20.3	2.1	8.2	3.3	31.7
TH02	4.66	2.14	23.1	20.0	34.5	23.9	3.0	11.2	4.7	31.5
TH04	4.43	2.09	22.7	20.1	33.7	19.5	2.5	10.0	4.3	27.6
TH05	4.52	2.07	24.3	21.2	34.5	18.3	1.9	7.9	3.8	30.7
VN01	4.62	1.99	24.6	20.5	36.1	19.0	2.5	8.8	4.3	28.3
VN02	4.67	2.04	23.8	20.9	35.7	22.7	3.2	8.3	4.5	28.4
VN03	4.54	2.03	21.5	---	---	24.5	3.1	9.3	4.4	25.9
VN04	4.64	2.15	23.6	21.0	35.2	22.4	3.4	8.5	4.6	28.8
VN05	4.05	2.10	22.8	21.9	37.7	16.8	2.3	14.4	3.7	19.6
Prepared value	4.60	2.16	23.7	20.8	35.4	20.4	2.3	9.1	4.3	29.2
Number of data	31	31	31	30	29	31	31	30	30	30
Average	4.63	2.08	23.4	20.6	35.3	20.3	2.4	9.1	4.2	29.1
Minimum	4.43	1.93	19.5	18.9	33.5	16.8	1.7	7.4	3.0	25.8
Maximum	4.73	2.36	26.5	22.4	38.2	24.5	3.4	11.9	4.8	31.7
Standard deviation	0.06	0.09	1.29	0.82	1.24	1.71	0.40	1.00	0.43	1.53

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

"---", Not measured

Appendix 2.2 Normalized Data

Appendix Table 2.2.1 Deviation% from prepared values of high conc. sample No. 111w

Sample No. 111w

Lab. ID	pH %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %	NH ₄ ⁺ %
KH01	-5.4	4.3	18.7	11.4	9.7	2.6	-7.7	-1.3	-1.5	2.8
CN01	-2.2	-2.0	2.2	2.9	10.2	-2.0	-6.7	7.6	0.7	6.3
CN02	-3.8	1.1	1.0	1.9	0.9	-1.3	-3.8	4.4	0.0	0.5
CN03	-3.4	-2.8	-2.5	-1.6	4.4	2.8	-8.7	7.8	1.5	-3.3
CN04	-4.2	0.9	1.2	-0.5	0.9	-5.2	-6.7	13.0	8.0	-3.7
ID01	-1.6	-1.1	5.0	1.3	0.5	-2.8	2.9	-4.6	-11.7	-6.3
ID02	0.9	-16.5	-8.2	-7.4	0.5	-1.7	4.8	2.9	4.4	-8.5
ID03	3.3	-4.5	-2.4	-0.5	-1.6	-5.4	4.8	-13.2	-2.9	-2.6
JP01	-2.0	1.4	-0.3	-0.5	-2.1	1.7	-6.7	-9.2	-6.6	1.4
JP03	-2.5	1.1	-0.1	-3.7	-1.9	-1.5	-1.0	2.5	0.0	-1.7
JP04	-0.7	-2.6	0.0	0.3	0.0	-5.6	1.0	4.0	1.5	-1.2
JP05	-2.7	-4.3	-4.2	-1.1	-0.9	-3.5	4.8	-4.0	-2.2	-3.7
JP07	-2.4	-3.4	-1.0	2.9	1.2	-5.4	-7.7	3.4	0.0	5.2
JP08	-1.1	-4.8	0.4	1.6	-0.2	0.9	-2.9	7.6	2.9	0.7
JP09	-0.2	-0.6	0.0	-1.9	-1.1	-2.2	0.0	-3.6	-3.6	-1.9
JP10	-0.9	-2.8	-3.5	-4.5	-4.1	-4.1	-5.8	-2.3	-3.6	-4.7
MY01	-1.3	-1.1	-1.4	-1.6	-0.5	-0.4	-9.6	-0.2	-13.9	2.3
MN01	-1.6	-2.3	---	---	---	---	---	---	---	---
MM01	2.9	-0.9	3.5	-2.6	1.8	1.3	-5.8	-0.2	-2.2	-3.7
PH01	-2.5	11.4	1.8	4.0	0.7	-2.4	3.8	8.6	4.4	-1.0
PH02	3.4	-2.8	0.3	0.5	-4.2	-4.7	2.9	18.3	25.5	-13.0
RU01	-6.3	-2.3	-1.3	3.7	3.4	2.6	-3.8	-9.5	-2.2	2.8
RU02	-5.1	0.3	4.5	8.7	8.1	11.0	-2.9	-9.9	8.0	6.4
TH01	-2.7	-0.9	-2.1	-4.0	-2.8	0.7	-2.9	2.5	-10.2	4.0
TH02	-2.9	-0.3	6.2	2.4	2.5	16.8	15.4	25.8	10.2	15.1
TH04	-6.0	-3.1	-1.7	0.3	-2.3	-4.3	16.3	1.9	-0.7	-4.0
TH05	-4.9	-2.3	2.6	1.6	-0.2	1.1	-10.6	22.1	8.0	24.9
VN01	-4.9	3.1	-2.2	19.0	0.0	-4.1	20.2	-0.4	0.0	-3.0
VN02	-7.1	-2.3	6.2	0.3	-0.2	-3.0	1.9	6.7	-0.7	-0.7
VN03	-7.2	-3.4	2.0	---	---	-2.2	19.2	3.2	4.4	-3.8
VN04	-6.7	0.6	5.5	0.0	-1.6	-2.2	0.0	7.1	-2.9	-1.2
VN05	-12.5	-7.1	3.1	2.4	1.6	-10.2	-58.7	15.1	-8.0	-11.1
Number of data	32	32	31	30	30	31	31	31	31	31
Average	-2.9	-1.6	1.1	1.2	0.8	-1.1	-1.7	3.4	0.2	-0.2
Minimum	-12.5	-16.5	-8.2	-7.4	-4.2	-10.2	-58.7	-13.2	-13.9	-13.0
Maximum	3.4	11.4	18.7	19.0	10.2	16.8	20.2	25.8	25.5	24.9

Note: "---", Not measured

Deviation from prepared value (Va/Vp): (Average (Va) / Prepared value (Vp) – 1) x 100 [%]

Appendix Table 2.2.2 Deviation% from prepared values of low conc. sample No. 112w

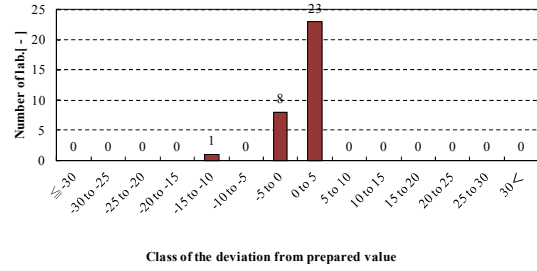
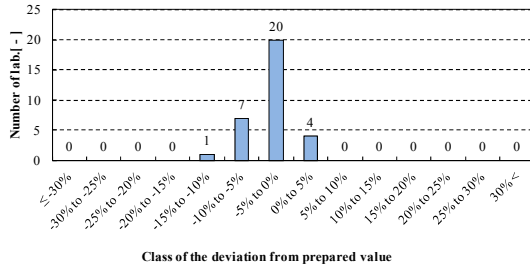
Sample No. 112w

Lab. ID	pH %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %	NH ₄ ⁺ %
KH01	-0.4	-9.7	11.8	7.7	5.9	-2.0	-26.1	-8.8	-2.3	1.0
CN01	0.9	-0.5	5.1	3.8	6.2	-1.0	13.0	11.0	4.7	-6.5
CN02	0.4	-2.3	0.8	1.4	2.0	1.5	0.0	7.7	7.0	-6.8
CN03	-0.4	-3.7	1.7	0.5	-3.4	2.0	26.1	-2.2	-16.3	-11.6
CN04	-0.2	-0.5	0.0	-1.0	-3.7	0.0	-13.0	30.8	11.6	-3.1
ID01	0.4	-5.1	1.7	0.0	-0.6	-4.4	21.7	-8.8	-23.3	0.0
ID02	1.7	-18.1	-17.7	-3.8	-18.4	-2.5	21.7	13.2	11.6	-2.1
ID03	0.2	-10.6	-3.4	-0.5	-3.4	-2.0	4.3	2.2	2.3	4.5
JP01	1.3	1.4	-3.0	-5.3	-4.0	2.9	8.7	-7.7	4.7	5.8
JP03	1.1	-0.5	-2.5	-1.4	-0.8	-2.5	0.0	1.1	-2.3	-0.7
JP04	1.1	-2.3	-1.3	-1.0	-0.6	-4.9	-13.0	-1.1	-7.0	-2.4
JP05	2.2	-6.5	-0.8	0.0	-0.6	-7.4	4.3	-7.7	-4.7	1.4
JP07	0.9	-3.2	2.1	1.4	-1.1	-8.3	13.0	-4.4	-4.7	-1.4
JP08	2.4	-10.2	0.0	1.0	-0.6	1.0	4.3	5.5	0.0	4.5
JP09	2.2	-2.8	-1.3	-1.4	-4.0	-1.5	4.3	-7.7	-4.7	-2.4
JP10	1.1	-2.8	-10.1	-9.1	-5.4	-4.9	-8.7	-5.5	-7.0	-4.1
MY01	0.9	0.5	-4.2	-3.8	0.3	-5.9	-21.7	-18.7	-30.2	6.8
MN01	2.0	-3.2	---	---	---	---	---	---	---	---
MM01	2.2	-6.5	4.6	-4.3	-0.6	-2.0	-8.7	-2.2	-4.7	5.8
PH01	1.5	9.3	2.1	-9.1	3.4	-8.3	0.0	12.1	-2.3	-1.7
PH02	2.8	-5.6	0.4	1.0	-3.7	-5.4	13.0	-18.7	65.1	4.1
RU01	-1.1	-1.9	-0.4	1.9	1.4	1.0	0.0	0.0	-2.3	-0.3
RU02	-0.2	-9.7	-5.1	6.3	7.9	20.1	4.3	2.2	2.3	6.2
TH01	0.2	-3.2	-11.8	-6.7	-3.1	-0.5	-8.7	-9.9	-23.3	8.6
TH02	1.3	-0.9	-2.5	-3.8	-2.5	17.2	30.4	23.1	9.3	7.9
TH04	-3.7	-3.2	-4.2	-3.4	-4.8	-4.4	8.7	9.9	0.0	-5.5
TH05	-1.7	-4.2	2.5	1.9	-2.5	-10.3	-17.4	-13.2	-11.6	5.1
VN01	0.4	-7.9	3.8	-1.4	2.0	-6.9	8.7	-3.3	0.0	-3.1
VN02	1.5	-5.6	0.4	0.5	0.8	11.3	39.1	-8.8	4.7	-2.7
VN03	-1.3	-6.0	-9.3	---	---	20.1	34.8	2.2	2.3	-11.3
VN04	0.9	-0.5	-0.4	1.0	-0.6	9.8	47.8	-6.6	7.0	-1.4
VN05	-12.0	-2.8	-3.8	5.3	6.5	-17.6	0.0	58.2	-14.0	-32.9
Number of data	32	32	31	30	30	31	31	31	31	31
Average	0.3	-4.0	-1.4	-0.8	-0.9	-0.5	6.2	1.4	-0.9	-1.2
Minimum	-12.0	-18.1	-17.7	-9.1	-18.4	-17.6	-26.1	-18.7	-30.2	-32.9
Maximum	2.8	9.3	11.8	7.7	7.9	20.1	47.8	58.2	65.1	8.6

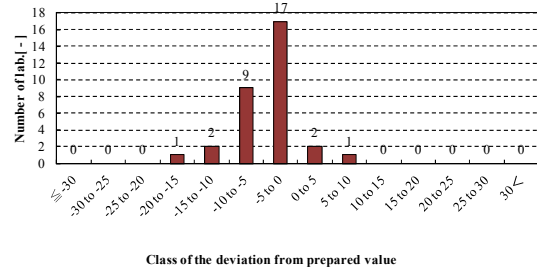
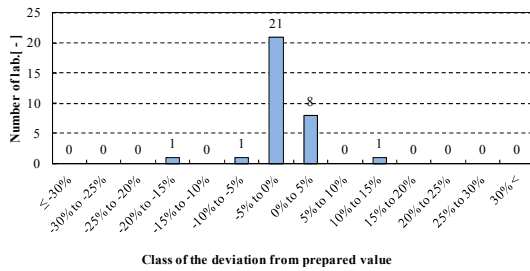
Note: "---", Not measured

Deviation from prepared value (Va/Vp): (Average (Va) / Prepared value (Vp) – 1) x 100 [%]

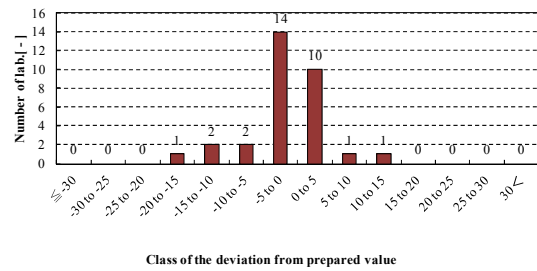
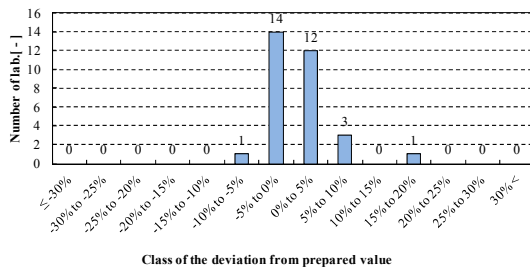
Appendix 2.3 Data Distribution



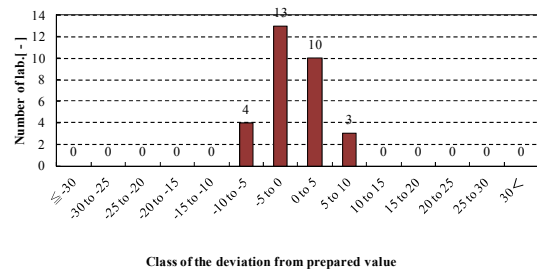
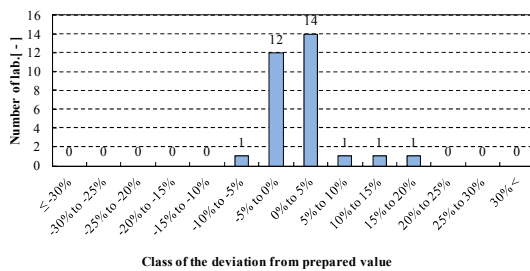
Appendix Figure 2.3.1 Data Distribution for pH (Left: 111w, Right: 112w)



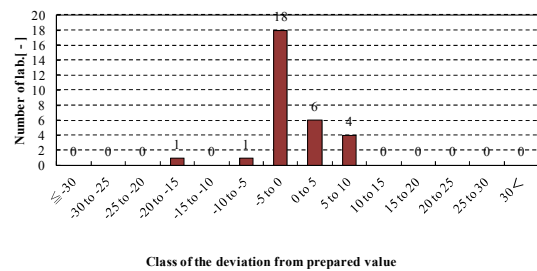
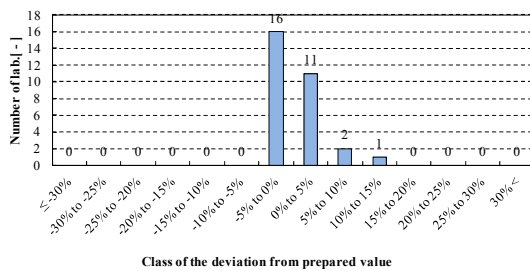
Appendix Figure 2.3.2 Data Distribution for EC (Left: 111w, Right: 112w)



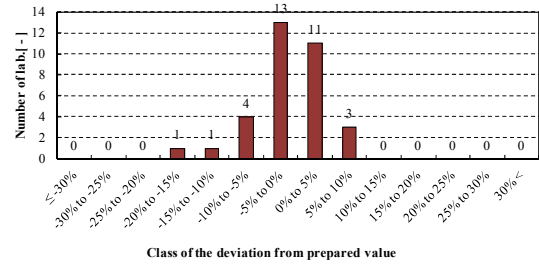
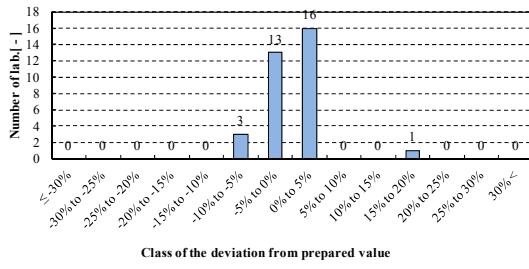
Appendix Figure 2.3.3 Data Distribution for SO_4^{2-} (Left: 111w, Right: 112w)



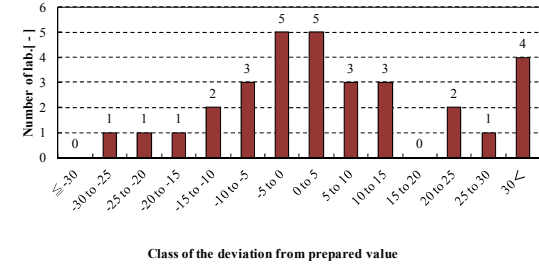
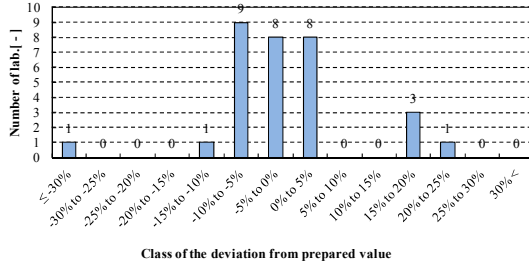
Appendix Figure 2.3.4 Data Distribution for NO_3^- (Left: 111w, Right: 112w)



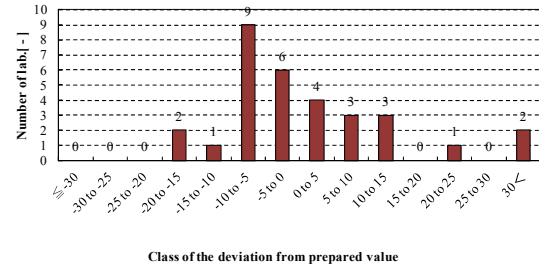
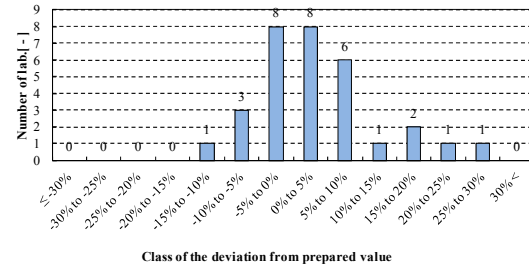
Appendix Figure 2.3.5 Data Distribution for Cl^- (Left: 111w, Right: 112w)



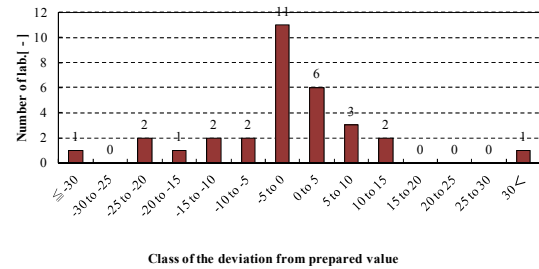
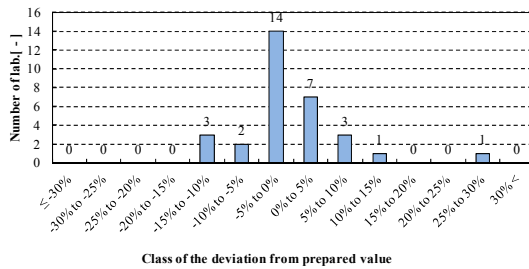
Appendix Figure 2.3.6 Data Distribution for Na⁺ (Left: 111w, Right: 112w)



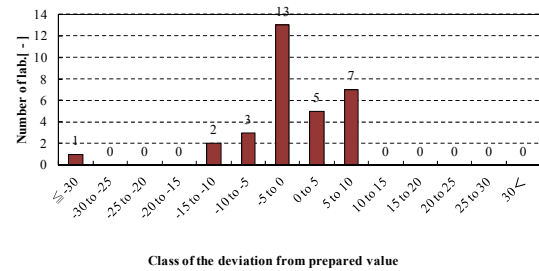
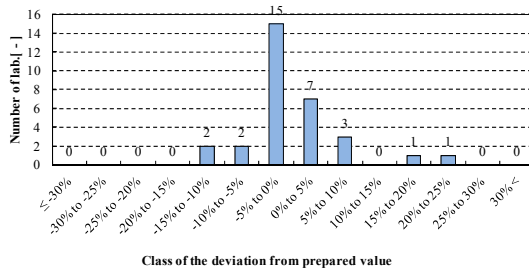
Appendix Figure 2.3.7 Data Distribution for K⁺ (Left: 111w, Right: 112w)



Appendix Figure 2.3.8 Data Distribution for Ca²⁺ (Left: 111w, Right: 112w)



Appendix Figure 2.3.9 Data Distribution for Mg²⁺ (Left: 111w, Right: 112w)



Appendix Figure 2.3.10 Data Distribution for NH₄⁺ (Left: 111w, Right: 112w)

3. 7th 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 2011. 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 26 laboratories in charge of EANET monitoring in 12 countries of EANET participated in this seventh activity. All participating laboratories and their codes are listed 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.111d-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.111d-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.112d-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.112d-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.113d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Blank
No.113d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	Blank

3.2.3 Analytes

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

3.2.4 Analytical Methodologies

The recommended procedure for sample analysis 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.111d-1, No.112d-1, No.113d-1

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

(2) Sample No.111d-2, No.112d-2, No.113d-2

Add 20 mL of pure water ($EC < 0.15 \text{ mS L}^{-1}$) 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 $0.45 \mu m$). 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 analysis 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 $4^\circ C$.

The participating laboratories were expected to use the analytical methods specified in the Technical Document (EANET, 2000b) in Table 3.2.

Table 3.2 Analytical methods specified in the Technical Document

Analyte	Analytical method
$\text{SO}_4^{2-}, \text{Cl}^-$	Ion Chromatography 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 (mg 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.111d-1, No.111d-2, No.112d-1 and No.112d-2;

$M_{\text{sol, Blank}}$: the average quantity (μg) in the filtrate from blank sample No.113d-1 and No.113d-2.

3.3 Results

The NC distributed the filter samples to 26 laboratories in the participating countries of EANET, and received their results from 22 laboratories. The results compared to the prepared values are summarized in Table 3.3. The average, minimum (Min.), maximum (Max.), standard deviation (S.D.) and number of data (N) were calculated from each analyzed ion quantity. Analytical results of Samples No.111d and No.112d are shown in Table 3.5 and Table 3.7.

Outliers exceeding three times the standard deviation (S.D.) were rejected before calculation. In this study, three data were rejected. One laboratory reported their results in unit other than we requested, therefore their submitted values were converted into microgram after correspondence with the laboratory.

As shown in Table 3.3, the deviations ($\Delta V/V_p$) for Cl⁻ in Sample No. 111d and Sample No.112d were -9.40% and -5.27%. The other deviations were within $\pm 5\%$.

The Data Quality Objectives (DQOs) of EANET is 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.111d and No.112d 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
(The results do not include outliers.)

Analyte	Prepared* (Vp)	Average (Va)	$\Delta V/Vp^*$ (%)	S.D.	Number (N)	Min.	Max.
<u>Sample No. 111d</u>							
SO ₄ ²⁻ (µg)	73	70.4	-3.54	3.53	22	62.9	77.9
Cl ⁻ (µg)	3.0	2.72	-9.40	0.40	21	1.89	3.87
NH ₄ ⁺ (µg)	8.0	8.25	3.18	0.97	22	6.06	10.1
<u>Sample No. 112d</u>							
SO ₄ ²⁻ (µg)	110	107	-3.15	6.86	22	91.6	127
Cl ⁻ (µg)	32	30.3	-5.27	3.20	21	20.6	36.3
NH ₄ ⁺ (µg)	26	25.7	-1.15	1.52	21	23.0	30.7

* Prepared: Prepared values

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

3.3.1 Evaluation of Laboratories' Performance (by sample)

Samples No. 111d-1, No.111d-2

For Sample No.111d, 11 analytical data in 66 results were flagged E, and 3 analytical data were flagged X. The total percentage of flagged samples was 21.2%. (Figure 3.2, Table 3.4 and 3.5).

Table 3.4 Number of flagged data for Sample No.111d

	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	Total
Flag E *	0	4	7	11
Flag X *	0	3	0	3
Data within DQOs	22	15	15	52
Ratio of Flagged (%)	0.0	31.8	31.8	21.2

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

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

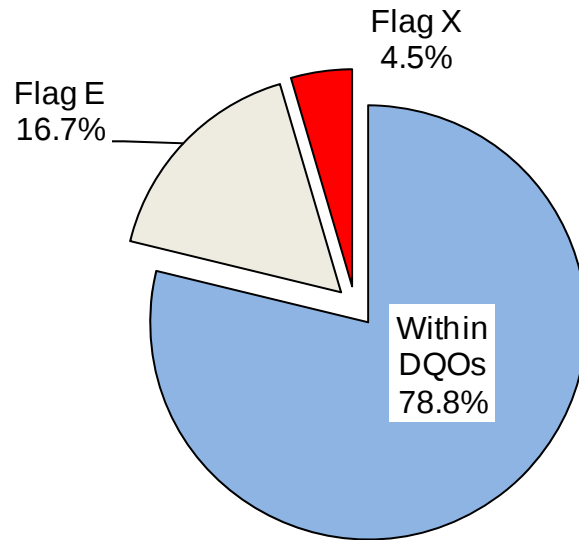


Figure 3.2 Percentage of flagged data for Sample No.111d

Table 3.5 Average analytical results of Sample No.111d

Lab. Code	SO ₄ ²⁻ (µg)	Cl ⁻ (µg)	NH ₄ ⁺ (µg)
KH01	77.9	2.89	8.54
CN04	70.2	2.83	7.90
ID01	74.8	2.92	9.46 E
ID03	70.4	7.60 X	6.06 E
JP01	73.6	2.62	7.60
JP02	72.0	2.99	8.22
JP03	71.2	2.68	7.79
JP04	73.3	2.66	7.82
JP05	71.8	2.75	7.62
JP08	72.0	2.87	8.72
JP09	67.1	2.78	6.61 E
JP10	68.7	2.68	8.01
MY01	67.1	2.68	8.61
PH01	65.2	2.06 X	9.25 E
PH02	62.9	1.89 X	7.57
KR01			
RU01	63.5	2.39 E	10.1 E
TH01	70.3	3.04	9.09
TH02	70.7	2.73	8.24

TH04	69.6	2.53 E	7.88
TH05	70.6	2.13 E	9.81 E
VN01	73.9	3.09	9.25 E
VN02	72.3	3.87 E	7.44

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

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

Samples No. 112d-1, No.112d-2

For Sample No.112d, 6 analytical data in 66 results were flagged E and 2 analytical data were flagged X. The total percentage of flagged samples was 12.1%. (Figure 3.3, Table 3.6 and 3.7).

Table 3.6 Number of flagged data for Sample No.112d

	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	Total
Flag E *	2	2	2	6
Flag X *	0	2	0	2
Data within DQOs	20	18	20	58
Ratio of Flagged (%)	9.1	18.2	9.1	12.1

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

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

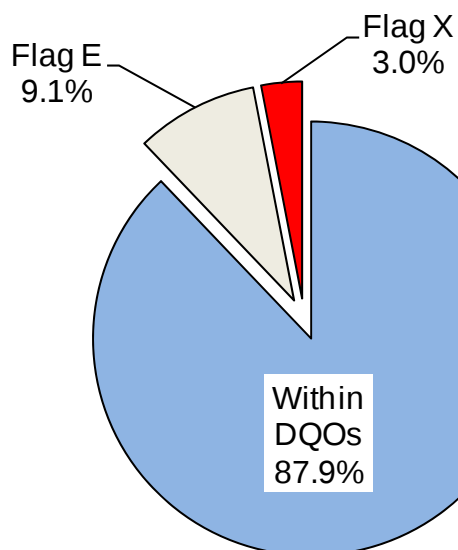


Figure 3.3 Percentage of flagged data for Sample No.112d

Table 3.7 Average analytical results of Sample No.112d

Lab. Code	SO ₄ ²⁻ (μg)	Cl ⁻ (μg)	NH ₄ ⁺ (μg)
KH01	127 E	33.8	27.1
CN04	101	30.7	26.4
ID01	116	31.5	26.6
ID03	105	47.5 X	24.6
JP01	111	31.6	24.5
JP02	110	31.9	25.7
JP03	108	30.1	25.2
JP04	111	31.7	25.5
JP05	107	30.8	25.3
JP08	109	31.4	25.0
JP09	104	29.1	23.9
JP10	106	31.0	25.5
MY01	104	30.5	25.2
PH01	102	26.6 E	26.2
PH02	99.1	24.7 E	23.0
KR01			
RU01	91.6 E	20.6 X	26.8
TH01	111	33.9	26.1
TH02	105	30.6	30.7 E
TH04	105	30.3	24.0
TH05	97.1	28.7	32.8 E
VN01	105	36.3	26.8
VN02	109	30.8	25.6

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

Blank Sample (No.113d)

Each quantity of SO₄²⁻, Cl⁻, and NH₄⁺ was determined for blank sample No.113d-1 and No.113d-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. Light gray color cells indicate that the sample was flagged E and dark gray color cells indicate that the sample was flagged X. At some laboratories, results were not flagged even though some blank values were high.

Table 3.8 Analytical results of Sample No.113d (blank)

Lab. Code	SO ₄ ²⁻ (μg)	Cl ⁻ (μg)	NH ₄ ⁺ (μg)
KH01	1.40	0.97	0.00
CN04	0.00	0.37	0.18
ID01	0.93	1.09	4.12
ID03	25.44	0.00	5.17
JP01	0.10	0.27	0.12
JP02	0.25	1.09	0.59
JP03	0.00	0.74	0.12
JP04	0.32	0.35	0.09
JP05	0.00	0.50	0.33
JP08	0.00	0.45	0.32
JP09	0.08	0.89	0.58
JP10	0.06	0.26	0.16
MY01	0.24	0.64	0.32
PH01	2.67	1.74	0.33
PH02	3.60	1.59	1.73
KR01			
RU01	0.00	0.00	0.30
TH01	0.31	0.48	0.33
TH02	0.32	0.67	0.56
TH04	0.00	0.00	0.15
TH05	2.16	1.41	0.00
VN01	0.00	0.00	0.07
VN02	0.00	0.00	2.26
Average	1.72	0.61	0.81
Median	0.17	0.49	0.32
Minimum	0.00	0.00	0.00
Maximum	25.44	1.74	5.17
Standard deviation	5.27	0.53	1.33

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

Lab. Code	Sample No.111d			Sample No.112d		
	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺
KH01	1.8	25.1	0.0	1.1	2.8	0.0
CN04	0.0	11.5	2.3	0.0	1.2	0.7
ID01	1.2	27.1	30.3	0.8	3.3	13.4
ID03	26.5	0.0	46.0	19.5	0.0	17.3
JP01	0.1	9.2	1.6	0.1	0.8	0.5
JP02	0.3	26.7	6.7	0.2	3.3	2.3
JP03	0.0	21.6	1.5	0.0	2.4	0.5
JP04	0.4	11.7	1.1	0.3	1.1	0.3
JP05	0.0	15.4	4.1	0.0	1.6	1.3
JP08	0.0	13.5	3.5	0.0	1.4	1.3
JP09	0.1	24.2	8.0	0.1	3.0	2.4
JP10	0.1	9.0	2.0	0.1	0.9	0.6
MY01	0.3	19.4	3.5	0.2	2.1	1.2
PH01	3.9	45.8	3.4	2.5	6.1	1.2
PH02	5.4	45.6	18.6	3.5	6.0	7.0
KR01						
RU01	0.0	0.0	2.9	0.0	0.0	1.1
TH01	0.4	13.6	3.5	0.3	1.4	1.2
TH02	0.5	19.8	6.4	0.3	2.2	1.8
TH04	0.0	0.0	1.9	0.0	0.0	0.6
TH05	3.0	39.7	0.0	2.2	4.7	0.0
VN01	0.0	0.0	0.8	0.0	0.0	0.3
VN02	0.0	0.0	23.3	0.0	0.0	8.1
		: Data flagged E				
		: Data flagged X				

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 (SO₄²⁻, Cl⁻ and NH₄⁺). 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.

SO₄²⁻ (Sulfate)

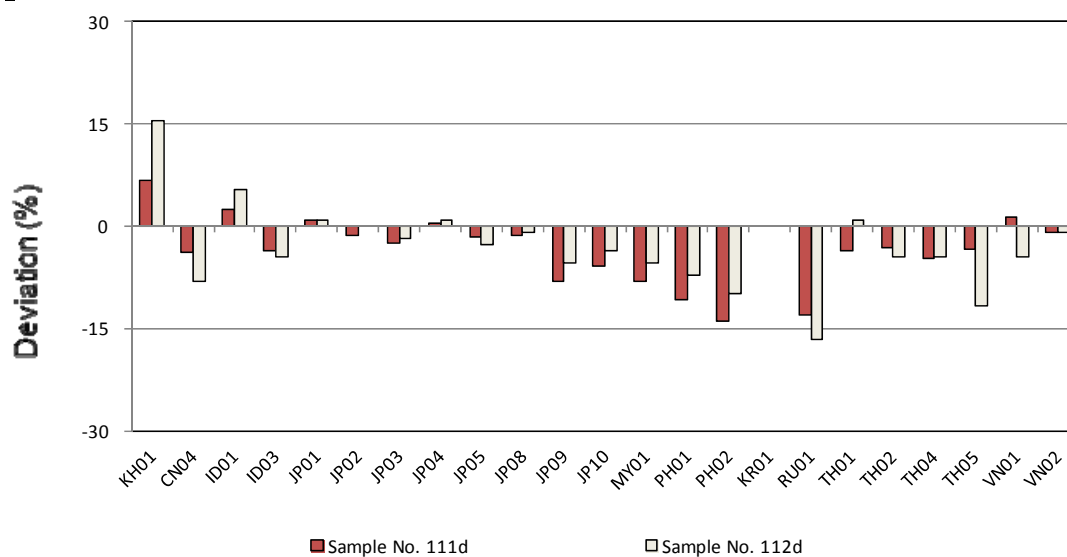


Figure 3.4 Deviation for SO₄²⁻

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

Table 3.10.1 Analytical method of SO₄²⁻

Analytical Method

Ion Chromatography 22/22

Table 3.10.2 Flagged data of SO₄²⁻

<u>Flagged Data</u>	Flag E	Flag X	Flagged (%)
Sample No.111d	0	0	0
Sample No.112d	2	0	9.1

All participating laboratories used Ion Chromatography for the determination of SO₄²⁻.
Two laboratories were flagged E for Sample No. 112d.

Cl⁻ (Chloride)

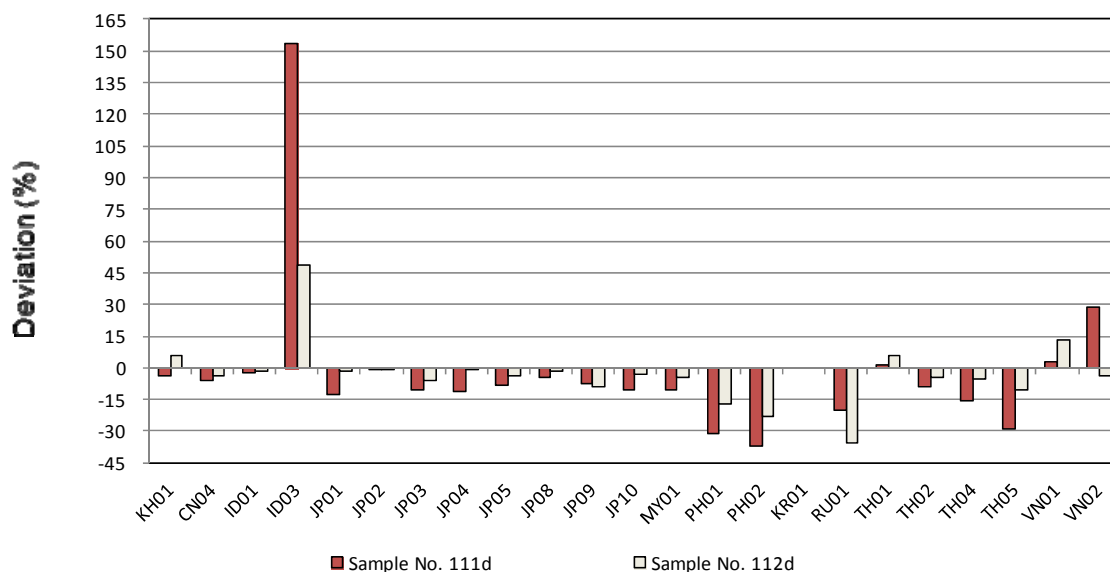


Figure 3.5 Deviation for Cl⁻

Table 3.11.1 Analytical method of Cl⁻

Analytical Method

Ion Chromatography 22/22

Table 3.11.2 Flagged data of Cl⁻

Flagged Data

	Flag E	Flag X	Flagged (%)
Sample No.111d	4	3	31.8
Sample No.112d	2	2	18.2

As with the analysis of SO₄²⁻, all laboratories used Ion Chromatography for the determination of Cl⁻. E flag appeared at 4 laboratories and X flag appeared at 3 laboratories for Sample No.111d. Two flags of each (E and X) appeared at 2 laboratories for Sample No. 112d. Four laboratories were flagged E or X for both samples.

NH₄⁺ (Ammonium)

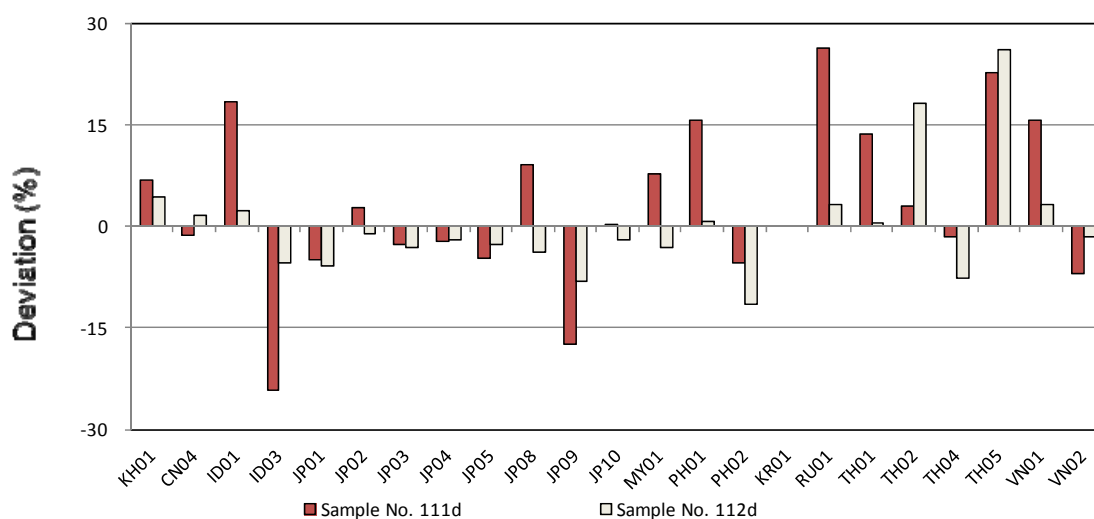


Figure 3.6 Deviation for NH₄⁺

Table 3.12.1 Analytical method of NH₄⁺

Analytical Method

Ion Chromatography	20/22
Spectrophotometry (Indophenol blue)	1/22
Spectrophotometry (Nessler)	1/22

Table 3.12.2 Flagged data of NH₄⁺

<u>Flagged Data</u>	Flag E	Flag X	Flagged (%)
Sample No.111d	7	0	31.8
Sample No.112d	2	0	9.1

Twenty laboratories used Ion Chromatography, one laboratory used Spectrophotometry (Indophenol Blue) and one laboratory used Spectrophotometry (Nessler). There were seven E flags for Sample No.111d, and two E flags for Sample No.112d.

3.3.3 Information on Laboratories

Methodologies used

As shown in Table 3.13, most participating laboratories used the recommended methods of EANET and all laboratories used Ion Chromatography for the determination of anions. On the other hand, for the determination of NH_4^+ , twenty laboratories used Ion Chromatography, one laboratory used Spectrophotometry (Indophenol Blue), and one laboratory used Spectrophotometry (Nessler) .

Table 3.13 Analytical methods used for sample analysis

Lab. Code	$\text{SO}_4^{2-}, \text{Cl}^-$	NH_4^+
KH01		Ion Chromatography
CN04		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
MY01		Ion Chromatography
PH01		Ion Chromatography
PH02	Ion Chromatography	Spectrophotometry (Indophenol Blue)
KR01		
RU01	Ion Chromatography	Spectrophotometry (Nessler)
TH01		Ion Chromatography
TH02		Ion Chromatography
TH04		Ion Chromatography
TH05		Ion Chromatography
VN01		Ion Chromatography
VN02		Ion Chromatography

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.111d or 112d. Data in dark gray color cells indicate flagged data in both Sample No.111d and No.112d.

Table 3.14 Years of staff experience (unit: year)

Lab. Code	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺
KH01	3	3	3
CN04	16	16	16
ID01	10	10	10
ID03	2	2	3
JP01	27	27	27
JP02	6	6	6
JP03	<1	<1	<1
JP04	4	4	4
JP05	2	2	2
JP08	1	1	1
JP09	3	3	3
JP10	21	21	21
MY01	1	1	1
PH01	8	8	8
PH02	4	4	8
KR01			
RU01	13	13	13
TH01	2	2	2
TH02	14	14	14
TH04	5	5	5
TH05	8	8	8
VN01	18	18	18
VN02	7	7	7

: One datum (either sample) is flagged.

: Two data (both samples) are flagged.

Flagged Data

In the results of Sample No.111d and 112d, the total number of flagged data was 22 (E: 17, X: 5) in the whole values (132). The number of flagged data in each laboratory is shown in Figure 3.8. Ten laboratories met DQOs (45.5%).

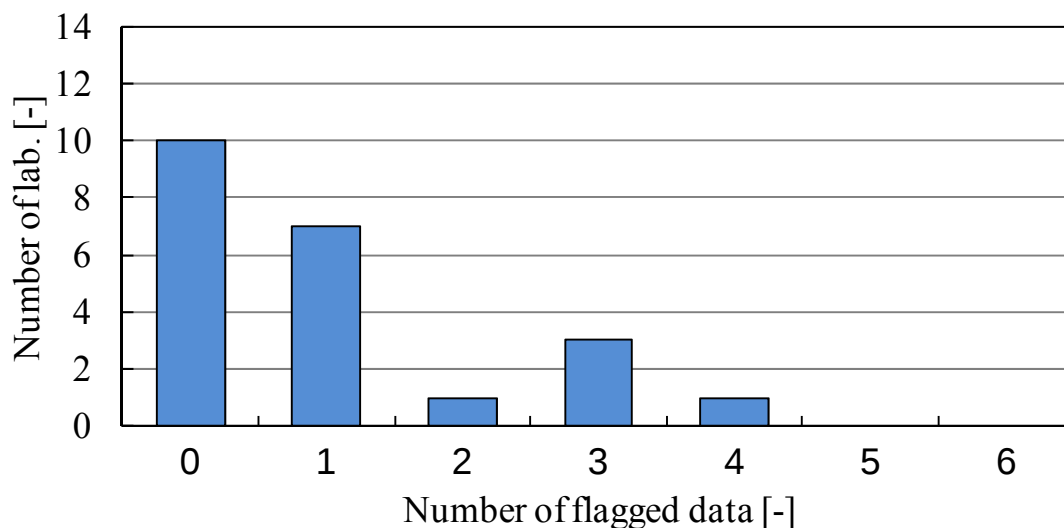


Figure 3.8 Number of flagged data and laboratories

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 higher than that of the prepared value.

Each concentration of prepared value 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⁻ (μmol L ⁻¹)		Cl ⁻ (μmol L ⁻¹)		NH ₄ ⁺ (μmol L ⁻¹)	
	Lowest	Highest	Lowest	Highest	Lowest	Highest
KH01	0	52.1	0	141	0	277
CN04	0	39.0	0	42.3	0	367
ID01	0	52.1	0	141	0	167
ID03	0	93.8	0	101	0	111
JP01	0	105	0	282	0	278
JP02	0	104	0	282	0	166
JP03	0	156	0	84.6	0	166
JP04	0	104	0	141	0	277
JP05	0	104	0	141	0	277
JP08	0	83.4	0	113	0	111
JP09	0	104	0	282	0	554
JP10	0	104	0	70.5	0	111
MY01	0	62.5	0	113	0	166
PH01	0	208	0	564	0	554
PH02	0	208	0	564	0	111
KR01						
RU01	0	104	0	282	0	222
TH01	0	105	0	283	0	166
TH02	0	104	0	282	0	139
TH04	0	83.3	0	56.4	0	111
TH05	0	83.3	0	113	0	111
VN01	0	104	0	141	0	277
VN02	0	108	0	113	0	106
*Sample No. 111d	38.0		4.23		22.2	
*Sample No. 112d	57.3		45.1		72.1	

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

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

*Sample concentration (μmol L⁻¹) = Prepared value (μg) / Solvent (mL) / M

M: molecular weight (g)

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 3.9.

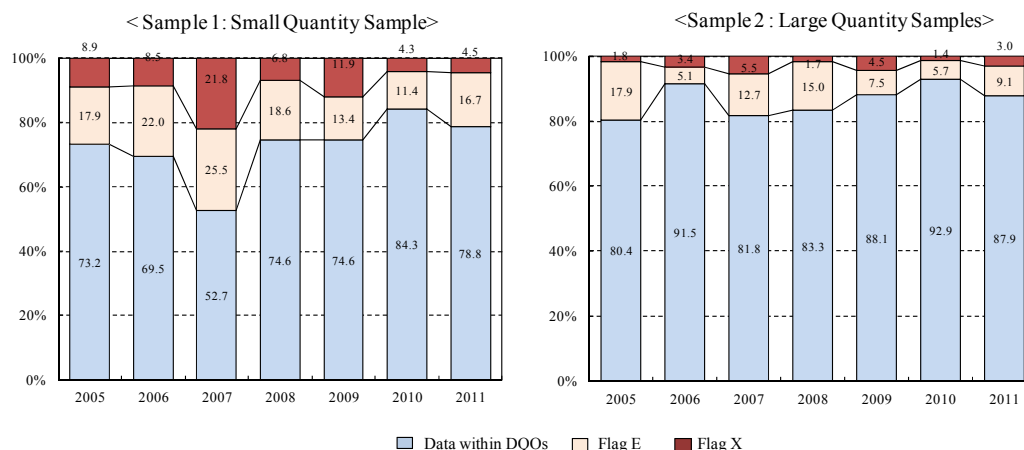


Figure 3.9 Comparison of DQOs' results for the past years

The comparison for each analyte in Inter-laboratory Comparison on dry deposition year-by-year is shown in Figure 3.10.

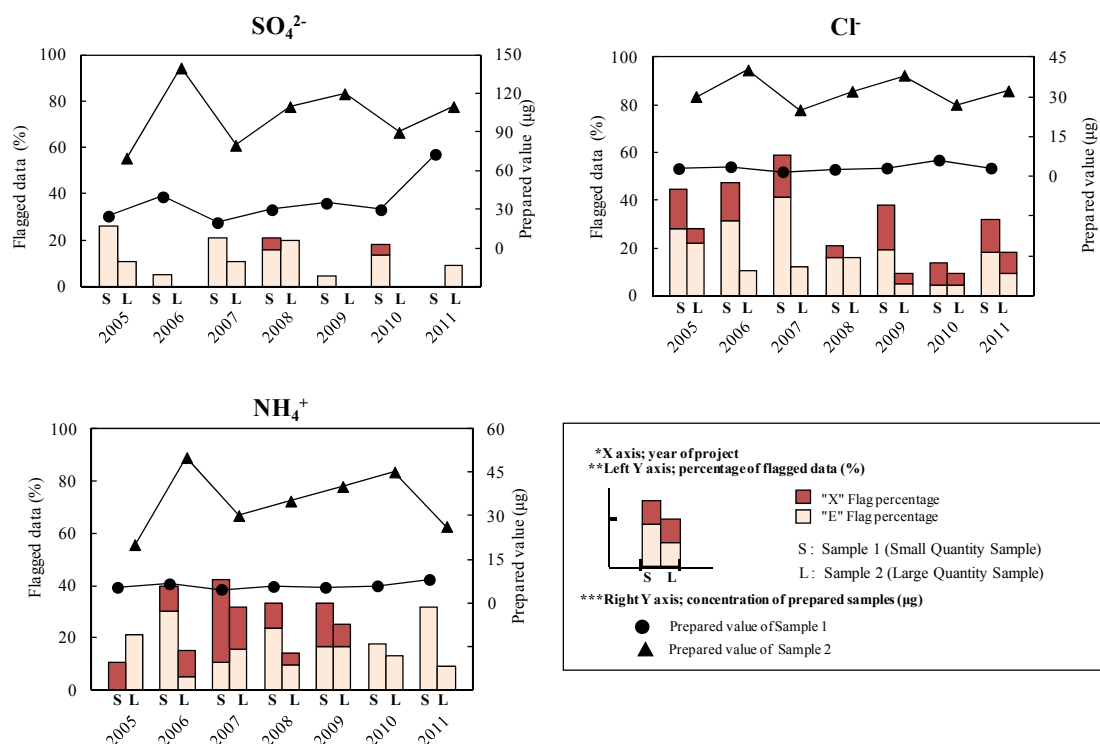


Figure 3.10 Comparison for each parameter in inter-laboratory comparison project

References

- EANET (2000a). *Guidelines for Acid Deposition Monitoring in East Asia*. Niigata.
- EANET (2003). *Technical Document for Filter Pack Method in East Asia*. Niigata.
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- EANET (2009). *Report of the Inter-laboratory Comparison Project 2008*. Niigata, Japan: Acid Deposition and Oxidant Research Center.
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4. 13th 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 13th project, Network Center (NC) provided two soil samples (No.111 and No.112) 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

Eighteen laboratories of 9 countries participated in the 13th project. 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. 111: Cambisols

Sample No. 112: Cambisols

Soils for Sample No.111 and No.112 were collected in Japanese cedar (*Cryptomeria japonica*) plantation established about 30 and 50 years ago, respectively, 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 300 - 400 g were weighed out, packed in 500 ml plastic bottles, and then, sterilized using radioisotope (20kGy) 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.111 and 112
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 cannot be obtained, 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 18 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. Both samples in the 13th inter-laboratory project had similar level of pH, whereas a cation exchangeable capacity was clearly different between the samples. Exchangeable base and acidic cations were higher in No.112 than in No.111. In both samples, we observed the large variations in the analyzed data of exchangeable base cations (Ex-Ca²⁺, Mg²⁺, K⁺ and Na⁺). CVs were high in those properties (e.g. 366% and 210% in Ex-Ca of No.111 and No.112) whereas CVs were low in pH (H₂O) and pH (KCl) (less than 5 %). Ex-acidity had moderately high CVs (66% and 40% of No.111 and No.112).

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. 111								
Number of Laboratories	18	18	16	16	16	16	18	18	18
Total average	4.8	4.1	3.0	0.4	0.2	0.3	2.4	1.8	0.6
Median	4.8	4.1	0.1	0.1	0.1	0.0	2.0	1.6	0.4
Maximum	5.1	4.2	43.8	3.8	1.6	3.8	8.6	5.1	3.4
Minimum	4.3	3.7	0.0	0.0	0.0	0.0	1.5	0.5	0.0
Standard deviation	0.2	0.1	10.9	0.9	0.4	0.9	1.6	1.0	0.8
CV (%) ^{*1}	4.5	3.6	366.6	253.5	211.3	324.9	66.3	55.8	128.9
No. 112									
Number of Laboratories	18	18	16	16	16	16	18	18	18
Total average	4.6	3.6	7.44	2.62	1.16	0.49	23.39	21.21	2.33
Median	4.6	3.6	3.50	1.69	0.65	0.29	20.82	18.84	1.99
Maximum	4.8	3.8	65.63	15.23	6.80	3.31	59.66	52.37	7.20
Minimum	4.1	3.0	0.92	0.42	0.19	0.08	16.92	14.98	0.02
Standard deviation	0.2	0.2	15.64	3.50	1.57	0.76	9.46	8.16	1.69
CV (%) ^{*1}	4.4	5.0	210.3	133.8	135	156	40.4	38.5	72

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

We also have an overview of the data by box-and-whisker plot (Figure 4.1) of No.111 and 102 analyzed by 18 laboratories. Box-and-whisker plot provides the five-number summaries: 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 ranges from lower quartile to upper quartile were around 0.2 in pH, less than 1.0 cmol_c kg⁻¹ in exchangeable base cations and less than 3.0 in exchangeable acidity. Meanwhile, the plots showed two or three clear non-parametrical outliers in each parameter. Those outliers might be produced by miss

calculation, wrong 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.

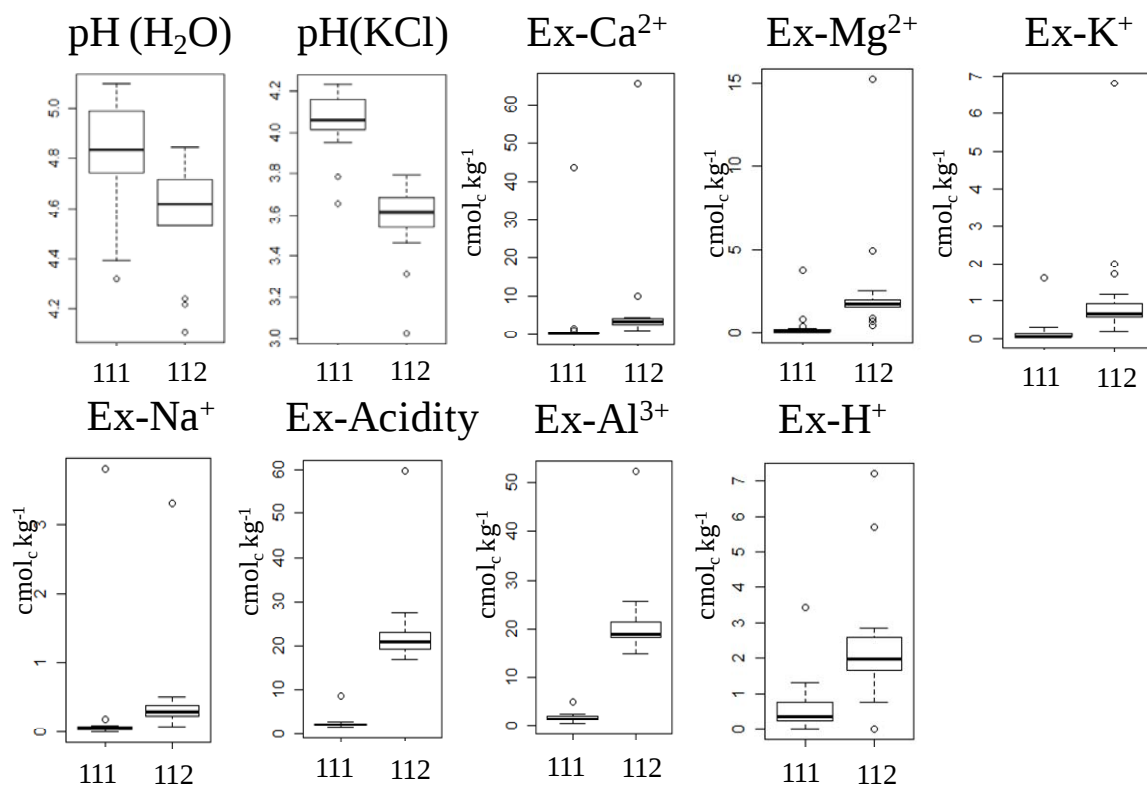


Figure 4.1 Data variability of No.111 and No.112 among 18 laboratories

Table 4.3 Data verification by Cochran-Grubbs methods

No.111

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	4.0	0.1	0.0	0.0	0.0	1.8	0.5	1.3	g
		2nd	4.9	4.0	0.1	0.0	0.0	0.0	1.8	0.5	1.3	g
	CN02	1st	4.9	4.0	0.1	0.0	0.0	0.0	1.8	1.0	0.9	c
		2nd	4.9	4.0	0.1	0.0	0.0	0.0	1.8	1.1	0.7	c
	CN03	1st	4.8	4.1	0.0	0.1	0.1	0.1	1.7	1.4	0.3	
		2nd	4.8	4.1	0.1	0.1	0.1	0.1	1.6	1.4	0.3	
	CN04	1st	4.8	4.1	0.1	0.0	0.0	0.0	1.4	0.7	0.7	
		2nd	4.8	4.1	0.1	0.0	0.0	0.0	1.5	0.8	0.8	
Indonesia	ID01	1st	4.8	4.0	0.0 c	0.0 c	0.0 c	0.0	1.9	1.6	0.3	
		2nd	4.8	4.0	2.8 c	1.5 c	0.6 c	0.0	1.9	1.6	0.3	
	ID04	1st	4.4	4.1	0.9 g	0.2 g	0.1	0.0	1.5	1.3	0.0	
		2nd	4.3	4.1	0.9 g	0.2 g	0.1	0.1	1.5	1.3	0.0	
Japan	JP04	1st	5.0	4.1	0.0	0.0	0.0	0.0	2.0	1.6	0.3	
		2nd	5.0	4.1	0.0	0.0	0.0	0.0	2.0	1.6	0.4	
	JP06	1st	4.8	4.1 c	0.0 c	0.0	0.0	0.0	1.8	1.4	0.4	
		2nd	4.9	4.3 c	0.1 c	0.0	0.0	0.0	1.7	1.3	0.4	
Mongolia	MN01	1st	4.4	3.6					2.3	1.2	0.8	
		2nd	4.4	3.7					2.3	1.2	0.8	
Malaysia	MY04	1st	4.7	4.1	0.1	0.1	0.0	0.0	8.1 c	5.1 g	2.9 c	
		2nd	4.8	4.1	0.1	0.1	0.0	0.0	9.2 c	5.2 g	3.9 c	
Phillipin	PH03	1st	4.5	3.8	43.6 c	3.8 c	1.6 c	3.9 c	2.4	2.1	0.3	
		2nd	4.6	3.8	43.9 c	3.7 c	1.6 c	3.7 c	2.4	2.1	0.3	
Russia	RU01	1st	4.9	4.2	0.2	0.1	0.0 c	0.1	2.3	1.9	0.1	
		2nd	4.9	4.2	0.2	0.1	0.1 c	0.1	2.1	1.8	0.1	
Thailand	TH01	1st	5.0	4.1 c	0.1	0.1	0.2	0.0	2.2	1.9	0.3	
		2nd	5.1	4.1 c	0.1	0.1	0.2	0.1	2.5	2.0	0.2	
	TH06	1st	5.1	4.2	0.3	0.1	0.1	0.1	2.1	2.0	0.1	
		2nd	5.1	4.2	0.3	0.1	0.1	0.1	2.1	2.0	0.1	
Vietnum	VN01	1st	5.0	4.2	0.0	0.0	0.0	0.0	2.0	1.3	0.7	
		2nd	5.0	4.2	0.0	0.0	0.0	0.0	2.0	1.3	0.7	
	VN02	1st	5.1	4.2					2.2	2.2	0.4	
		2nd	5.1	4.2					2.2	2.3	0.3	
	VN03	1st	4.8	4.0	0.2	0.4 g	0.2 g	0.2 g	2.8 g	2.5	0.2	
		2nd	4.7	4.0	0.2	0.4 g	0.2 g	0.2 g	2.9 g	2.6	0.2	
	VN04	1st	4.7	4.1	0.1	0.1	0.1	0.0	2.2	2.2	0.4	
		2nd	4.7	4.1	0.1	0.1	0.1	0.0	2.2	2.2	0.4	

No.112

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 _e kg ⁻¹						
China	CN01	1st	4.6	3.5	4.2	1.6	0.6	0.3	21.5	18.8	2.6
		2nd	4.6	3.5	4.2	1.6	0.6	0.3	21.5	18.8	2.7
	CN02	1st	4.7	3.5	3.2	1.6	0.6	0.3	19.0	16.0	2.9 c
		2nd	4.7	3.5	3.2	1.5	0.6	0.3	18.9	16.6	2.2 c
	CN03	1st	4.6	3.6	3.1	1.7	0.6	0.5	19.1	18.2	0.9
		2nd	4.6	3.6	3.2	1.7	0.6	0.5	19.6	18.7	0.9
	CN04	1st	4.6	3.6	3.3	1.8	0.6	0.4	20.9	18.3	3.0 c
		2nd	4.6	3.6	3.3	1.9	0.6	0.4	20.5	18.0	2.7 c
Indonesia	ID01	1st	4.7	3.6	0.0 c	0.0 c	0.0 c	0.3	20.6	18.3	2.3
		2nd	4.7	3.6	3.0 c	1.7 c	0.6 c	0.3	20.5	18.2	2.2
	ID04	1st	4.2	3.7	0.9	0.4 g	0.2 g	0.1	17.3	16.4	0.0
		2nd	4.2	3.7	0.9	0.4 g	0.2 g	0.1	17.3	16.4	0.0
Japan	JP04	1st	4.8	3.7	4.2	1.9	0.7	0.3	21.3	19.5	1.8
		2nd	4.8	3.6	4.1	2.1	0.7	0.3	20.8	19.1	1.7
	JP06	1st	4.8	3.7 c	3.9 c	2.0	0.6	0.3	20.9	18.0	2.9 c
		2nd	4.8	3.8 c	3.7 c	1.8	0.6	0.3	20.8	19.5	1.3 c
Mongolia	MN01	1st	4.1	3.0 g					24.5	18.5	5.8
		2nd	4.1	3.0 g					24.5	18.7	5.6
Malaysia	MY04	1st	4.5	3.6	3.8	1.8	0.7	0.3	60.4 c	53.1 g	7.2
		2nd	4.5	3.6	3.7	1.7	0.6	0.2	58.9 c	51.6 g	7.2
Phillipin	PH03	1st	4.2	3.3	64.8 c	15.4 g	6.9 c	3.3 g	20.8	18.9	1.9
		2nd	4.2	3.3	66.4 c	15.1 g	6.7 c	3.3 g	20.8	18.9	1.9
Russia	RU01	1st	4.7	3.7	3.4	2.5 g	0.6	0.4	25.8	25.8	0.8
		2nd	4.7	3.7	3.5	2.4 g	0.7	0.4	26.0	25.9	0.8
Thailand	TH01	1st	4.5 c	3.6 c	3.6	1.6	1.2 g	0.2	22.7	21.2	1.8 c
		2nd	4.7 c	3.6 c	3.5	1.7	1.2 g	0.2	23.1	22.4	0.6 c
	TH06	1st	4.7	3.7	4.4	1.6	0.7	0.4	23.1	21.4	1.7
		2nd	4.7	3.7	4.4	1.6	0.7	0.3	23.1	21.4	1.6
Vietnum	VN01	1st	4.8	3.8	2.1	1.7	0.7	0.2	16.8	15.0	1.8
		2nd	4.9	3.8	2.1	1.7	0.7	0.2	17.0	15.0	1.8
	VN02	1st	4.6	3.7					19.2	21.1	2.3
		2nd	4.6	3.7					19.2	21.2	2.4
	VN03	1st	4.6	3.5	9.9 g	4.8 g	1.7 g	0.5	27.4 g	20.1	1.8
		2nd	4.5	3.5	9.9 g	5.0 g	1.7 g	0.5	27.6 g	20.7	1.7
	VN04	1st	4.6	3.6	2.0	0.7 g	1.9 c	0.2	20.3	21.7	2.5
		2nd	4.6	3.6	2.0	0.7 g	2.0 c	0.2	20.2	21.8	2.4

Note; The outliers judged by Cochran and Grubbs methods were marked with **c** and **g**, 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. “ID01” in Ex-Ca, Mg and K of No.111. 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 1-6 outliers for each exchangeable base and acid cations. Meanwhile, only 1-3 outliers were detected in pH (H₂O) and pH (KCl). As a result of removing outliers, the “verified” dataset consisting of 15-18 laboratories in pH, 10-15 laboratories in base cations and 14-18 laboratories in acid cations 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.111 and No.112 were shown in Table 4.4. Although chemical properties in both soils were not largely changed by verification, the data variability of exchangeable cations decreased from entire dataset. Meanwhile, CVs were still high in Ex-Ca, Ex-Mg, Ex-Na and Ex-H (e.g. 77.5% and 66.9% in Ex-Ca and Ex-K in No.111, respectively). The variation included the many kinds of 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. 111								
Number of Laboratories	18	16	12	12	12	14	16	17	15
Total average	4.8	4.0	0.12	0.06	0.07	0.04	1.98	1.58	0.35
Median	4.8	4.1	0.09	0.05	0.04	0.04	1.99	1.58	0.29
Maximum	5.1	4.2	0.33	0.11	0.16	0.10	2.37	2.59	0.80
Minimum	4.3	3.7	0.01	0.02	0.03	0.01	1.46	0.53	0.02
Standard deviation	0.2	0.1	0.09	0.03	0.04	0.03	0.29	0.55	0.23
CV (%) ^{*1}	4.5	3.7	77.5	53.5	66.9	58.8	14.8	34.9	66.4
No. 112									
Number of Laboratories	17	15	12	10	10	15	16	17	14
Total average	4.6	3.6	3.18	1.73	0.64	0.30	20.86	19.38	2.37
Median	4.6	3.6	3.37	1.69	0.64	0.29	20.75	18.82	1.87
Maximum	4.8	3.8	4.36	2.01	0.71	0.51	25.90	25.88	7.20
Minimum	4.1	3.3	0.92	1.56	0.58	0.08	16.92	14.98	0.02
Standard deviation	0.2	0.1	1.03	0.15	0.05	0.11	2.39	2.56	1.90
CV (%) ^{*1}	4.5	3.2	32.4	8.5	8.1	38.0	11.5	13.2	80.1

Note: *1. CV, Coefficient of variance (%) = (standard deviation/average)*100, *2.dataset is verified removing outliers judged 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 pH and 10% in exchangeable base cations except Ex-Mg and Ex-Na in No.111. 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

High within-laboratory precision was also observed for most parameters. 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 5% in pH (H₂O) and pH (KCl). However, the CVs of exchangeable base and acid cations were large for both samples. CVs are high in exchangeable base cations and acid cations. We discussed the possible factor of the large 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. The reproducibility limit (inter-laboratories reproducibility limit) is also small for pH. Participating laboratories can detect the significant difference between the monitoring sites if the differences are more than about 0.3-0.6 pH units. Meanwhile, the reproducibility limit in the 13th Inter-laboratory comparison project should be improved for exchangeable Ca and acidity. For example, the estimation from No.112 showed that participating laboratories could detect the significant difference among the monitoring site if the differences are more than about 2.9 and 6.7 cmol_c kg⁻¹ in Ex-Ca and Ex-acidity, respectively.

Table 4.5 Analysis of variance for “verified” dataset

Statistics	No. 111								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	18	16	12	12	12	14	16	17	15
Total sum of square	270722	150614	75	19	22	14	36290	26033	1010
ST/lmd	2507	1569	1	0	0	0	378	255	11
Number of Data	108	96	72	72	72	84	96	102	90
Total sum	520.3	388.1	8.64	4.30	4.69	3.77	190.50	161.35	31.78
Total average	4.8	4.0	0.12	0.06	0.07	0.04	1.98	1.58	0.35
Sum of square inter-laboratories (S_R)	4.8	2.0	0.57	0.07	0.13	0.05	7.78	29.27	4.62
Sum of square within-laboratory (S_{RW})	0.1	0.0	0.00	0.00	0.00	0.00	0.20	0.14	0.03
Sum of square repeatability (S_i)	0.1	0.0	0.00	0.00	0.00	0.00	0.67	0.66	0.19
Total sum of square (S_T)	5.0	2.0	0.57	0.07	0.13	0.06	8.65	30.07	4.84
Inter-laboratories degree of freedom (ϕ_R)	17	15	11	11	11	13	15	16	14
Within-laboratory degree of freedom (ϕ_{RW})	18	16	12	12	12	14	16	17	15
Repeatability degree of freedom (ϕ_i)	72	64	48	48	48	56	64	68	60
Total degree of freedom (ϕ_T)	107	95	71	71	71	83	95	101	89
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.29	0.13	0.052	0.006	0.011	0.004	0.519	1.829	0.330
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.000	0.000	0.000	0.000	0.013	0.008	0.002
Repeatability variance ($V_i = S_i/\phi_i$)	0.00	0.00	0.000	0.000	0.000	0.000	0.010	0.010	0.003
Laboratory component of variance ($s_b^2 = (V_R - V_{RW})/(2*3)$)	0.05	0.02	0.009	0.001	0.002	0.001	0.084	0.304	0.055
Within-laboratory component of variance ($s_c^2 = (V_{RW} - V_i)/3$)	0.00	0.00	0.000	0.000	0.000	0.000	0.001	-0.001	0.000
Repeatability component of variance ($s_e^2 = V_i$)	0.00	0.00	0.000	0.000	0.000	0.000	0.010	0.010	0.003
Inter-laboratories standard deviation ($s_R = \text{SQRT}(s_b^2/(2*3) + s_c^2/2 + s_e^2)$)	0.2	0.1	0.09	0.03	0.04	0.03	0.29	0.55	0.23
Within-laboratory standard deviation ($s_{RW} = \text{SQRT}(s_c^2/3 + s_e^2)$)	0.0	0.0	0.01	0.00	0.00	0.00	0.06	0.05	0.03
Repeatability standard deviation ($s_i = \text{SQRT}(s_e^2)$)	0.0	0.0	0.01	0.01	0.01	0.01	0.10	0.10	0.06
Inter-laboratories precision CV (%)	4.5	3.7	77.49	53.54	66.87	58.77	14.81	34.91	66.42
Within-laboratory precision CV (%)	0.8	0.2	4.66	7.58	4.65	9.21	3.26	3.28	7.31
Repeatability precision CV (%)	0.6	0.4	7.14	12.56	8.06	15.92	5.15	6.21	15.93
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.61	0.42	0.260	0.090	0.122	0.074	0.823	1.546	0.657
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{RW}$)	0.10	0.03	0.016	0.013	0.008	0.012	0.181	0.145	0.072
Repeatability limit ($r = D(3, 0.95)*s_i$)	0.10	0.05	0.028	0.025	0.017	0.024	0.338	0.324	0.186

Statistics	No. 112								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	17	15	12	10	10	15	16	17	14
Total sum of square	218473	105365	52316	10743	1477	731	4010292	3905650	39540
ST/lmd	2142	1171	727	179	25	8	41774	38291	471
Number of Data	102	90	72	60	60	90	96	102	84
Total sum	467.4	324.6	228.73	103.65	38.43	27.04	2002.57	1976.27	198.85
Total average	4.6	3.6	3.18	1.73	0.64	0.30	20.86	19.38	2.37
Sum of square inter-laboratories (S_R)	4.2	1.1	69.72	1.17	0.15	1.09	515.47	628.95	280.46
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.06	0.16	0.01	0.01	1.53	6.77	0.05
Sum of square repeatability (S_i)	0.1	0.0	0.20	0.05	0.05	0.02	5.07	6.04	5.20
Total sum of square (S_T)	4.2	1.2	69.98	1.38	0.20	1.12	522.06	641.77	285.71
Inter-laboratories degree of freedom (ϕ_R)	16	14	11	9	9	14	15	16	13
Within-laboratory degree of freedom (ϕ_{RW})	17	15	12	10	10	15	16	17	14
Repeatability degree of freedom (ϕ_i)	68	60	48	40	40	60	64	68	56
Total degree of freedom (ϕ_T)	101	89	71	59	59	89	95	101	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.26	0.08	6.338	0.130	0.016	0.078	34.365	39.310	21.574
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.005	0.016	0.001	0.001	0.096	0.399	0.004
Repeatability variance ($V_i = S_i/\phi_i$)	0.00	0.00	0.004	0.001	0.001	0.000	0.079	0.089	0.093
Laboratory component of variance ($s_b^2 = (V_R - V_{RW})/(2*3)$)	0.04	0.01	1.056	0.019	0.003	0.013	5.712	6.485	3.595
Within-laboratory component of variance ($s_c^2 = (V_{RW} - V_i)/3$)	0.00	0.00	0.000	0.005	0.000	0.000	0.005	0.103	-0.030
Repeatability component of variance ($s_e^2 = V_i$)	0.00	0.00	0.004	0.001	0.001	0.000	0.079	0.089	0.093
Inter-laboratories standard deviation ($s_R = \text{SQRT}(s_b^2/(2*3) + s_c^2/2 + s_e^2)$)	0.2	0.1	1.03	0.15	0.05	0.11	2.39	2.56	1.90
Within-laboratory standard deviation ($s_{RW} = \text{SQRT}(s_c^2/3 + s_e^2)$)	0.0	0.0	0.04	0.07	0.01	0.01	0.18	0.36	0.03
Repeatability standard deviation ($s_i = \text{SQRT}(s_e^2)$)	0.0	0.0	0.07	0.04	0.04	0.02	0.28	0.30	0.30
Inter-laboratories precision CV (%)	4.5	3.2	32.35	8.51	8.09	37.96	11.47	13.21	80.10
Within-laboratory precision CV (%)	0.3	0.2	1.24	4.23	2.12	4.61	0.86	1.88	1.44
Repeatability precision CV (%)	0.8	0.5	2.06	2.07	5.54	5.37	1.35	1.54	12.87
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.58	0.33	2.878	0.412	0.145	0.319	6.701	7.167	5.309
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{RW}$)	0.04	0.02	0.110	0.204	0.038	0.039	0.500	1.021	0.096
Repeatability limit ($r = D(3, 0.95)*s_i$)	0.12	0.06	0.216	0.118	0.117	0.053	0.928	0.984	1.005

4.3.5 Inter-laboratory variations in each parameter

To assess the precision in each laboratories and properties, we showed scatter plots between No.111 and No.112 with its “verified” mean indicated by solid line. As a guide for comparison, 20% of verified mean is added by dashed lines, while 0.2 units from the average are used for pH. Outliers selected by Cochran and Grubbs method (as mentioned above) were denoted by§. Outliers within the 20 % total average are mainly due to poor repeatability in each laboratory (i.e. large within-laboratory

variation). The plot did not include extreme outliers for eye-friendly.

1) pH

Linear correlation between No.111 and No.112 indicated the systematic errors of the inter-laboratory variation in pH (Figure 4.2 and Figure 4.3). 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 0.2 pH unit for No.111 and No.112. Very few laboratories were judged by outliers using Cochran-Grubbs method for pH(H₂O) and pH(KCl). The result indicates enough capacity of participating countries for analyzing soil pH.

2) Base cations

Non-linearly distribution in the plot of exchangeable base cations (Figure 4.4 to 4.7) suggested large random error of inter-laboratory variations. Few laboratories were included in the range of 20% of verified mean for Ex-Ca and Ex-Mg in both samples. The random error led to the very large variation in the dataset and many outliers.

The error might be caused by not only the condition of ammonium acetate (extraction liquid), standard solution or dilution rate, but also the inconsistent procedure or erratic way for soil analysis. 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 harmonize the background with that of the samples. Wrong dilution rate also may result in this kind of large error.

3) Acidity

The plots of Ex-acidity, Ex-Al and Ex-H moderately indicated systematic error of inter-laboratory variation (Figure 4.8 to 4.10). In Ex-acidity, almost all laboratories were included in the 20% range of verified mean of No.111 and No.112.

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).

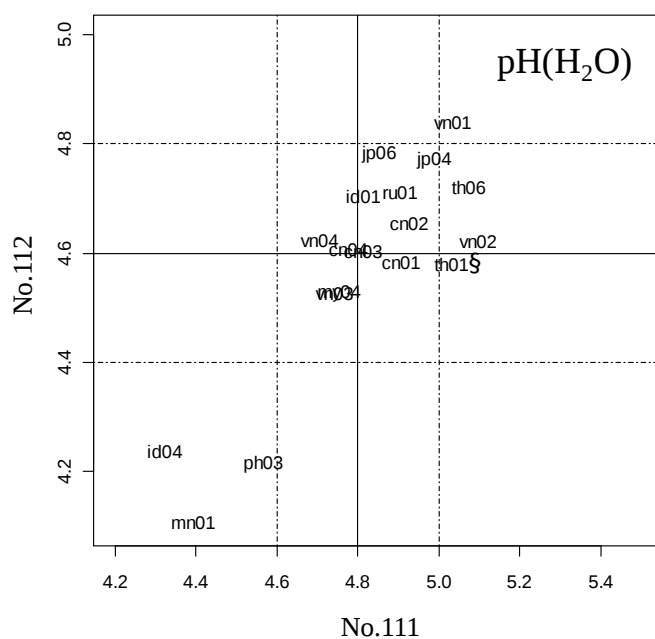


Figure 4.2 Scatter diagram of pH (H₂O) between No.111 and No.112 (Solid lines show mean of verified datasets and dashed lines show 0.2 pH units from the mean. Outliers selected by Cochran and Grubbs method were denoted by §.)

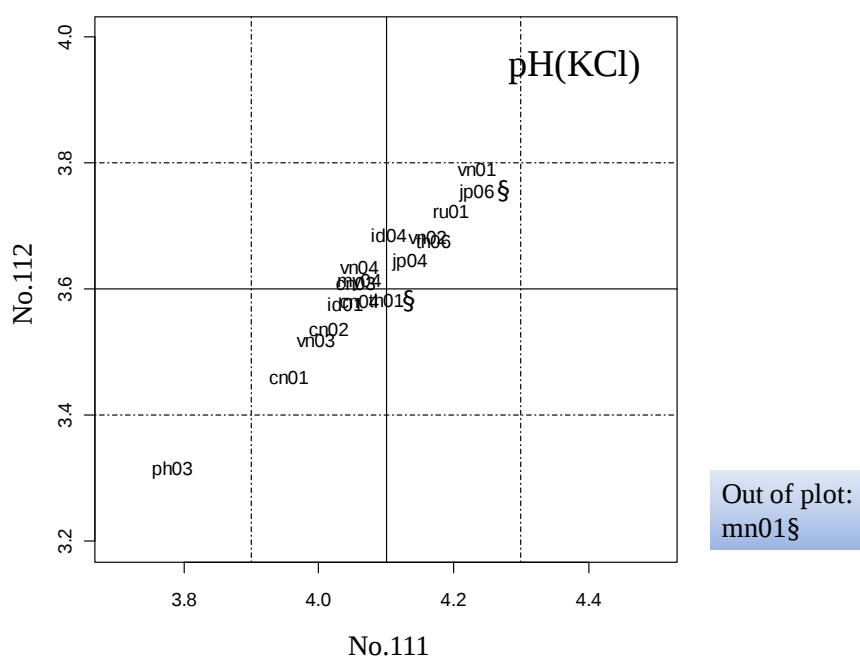


Figure 4.3 Scatter diagram of pH (KCl) between No.111 and No.112 (Solid lines show mean of verified datasets and dashed lines show 0.2 pH units from the mean. Outliers selected by Cochran and Grubbs method were denoted by §.)

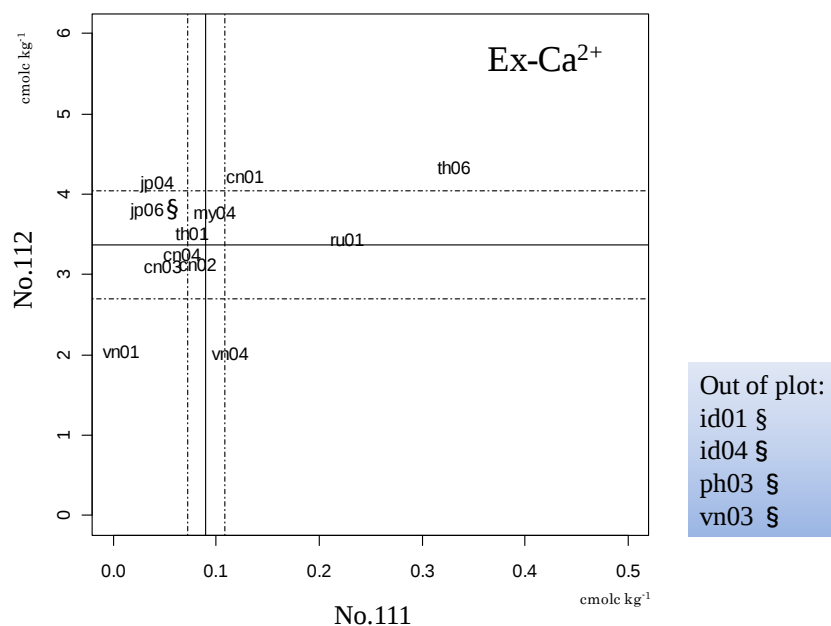


Figure 4.4 Scatter plot of Ex-Ca between No.111 and No.112 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cohcran and Grubbs method were denoted by §.)

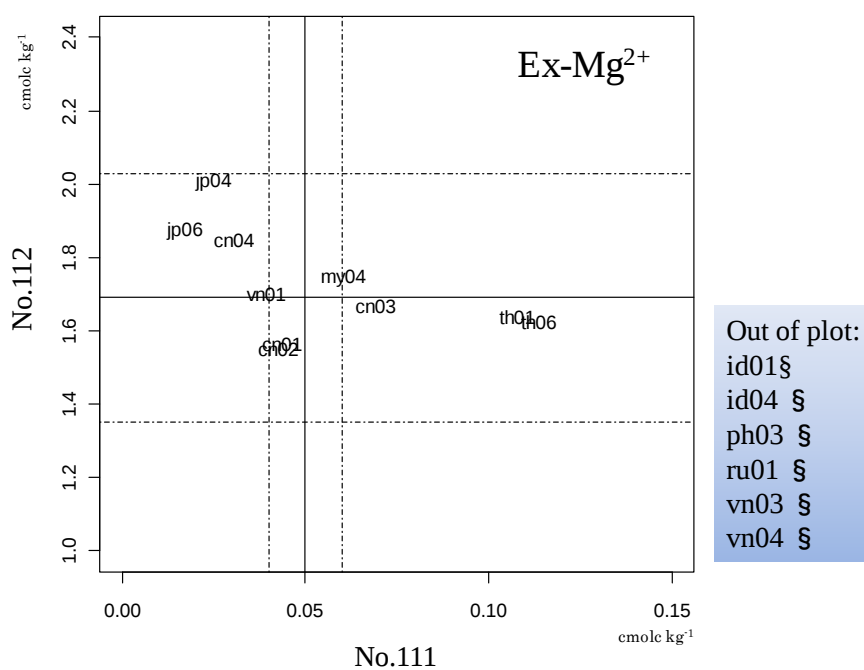


Figure 4.5 Scatter plot of Ex-Mg between No.111 and No.112 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cohcran and Grubbs method were denoted by §.)

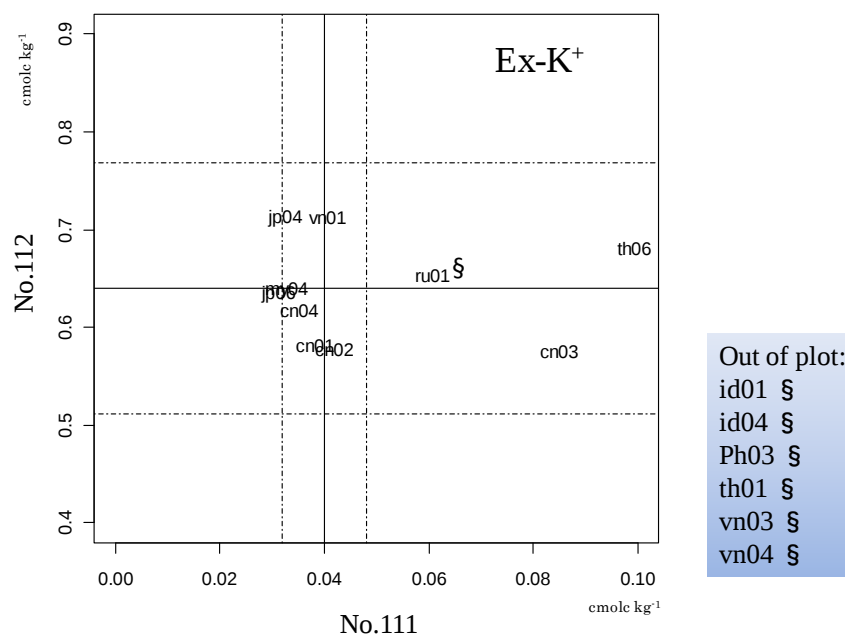


Figure 4.6 Scatter plot of Ex-K between No.111 and No.112 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cochran and Grubbs method were denoted by §.)

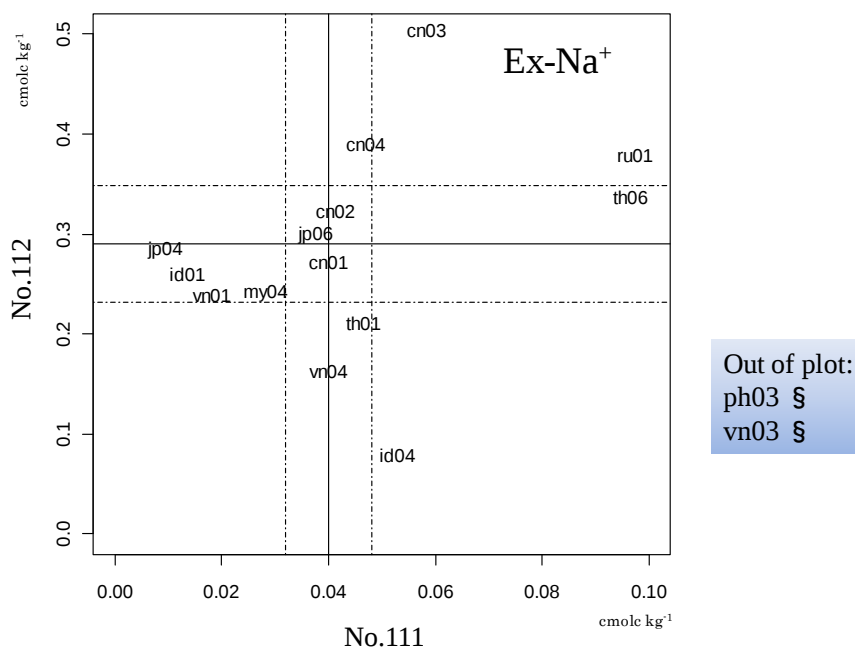
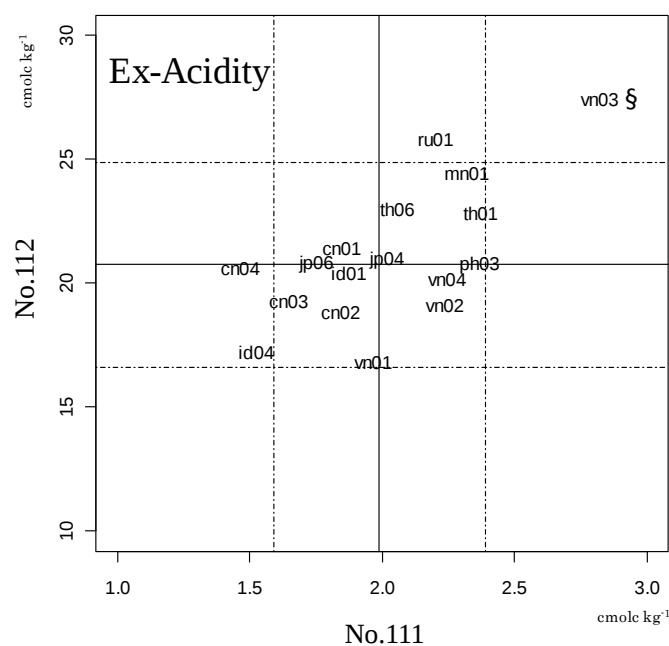
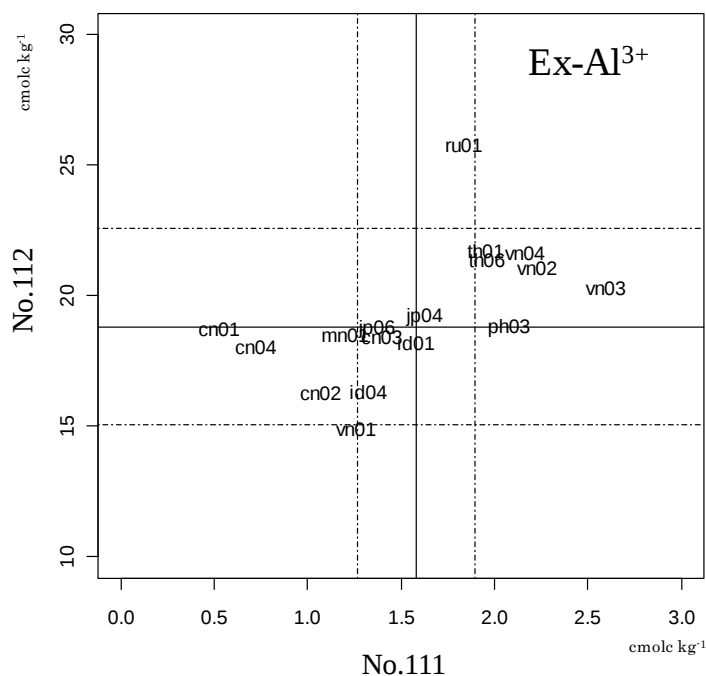


Figure 4.7 Scatter plot of Ex-Na between No.111 and No.112 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cochran and Grubbs method were denoted by §.)



Out of plot:
my04 §

Figure 4.8 Scatter plot of Ex-acidity between No.111 and No.112 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cochran and Grubbs method were denoted by §.)



Out of plot:
my04 §

Figure 4.9 Scatter plot of Ex-Al between No.111 and No.112 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cochran and Grubbs method were denoted by §.)

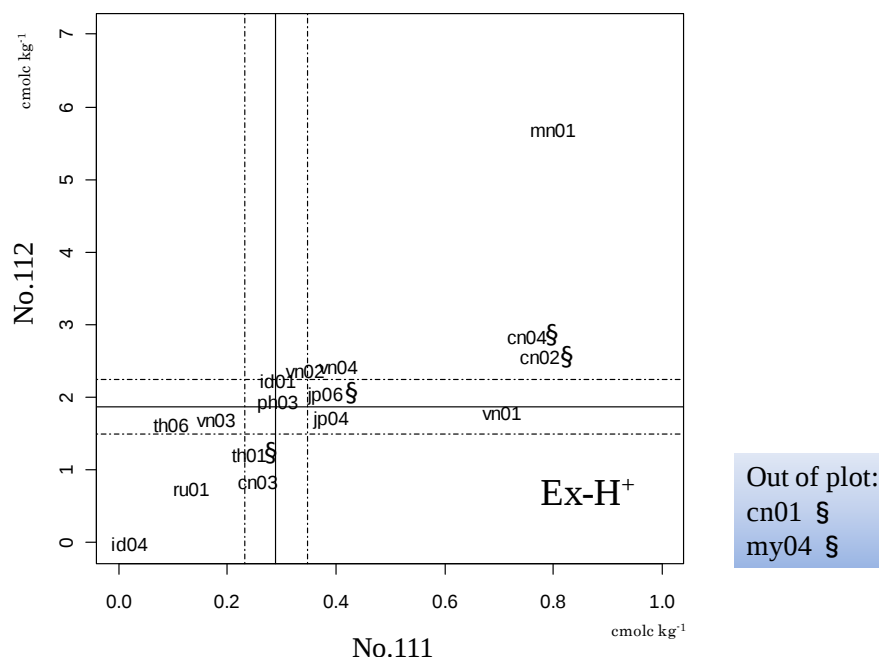


Figure 4.10 Scatter plot of Ex-H between No.111 and No.112 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cochran and Grubbs method were denoted by §.)

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. Almost all laboratories used AAS for measurement of Ex-Ca and Mg, and 4 laboratories used FEP for Ex-K and Na. One laboratory used ICP for measurement of Ex-Ca, Mg, K and Na. Years in use of instruments ranged from 2 to 26. Ten laboratories applied Sr or La for measurements of Ex-Ca and Mg by AAS.

Nine laboratories used percolation tube procedures for extraction of exchangeable base cations, while Buchner funnel procedures, centrifuge procedures and automatic extractor procedures were used in 1, 3 and 2 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 10 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. Most laboratories carried out the analysis by February 2012. There were 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 41 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. 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	2	9	7	2	9	7	s
CN02	1	13	13	1	22	22	d
CN03	1	15	12	1	15	12	s
CN04	1	26	8	1	5	3	d
ID01	1	8	5	1	8	5	s
ID04	1	n	n	1	14	12	d
JP04	1	3	1	1	3	1	s
JP06	1	18	1	1	18	1	s
MN01	-	-	-	1	18	18	-
MY04	1	13	13	1	13	13	s
PH03	1	23	4	1	35	35	d
RU01	1	26	13	1	11	8	d
TH01	1	7	6	1	17	2	d
TH06	2	7	3	2	7	3	s
VN01	1	19	14	1	19	14	s
VN02	-	-	-	1	7	3	-
VN03	1	8	8	1	5	5	d
VN04	1	10	8	1	8	7	d

Note: -, Not measured; 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			Ex-K		Ex-Na			Procedures for extraction of Ex-base cations	method	Ex-Acidity, Al and H Size of burette (ml)	
		Instrument	Years ^{*1}	Instrument	Years		Instrument	Years	Instrument	Years				Capacity	Minimum graduate
CN01	No.111	AAS	7	AAS	7	Sr	AAS	7	AAS	7	na	Centrifuge	Titration	10	0.05
	No.112	AAS	7	AAS	7	Sr	AAS	7	AAS	7	na				
CN02	No.111	AAS	13	AAS	13	Sr	AAS	13	AAS	13	Sr	Percolation tube	Titration	50	0.1
	No.112	AAS	13	AAS	13	Sr	AAS	13	AAS	13	Sr				
CN03	No.111	AAS	4	AAS	4	Sr	AAS	4	AAS	4	Sr	Automatic extractor	Titration	13	0.00125
	No.112	AAS	4	AAS	4	Sr	AAS	4	AAS	4	Sr				
CN04	No.111	AAS	6	AAS	6	Sr	AAS	6	AAS	6	Sr	Automatic extractor	Titration	25	0.1
	No.112	AAS	6	AAS	6	Sr	AAS	6	AAS	6	Sr				
ID01	No.111	AAS	6	AAS	6	Sr	AAS	6	AAS	6	Sr	Centrifuge	Titration	50	0.05
	No.112	AAS	6	AAS	6	Sr	AAS	6	AAS	6	Sr				
ID04	No.111	AAS	21	AAS	21	+	AAS	21	AAS	21	+	Percolation tube	Titration	50	0.02
	No.112	AAS	21	AAS	21	+	AAS	21	AAS	21	+				
JP04	No.111	AAS	22	AAS	22	Sr	FEP	22	FEP	22	na	Percolation tube	Titration	25	0.1
	No.112	AAS	22	AAS	22	Sr	FEP	22	FEP	22	na				
JP06	No.111	AAS	26	AAS	26	Sr	FEP	26	FEP	26	na	Percolation tube	Titration	25	0.1
	No.112	AAS	26	AAS	26	Sr	FEP	26	FEP	26	na				
MN01	No.111	-	-	-	-	-	-	-	-	-	-	-	Titration	25	0.1
	No.112	-	-	-	-	-	-	-	-	-	-				
MY04	No.111	AAS	8	AAS	8	na	AAS	8	AAS	8	na	Centrifuge	Titration	50	0.05
	No.112	AAS	8	AAS	8	na	AAS	8	AAS	8	na				
PH03	No.111	AAS	2	AAS	2	Sr	AAS	2	AAS	2	na	Buchner funnel	Titration	50	0.01
	No.112	AAS	2	AAS	2	Sr	AAS	2	AAS	2	na				
RU01	No.111	AAS	26	AAS	26	La	FEP	26	FEP	26	La	Percolation tube	Titration	25	0.1
	No.112	AAS	26	AAS	26	La	FEP	26	FEP	26	La				
TH01	No.111	ICP	4	ICP	4	na	ICP	4	ICP	4	na	Percolation tube	Titration	25	0.05
	No.112	ICP	4	ICP	4	na	ICP	4	ICP	4	na				
TH06	No.111	AAS	4	AAS	4	Sr	FEP	4	FEP	4	Sr	Percolation tube	Titration	25	0.05
	No.112	AAS	4	AAS	4	Sr	FEP	4	FEP	4	Sr				
VN01	No.111	AAS	5	AAS	5	na	AAS	5	AAS	5	na	Buchner funnel	Titration	10	0.05
	No.112	AAS	5	AAS	5	na	AAS	5	AAS	5	na				
VN02	No.111	-	-	-	-	-	-	-	-	-	-	-	Titration	10	0.05
	No.112	-	-	-	-	-	-	-	-	-	-				
VN03	No.111	AAS	6	AAS	6	na	AAS	6	AAS	6	na	Percolation tube	Titration	10	0.02
	No.112	AAS	6	AAS	6	na	AAS	6	AAS	6	na				
VN04	No.111	AAS	8	AAS	8	na	AAS	8	AAS	8	na	Percolation tube	Titration	10	0.05
	No.112	AAS	8	AAS	8	na	AAS	8	AAS	8	na				

Note: AAS, Atomic absorption spectrometry; FEP, Flame (emission) photometry; na, Not added; -, Not measured; +, No information. *1. Years in use of instrument.

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}	Date ^{*1}	Analysis ^{*2}	Interval ^{*3}		
															Days	Days
CN01	1st	2011/11/20	1	1	2011/11/22	2	2	2011/11/21	2011/11/22	2	2	2011/11/20	1	2		
	2nd	2011/11/21	1		2011/11/24	2		2011/11/23	2011/11/24	2		2011/11/22	1			
CN02	1st	2012/1/12	1	1	2012/1/11	2	7	2012/1/10	2012/1/11	2	7	2012/1/20	3	25		
	2nd	2012/1/13	1		2012/1/18	2		2012/1/17	2012/1/18	2		2012/2/16	5			
CN03	1st	2011/12/2	2	20	2011/12/2	2	20	2011/12/1	2011/12/2	2	20	2011/12/7	3	21		
	2nd	2011/12/22	2		2011/12/22	2		2011/12/21	2011/12/22	2		2011/12/27	2			
CN04	1st	2012/2/3	1	7	2012/2/1	1	7	2012/2/1	2012/2/1	1	7	2012/2/16	5	3		
	2nd	2012/2/10	1		2012/2/8	1		2012/2/8	2012/2/8	1		2012/2/16	2			
ID01	1st	2012/1/9	1	4	2012/2/1	16	2	2012/1/17	2012/2/1	16	2	2012/1/12	1	4		
	2nd	2012/1/13	1		2012/2/1	14		2012/1/19	2012/2/1	14		2012/1/16	1			
ID04	1st	2012/1/12	4	7	2012/1/12	4	7	2012/1/9	2012/1/12	4	7	2012/1/12	4	7		
	2nd	2012/1/19	4		2012/1/19	4		2012/1/16	2012/1/19	4		2012/1/19	4			
JP04	1st	2011/11/16	1	41	2011/12/26	11	19	2011/12/16	2012/1/4	20	9	2011/12/1	4	29		
	2nd	2011/12/27	1		2012/1/13	10		2012/1/4	2012/1/13	10		2011/12/28	2			
JP06	1st	2012/1/17	2	2	2012/1/10	7	13	2012/1/4	2012/1/10	7	13	2012/1/26	2	0		
	2nd	2012/1/18	1		2012/1/27	11		2012/1/17	2012/1/27	11		2012/1/27	3			
MN01	1st	2012/3/1	1	0										2012/3/5	1	1
	2nd	2012/3/1	1											2012/3/6	1	
MY04	1st	2012/3/15	1	3	2012/3/20	5	14	2012/3/16	2012/3/20	5	14	2012/4/6	1	14		
	2nd	2012/3/18	1		2012/4/4	6		2012/3/30	2012/4/4	6		2012/4/20	1			
PH03	1st	2012/1/10	1	7	2012/2/1	1	7	2012/2/1	2012/2/1	1	7	2012/1/19	1	7		
	2nd	2012/1/17	1		2012/2/8	1		2012/2/8	2012/2/8	1		2012/1/26	1			
RU01	1st	2012/1/16	1	1	2012/1/20	5	3	2012/1/16	2012/1/20	5	3	2012/1/17	1	1		
	2nd	2012/1/17	1		2012/1/20	2		2012/1/19	2012/1/20	2		2012/1/18	1			
TH01	1st	2012/4/11	1	15	2012/4/9	2	12	2012/4/8	2012/4/9	2	12	2012/3/29	1	6		
	2nd	2012/4/26	1		2012/4/21	2		2012/4/20	2012/4/21	2		2012/4/4	1			
TH06	1st	2012/2/16	1	5	2012/2/18	2	6	2012/2/17	2012/2/18	2	6	2012/2/16	1	5		
	2nd	2012/2/21	1		2012/2/24	2		2012/2/23	2012/2/24	2		2012/2/21	1			
VN01	1st	2011/12/12	1	2	2011/12/12	1	2	2011/12/12	2011/12/12	1	2	2011/12/12	1	2		
	2nd	2011/12/14	1		2011/12/14	1		2011/12/14	2011/12/14	1		2011/12/14	1			
VN02	1st	2011/10/12	1	31										2011/12/12	1	1
	2nd	2011/11/12	1		-			-			-			2011/12/13	1	
VN03	1st	2012/1/9	1	0	2012/1/12	1	0	2012/1/12	2012/1/12	1	0	2012/1/11	1	0		
	2nd	2012/1/9	1		2012/1/12	1		2012/1/12	2012/1/12	1		2012/1/12	2			
VN04	1st	2011/1/13	3	0	2012/1/20	5	0	2012/1/16	2012/1/20	5	0	2011/1/13	3	0		
	2nd	2011/1/13	3		2012/1/20	5		2012/1/16	2012/1/20	5		2011/1/13	3			

Note: *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 4.11 shows the change of outlier ratio in all properties and laboratories from 2002 to 2011 (the ratio is calculated by N of outliers / N of all data). Although the ratio decreased from first experiment in 2002, this is still high (10-20% from 2003 to 2011). 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.

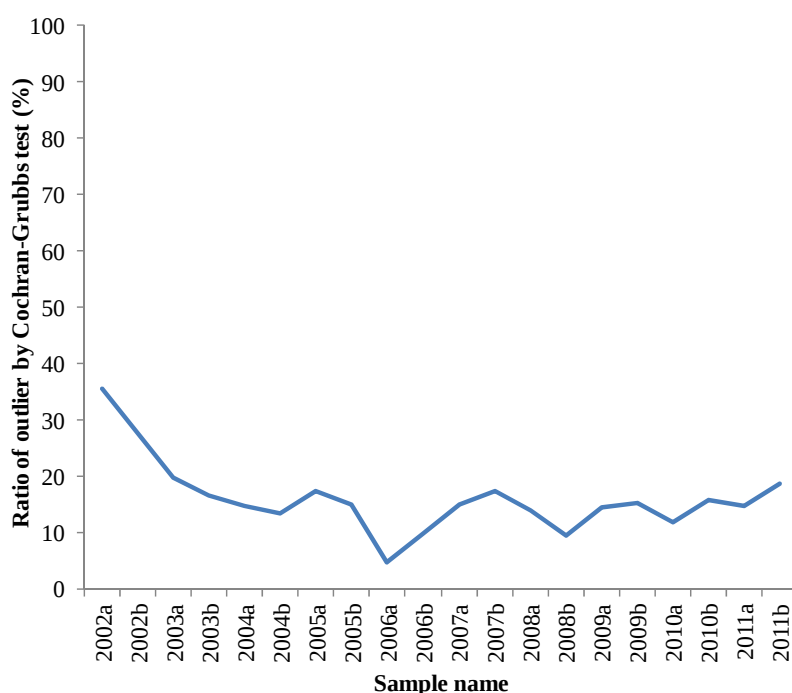


Figure 4.11 Change of the outlier ratio in all properties and laboratories from 2002 to 2010 (N of outliers / N of all data)

4.5 Recommendations

Reducing the outliers (about 20% of all data) in exchangeable base and acid cations will be considered firstly. The condition of standard solution, extraction liquid (potassium chloride and ammonium acetate), dilution rate and calculation will be checked. Precision for exchangeable acidity should be more improved to evaluate the actual monitoring data. Analyst needs an effort to improve the manipulation of titration in terms of appropriate reagent concentration, volume and so on. Not only analytical procedures but also reporting procedures should be checked carefully in the respective laboratories.

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Appendix Table 4.1 Results submitted by the laboratories (sample No. 111)

Lab.	pH(H ₂ O)			pH(KCl)			Ex-Ca (cmol.kg ⁻¹)			Ex-Mg (cmol.kg ⁻¹)			Ex-K (cmol.kg ⁻¹)			Ex-Na (cmol.kg ⁻¹)			Ex-acidity (cmol.kg ⁻¹)			Ex-Al (cmol.kg ⁻¹)			Ex-H (cmol.kg ⁻¹)					
	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat			
CN01	4.9	4.9 (0.0)	4.9	4.0	4.0 (0.0)	4.0	0.13	0.13 (0.01)	0.14	0.04	0.04 (0.00)	0.04	0.04	0.04 (0.00)	0.04	0.04	0.04 (0.01)	0.04	0.04	0.04 (0.01)	0.04	1.85	1.85 (0.05)	1.90	0.53	0.53 (0.03)	0.56	1.33	1.32 (0.04)	1.34
			4.9	4.0		3.9			0.12		0.05		0.04		0.05		0.04		0.05		1.80		0.53		0.50		1.27			
			4.9	4.0		4.0		0.13 (0.01)	0.12		0.04		0.04		0.03		0.04		0.03		1.85		0.50		1.35					
		4.9 (0.0)	4.9	4.0 (0.0)	4.0			0.13 (0.01)	0.12		0.04 (0.00)	0.04	0.04	0.04 (0.00)	0.04	0.04	0.04 (0.00)	0.04	0.04	0.04 (0.00)	0.04	1.85	1.85 (0.03)	1.84	0.52	0.52 (0.03)	0.52	1.33 (0.00)	1.32	
			4.9	4.0		4.0			0.14		0.04		0.04		0.04		0.04		0.04		1.82		0.50		1.32					
CN02	4.9	4.9 (0.0)	4.9	4.0	4.0 (0.0)	4.0	0.08	0.08 (0.01)	0.07	0.04	0.04 (0.01)	0.07	0.04	0.04 (0.01)	0.04	0.04	0.04 (0.01)	0.04	0.04	0.04 (0.01)	0.04	1.85	1.85 (0.07)	1.87	1.07	1.00 (0.09)	0.93	0.78	0.85 (0.16)	0.93
			4.9	4.0		4.0			0.09		0.04		0.04		0.05		0.04		0.05		1.91		0.96		1.10		0.67			
			4.9	4.0		4.0			0.08		0.08		0.05		0.04		0.04		0.04		1.77		1.10		0.70 (0.06)	0.71				
		4.9 (0.0)	4.9	4.0 (0.0)	4.0			0.08 (0.00)	0.08		0.04 (0.00)	0.04	0.05	0.04 (0.00)	0.04	0.04	0.04 (0.00)	0.04	0.04	0.04 (0.00)	0.04	1.84	1.84 (0.04)	1.81	1.14	1.14 (0.05)	1.10	0.26 (0.02)	0.28	
			4.9	4.0		4.0			0.08		0.04		0.04		0.04		0.04		0.04		1.89		1.14		0.75		0.63			
CN03	4.8	4.8 (0.0)	4.8	4.1	4.1 (0.0)	4.1	0.05	0.04 (0.00)	0.04	0.07	0.07 (0.00)	0.07	0.09	0.08 (0.01)	0.09	0.06	0.06 (0.00)	0.06	0.06	0.06 (0.00)	0.06	1.65	1.69 (0.07)	1.76	1.39	1.43 (0.05)	1.48	0.26	0.26 (0.02)	0.28
			4.8	4.1		4.1			0.04		0.04		0.08		0.06		0.08		0.06		1.68		1.43		0.24					
			4.8	4.1		4.1		0.05 (0.00)	0.05		0.06 (0.00)	0.06	0.08	0.09 (0.01)	0.09	0.06	0.05 (0.00)	0.06	0.06	0.05 (0.00)	0.06	1.61	1.61 (0.07)	1.60	1.35	1.35 (0.09)	1.32	0.26 (0.02)	0.24	
		4.8 (0.0)	4.8	4.1 (0.0)	4.1				0.05		0.06		0.06		0.06		0.08		0.05		1.55		1.29		0.26					
			4.8	4.1		4.1			0.05		0.06		0.06		0.06		0.08		0.05		1.55		1.29		0.26					
CN04	4.8	4.8 (0.0)	4.8	4.1	4.1 (0.0)	4.1	0.07	0.07 (0.00)	0.07	0.03	0.03 (0.00)	0.03	0.04	0.04 (0.00)	0.04	0.05	0.05 (0.00)	0.05	0.05	0.05 (0.00)	0.05	1.47	1.41 (0.10)	1.29	0.73	0.69 (0.03)	0.69	0.75	0.73 (0.08)	0.64
			4.8	4.1		4.1			0.06		0.03		0.03		0.03		0.04		0.05		1.44		0.69		0.76		0.72			
			4.8	4.1		4.1			0.07		0.03		0.03		0.03		0.03		0.05		1.49		0.72		0.79		0.79			
		4.8 (0.0)	4.8	4.1 (0.0)	4.1			0.07 (0.00)	0.07		0.03 (0.00)	0.03	0.03	0.03 (0.00)	0.03	0.03	0.05 (0.00)	0.05	0.05	0.05 (0.00)	0.05	1.52	1.52 (0.07)	1.46	0.76	0.76 (0.03)	0.79	0.77 (0.08)	0.68	
			4.8	4.1		4.1			0.07		0.03		0.03		0.03		0.04		0.04		1.59		0.76		0.85					
ID01	4.8	4.8 (0.0)	4.8	4.0	4.0 (0.0)	4.0	1.42	0.04 (0.00)	0.04	0.77	0.04 (0.00)	0.04	0.31	0.04 (0.00)	0.04	0.01	0.01 (0.00)	0.01	0.01	0.01 (0.00)	0.01	1.88	1.88 (0.00)	1.88	1.58	1.58 (0.00)	1.58	0.29	0.29 (0.00)	0.29
			4.8	4.0		4.0			0.03		0.03		0.04		0.04		0.04		0.01		1.88		1.58		0.29					
			4.8	4.0		4.0			0.04		0.04		0.04		0.03		0.03		0.01		1.88		1.58		0.29					
		4.8 (0.0)	4.8	4.0 (0.0)	4.1			2.79 (0.07)	2.72		1.50 (0.01)	1.49	0.57	0.57 (0.01)	0.58	0.01	0.01 (0.00)	0.01	0.01	0.01 (0.00)	0.01	1.87	1.87 (0.00)	1.87	1.58	1.58 (0.00)	1.58	0.29	0.29 (0.00)	0.29
			4.8	4.1		4.1			2.82		1.50		0.56		0.56		0.01	0.01 (0.00)	0.01	0.01	0.01 (0.00)	0.01	1.87	1.87 (0.00)	1.87	1.58	1.58 (0.00)	1.58	0.29	0.29 (0.00)
ID04	4.4	4.4 (0.0)	4.3	4.1	4.1 (0.0)	4.1	0.87	0.86 (0.02)	0.87	0.22	0.22 (0.01)	0.23	0.14	0.13 (0.01)	0.14	0.06	0.05 (0.01)	0.04	0.05	0.05 (0.01)	0.04	1.53	1.53 (0.00)	1.53	1.33	1.33 (0.01)	1.32	0.02	0.02 (0.00)	0.02
			4.4	4.1		4.1			0.83		0.22		0.22		0.13		0.05		0.05		1.53		1.34		0.02		1.34			
			4.3	4.1		4.1			0.87		0.22		0.13		0.13		0.05		0.05		1.53		1.34		0.02		1.34			
		4.3 (0.1)	4.2	4.1 (0.0)	4.1			0.87 (0.01)	0.86		0.21 (0.01)	0.20	0.14	0.14 (0.00)	0.14	0.06	0.06 (0.01)	0.06	0.06	0.06 (0.01)	0.06	1.53	1.53 (0.00)	1.53	1.32	1.32 (0.01)	1.32	0.02	0.02 (0.00)	0.02
			4.4	4.1		4.1			0.87		0.22		0.22		0.13		0.05		0.05		1.53		1.34		0.02		1.34			
JP04	5.0	5.0 (0.0)	5.0	4.1	4.1 (0.0)	4.1	0.04	0.04 (0.00)	0.04	0.03	0.03 (0.00)	0.03	0.03	0.03 (0.00)	0.03	0.01	0.01 (0.00)	0.01	0.01	0.01 (0.00)	0.01	2.02	1.99 (0.21)	2.02	1.63	1.65 (0.15)	1.58	0.39	0.34 (0.11)	0.44
			5.0	4.2		4.2			0.05		0.03		0.03		0.03		0.03		0.01		1.77		1.54		0.23					
			5.0	4.1		4.1			0.05		0.03		0.03		0.03		0.04		0.01		2.19		1.83		0.37					
		5.0 (0.0)	5.0	4.1 (0.0)	4.1			0.04 (0.00)	0.05		0.03 (0.00)	0.03	0.03	0.03 (0.00)	0.03	0.03	0.01 (0.00)	0.01	0.01	0.01 (0.00)	0.01	2.05	2.05 (0.23)	2.05	1.61	1.61 (0.18)	1.42	0.44	0.44 (0.08)	0.37
			5.0	4.1		4.1			0.04		0.03		0.03		0.03		0.03		0.01		2.21		1.78		0.42					
JP06	4.9	4.8 (0.1)	4.8	4.2	4.1 (0.0)	4.1	0.04	0.00 (0.01)	0.00	0.02	0.02 (0.00)	0.02	0.04	0.04 (0.00)	0.03	0.04	0.04 (0.00)	0.03	0.04	0.04 (0.00)	0.03	1.75	1.84 (0.10)	1.94	1.37	1.45 (0.20)	1.42	0.38	0.40 (0.19)	0.53
			4.7	4.2		4.2			0.00		0.02		0.02		0.04		0.04		0.04		1.74		1.26		0.49					
			4.9	4.2		4.2			0.01		0.02		0.02		0.04		0.04		0.04		1.84		1.66		0.18					
		4.9 (0.0)	4.9	4.3 (0.0)	4.3			0.07 (0.05)	0.04		0.01 (0.02)	0.00	0.03	0.03 (0.00)	0.03	0.03	0.04 (0.01)	0.03	0.03	0.03 (0.01)	0.03	1.72	1.66 (0.11)	1.72	1.29	1.29 (0.15)	1.38	0.36	0.36 (0.04)	0.34
			4.9	4.3		4.3			0.04		0.04		0.00		0.00		0.02		0.03		1.73		1.39		0.34					
MN01	4.4	4.4 (0.0)	4.4	3.7	3.6 (0.0)	3.7			0.12		0.03		0.03		0.03				0.05		1.54		1.12		0.42					
			4.4	3.7		3.7															2.32		2.30		1.20		1.20		0.80	
			4.4	3.6		3.6															2.30		1.20		0.80					
		4.4 (0.0)	4.4	3.7 (0.0)	3.7																2.30		1.20		0.80					
			4.4	3.7		3.7															2.30		1.20		0.80					

Appendix Table 4.1 continued

Lab.	pH(H ₂ O)			pH(KCl)			Ex-Ca (cmol kg ⁻¹)			Ex-Mg (cmol kg ⁻¹)			Ex-K (cmol kg ⁻¹)			Ex-Na (cmol kg ⁻¹)			Ex-actdity (cmol kg ⁻¹)			Ex-Al (cmol kg ⁻¹)			Ex-H (cmol kg ⁻¹)		
	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat
MY04	4.8	4.7 (0.0)	4.7	4.1	4.1 (0.0)	4.0	0.10	0.10 (0.00)	0.10	0.06	0.05 (0.00)	0.05	0.04	0.04 (0.00)	0.04	0.03	0.03 (0.00)	0.03	8.64	8.11 (1.45)	7.27	5.13	5.09 (0.50)	4.69	3.43	2.94 (0.96)	2.50
			4.7			4.1	0.10		0.10			0.05			0.04			0.03			9.78			5.66		4.04	
			4.7			4.1	0.10		0.10			0.06			0.03			0.03			7.27			4.93		2.26	
		4.8 (0.1)	4.9	4.1 (0.0)	4.1	0.10 (0.00)	0.10	0.00	0.10	0.07 (0.01)	0.06	0.03 (0.01)	0.06	0.03	0.03 (0.01)	0.03	0.03 (0.00)	0.03	9.16 (1.21)	9.21	5.17 (0.64)	4.43	5.17 (0.64)	4.43	3.91 (1.43)	4.70	
PH03			4.8			4.1	0.10		0.10			0.07			0.03			0.03			7.92			5.58		2.26	
			4.7			4.1	0.10		0.10			0.07			0.03			0.03			10.34			5.49		4.77	
	4.6	4.5 (0.1)	4.5	3.8	3.8 (0.0)	3.8	43.79	43.64 (0.89)	42.7	3.77	3.81 (0.21)	3.6	1.61	1.60 (0.11)	1.7	3.82	3.88 (0.07)	3.8	2.37	2.36 (0.18)	2.52	2.08	2.07 (0.17)	2.20	0.29 (0.03)	0.33	
	4.6		4.6	3.8		3.8			43.9		4.0				1.6			3.9			2.16			1.88		0.28	
RU01			4.5			3.8			44.4		3.8				1.5			4.0			2.40			2.14		0.26	
		4.6 (0.0)	4.6	3.8 (0.1)	3.7	43.94 (0.78)	43.5	3.9	3.72 (0.18)	43.5	3.9	1.62 (0.04)	1.6	3.75 (0.10)	1.6	3.75 (0.10)	3.9	2.38 (0.17)	2.52	2.08 (0.17)	2.20	0.30 (0.03)	0.33	0.30 (0.03)	0.33		
	4.6		4.6	3.8		3.8			43.5		3.7				1.6			3.7			2.19			1.88		0.31	
	4.6		4.6	3.8		3.8			44.8		3.5				1.7			3.7			2.42			2.16		0.26	
RU01	4.9	4.9 (0.0)	4.9	4.2	4.2 (0.0)	4.2	0.23	0.22 (0.00)	0.22	0.09	0.09 (0.02)	0.10	0.06	0.05 (0.01)	0.06	0.10	0.09 (0.02)	0.10	2.21	2.27 (0.10)	2.19	1.84	1.89 (0.12)	1.82	0.13	0.13 (0.06)	0.20
			4.9			4.2			0.21			0.10			0.04			0.07			2.38			2.02		0.10	
			4.9			4.2			0.21			0.07			0.04			0.10			2.24			1.82		0.10	
	4.9 (0.0)	4.9	4.2 (0.0)	4.2	0.24 (0.03)	0.21	0.08 (0.02)	0.10	0.07 (0.03)	0.08	0.11 (0.02)	0.12	0.14 (0.00)	2.14	1.79 (0.12)	1.72	0.13 (0.06)	0.10									
TH01			4.9			4.2			0.25		0.07				0.09			0.11			2.14			1.72		0.20	
			4.9			4.2			0.25		0.07				0.04			0.08			2.14			1.92		0.10	
	5.1	5.0 (0.0)	5.0	4.1	4.1 (0.0)	4.1	0.08	0.08 (0.01)	0.07	0.11	0.11 (0.01)	0.10	0.16	0.16 (0.01)	0.14	0.05	0.04 (0.01)	0.04	2.37	2.25 (0.09)	2.17	1.96	1.89 (0.23)	1.62	0.24	0.28 (0.10)	0.40
	5.0		5.0	0.09	0.17	0.17	0.08 (0.02)	0.10	0.07 (0.03)	0.08	0.11 (0.02)	0.12	0.16	0.16 (0.01)	0.17	0.06	0.05 (0.00)	0.05	2.49 (0.31)	2.20	2.02	2.02 (0.00)	2.02	0.20	0.20 (0.00)	0.20	
TH06			5.1			4.1			0.07		0.11				0.14			0.05			2.80			2.02		0.20	
			5.1			4.1			0.07		0.11				0.17			0.05			2.49			2.02		0.20	
			5.1			4.1			0.07		0.11				0.17			0.05			2.49			2.02		0.20	
	5.1	5.1 (0.0)	5.1	4.2	4.2 (0.0)	4.2	0.33	0.34 (0.01)	0.33	0.11	0.11 (0.00)	0.12	0.10	0.10 (0.01)	0.11	0.10	0.10 (0.01)	0.10	2.06	2.06 (0.00)	2.06	1.96	1.95 (0.00)	1.95	0.10	0.10 (0.00)	0.10
VN01			5.1			4.2			0.35		0.11				0.10			0.10			2.06			1.95		0.10	
			5.1			4.2			0.33		0.11				0.09			0.09			2.06			1.95		0.10	
			5.1			4.2			0.33		0.11				0.11			0.10			2.06			1.97		0.10	
	5.1 (0.0)	5.1	4.2 (0.0)	4.2	0.32 (0.01)	0.33	0.11 (0.00)	0.12	0.10 (0.00)	0.10	0.10 (0.00)	0.10	0.10 (0.00)	2.06	1.97 (0.02)	1.95	0.09 (0.02)	0.10									
VN02			5.1			4.2			0.33		0.11				0.10			0.10			2.06			1.95		0.10	
			5.1			4.2			0.31		0.11				0.10			0.10			2.06			1.99		0.06	
	5.0	5.0 (0.0)	5.1	4.2	4.2 (0.0)	4.2	0.01	0.01 (0.00)	0.01	0.04	0.04 (0.00)	0.04	0.04	0.04 (0.00)	0.04	0.02	0.02 (0.00)	0.02	1.97	1.96 (0.00)	1.96	1.26	1.26 (0.00)	1.26	0.71	0.71 (0.00)	0.70
	5.0		5.0	0.01	0.04	0.04	0.04 (0.00)	0.04	0.04	0.04 (0.00)	0.04	0.04	0.04 (0.00)	1.96	1.96 (0.00)	1.96	1.26	1.26 (0.00)	1.26	0.71	0.71 (0.00)	0.71					
VN03			5.0			4.3			0.01		0.04				0.04			0.02			1.97			1.26		0.71	
			5.0			4.2			0.01		0.04				0.04			0.02			1.97			1.26		0.71	
	5.0 (0.0)	5.0	4.2 (0.0)	4.2	0.01 (0.00)	0.01	0.04 (0.00)	0.01	0.04 (0.00)	0.04	0.02 (0.00)	0.02	1.97 (0.00)	1.26	0.71 (0.00)	0.71											
			5.0			4.2			0.01		0.04				0.04			0.02			1.97			1.26		0.71	
VN02			5.1			4.2			0.01		0.04				0.04			0.02			1.97			1.26		0.71	
			5.1			4.2			0.01		0.04				0.04			0.02			1.97			1.26		0.71	
	5.1 (0.0)	5.1	4.2 (0.0)	4.2	0.22 (0.00)	0.21	0.09 (0.00)	0.11	0.09	0.09 (0.00)	0.09	0.06	0.06 (0.00)	0.06	0.04	0.04 (0.00)	0.04	2.25	2.24 (0.03)	2.23	2.16	2.16 (0.12)	2.23	0.41	0.40 (0.00)	0.40	
			5.1			4.2			0.12		0.08				0.06			0.04			2.23			2.02		0.40	
VN04			4.7			4.0			0.22		0.38				0.18			0.20			2.84			2.59		0.19	
			4.7			4.0			0.22		0.38				0.18			0.20			2.84			2.59		0.19	
	4.8	4.8 (0.0)	4.8	4.0	4.0 (0.0)	4.0	0.22	0.21 (0.01)	0.20	0.38	0.37 (0.00)	0.37	0.18	0.18 (0.00)	0.18	0.19	0.18 (0.01)	0.18	2.83	2.78 (0.11)	2.84	2.59	2.54 (0.04)	2.50	0.18	0.19 (0.02)	0.17
			4.8			4.0			0.20			0.37			0.18			0.18			2.65			2.59		0.21	
VN04			4.7			4.0			0.21			0.37			0.18			0.19			2.85			2.54		0.21	
			4.7			4.0			0.22		0.38				0.18			0.20			2.87			2.63		0.17 (0.02)	0.15
	4.7 (0.0)	4.7	4.0 (0.0)	4.0	0.22 (0.00)	0.22	0.38 (0.00)	0.38	0.38 (0.00)	0.38	0.18	0.18 (0.00)	0.18	0.20 (0.01)	0.20	0.20 (0.01)	0.20	2.87 (0.08)	2.87	2.64 (0.06)	2.64	0.17 (0.02)	0.15				
			4.7			4.0			0.22		0.38				0.18			0.20			2.84			2.59		0.19	
VN04			4.8			4.0			0.23			0.38			0.18			0.20			2.81			2.71		0.17	
			4.7			4.1			0.11		0.09				0.06			0.04			2.23			2.23		0.40	
	4.7 (0.0)	4.7	4.1 (0.0)	4.1	0.11 (0.00)	0.11	0.09 (0.00)	0.11	0.09	0.09 (0.00)	0.09	0.06	0.06 (0.00)	0.06	0.04	0.04 (0.00)	0.04	2.25	2.24 (0.03)	2.23	2.16	2.16 (0.12)	2.23	0.41	0.40 (0.00)	0.40	
			4.7			4.1			0.11		0.09				0.06			0.04			2.28			2.23		0.40	
VN04			4.7			4.1			0.12		0.08				0.06			0.04			2.23			2.02		0.40	
			4.7			4.1			0.12		0.08				0.06			0.04			2.23			2.02		0.40	
	4.7 (0.0)	4.7	4.1 (0.0)	4.1	0.11 (0.00)	0.12	0.08 (0.00)	0.12	0.08 (0.00)	0.08	0.05 (0.00)	0.05	0.04 (0.00)	0.04	0.04 (0.00)	0.04	2.25 (0.03)	2.25	2.16 (0.12)	2.16	0.41 (0.00)	0.41					
			4.7			4.1			0.12		0.08				0.05			0.04			2.23			2.23		0.41	

Appendix Table 4.2 Results submitted by the laboratories (sample No. 112)

Appendix Table 4.2 continued

Lab.	pH(H ₂ O)			pH(KCl)			Ex-Ca (cmol kg ⁻¹)			Ex-Mg (cmol kg ⁻¹)			Ex-K (cmol kg ⁻¹)			Ex-Na (cmol kg ⁻¹)			Ex-acidity (cmol kg ⁻¹)			Ex-Al (cmol kg ⁻¹)			Ex-H (cmol kg ⁻¹)				
	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat	Lab. Ave.	Ave. (S.D.)	repeat		
MY04	4.5	4.5 (0.0)	4.5	3.6	3.6 (0.0)	3.6	3.77	3.81 (0.15)	3.91	1.75	1.81 (0.07)	1.85	0.64	0.66 (0.02)	0.67	0.25	0.26 (0.00)	0.25	59.7	60.4 (1.99)	58.1	52.4	53.1 (2.68)	50.6	7.2	7.2 (1.41)	7.4	5.7	
	4.6		4.6	3.6		3.6			3.88		1.86		0.64		0.64		0.25		61.7		61.7		56.0		7.4		5.7		
	4.5		4.5	3.6		3.6		3.64		3.64		1.74		0.67		0.26		61.4		61.4		52.8		8.5		8.5			
	4.5	4.5 (0.0)	4.5	3.6	3.6 (0.0)	3.6	3.73 (0.06)		3.74	1.69 (0.05)	1.74	0.62 (0.10)	0.73	0.56	0.56	0.23 (0.02)	0.26	58.9 (5.07)	53.2	51.6 (5.01)	45.9	7.2 (0.41)	7.2	7.2 (0.41)	7.2	7.2 (0.41)	7.2		
	4.6		4.6	3.6		3.6		3.78		3.78		1.69		0.64		0.22		63.0		63.0		55.3		7.6		7.6			
PH03	4.5		4.5	3.6		3.6		3.67		3.67		1.63		0.57		0.22		60.5		60.5		53.6		6.8		6.8			
	4.2	4.2 (0.1)	4.2	3.3	3.3 (0.0)	3.3	65.64	64.82 (0.87)	64.18	15.24	15.36 (0.32)	15.07	6.81	6.88 (0.34)	6.52	3.31	3.32 (0.08)	3.33	20.8	20.8 (0.26)	21.0	18.9	18.9 (0.20)	18.8	1.9	1.9 (0.25)	2.2	2.2	
	4.2		4.2	3.3		3.3		64.45		15.30		6.91		3.22		20.5		18.7						1.8		1.8		1.8	
	4.3		4.3	3.3		3.3		65.81		15.70		7.19		3.39		20.8		19.1						1.8		1.8		1.8	
	4.2	4.2 (0.0)	4.2	3.4	3.3 (0.1)	3.4	66.45 (0.96)		65.54	15.11 (0.37)	14.71	6.73 (0.28)	6.69	3.30 (0.08)	3.22	20.8 (0.28)	21.0	18.9 (0.20)	18.8	1.9 (0.25)	2.2	2.2	2.2	2.2	2.2 (0.25)	2.2	2.2		
RU01	4.2		4.2	3.3		3.3		66.36		15.16		6.47		3.38		20.5		18.7						1.8		1.8		1.8	
	4.7	4.7 (0.0)	4.7	3.7	3.7 (0.0)	3.7	3.47	3.43 (0.02)	3.45	2.49	2.54 (0.10)	2.50	0.66	0.64 (0.03)	0.64	0.39	0.40 (0.05)	0.42	25.9	25.8 (0.11)	25.7	25.9	25.9 (0.18)	25.8	0.8	0.8 (0.18)	0.8	0.8	
	4.7		4.7	3.7		3.7		3.41		2.46		0.60		0.34		25.9		26.0						0.6		0.6			
	4.7		4.7	3.7		3.7		3.43		2.66		0.67		0.43		25.8		25.7						0.9		0.9			
	4.7	4.7 (0.0)	4.7	3.8	3.7 (0.0)	3.8	3.50 (0.20)	3.41	2.43 (0.14)	2.37	0.69	0.37 (0.04)	0.38	26.0 (0.13)	25.9	25.9 (0.11)	25.8	0.8 (0.13)	0.7					0.7		0.7			
TH01	4.7		4.7	3.7		3.7		3.36		2.34		0.56		0.32		26.2		26.0						0.9		0.9			
	4.7		4.7	3.7		3.7		3.72		2.60		0.78		0.39		25.9		25.9						0.7		0.7			
	4.6	4.5 (0.0)	4.5	3.6	3.6 (0.0)	3.6	3.53	3.56 (0.04)	3.51	1.65	1.63 (0.09)	1.66	1.16	1.16 (0.02)	1.17	0.22	0.20 (0.00)	0.19	22.9	22.7 (0.23)	22.9	21.8	21.2 (0.55)	21.8	1.3	1.9 (0.36)	1.4	1.4	
	4.5		4.5	3.6		3.6		3.58		1.70		1.15		0.20		22.6		21.1						2.1		2.1		2.1	
	4.5		4.5	3.6		3.6		3.59		1.53		1.17		0.20		22.5		20.7						2.0		2.0		2.0	
TH06	4.7	4.7 (0.0)	4.7	3.7	3.6 (0.0)	3.7	3.48	3.50 (0.08)	3.48	1.66 (0.04)	1.61	1.16 (0.02)	1.18	0.23 (0.02)	0.23	23.1 (0.37)	23.0	22.4 (0.91)	23.1	0.6 (0.08)	0.2			0.6 (0.08)	0.2		0.2		
	4.7		4.7	3.6		3.6		3.42		1.69		1.15		0.25		23.5		22.7						0.1		0.1			
	4.7		4.7	3.7		3.7		3.59		1.66		1.16		0.20		22.8		21.4						1.7		1.7			
	4.7		4.7	3.7		3.7		4.38		1.61		0.67		0.35		23.0		21.4						1.6		1.6			
	4.7	4.7 (0.0)	4.7	3.7	3.7 (0.0)	3.7	4.37	4.36 (0.05)	4.33	1.64 (0.01)	1.63	0.69	0.69 (0.03)	0.72	0.34	0.35 (0.01)	0.37	23.1	23.1 (0.06)	23.1	21.4	21.4 (0.03)	21.5	1.7	1.7 (0.06)	1.6	1.6		
VN01	4.7		4.7	3.7		3.7		4.36	4.35 (0.04)	4.30	1.63	1.62 (0.01)	1.63	0.69	0.69 (0.03)	0.72	0.34	0.35 (0.01)	0.37	23.1	23.1 (0.06)	23.1	21.4	21.4 (0.03)	21.5	1.7	1.7 (0.06)	1.6	1.6
	4.7		4.7	3.7		3.7		4.37		1.61		0.66		0.34		23.2		21.4						1.6		1.6			
	4.7		4.7	3.7		3.7		4.33		1.65	1.64 (0.01)	1.63	0.68	0.68 (0.00)	0.72	0.34	0.35 (0.01)	0.37	23.1	23.1 (0.06)	23.1	21.4	21.4 (0.03)	21.5	1.6	1.6 (0.03)	1.6	1.6	
	4.7		4.7	3.7		3.7		4.42		1.65		0.68		0.33		23.0		21.4						1.6		1.6			
	4.7		4.7	3.7		3.7		4.34		1.63	1.63 (0.01)	1.67	0.71	0.71 (0.02)	0.70	0.24	0.24 (0.01)	0.23	16.9	16.8 (0.10)	16.7	15.0	15.0 (0.08)	14.9	1.8	1.8 (0.10)	1.9	1.9	
VN02	4.9	4.8 (0.0)	4.9	3.8	3.8 (0.0)	3.8	2.08	2.07 (0.02)	2.04	1.71	1.71 (0.03)	1.67	0.71	0.71 (0.02)	0.70	0.24	0.24 (0.01)	0.23	16.9	16.8 (0.10)	16.7	15.0	15.0 (0.08)	14.9	1.8	1.8 (0.10)	1.9	1.9	
	4.8		4.8	3.8		3.8		2.08		1.72		0.70		0.24		16.7		15.0						1.7		1.7		1.7	
	4.8		4.8	3.8		3.8		2.08		1.73		0.74		0.26		16.9		15.0						1.9		1.9			
	4.9	4.9 (0.0)	4.8	3.8	3.8 (0.0)	3.8	2.08 (0.01)		2.09	1.70 (0.03)	1.70	0.71 (0.01)	0.73	0.24 (0.00)	0.23	17.0 (0.09)	16.9	15.0 (0.07)	15.0	1.8 (0.12)	1.7			1.8 (0.12)	1.7	1.7			
	4.9		4.9	3.8		3.8		2.08		1.73		0.72		0.24		17.1		14.9						1.9		1.9			
VN03	4.6	4.6 (0.0)	4.6	3.7	3.7 (0.0)	3.7			2.08		1.67		0.70	0.70	0.24	17.1		14.9						1.9		1.9		1.9	
	4.6		4.6	3.7		3.7		9.88 (0.08)	9.85	4.90	4.79 (0.14)	4.74	1.73	1.74 (0.07)	1.73	0.50	0.52 (0.00)	0.52	27.5	27.4 (0.14)	27.5	20.4	20.1 (0.28)	19.8	1.7	1.8 (0.16)	1.8	1.8	
	4.6		4.6	3.5		3.5		9.97		4.94		1.67		0.52		27.5		20.4						1.6		1.6			
	4.6		4.6	3.5		3.5		9.82		4.68		1.81		0.51		27.3		20.0						1.9		1.9			
	4.5	4.5 (0.0)	4.5	3.5	3.5 (0.0)	3.5	9.92 (0.03)	9.91	5.01 (0.02)	5.00	1.72 (0.01)	1.72	0.48 (0.01)	0.47	27.6 (0.08)	27.6	20.7 (0.17)	20.5	1.7 (0.09)	1.8					1.8	1.8			
VN04	4.5		4.5	3.5		3.5		9.89		5.03		1.72		0.49		27.6		20.8						1.6		1.6		1.6	
	4.5		4.5	3.5		3.5		9.96		4.99		1.71		0.48		27.7		20.8						1.6		1.6			
	4.7	4.6 (0.0)	4.7	3.6	3.6 (0.0)	3.6	2.04	2.04 (0.01)	2.05	0.70	0.69 (0.00)	0.69	1.98	1.94 (0.00)	1.94	0.17	0.17 (0.00)	0.17	20.3	20.3 (0.03)	20.2	21.8	21.7 (0.13)	21.8	2.5	2.5 (0.13)	2.5	2.5	
	4.6		4.6	3.6		3.6		2.03		0.70		1.94		0.17		20.3		21.6						2.5		2.5		2.5	
	4.6		4.6	3.7		3.7		2.05		0.69		1.94		0.16		20.3		21.6						2.3		2.3		2.3	
VN04	4.6	4.6 (0.0)	4.6	3.7	3.6 (0.0)	3.7	2.04 (0.01)		2.03	0.70 (0.00)	0.71	2.02 (0.01)	2.02	0.16	0.16 (0.00)	0.16	20.2 (0.03)	20.3	21.8 (0.00)	21.8	2.5 (0.13)	2.5			2.5 (0.13)	2.5	2.5		
	4.7		4.7	3.6		3.6		2.05		0.70		2.03		0.16	0.16 (0.00)	0.16	20.2 (0.03)	20.3	21.8 (0.00)	21.8	2.5 (0.13)	2.5			2.5 (0.13)	2.5	2.5		
	4.7		4.7	3.6		3.6		2.05		0.70		2.03		0.16	0.16 (0.00)	0.16	20.2 (0.03)	20.3	21.8 (0.00)	21.8	2.5 (0.13)	2.5			2.5 (0.13)	2.5	2.5		
	4.7		4.7	3.6		3.6		2.05		0.70		2.03		0.16	0.16 (0.00)	0.16	20.2 (0.03)	20.3	21.8 (0.00)	21.8	2.5 (0.13)	2.5			2.5 (0.13)	2.5	2.5		
	4.6		4.6	3.7		3.7		2.05		0.70		2.03		0.16	0.16 (0.00)	0.16	20.2 (0.03)	20.3	21.8 (0.00)	21.8	2.5 (0.13)	2.5			2.5 (0.13)	2.5	2.5		

5. 12th INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENT

5.1 Introduction

In the 12th Inter-laboratory Comparison Project on inland aquatic environment, an artificial inland water sample containing known concentrations of major ions, were prepared and sent to the EANET participating countries by the Network Center (NC) in October 2011. Almost all the participating laboratories submitted their analytical data to the NC. The measured results of pH, EC, alkalinity and concentrations of SO_4^{2-} , NO_3^- , Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+ in the participating laboratories were compared with the prepared values and the results were statistically analyzed.

5.2 Procedures

5.2.1 Participating Laboratories

The NC shipped an artificial inland water samples on October 3, 2011 to 23 laboratories involved in the EANET activities, and most of them submitted their analytical data to the NC by February 29, 2012. Participating laboratories and their identification codes are listed in Table 1.1. For this attempt, the laboratory MY03 and MN01 submitted the data of 3 parameters, pH, EC, and alkalinity, and the laboratory VN03 submitted all the data except NO_3^- .

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 that are specified in the “Technical Manual for Monitoring on Inland Aquatic Environment in East Asia (2000)” and the “QA/QC Program for Monitoring on Inland Aquatic Environment in East Asia (2000)”. Analytical methods specified in the manual are described in Table 5.4.

Table 5.4 Analytical methods specified in the Technical Manual for Monitoring on Inland Aquatic Environment in East Asia

Parameter	Analytical method
pH	Glass electrode
EC	Conductivity cell
Alkalinity	Titration by Burette or Digital Burette with pH Meter (end-point pH4.8)
SO ₄ ²⁻ NO ₃ ⁻	Ion Chromatography or Spectrophotometry
Cl ⁻	Ion Chromatography or Titration
Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
NH ₄ ⁺	Ion Chromatography or Spectrophotometry (Indophenol blue)

5.2.4 Data Checking Procedures

a) Calculation of ion balance (R_1)

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

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

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 Monitoring on Inland Aquatic Environment in East Asia (2000)”

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;

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

(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 Monitoring on Inland Aquatic Environment in East Asia (2000)”

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 apart 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 $\pm 10\%$.

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

Constituents	Prepared	Average	S.D.	N	Min.	Max.
pH	7.20	7.18	0.12	21	7.02	7.44
EC (mS m^{-1})	5.48	5.37	0.20	21	5.18	6.08
Alkalinity (meq L^{-1})	0.225	0.236	0.02	22	0.190	0.270
SO_4^{2-} (mg L^{-1})	7.33	7.41	0.25	19	7.04	7.93
NO_3^- (mg L^{-1})	1.57	1.62	0.16	19	1.26	2.06
Cl^- (mg L^{-1})	2.20	2.20	0.22	19	1.55	2.53
Na^+ (mg L^{-1})	5.34	5.37	0.15	19	5.07	5.68
K^+ (mg L^{-1})	1.40	1.37	0.12	20	1.12	1.60
Ca^{2+} (mg L^{-1})	2.59	2.67	0.26	19	1.95	3.10
Mg^{2+} (mg L^{-1})	0.53	0.54	0.04	19	0.48	0.63
NH_4^+ (mg L^{-1})	0.42	0.43	0.06	20	0.30	0.54

(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 sample 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 circumstance of analysis 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 circumstances of analysis 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	5	1	2	2	0	2	3	2	7	24	10.7%
X	0	1	0	0	1	1	1	0	1	1	0	6	2.7%
Data within DQOs	22	21	17	19	16	17	19	18	16	17	13	195	86.7%
Flagged(%)	0.0	4.5	22.7	5.0	15.8	15.0	5.0	10.0	20.0	15.0	35.0	13.3	

*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 $> 30\%$)

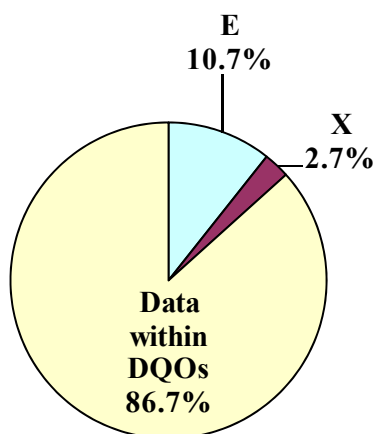


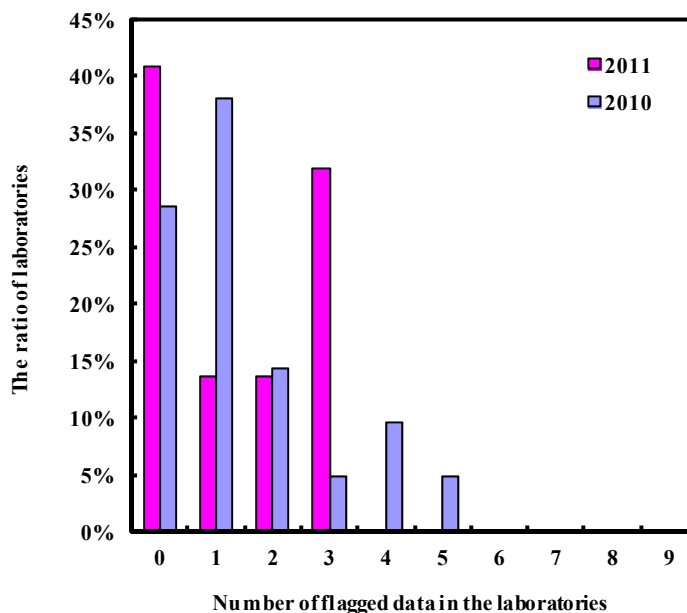
Figure 5.1 Percentage of flagged data

The data flagged by "E", which exceeded the DQOs within a factor of 2, shared 10.7% of all the reported data of samples. Furthermore, the data flagged by "X", which exceeded the DQOs more than a factor of 2, shared 2.7% of all the reported data of samples. Concerning respective parameters, the percentage of flagged NH₄⁺ was comparatively high, more than 30%.

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	9	41%
1	3	14%
2	3	14%
3	7	32%
4	0	0%
5	0	0%
6	0	0%
7	0	0%
8	0	0%
9	0	0%
Total	22	100%

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

The percentage of the laboratories without flagged data was 41% in this attempt, while that in the last attempt (2010) was 29%.

The Analytical data submitted by the participating laboratories were shown in Table 5.10 with flags. In seven laboratories, three flagged data were observed.

Table 5.10 Analytical Results of Sample No.111i (artificial inland aquatic environment sample : EANET in 2011)

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	7.05	5.42	0.227	9.21 E	1.76	2.53 E	5.59	1.33	2.62	0.48	0.40	-4.84	-
CN01	7.20	5.35	0.231	7.69	1.70	2.51	5.33	1.38	2.94	0.54	0.42	-0.75	3.69
CN02	7.17	5.37	0.231	7.33	1.59	2.23	5.31	1.40	2.55	0.54	0.39	-1.38	1.08
CN03	7.02	5.30	0.228	7.42	1.56	2.18	5.33	1.41	2.71	0.55	0.30 E	-0.41	1.89
CN04	7.14	5.35	0.238	7.41	1.56	2.08	5.31	1.29	3.10 E	0.63 E	0.41	1.81	3.10
ID01	7.05	5.36	0.240	7.77	1.63	2.24	5.30	1.30	2.55	0.49	0.49 E	-3.42	2.26
ID05	7.10	5.40	0.190 E	7.40	1.26 E	2.00	5.27	1.33	2.35	0.53	0.51 E	3.64	-1.92
JP04	7.34	5.32	0.240	7.24	1.50	2.09	5.07	1.37	2.97	0.56	0.43	0.01	2.25
JP05	7.44	5.18	0.240	7.36	1.58	2.18	5.35	1.37	2.88	0.53	0.42	-0.15	4.23
MY01	7.29	5.22	0.230	7.24	1.50	2.17	5.35	1.37	2.71	0.51	0.42	0.19	2.59
MY03	7.09	41.77 X	0.270 E									-	-
MN01	7.19	5.24	0.230									-	-
PH01	7.03	6.08	0.237	7.59	2.06 X	2.26	5.67	1.51	2.99 E	0.56	0.33 E	0.69	-2.06
PH02	7.30	5.32	0.240	7.32	1.69	2.11	5.46	1.40	2.58	0.58	0.46	-0.44	2.54
RU01	7.31	5.36	0.240	7.20	1.53	1.55 E	5.22	1.44	2.52	0.54	0.44	-0.03	-0.10
RU02	7.25	5.37	0.224	7.10	1.66	2.53	5.25	1.49	2.60	0.57	0.41	-0.44	1.51
TH01	7.26	5.74	0.227	7.20	1.58	2.16	5.42	1.40	2.72	0.55	0.44	1.49	-1.81
TH02	6.65	5.33	0.220	7.93	1.60	2.29	7.07 X	1.60	4.64 X	0.63 E	0.46	16.08 I	11.22 C
VN01	7.12	5.23	0.260 E	7.14	1.89 E	2.34	5.68	1.53	2.59	0.50	0.32 E	-3.17	4.46
VN02	7.17	5.31	0.270 E	7.69	1.62	2.22	5.42	1.14 E	2.74	0.52	0.53 E	-4.56	4.44
VN03	7.02	5.24	0.220	7.04		6.55 X	5.47	1.31	1.95 E	1.41 X	0.40	-	-
VN04	7.17	5.31	0.260 E	7.72	1.55	2.23	5.31	1.12 E	2.62	0.50	0.54 E	-4.79	3.54
Expected value	7.20	5.48	0.225	7.33	1.57	2.20	5.34	1.40	2.59	0.53	0.42	-	-

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 general overviews of data are presented below in Figures 5.3 to 5.13 for each analytical parameter. The results received from each laboratory are normalized by the prepared values to evaluate deviation from the prepared values.

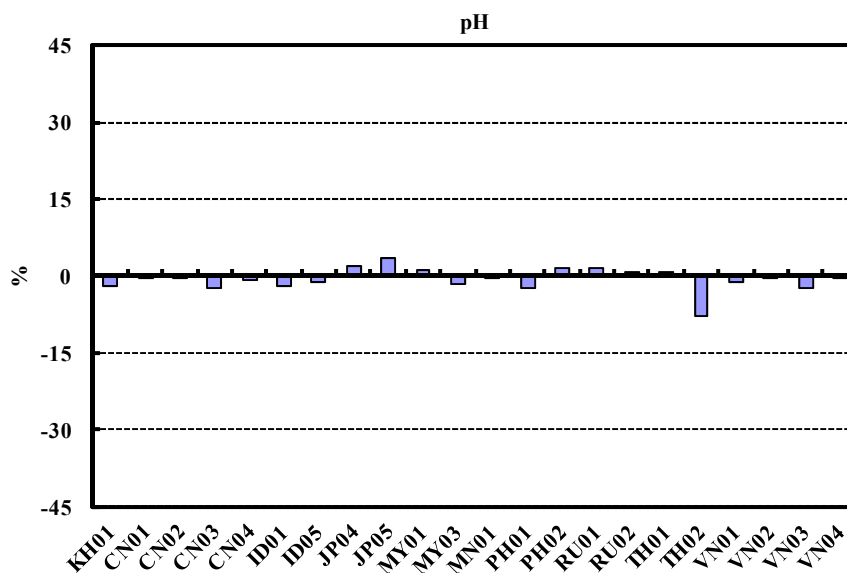


Figure 5.3 Distribution of results for pH (normalized by the prepared value)

All the submitted data of pH were within DQOs, and almost all of them agreed well with the prepared value.

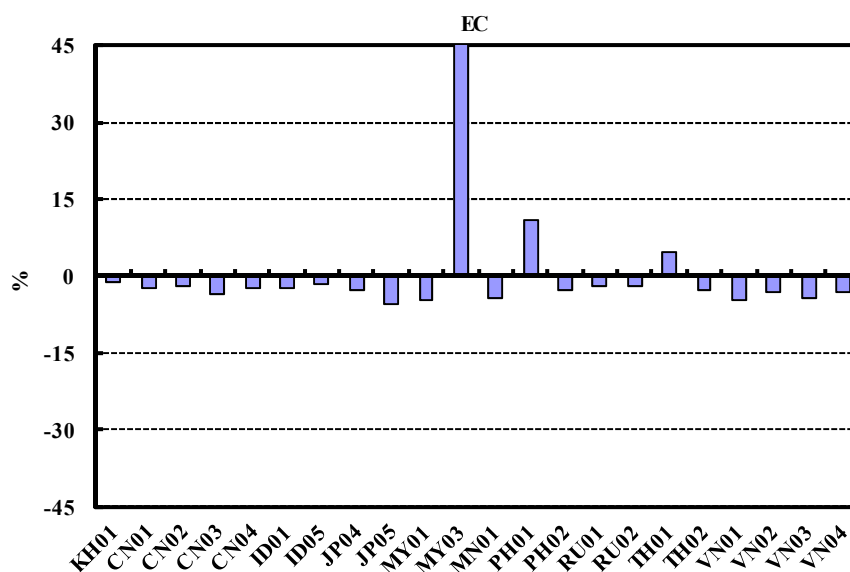


Figure 5.4 Distribution of results for EC (normalized by the prepared value)

Except for MY03, all the submitted data of EC were within DQO, 15%. Most of them were lower than the prepared value and their differences between laboratories were small, although the data of MY03 exceeds DQOs extremely.

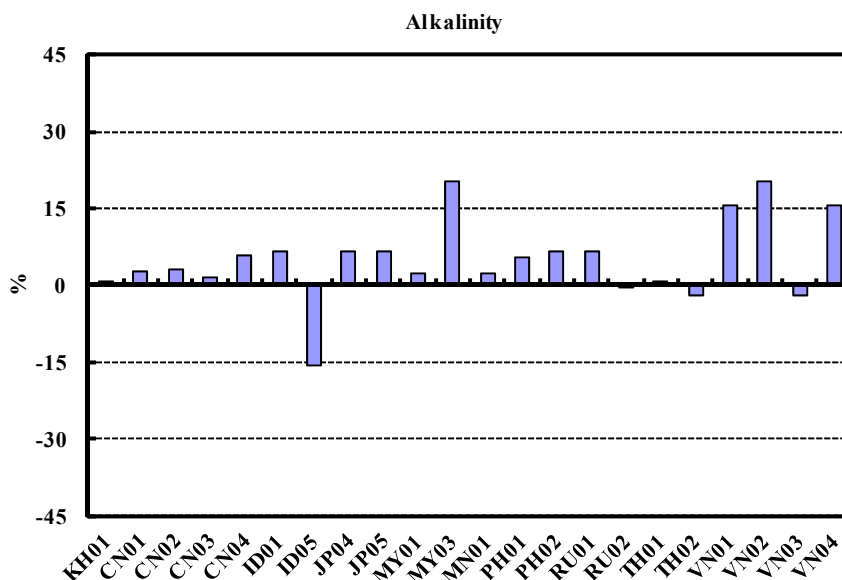


Figure 5.5 Distribution of results for alkalinity (normalized by prepared concentration)

Data from five laboratories were flagged, however, they were all within 30%.

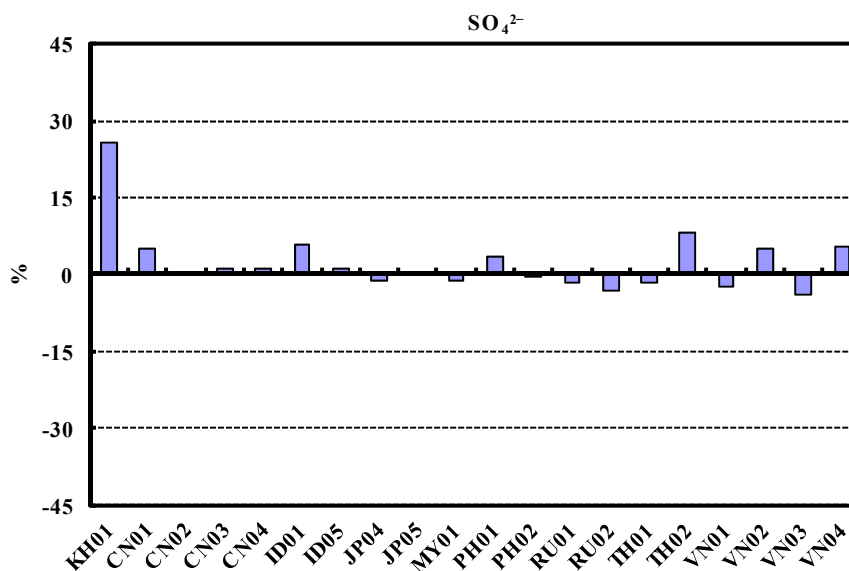


Figure 5.6 Distribution of results for SO₄²⁻ (normalized by prepared concentration)

One data was flagged, and that stayed within 30%. Most of the participating laboratories used ion chromatography for the determination of SO₄²⁻, and also the flagged data was obtained

through this method.

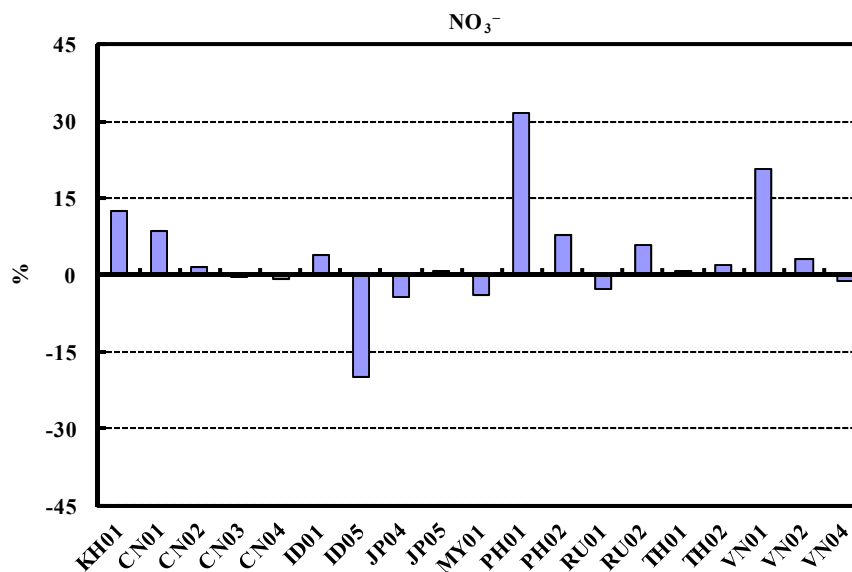


Figure 5.7 Distribution of results for NO₃⁻ (normalized by prepared concentration)

Data from three laboratories were flagged, and one of them was more than 30% deviated from the prepared value. Most of the participating laboratories used ion chromatography for the determination of NO₃⁻, while two laboratories used spectrophotometry. Flagged data was found in the data obtained through both methods.

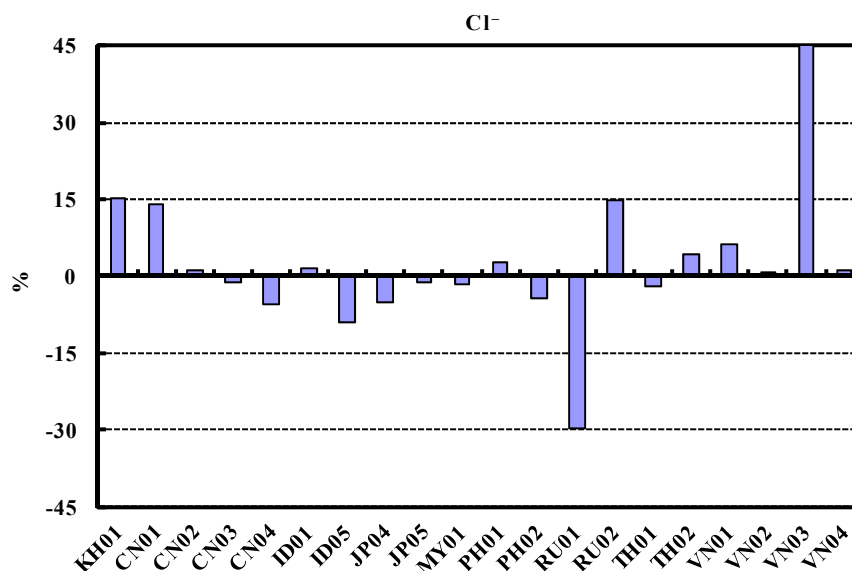


Figure 5.8 Distribution of results for Cl⁻ (normalized by prepared concentration)

Data from three laboratories were flagged. In particular, the data submitted by laboratory VN03

was significantly deviated from the prepared value. Most of the participating laboratories used ion chromatography for the determination of Cl^- , while four laboratories used the titration method. The most deviant data of flagged ones was obtained through the titration method.

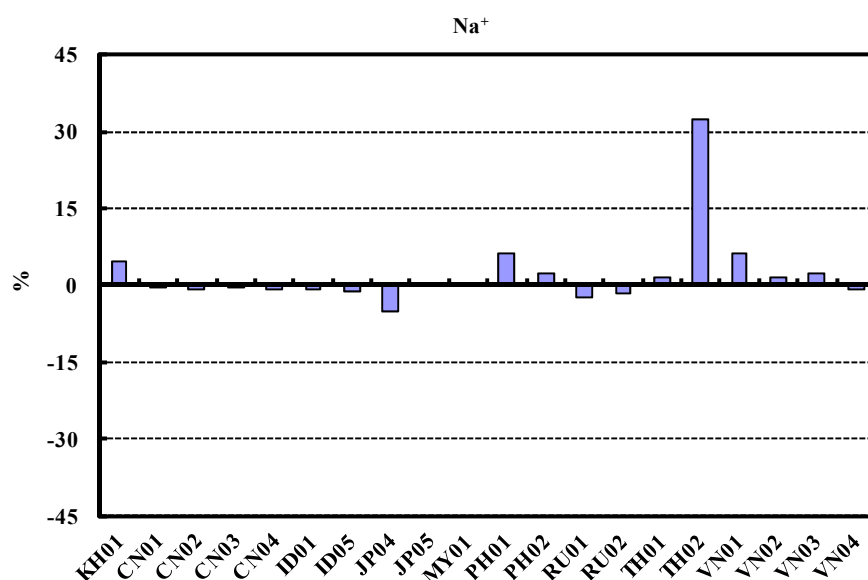


Figure 5.9 Distribution of results for Na^+ (normalized by prepared concentration)

One data was flagged and more than 30% deviated from the prepared value, however, all the others were within 10%. Most of the participating laboratories used ion chromatography for the determination of Na^+ , and also the flagged data was obtained through this method.

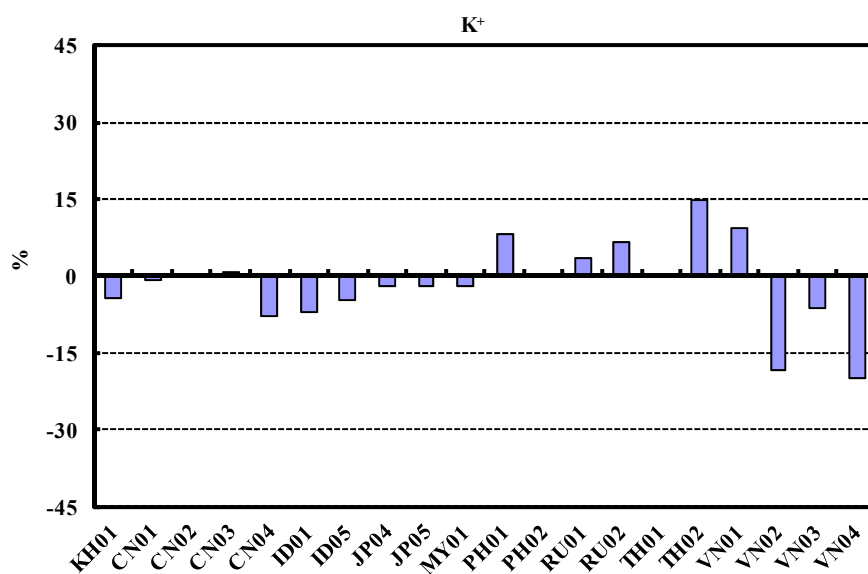


Figure 5.10 Distribution of results for K^+ (normalized by prepared concentration)

Data from two laboratories were flagged, and they stayed within 30%. Most of the participating laboratories used ion chromatography for the determination of K^+ , and also the two flagged data were obtained through this method.

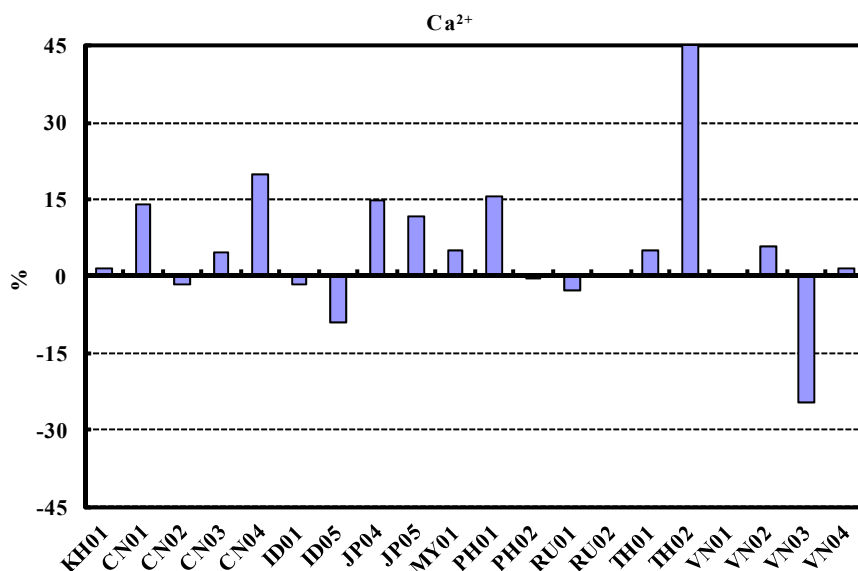


Figure 5.11 Distribution of results for Ca^{2+} (normalized by prepared concentration)

Data from four laboratories were flagged. In particular, the data submitted by laboratory TH02 was significantly deviated from the prepared value. Most of the participating laboratories used ion chromatography for the determination of Ca^{2+} , while five laboratories used atomic absorption spectrometry / flame (emission) photometry. Three of four flagged data, which includes the significantly deviant one, were obtained through ion chromatography.

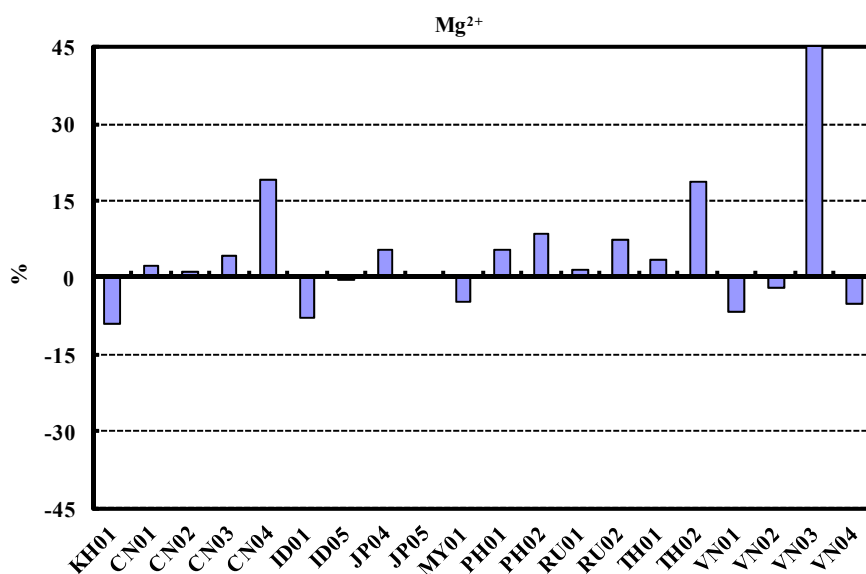


Figure 5.12 Distribution of results for Mg^{2+} (normalized by prepared concentration)

Data from three laboratories were flagged. In particular, the data submitted by laboratory VN03 was significantly deviated from the prepared value. Most of the participating laboratories used ion chromatography for the determination of Mg^{2+} , while five laboratories used atomic absorption spectrometry / flame (emission) photometry. One of three flagged data, which is the significantly deviant one was obtained through atomic absorption spectrometry.

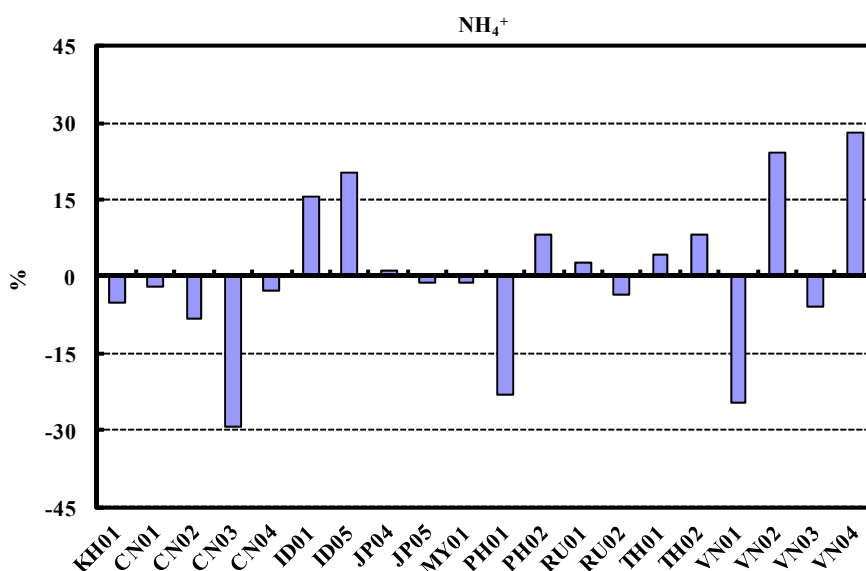


Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

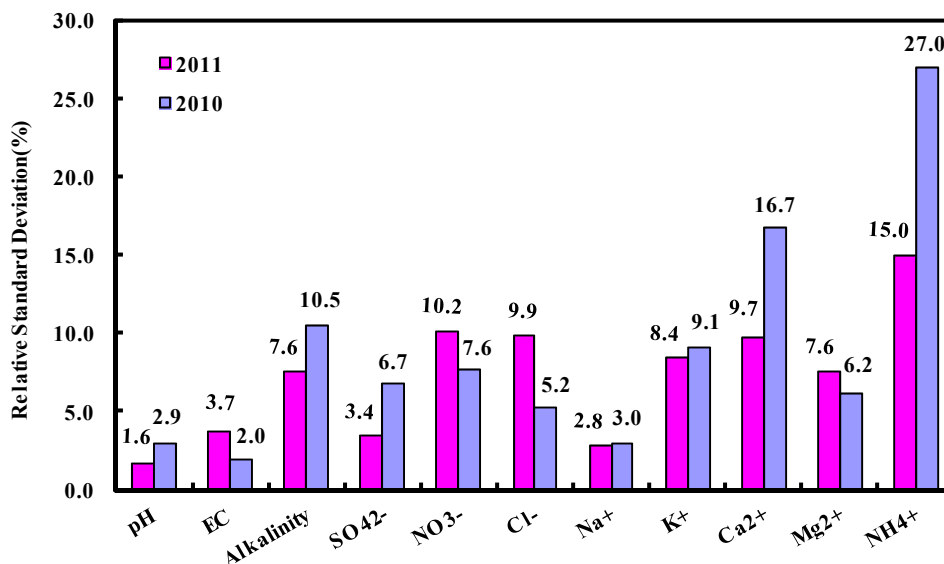
Data from seven laboratories were flagged, however, they were all within 30%. Among 20 participating laboratories, 14 laboratories used ion chromatography, 4 laboratories used

spectrophotometry (Indophenol) and 2 laboratory used spectrophotometry (other method) for the determination of NH_4^+ . Five of seven flagged data were obtained through ion chromatography. The other two were obtained through spectrophotometry (Indophenol). There was no flagged data obtained through spectrophotometry (other method).

NH_4^+ was the parameter that has the highest flagged percentage in this attempt, too. This parameter had also the highest flagged percentage in the attempts in 2003-2010. It may be necessary to pay more attention to the accuracy of NH_4^+ analyze in the inland water sample in each laboratories.

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 (2010).



(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 of NH_4^+ results from laboratories had tendency to be larger than the other parameters comparatively as similar to that of the last attempt. However, in most parameters, these values decreased in this attempt. In particular, it's clear concerning Ca^{2+} and NH_4^+ , these were from 16.7% to 9.7%, and from 27.0% to 15.0%, respectively. On the other hand, as to NO_3^- and Cl^- , these values increased from 7.6% to 10.2%, and from 5.2% to 9.9%, respectively. Although the relative standard deviation of NH_4^+ decreased, that value was the largest in this attempt in the same manner as before. Thus, it may be necessary to pay more attention to the variation among the laboratories of NH_4^+ analysis in the inland water than other analytical parameters.

5.3.4 Information on laboratories

Methodologies used

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

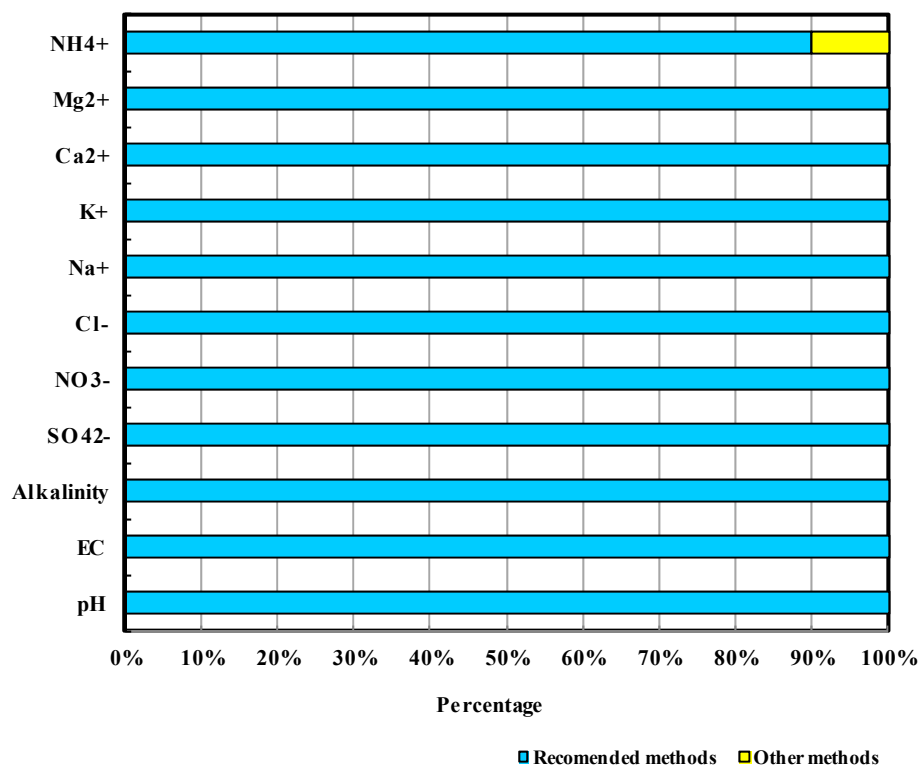


Figure 5.15 Percentage of laboratories using the recommended methods

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	22										
1		22(1)									
2			22(5)			3(1)					
3							5	5	5(1)	5(1)	
4				17(1)	17(2)	17(2)	15(1)	15(2)	15(3)	15(2)	14(5)
5											
6											
7				3	2(1)						2
8											4(2)
9											
10											
11											
Flagged E	0	0	5	1	2	2	0	2	3	2	7
Flagged X	0	1	0	0	1	1	1	0	1	1	0

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 NH₄⁺. Two laboratories used spectrophotometry without indophenol blue for NH₄⁺ analysis. Their data were not flagged.

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 for data obtained through other recommended methods, there was no flagged data in the particular case of SO₄²⁻, Na⁺ and

K⁺. As a result, 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	2	A	A	B	A	A	-	A	-	-	-	-
CN01	1	A	A	A	A	A	A	A	A	A	A	A
CN02	3	A	A	B	C	C	C	B	B	B	B	C
CN03	2	A	A	B	B	B	B	B	B	B	B	B
CN04	2	A	A	A	B	B	B	B	B	B	B	B
ID01	1	A	A	A	A	A	A	A	A	A	A	A
ID05	6	A	A	A	B	C	D	E	E	E	E	F
JP04	1	A	A	A	A	A	A	A	A	A	A	A
JP05	1	A	A	A	A	A	A	A	A	A	A	A
MY01	3	A	A	A	B	B	B	C	C	C	C	C
MY03	1	A	A	A								
MN01	2	A	A	B								
PH01	3	A	A	B	A	A	A	A	A	A	A	C
PH02	3	A	A	B	C	C	C	C	C	C	C	C
RU01	3	A	A	A	B	B	B	C	C	C	C	-
RU02	3	A	A	A	B	B	A	C	C	C	C	B
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	B	B	B		B	C	C	C	C	B
VN04	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 ⁺	Unit : year		
									Ca ²⁺	Mg ²⁺	NH ₄ ⁺
KH01	6	6	-	6	6	-	6	-	-	-	-
CN01	20	20	20	20	20	20	20	20	20	20	20
CN02	21	21	6	6	6	6	6	6	6	6	6
CN03	1	1	15	15	15	15	15	15	15	15	15
CN04	5	5	5	26	26	26	26	26	26	26	26
ID01	14	14	14	14	14	14	14	14	14	14	14
ID05	29	29	29	1	5	3	3	3	3	3	5
JP04	3	3	3	3	3	3	3	3	3	3	3
JP05	1	1	1	1	1	1	1	1	1	1	1
MY01	5	5	5	1	1	5	9	9	9	9	9
MY03	1	1	1								
MN01	1	1	10								
PH01	2	2	6	4	4	4	14	14	14	14	1
PH02	21	21	7	20	20	20	20	20	20	20	20
RU01	18	18	18	16	16	16	26	26	26	26	-
RU02	51	51	51	17	17	51	20	20	20	20	17
TH01	7	7	7	7	7	7	7	7	7	7	7
TH02	14	8	14	8	8	8	14	14	14	14	14
VN01	3	3	19	19	19	19	19	19	19	19	19
VN02	5	5	7	19	19	19	19	19	19	19	19
VN03	5	5	5	5		5	8	8	8	8	5
VN04	7	7	8	8	8	8	8	8	8	8	8

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 12 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.

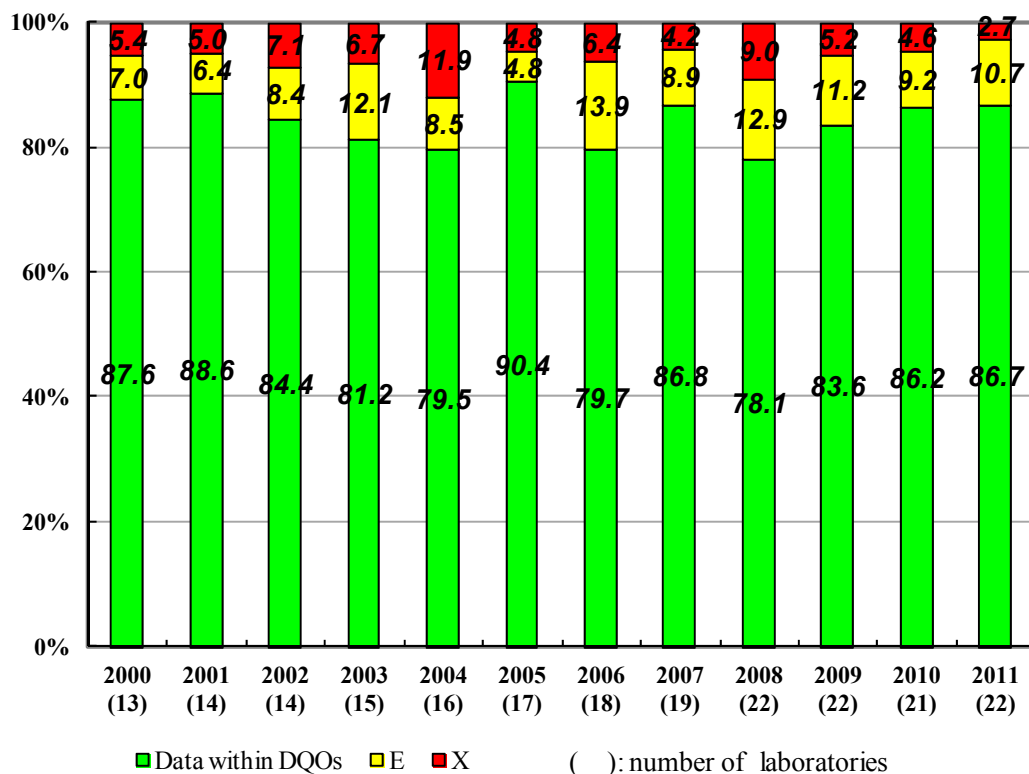


Figure 5. 16 Comparison of the results from the inter-laboratory comparison projects

The number of participating laboratories was not really change since 2008, and the percentage of data that satisfied the DQOs kept on increasing in this term. On the other hand, the percentage of flagged data exceeding the DQOs more than a factor of 2 showed the lowest value up to the present.

The comparison for each parameter from the 1st to 12th project with the percentage of flagged data is shown in Figure 5.17.

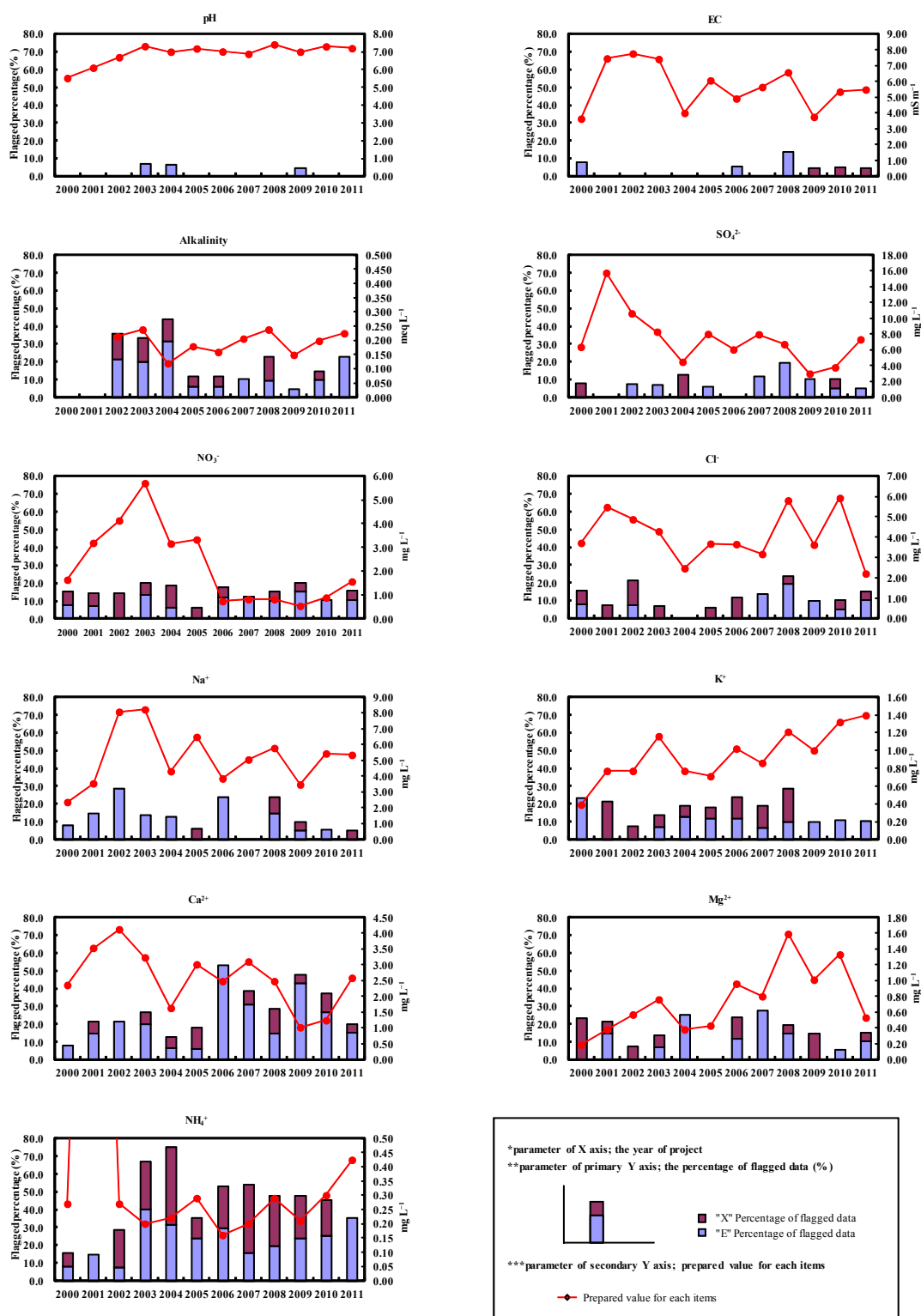


Figure 5.17 Comparison of the percentage of flagged data for each parameter in inter-laboratory comparison projects

The percentage of flagged data of NH_4^+ had maintained high level since 2003 when its concentration was prepared low. However, in the recent attempts, it seemed that the percentage decreased with increase of concentrations, and a similar transition was observed as to Ca^{2+} , too. In fact, no laboratory produced the flagged data with “X” for NH_4^+ in this attempt, whose prepared value was the highest in the period from 2003 to 2011. Concerning the other parameters, eventually, there was no clear relationship between the concentration and the percentage of flagged data.

The percentages of flagged cations’ data seemed generally to be larger than those of anions throughout the projects. Furthermore, the percentage of flagged data was larger for 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. However, the reason was not clear. Actually, concentration of NH_4^+ is relatively low or under detection limit in inland water samples in some monitoring sites. It might be important to detect the targeted level for evaluation of nitrogen cycle in the monitoring sites. Therefore, it is necessary to pay more attention to the analysis not only of NH_4^+ but also of Ca^{2+} , in the inland water than the other analytical parameters.

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.

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Appendix Table 5.1 Results submitted by the laboratories

Lab. ID	pH	EC - (mS m ⁻¹)	Alkalinity (meq L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	NH ₄ ⁺ (mg L ⁻¹)
KH01	7.05	5.42	0.227	9.21	1.76	2.53	5.59	1.33	2.62	0.48	0.40
CN01	7.20	5.35	0.231	7.69	1.70	2.51	5.33	1.38	2.94	0.54	0.42
CN02	7.17	5.37	0.231	7.33	1.59	2.23	5.31	1.40	2.55	0.54	0.39
CN03	7.02	5.30	0.228	7.42	1.56	2.18	5.33	1.41	2.71	0.55	0.30
CN04	7.14	5.35	0.238	7.41	1.56	2.08	5.31	1.29	3.10	0.63	0.41
ID01	7.05	5.36	0.240	7.77	1.63	2.24	5.30	1.30	2.55	0.49	0.49
ID05	7.10	5.40	0.190	7.40	1.26	2.00	5.27	1.33	2.35	0.53	0.51
JP04	7.34	5.32	0.240	7.24	1.50	2.09	5.07	1.37	2.97	0.56	0.43
JP05	7.44	5.18	0.240	7.36	1.58	2.18	5.35	1.37	2.88	0.53	0.42
MY01	7.29	5.22	0.230	7.24	1.50	2.17	5.35	1.37	2.71	0.51	0.42
MY03	7.09	41.77	0.270								
MN01	7.19	5.24	0.230								
PH01	7.03	6.08	0.237	7.59	2.06	2.26	5.67	1.51	2.99	0.56	0.33
PH02	7.30	5.32	0.240	7.32	1.69	2.11	5.46	1.40	2.58	0.58	0.46
RU01	7.31	5.36	0.240	7.20	1.53	1.55	5.22	1.44	2.52	0.54	0.44
RU02	7.25	5.37	0.224	7.10	1.66	2.53	5.25	1.49	2.60	0.57	0.41
TH01	7.26	5.74	0.227	7.20	1.58	2.16	5.42	1.40	2.72	0.55	0.44
TH02	6.65	5.33	0.220	7.93	1.60	2.29	7.07	1.60	4.64	0.63	0.46
VN01	7.12	5.23	0.260	7.14	1.89	2.34	5.68	1.53	2.59	0.50	0.32
VN02	7.17	5.31	0.270	7.69	1.62	2.22	5.42	1.14	2.74	0.52	0.53
VN03	7.02	5.24	0.220	7.04		6.55	5.47	1.31	1.95	1.41	0.40
VN04	7.17	5.31	0.260	7.72	1.55	2.23	5.31	1.12	2.62	0.50	0.54
Expected value	7.20	5.48	0.225	7.33	1.57	2.20	5.34	1.40	2.59	0.53	0.42
Number of data	22	22	22	20	19	20	20	20	20	20	20
Average	7.15	7.03	0.236	7.50	1.62	2.42	5.46	1.37	2.77	0.59	0.43
Minimum	6.65	5.18	0.190	7.04	1.26	1.55	5.07	1.12	1.95	0.48	0.30
Maximum	7.44	41.77	0.270	9.21	2.06	6.55	7.07	1.60	4.64	1.41	0.54

blank: not analyzed

Appendix Table 5.2 Data normalized by the prepared value

Lab. ID	(Original data / Expected Value - 1) × 100 (%)												
	pH (%)	EC (%)	Alkalinity (%)	SO ₄ ²⁻ (%)	NO ₃ ⁻ (%)	Cl ⁻ (%)	Na ⁺ (%)	K ⁺ (%)	Ca ²⁺ (%)	Mg ²⁺ (%)	NH ₄ ⁺ (%)		
KH01	-2.0	-1.2	0.8	25.7	12.5	15.1	4.7	-4.5	1.5	-9.0	-5.0		
CN01	0.0	-2.5	2.8	5.0	8.7	13.9	-0.2	-0.9	13.8	2.3	-1.9		
CN02	-0.4	-2.0	2.9	0.0	1.5	1.3	-0.6	0.3	-1.5	1.0	-8.1		
CN03	-2.5	-3.4	1.4	1.2	-0.4	-1.1	-0.3	0.8	4.8	4.2	-29.3		
CN04	-0.8	-2.4	5.9	1.1	-0.6	-5.5	-0.7	-7.8	19.9	19.2	-2.6		
ID01	-2.0	-2.2	6.8	6.0	3.8	1.6	-0.7	-6.9	-1.5	-7.8	15.4		
ID05	-1.3	-1.5	-15.5	1.0	-19.8	-9.1	-1.4	-4.7	-9.1	0.0	20.1		
JP04	2.0	-2.9	6.8	-1.2	-4.3	-5.0	-5.0	-2.1	15.0	5.4	1.3		
JP05	3.3	-5.6	6.8	0.4	0.6	-1.1	0.1	-1.8	11.5	0.4	-1.1		
MY01	1.3	-4.8	2.3	-1.2	-4.0	-1.4	0.1	-2.1	4.9	-4.6	-1.1		
MY03	-1.5	662.1	20.1										
MN01	-0.1	-4.4	2.3										
PH01	-2.3	10.9	5.3	3.6	31.5	2.7	6.1	8.2	15.5	5.4	-23.1		
PH02	1.5	-2.9	6.8	-0.1	7.9	-4.1	2.2	0.3	-0.2	8.6	8.3		
RU01	1.6	-2.2	6.8	-1.7	-2.6	-29.6	-2.4	3.4	-2.7	1.7	2.9		
RU02	0.7	-2.0	-0.3	-3.1	6.0	15.0	-1.7	6.8	0.6	7.3	-3.4		
TH01	0.9	4.7	0.8	-1.7	0.6	-1.8	1.5	0.1	5.1	3.5	4.4		
TH02	-7.6	-2.8	-2.1	8.2	2.1	4.2	32.4	14.6	79.6	18.6	8.3		
VN01	-1.1	-4.6	15.7	-2.5	20.8	6.3	6.3	9.4	0.3	-6.5	-24.6		
VN02	-0.4	-3.1	20.1	4.9	3.2	0.9	1.5	-18.3	5.8	-2.1	24.1		
VN03	-2.5	-4.4	-2.1	-3.9		197.6	2.4	-6.1	-24.6	165.5	-5.8		
VN04	-0.3	-3.2	15.7	5.4	-1.1	1.2	-0.6	-19.8	1.5	-5.2	28.0		
Minimum	-7.6	-5.6	-15.5	-3.9	-19.8	-29.6	-5.0	-19.8	-24.6	-9.0	-29.3		
Maximum	3.3	662.1	20.1	25.7	31.5	197.6	32.4	14.6	79.6	165.5	28.0		
Average	-0.6	28.2	5.0	2.4	3.5	10.1	2.2	-1.6	7.0	10.4	0.3		

blank: not analyzed

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