Acid Deposition Monitoring Network
in East Asia (EANET)

Report of the Inter-laboratory Comparison Project 2012

15th Inter-laboratory Comparison Project on Wet Deposition

8th Inter-laboratory Comparison Project on Dry Deposition

14th Inter-laboratory Comparison Project on Soil

13th Inter-laboratory Comparison Project on Inland Aquatic Environment

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Contents

1. INTRODUCTION

The Inter-laboratory Comparison Project was conducted among the analytical laboratories in participating countries of the Acid Deposition Monitoring Network in East Asia (EANET), based on the Quality Assurance / Quality Control (QA/QC) 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 15th Inter-laboratory Comparison Project on wet deposition, 8th Inter-laboratory Comparison Project on dry deposition, 14th Inter-laboratory Comparison Project on soil, and 13th 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.

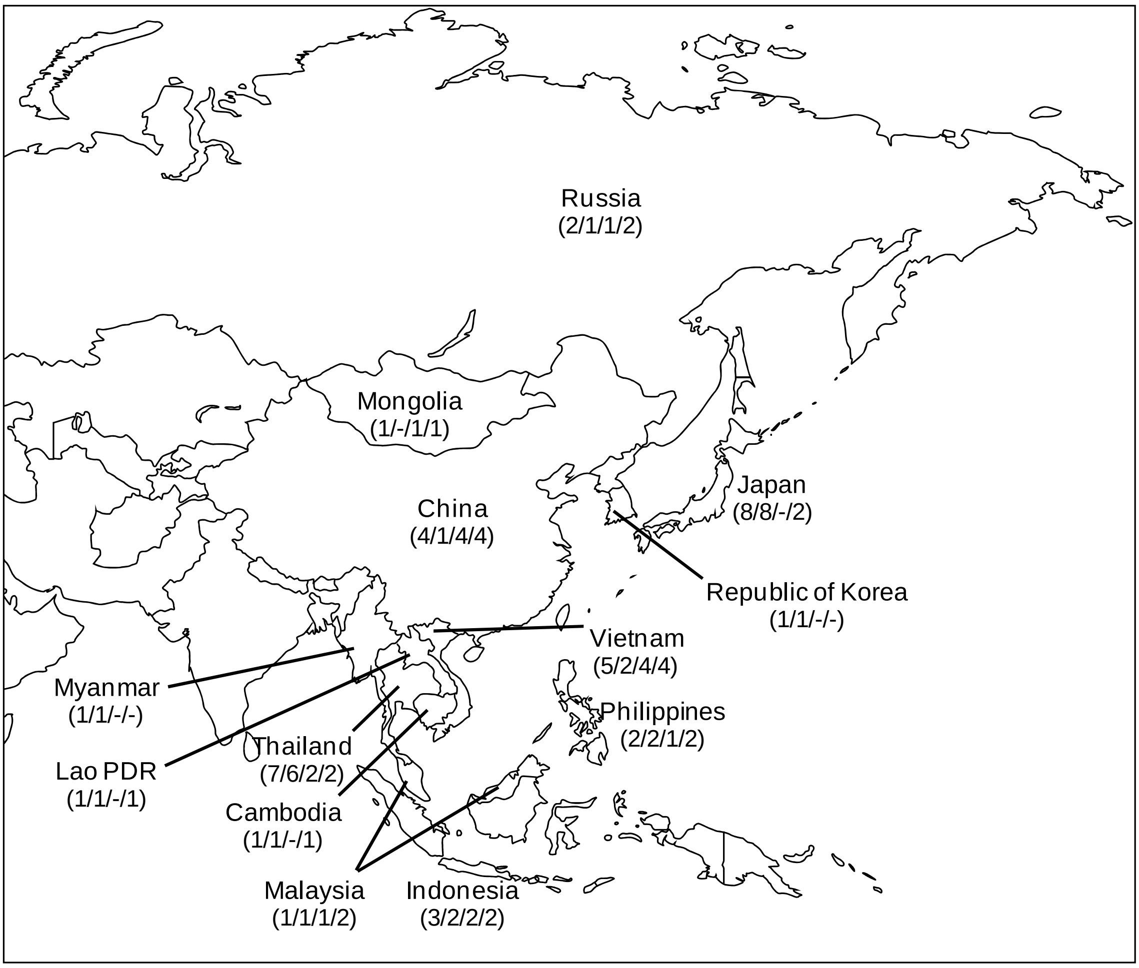


Figure 1.1 Number of participating laboratories in 2012

* 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	**CN01**	✔		✔	✔
Xiamen Environmental Monitoring Station	**CN02**	✔	✔	✔	✔
Xi’an Environmental Monitoring Center Station	**CN03**	✔		✔	✔
Chongqing Institute of Environmental Science	**CN04**	✔		✔	✔
Indonesia					
Environmental Management Center (EMC), Environmental Impact Management Agency (BAPEDAL)	**ID01**	✔	✔	✔	✔
Climatology,Meteorological and Geophysical Agency (BMKG)	**ID02**	✔			
Indonesian National Institute of Aeronautic and Space (LAPAN)	**ID03**	✔	✔		
Indonesian Soil Research Institute (ISRI)	**ID04**			✔	
Research Center for Water Resources (RCWR), Agency for Research and Development, Ministry of Public Works	**ID05**				✔
Japan					
Institute of Environmental Sciences, Hokkaido Research Organization	**JP01**	✔	✔		
Niigata Prefectural Institute of Public Health and Environmental Sciences	**JP02**		✔		
Nagano Environmental Conservation Research Institute	**JP03**	✔	✔		
Gifu Prefectural Research Institute for Health and Environmental Sciences	**JP04**	✔	✔		✔
Shimane Prefectural Institute of Public Health and Environmental Science	**JP05**	✔	✔		✔
Kochi Prefectural Environmental Research Center	**JP07**	✔			
Okinawa Prefectural Institute of Health and Environment	**JP08**	✔	✔		
Asia Center for Air Pollution Research (ACAP)	**JP09**	✔	✔		
Japan Environmental Sanitation Center (JESC)	**JP10**	✔	✔		
Lao PDR					
Environment Quality Monitoring Center, Environment Research Institute, Science technology and Environment Agency	**LA01**	✔	✔		✔
Malaysia					
Division of Environmental Health, Department of Chemistry (DOC)	**MY01**	✔	✔		✔
Faculty of Applied Science, University Technology Mara (UiTM)	**MY03**				✔
Universiti Putra Malaysia, Bintulu Sarawak Kampus (UPMKB)	**MY04**			✔	
Mongolia					
Central Laboratory of Environment and Metrology	**MN01**	✔		✔	✔
Myanmar					
Department of Meteorology and Hydrology (DMH)	**MM01**	✔	✔		
Philippines					
Environmental Management Bureau - Central Office (EMB-CO)	**PH01**	✔	✔		✔
Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR)	**PH02**	✔	✔		✔
University of the Philippines Los Baños (UPLB)	**PH03**			✔	
Republic of Korea					
Korea Environment Corporation (KECO)	**KR02**	✔	✔		
Russia					
Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB)	**RU01**	✔	✔	✔	✔
Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	**RU02**	✔			✔
Thailand					
Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MONRE)	**TH01**	✔	✔	✔	✔
Environmental Research and Training Centre (ERTC), Department of Research and Environmental Quality Promotion	**TH02**	✔	✔		✔
Chemistry Department, Science Faculty, Chiangmai University (CMU)	**TH04**	✔	✔		
Khon Kaen University (KKU)	**TH05**	✔	✔		
King Mongkut’s University of Technology Thonburi (KMUTT)	**TH06**	✔	✔	✔	
Kasetsart University	**TH07**	✔	✔		
Songkla University	**TH08**	✔			
Vietnam					
Environmental Laboratory - Center for Environmental Research - Vietnam Institute of Meteorology, Hydrology and Environment (IMHEN)- MoNRE	**VN01**	✔	✔	✔	✔
Mid- Central Regional Hydro Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	**VN02**	✔	✔	✔	✔
Sub-Institute of HydroMeteorology and Environment of South Vietnam (SIHYMETE)	**VN03**	✔		✔	✔
Center for Hydro-Meteorological and Environmental Networks, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	**VN04**	✔		✔	✔
Southern Region Hydro-Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	**VN05**	✔			
Total :		**37**	**27**	**16**	**23**

2. 15th INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

2.1 Introduction

In the 15th 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 1 October 2012. Their analytical results were required to be submitted to the NC by 28 February 2013.

2.2 Procedures

2.2.1 Participating Laboratories

The NC distributed the artificial rainwater samples to 37 laboratories in charge of chemical analysis in 13 countries of EANET. All 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. 121w No. 122w	100mL each	Polypropyrene bottle 100mL	One bottle each	- Fixed quantity of reagents are dissolved in deionized water - Samples do not include other ions than shown in Table 2.2

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

Table 2.2 Prepared values/concentrations of analytical parameters*

	pH -	EC mS m^{-1}	SO_4^{2-} μmol L^{-1}	NO_3^- μmol L^{-1}	Cl^- μmol L^{-1}	Na^+ μmol L^{-1}	K^+ μmol L^{-1}	Ca^{2+} μmol L^{-1}	Mg^{2+} μmol L^{-1}	NH_4^+ μmol L^{-1}
No. 121w	4.60	3.25	37.1	32.9	78.7	58.7	6.3	18.6	10.8	37.1
No. 122w	5.10	1.31	9.7	21.6	40.4	40.4	2.5	5.6	5.6	8.3

* For 100 times diluted samples.

2.2.3 Analytical Methods and Data Checking Procedures

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

All participating laboratories were expected to analyze the diluted samples for the following 10 parameters; pH, EC, concentrations of SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+.

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 (R_1) and total electric conductivity agreement (R_2).

Calculation of ion balance (R_1)

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

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

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

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

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

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

(3) Calculation of ion balance (R_1)

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

(4) R_1 calculated by the above equation was compared with allowable ranges in Table 2.4. If R_1 was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

Table 2.4 Allowable ranges for R_1 in different concentration ranges

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

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

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

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

$$\begin{aligned}\Lambda \text{ calc } [\text{mS m}^{-1}] = \{&349.7 \times 10\ (6\text{-pH}) + 80.0 \times 2c\ (SO_4^{2-}) + 71.5 \times c\ (NO_3^-) \\ &+76.3 \times c\ (Cl^-) + 73.5 \times c\ (NH_4^+) + 50.1 \times c\ (Na^+) + 73.5 \times c\ (K^+) \\ &+ 59.8 \times 2c\ (Ca^{2+}) + 53.3 \times 2c\ (Mg^{2+})\} / 10000\end{aligned}$$

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

(2) Electrical conductivity comparison (R_2) was calculated as follows;

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

Λ meas: measured conductivity

(3) R_2 calculated by the above equation was compared with allowable ranges in Table 2.5. If R_2 was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

Table 2.5 Allowable ranges for R_2 in different ranges of EC

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

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

2.3 Results

The NC received the analytical results from 37 laboratories in the participating countries of EANET. The original data submitted by the laboratories were shown in Appendix 2.2.

Basic statistics of submitted data summarized in Table 2.6 were calculated for each parameter of the artificial rainwater samples such as: average (Va), minimum (Min.), maximum (Max.), standard deviation (S.D.), and number of data (N). The outliers which are apart from the average greater than a factor of 3 of S.D. were not included for the statistics calculation. As shown in Table 2.6, Va agreed with prepared value (Vp) fairly well. The range of ΔV/Vp was between -3.7% to 1.7% for the sample No. 121w, and -3.3% to 10.1% for the sample No. 122w.

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

Sample No. 121w

Constituents	Prepared (Vp)	Average (Va)	ΔV/Vp[*1] %	S.D.	N	Min.	Max.
pH	4.60	4.68	1.7	0.11	37	4.48	4.97
EC [mS m^{-1}]	3.25	3.13	-3.7	0.18	37	2.59	3.67
SO_4^{2-} [μmol L^{-1}]	37.1	36.4	-1.9	2.32	34	28.7	40.8
NO_3^- [μmol L^{-1}]	32.9	31.7	-3.5	1.56	33	25.9	35.2
Cl^- [μmol L^{-1}]	78.7	76.1	-3.4	4.21	33	59.2	80.5
Na^+ [μmol L^{-1}]	58.7	59.2	0.9	3.52	33	52.7	68.9
K^+ [μmol L^{-1}]	6.3	6.4	1.3	1.14	33	5.0	10.4
Ca^{2+} [μmol L^{-1}]	18.6	18.5	-0.3	1.59	33	14.3	24.5
Mg^{2+} [μmol L^{-1}]	10.8	10.5	-2.8	0.96	34	7.8	12.5
NH_4^+ [μmol L^{-1}]	37.1	37.7	1.5	2.58	33	29.2	42.1

Sample No. 122w

Constituents	Prepared (Vp)	Average (Va)	ΔV/Vp[*1] %	S.D.	N	Min.	Max.
pH	5.10	5.18	1.5	0.15	36	4.96	5.60
EC [mS m^{-1}]	1.31	1.28	-2.0	0.08	36	1.10	1.41
SO_4^{2-} [μmol L^{-1}]	9.7	9.4	-3.3	0.95	34	7.4	11.2
NO_3^- [μmol L^{-1}]	21.6	21.0	-2.7	1.29	33	16.7	23.1
Cl^- [μmol L^{-1}]	40.4	39.6	-2.0	2.44	33	31.0	44.9
Na^+ [μmol L^{-1}]	40.4	40.9	1.2	2.94	33	31.6	47.7
K^+ [μmol L^{-1}]	2.5	2.5	-1.9	0.67	34	0.6	4.1
Ca^{2+} [μmol L^{-1}]	5.6	6.2	10.1	1.36	34	3.8	10.0
Mg^{2+} [μmol L^{-1}]	5.6	5.8	4.1	0.82	34	3.5	8.0
NH_4^+ [μmol L^{-1}]	8.3	8.5	2.0	1.39	33	5.7	11.5

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

The Data Quality Objective for accuracy (hereafter referred to as DQO) was specified in the QA/QC program of the EANET for every parameter to be within ±15% of deviation from Vp. In this report, analytical data of the artificial rainwater samples were compared with Vp, and the data exceed DQO were marked with flags. Flag "E" was put to the data exceed DQO within a factor of 2 (±15% to ±30%), and flag "X" was put to the data exceed DQO more than a factor of 2 (over ±30%).

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

The results were evaluated by the following three aspects:
i) Comparison of concentration dependence on level of their concentration
– sample No. 121w and No. 122w,
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. 121w and No. 122w 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. 121w

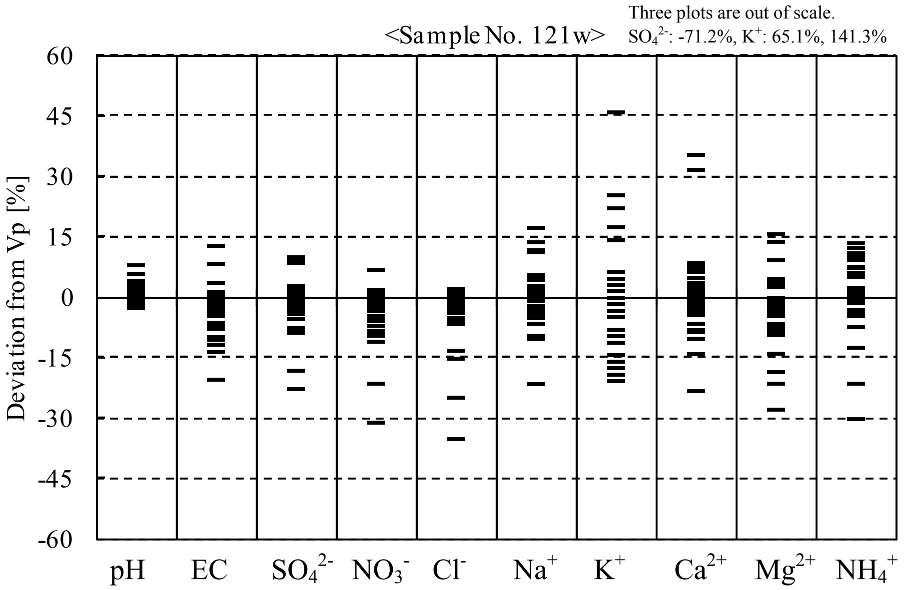
The number and percentage of flagged data for the sample No. 121w were shown in Table 2.7. 23 analytical data out of 347 exceeded DQO within a factor of 2 and were flagged by "E". 9 analytical data out of 347 exceeded DQO more than a factor of 2 and were flagged by "X". Data flagged by "E" and "X" shared 8.5 percent of all the submitted data for sample No. 121w.
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. 121w

Charactarization of data	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total
Data within DQO	37	36	32	32	31	32	22	31	30	32	315
Data with flag E[*1]	0	1	2	1	2	2	9	1	4	1	23
Data with flag X[*2]	0	0	1	1	1	0	3	2	0	1	9
Flagged data [%]	0.0	2.7	8.6	5.9	8.8	5.9	35.3	8.8	11.8	5.9	9.2

(Total data = 347)

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



Three plots are out of scale.
SO_4^{2-}: -71.2%, K^+: 65.1%, 141.3%

Figure 2.1 Distribution of the data normalized by prepared value in each parameter for sample No. 121w

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

Table 2.8 Analytical Results of Sample No. 121w

Lab. ID[*1]	pH	EC mS m^{-1}	SO$_4^{2-}$ μmol L^{-1}	NO$_3^-$ μmol L^{-1}	Cl$^-$ μmol L^{-1}	Na$^+$ μmol L^{-1}	K$^+$ μmol L^{-1}	Ca^{2+} μmol L^{-1}	Mg^{2+} μmol L^{-1}	NH$_4^+$ μmol L^{-1}	R$_1$ %	R$_2$ %
KH01	4.59	2.59 E	30.4 E	25.9 E	66.8 E	54.9	5.2 E	16.7	10.4	36.0	6.8	6.8
CN01	4.73	3.30	36.0	31.3	77.1	68.9 E	7.2	19.8	11.1	39.1	4.0	-3.5
CN02	4.57	3.37	40.3	32.4	79.2	61.3	6.4	19.8	10.5	41.7	1.2	0.9
CN03	4.60	3.30	40.6	31.3	76.9	65.6	6.7	20.0	11.2	39.4	2.5	1.0
CN04	4.57	3.26	40.8	32.3	79.4	61.8	6.3	17.1	8.8 E	39.0	-2.0	1.7
ID01	4.79	3.12	36.9	35.2	73.7	56.7	5.7	17.4	10.3	39.9	-2.5	-3.5
ID02	4.67	3.03	38.0	32.6	78.8	58.2	6.1	19.5	11.1	35.6	-1.3	1.8
ID03	4.87	2.81	36.5	32.7	78.0	58.5	7.4 E	18.3	11.8	37.3	-1.9	0.7
JP01	4.65	3.20	36.3	32.0	76.5	61.9	6.4	19.9	11.2	40.6	3.3	-0.2
JP03	4.65	3.18	36.2	32.0	79.2	58.3	5.8	18.2	10.1	36.6	-1.1	-0.9
JP04	4.67	3.15	35.8	32.2	77.5	56.6	6.1	18.8	10.8	37.6	-0.1	-1.0
JP05	4.54	3.13	36.4	32.0	74.8	56.7	6.6	17.0	10.5	35.4	0.8	2.6
JP07	4.62	3.28	36.6	33.2	77.2	57.3	5.0 E	18.0	10.5	37.3	-0.8	-1.6
JP08	4.97	3.10	37.4	33.0	78.7	57.5	6.0	18.5	10.5	36.9	-4.9	-6.1
JP09	4.68	3.10	36.4	31.2	76.4	59.4	6.1	18.5	9.8	36.7	-0.2	-0.7
JP10	4.69	3.11	35.6	31.1	74.2	56.4	6.1	17.9	10.5	35.9	-0.3	-2.0
LA01	4.71	2.93	10.7 X	22.7 X	51.1 X	---	---	---	---	---	---	---
MY01	4.71	3.17	37.5	31.9	77.8	58.2	5.7	19.3	9.9	37.3	-1.5	-2.0
MN01	4.58	3.12	---	---	---	---	---	---	---	---	---	---
MM01	4.68	3.52	37.9	31.8	80.5	65.3	5.6	17.8	9.3	42.1	0.0	-5.3
PH01	4.77	2.87	28.7 E	29.8	59.2 E	46.1 E	5.4	14.3 E	8.5 E	29.2 E	-1.1	-7.6
PH02	4.67	3.16	37.5	32.5	73.5	59.8	6.2	18.9	10.8	39.8	1.5	-0.6
KR02	4.63	3.13	37.8	30.6	78.4	59.0	5.8	18.3	10.0	39.1	-0.2	1.0
RU01	4.62	3.22	33.9	32.4	78.6	57.5	6.2	17.8	11.3	37.6	1.3	-1.0
RU02	4.67	3.13	36.4	33.5	78.9	58.6	6.2	18.5	10.7	38.0	-0.7	-0.1
TH01	4.79	3.10	34.3	29.3	75.9	58.3	5.2 E	16.0	7.8 E	39.9	-1.9	-5.0
TH02	4.65	3.27	35.8	30.2	73.6	59.3	6.5	19.1	10.8	37.1	2.7	-2.8
TH04	4.71	3.10	36.6	33.2	78.9	60.4	7.4 E	24.5 X	12.5 E	40.8	4.3	1.4
TH05	4.48	3.22	38.2	31.4	76.0	58.2	5.7	18.8	11.3	36.7	2.7	4.5
TH06	4.71	3.05	36.9	30.0	79.0	55.7	7.9 E	20.2	12.3	34.4	-0.1	0.0
TH07	4.97	3.67	35.8	32.8	80.0	66.8	15.2 X	18.6	9.8	25.9 X	-2.5	-14.2 C
TH08	4.54	3.10	---	---	---	---	---	---	---	---	2.4 [*2]	4.3 [*2]
VN01	4.69	3.04	37.6	32.8	75.8	62.0	7.7 E	18.7	10.6	37.2	0.6	1.1
VN02	4.71	2.91	36.8	32.4	68.4	60.0	10.4 X	18.7	10.1	37.1	2.8	1.6
VN03	4.64	3.03	34.2	---	---	53.2	5.3 E	19.1	9.8	41.2	---	---
VN04	4.71	3.02	36.1	31.4	74.7	59.3	9.2 X	18.1	11.2	37.7	1.7	0.2
VN05	4.53	3.00	35.1	31.0	76.4	52.7	5.1 E	25.2 X	11.1	32.5	4.0	5.6
Vp	4.60	3.25	37.1	32.9	78.7	58.7	6.3	18.6	10.8	37.1	0.1	0.1
N of data	37	37	35	34	34	34	34	34	34	34		
Within DQO	37	36	32	32	31	32	22	31	30	32		
Flag E	0	1	2	1	2	2	9	1	4	1		
Flag X	0	0	1	1	1	0	3	2	0	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 (R$_1$); "C", Poor conductivity agreement (R$_2$); "---", Not measured; "Vp", Prepared values of parameters;
[*1] : The abbreviated name and code are given in Chapter 1
[*2] : R$_1$ and R$_2$ for TH08 were calculated with results of ion concentration from TH06.

2) Sample No. 122w

The number and percentage of flagged data for the sample No. 122w were shown in Table 2.9. 45 analytical data out of 347 exceeded the DQO within a factor of 2 and were flagged by "E". 29 analytical data out of 347 exceeded the DQO more than a factor of 2 and were flagged by "X". Data marked with flags shared up to 20.8 percent of all the submitted data for sample No. 122w.

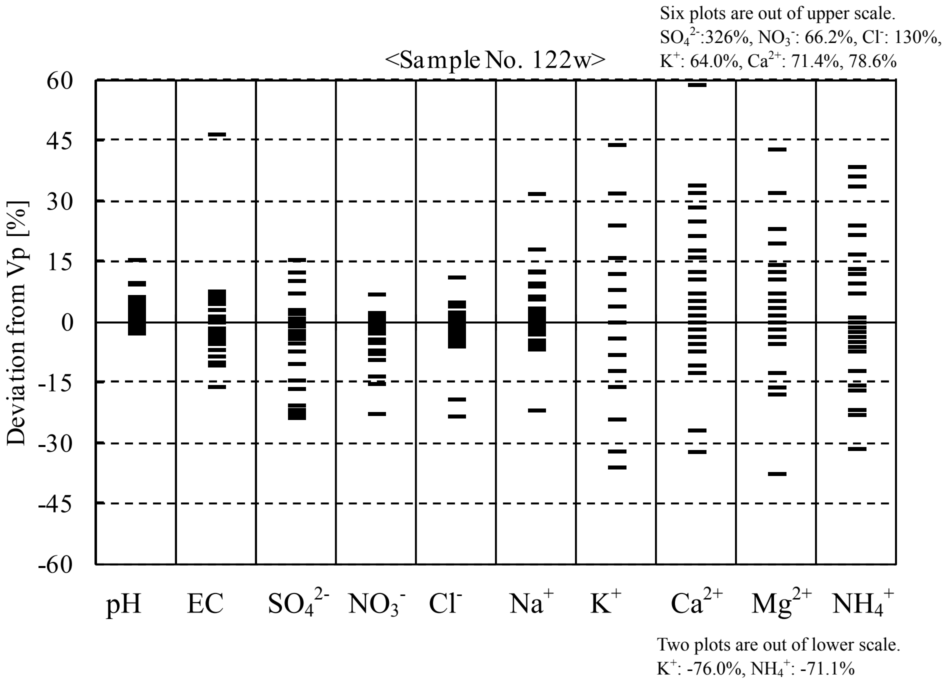
The normalized data by prepared value in each parameter were shown in Figure 2.2.

Table 2.9 Number of flagged data for the Sample No. 122w

Charactarization of data	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total
Data within DQO	36	35	27	31	31	31	16	19	26	21	273
Data with flag E*1	1	1	7	2	2	2	8	9	5	8	45
Data with flag X*2	0	1	1	1	1	1	10	6	3	5	29
Flagged data [%]	2.7	5.4	22.9	8.8	8.8	8.8	52.9	44.1	23.5	38.2	21.3

(Total data = 347)

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



Six plots are out of upper scale.
SO_4^{2-}:326%, NO_3^-: 66.2%, Cl^-: 130%, K^+: 64.0%, Ca^{2+}: 71.4%, 78.6%

Two plots are out of lower scale.
K^+: -76.0%, NH_4^+: -71.1%

Figure 2.2 Distribution of the data normalized by prepared value for each parameter for sample No. 122w

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. 122w

Lab. ID[*1]	pH	EC mS/m	SO_4^{2-} µmol L^{-1}	NO_3^- µmol L^{-1}	Cl^- µmol L^{-1}	Na^+ µmol L^{-1}	K^+ µmol L^{-1}	Ca^{2+} µmol L^{-1}	Mg^{2+} µmol L^{-1}	NH_4^+ µmol L^{-1}	R_1 %	R_2 %
KH01	5.15	1.10 E	7.4 E	16.7 E	32.7 E	38.0	1.7 X	4.9	5.8	5.7 X	7.0	0.0
CN01	5.21	1.39	11.2 E	21.8	42.4	47.7 E	3.6 X	9.6 X	6.9 E	8.1	6.5	-0.1
CN02	4.96	1.41	10.9	21.9	42.0	43.0	2.5	6.5 E	5.5	7.3	1.2	1.7
CN03	5.08	1.40	11.2 E	22.1	40.3	45.4	3.6 X	6.5 E	5.8	8.3	3.1	-0.4
CN04	5.07	1.28	10.0	21.4	41.2	44.0	2.8	5.7	5.8	7.0 E	1.6	2.6
ID01	5.33	1.33	9.0	21.3	38.8	40.9	2.6	6.0	5.7	6.4 E	-0.1	-6.8
ID02	5.05	1.29	10.7	21.9	40.5	42.7	2.8	6.6 E	6.4	7.3	2.3	3.5
ID03	5.58	1.37	9.6	21.5	39.5	45.5	3.1 E	7.4 X	6.9 E	8.1	4.6	-7.7
JP01	5.11	1.35	9.6	20.5	38.7	44.3	2.4	5.4	5.4	8.2	3.6	-2.3
JP03	5.10	1.27	10.4	21.9	40.2	40.2	2.2	5.8	5.4	7.8	-1.4	1.5
JP04	5.18	1.28	9.4	21.3	40.0	37.8	2.9 E	6.3	5.9	7.9	-0.3	-1.3
JP05	5.11	1.25	9.6	21.5	40.2	39.2	2.4	5.0	5.3	7.9	-1.9	0.9
JP07	5.08	1.38	10.0	21.9	41.0	39.4	1.6 X	5.3	5.7	9.1	-1.5	-2.2
JP08	5.20	1.26	9.7	21.6	39.7	39.6	2.3	5.4	5.4	10.1 E	-0.5	-0.6
JP09	5.22	1.28	9.7	21.0	39.9	41.4	2.2	6.2	5.5	7.7	0.3	-1.9
JP10	5.14	1.22	9.2	21.2	38.0	38.4	2.3	5.5	5.3	8.0	0.0	0.5
LA01	5.24	1.18	41.3 X	35.9 X	92.9 X	---	---	---	---	---	---	---
MY01	5.12	1.33	9.6	20.7	39.6	39.6	2.4	5.9	4.9	8.2	-0.1	-2.4
MN01	5.00	1.29	---	---	---	---	---	---	---	---	---	---
MM01	5.20	1.41	9.8	20.7	40.5	45.4	2.1 E	5.2	4.6 E	11.1 X	2.2	-5.2
PH01	5.15	1.25	7.6 E	18.3 E	31.0 E	31.6 E	2.2	4.1 E	4.7 E	6.5 E	0.4	-8.3
PH02	5.14	1.32	9.6	21.7	38.2	41.8	2.5	7.5 X	5.9	9.4	5.2	-0.6
KR02	5.03	1.31	9.4	19.9	39.8	40.6	1.9 E	5.9	5.4	6.9 E	1.8	0.3
RU01	5.02	1.38	9.0	23.1	42.1	39.3	2.7	5.6	6.2	8.9	0.5	0.0
RU02	5.12	1.25	9.2	23.1	41.4	41.2	2.4	5.3	6.0	9.3	0.1	2.5
TH01	5.05	1.17	7.7 E	18.7	38.5	39.5	1.7 X	3.8 X	3.5 X	8.4	0.4	2.0
TH02	5.11	1.37	9.0	19.6	38.1	41.2	2.9 E	7.2 E	6.3	8.2	7.0	-3.1
TH04	5.60	1.26	9.5	21.9	40.2	42.9	3.3 X	10.0 X	8.0 X	11.5 X	8.5 I	-1.1
TH05	5.00	1.32	9.2	19.9	38.2	37.7	1.7 X	4.1 E	5.4	7.7	-0.3	-0.9
TH06	5.17	1.31	9.9	20.1	44.9	38.6	2.7	7.0 E	7.4 X	8.0	0.0	0.2
TH07	5.89 E	1.92 X	7.5 E	21.2	40.7	53.3 X	0.6 X	8.9 X	5.3	2.4 X	5.6	-28.0 C
TH08	5.15	1.24	---	---	---	---	---	---	---	---	0.2 [*2]	3.4 [*2]
VN01	5.30	1.20	9.8	21.6	40.1	40.5	1.9 E	6.8 E	6.4	9.7 E	1.3	1.2
VN02	5.39	1.17	9.3	21.4	40.8	39.8	1.9 E	7.0 E	6.7 E	10.3 E	1.6	1.3
VN03	5.42	1.22	8.3	---	---	39.5	3.3 X	5.8	6.0	11.3 X	---	---
VN04	5.35	1.18	8.1 E	21.9	38.5	41.4	2.1 E	5.6	6.4	10.3 E	3.6	-0.4
VN05	5.29	1.20	8.7	20.6	39.1	40.5	4.1 X	5.9	6.4	8.9	3.8	0.1
Vp	5.10	1.31	9.7	21.6	40.4	40.4	2.5	5.6	5.6	8.3	0.1	-0.2
N of data	37	37	35	34	34	34	34	34	34	34		
Within DQO	36	35	27	31	31	31	16	19	26	21		
Flag E	1	1	7	2	2	2	8	9	5	8		
Flag X	0	1	1	1	1	1	10	6	3	5		

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 (R_1); "C", Poor conductivity agreement (R_2); "---", Not measured; "Vp", Prepared values of parameters;
[*1] The abbreviated name and code are given in Chapter 1
[*2] R_1 and R_2 for TH08 were calculated with results of ion concentration from TH06.

3) Comparison of High and Low Concentration Sample

The percentage of flagged data for Sample No. 121w and 122w were shown in Figure 2.3. The percentage of the data within the DQO for the sample No. 121w and 122w were 90.8% and 78.7% respectively. The difference between both samples was 12.1%. In this project, the total number of flagged data was 100 (E: 68, X: 38) among the whole set of 694 data.

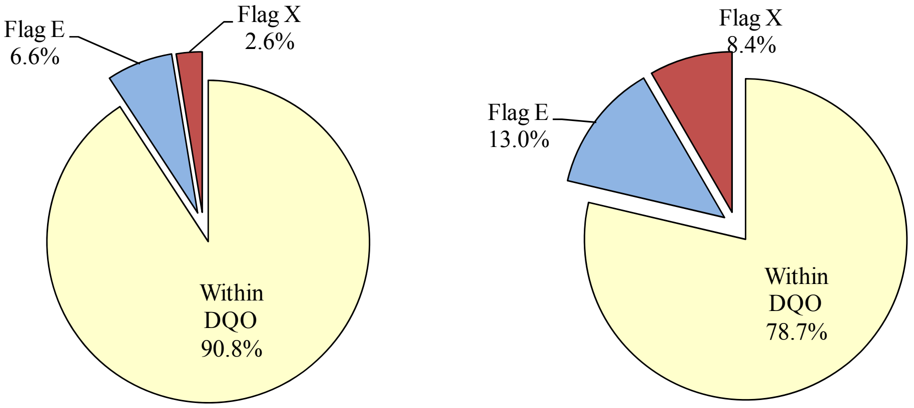


Figure 2.3 Percentage of flagged data for Sample No. 121w and No. 122w (Left: No. 121w, Right: No. 122w)

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

The number of laboratory by number of flags was shown in Figure 2.4. The number of laboratory without flagged data was 10, which corresponds to 27.0% of all the participating laboratories. On the other hand, 2 laboratories were added no less than 10 flags.

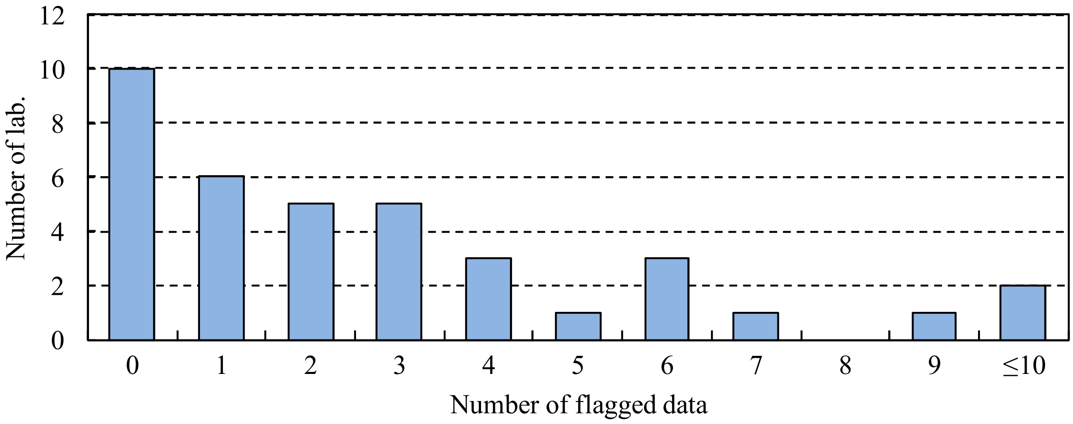


Figure 2.4 Distribution of the number of laboratory (by number of flags)

2.3.2 Evaluation of laboratories' performance (by analytical parameter)

The data normalized by Vp were shown in Figures 2.5 through 2.24 for each parameter. In scatter diagrams (lower figures), bold line means the prepared values of sample No. 121w and 122w, broken lines and dotted lines showed the values of Vp±15% and Vp±30% respectively.

1) pH

All participating laboratories used pH meter with glass electrode method for the measurement of pH. The data of sample No. 122w from TH07 exceeded the DQO and were marked with flag "E".

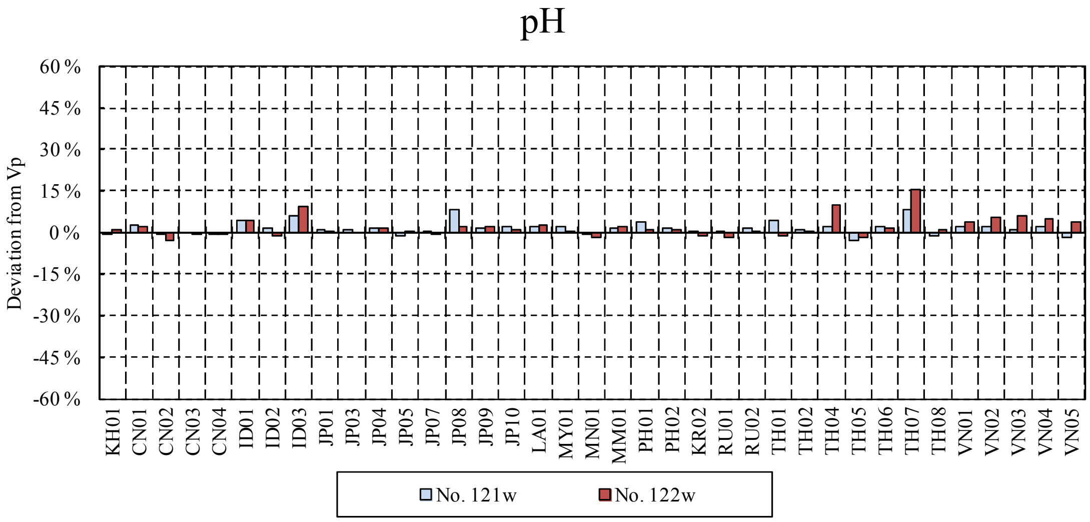


Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)

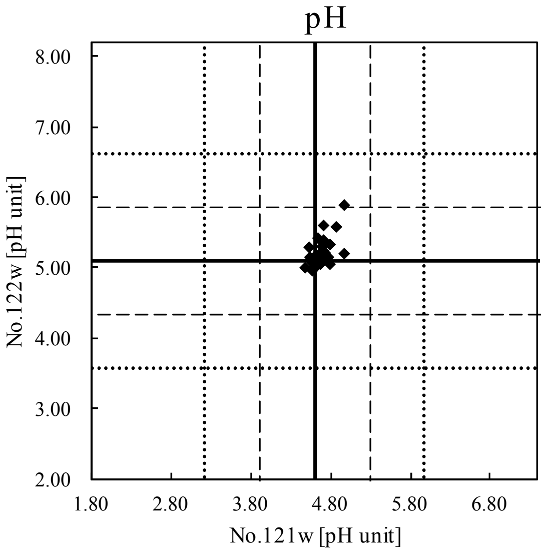


Figure 2.6 Scatter diagram for pH

2) EC

All participating laboratories used conductivity cell method for the measurement of EC. The data of sample No. 121w and No. 122w from KH01 exceeded the DQO and were marked with flag "E". Additionally, the data of sample No. 122w from TH07 exceeded the DQO more than a factor of 2 and were marked with flag "X".

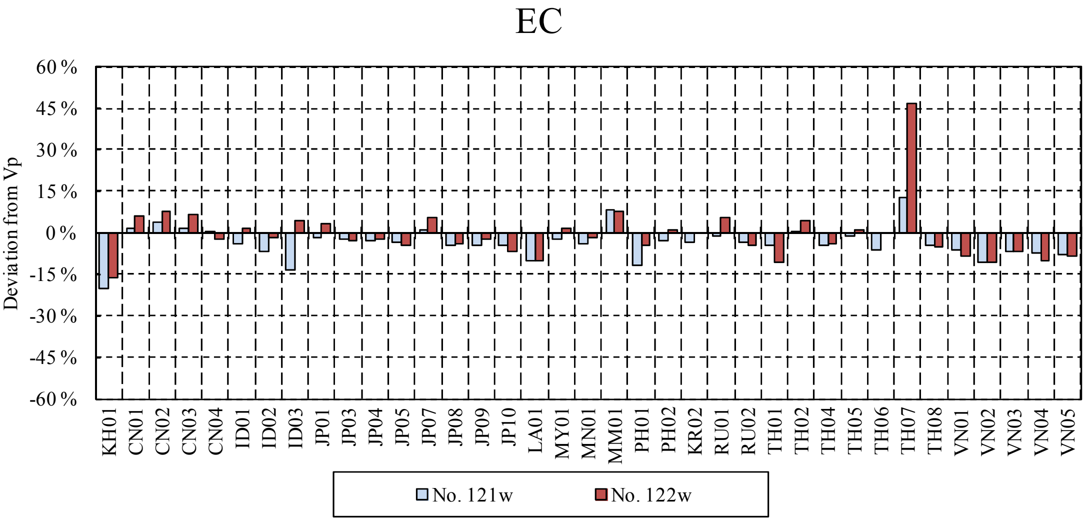


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)

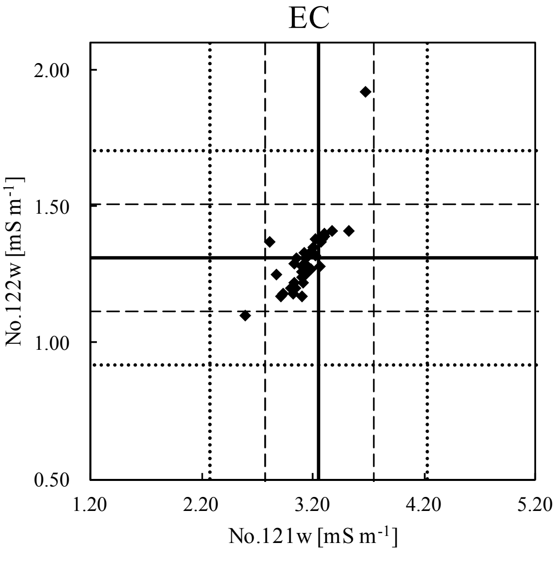


Figure 2.8 Scatter diagram for EC

3) SO_4^{2-}

The data of sample No. 121w from 2 laboratories (KH01 and PH01) and the data of sample No. 122w from 7 laboratories (KH01, CN01, CN03, PH01, TH01, TH07 and VN04) exceeded the DQO and were marked with flag "E". Additionally, the data of sample No. 121w and 122w from LA01 exceeded the DQO more than a factor of 2 and were marked with flag "X".

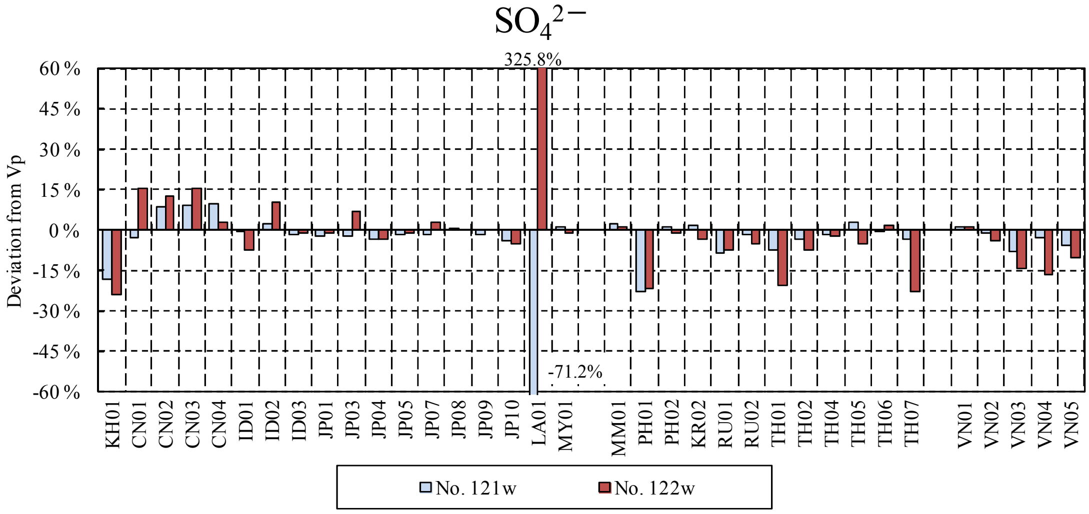


Figure 2.9 Deviation from prepared value for SO_4^{2-} (normalized by prepared value)

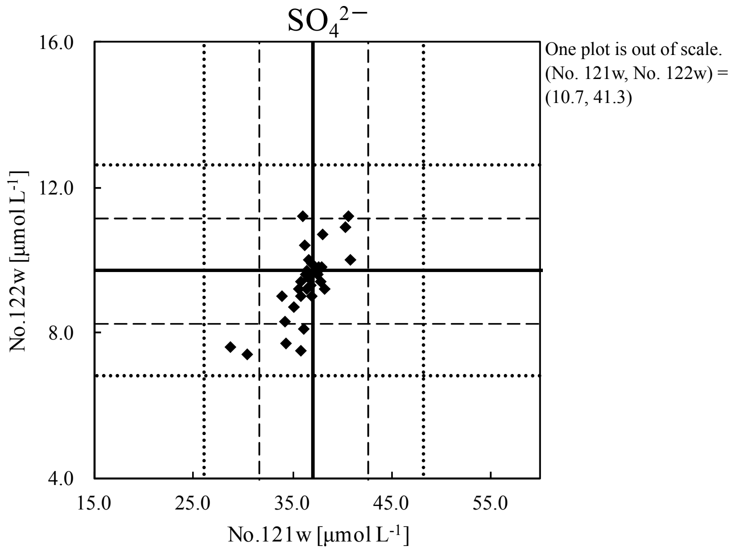


Figure 2.10 Scatter diagram for SO_4^{2-}

4) NO_3^-

The data of sample No. 121w from KH01 and the data of sample No. 122w from 2 laboratories (KH01 and PH01) exceeded the DQO and were marked with flag "E". Additionally, the data of sample No. 121w and 122w from LA01 exceeded the DQO more than a factor of 2 and were marked with flag "X".

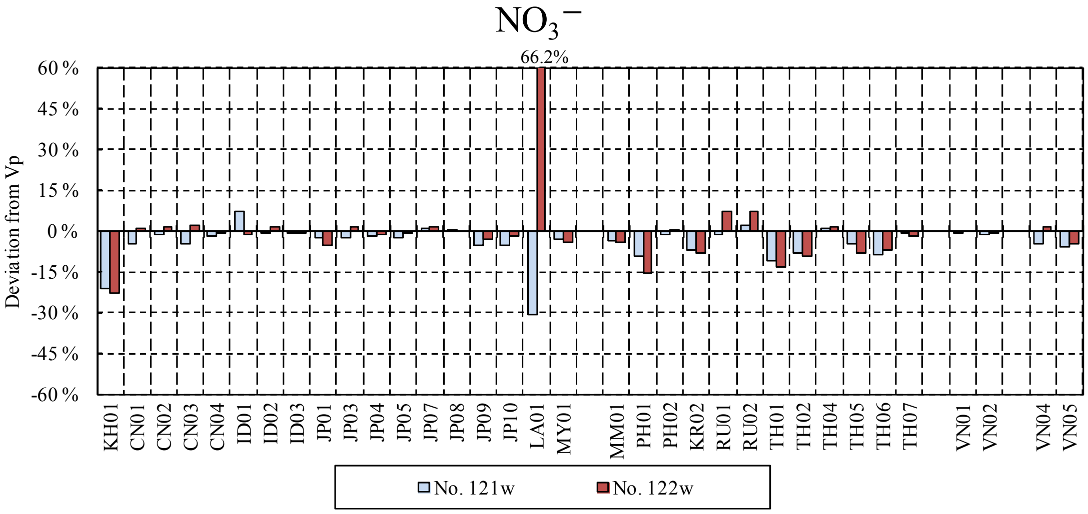


Figure 2.11 Deviation from prepared value for NO_3^- (normalized by prepared value)

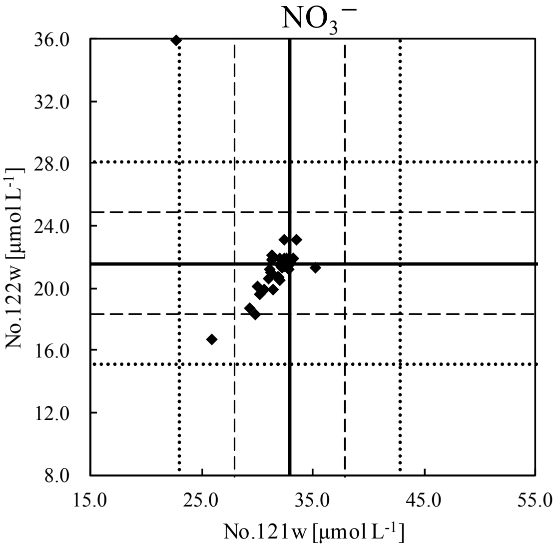


Figure 2.12 Scatter diagram for NO_3^-

5) Cl⁻

The data of sample No. 121w and No. 122w from 2 laboratories (KH01 and PH01) exceeded the DQO and were marked with flag "E". Additionally, the data of sample No. 121w and 122w from LA01 exceeded the DQO more than a factor of 2 and were marked with flag "X".

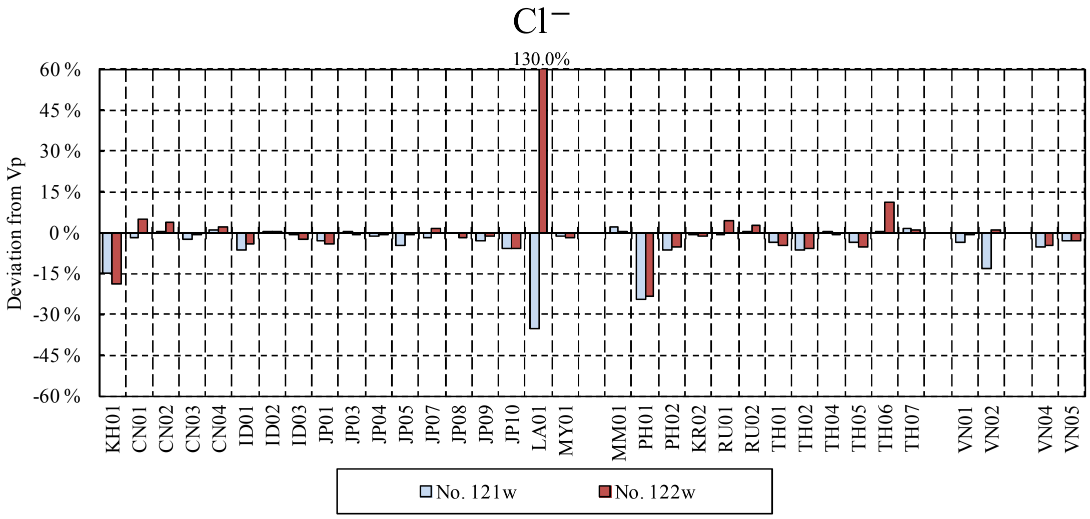
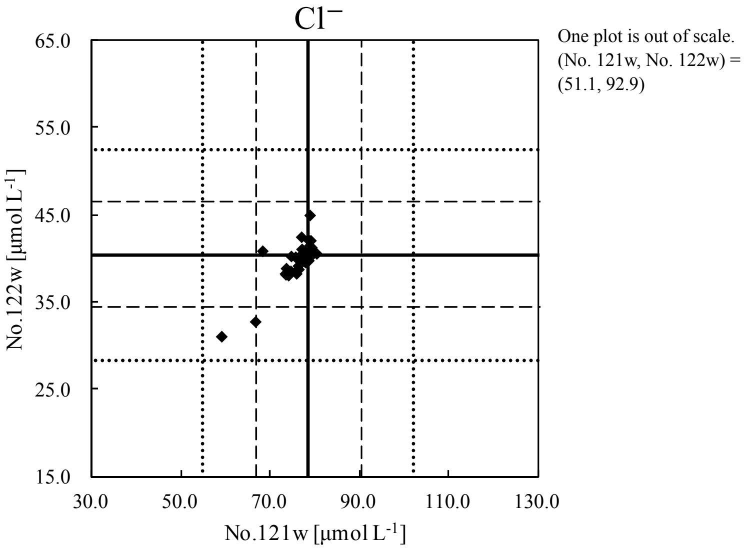


Figure 2.13 Deviation from prepared value for Cl$^-$ (normalized by prepared value)



One plot is out of scale.
(No. 121w, No. 122w) =
(51.1, 92.9)

Figure 2.14 Scatter diagram for Cl$^-$

6) Na^+

The data of sample No. 121w and No. 122w from 2 laboratories (CN01 and PH01) exceeded the DQO and were marked with flag "E". Additionally, the data of sample No. 122w from TH07 exceeded the DQO more than a factor of 2 and were marked with flag "X".

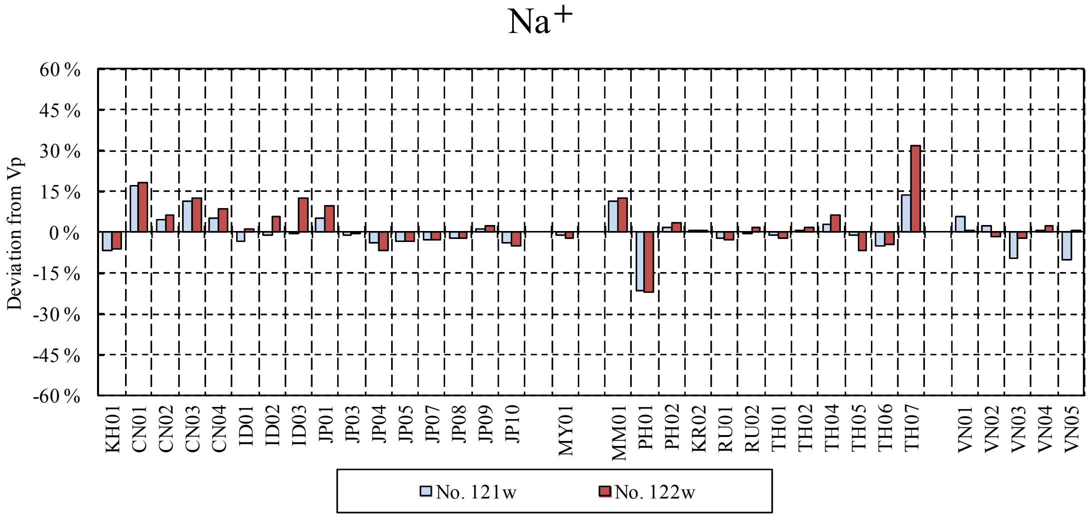


Figure 2.15 Deviation from prepared value for Na^+ (normalized by prepared value)

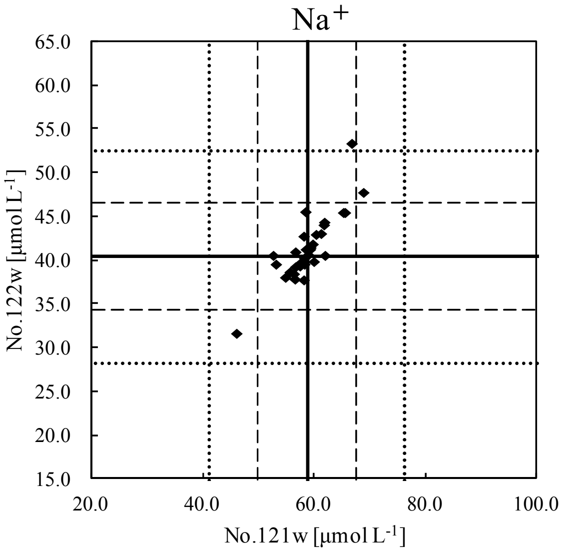


Figure 2.16 Scatter diagram for Na^+

7) K^+

The data of sample No. 121w from 9 laboratories (KH01, ID03, JP07, TH01, TH04, TH06, VN01, VN03 and VN05) and the data of sample No. 122w from 8 laboratories (ID03, JP04, MM01, KR02, TH02, VN01, VN02 and VN04) exceeded the DQO and were marked with flag "E". Additionally, the data of sample No. 121w from 3 laboratories (TH07, VN02 and VN04) and the data of sample No. 122w from 10 laboratories (KH01, CN01, CN03, JP07, TH01, TH04, TH05, TH07, VN03 and VN05) exceeded the DQO more than a factor of 2 and were marked with flag "X".

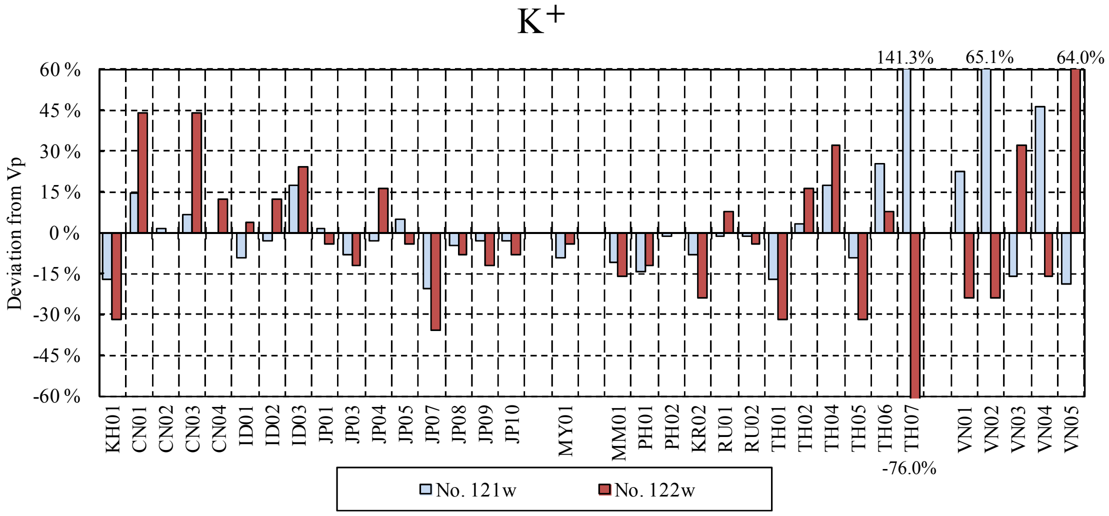


Figure 2.17 Deviation from prepared value for K^+ (normalized by prepared value)

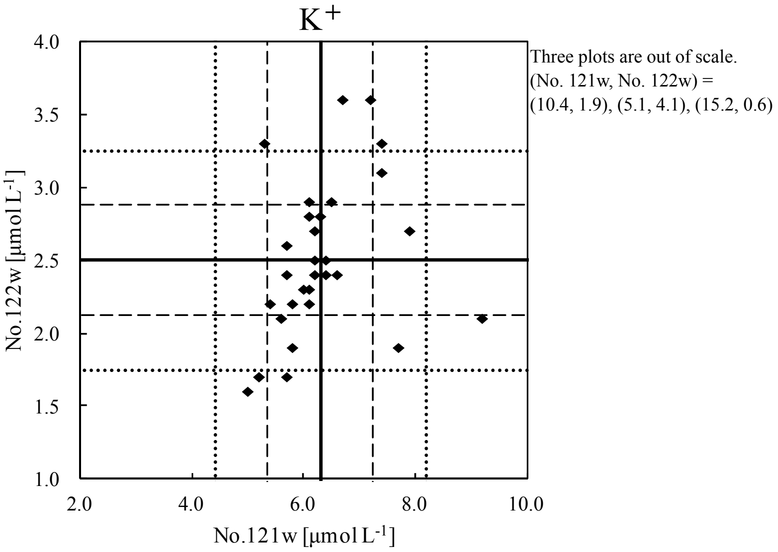


Figure 2.18 Scatter diagram for K^+

8) Ca^{2+}

The data of sample No. 121w from PH01 and the data of sample No. 122w from 9 laboratories (CN02, CN03, ID02, PH01, TH02, TH05, TH06, VN01 and VN02) exceeded the DQO and were marked with flag "E". Additionally, the data of sample No. 121w from 2 laboratories (TH04 and VN05) and the data of sample No. 122w from 6 laboratories (CN01, ID03, PH02, TH01, TH04 and TH07) exceeded the DQO more than a factor of 2 and were marked with flag "X".

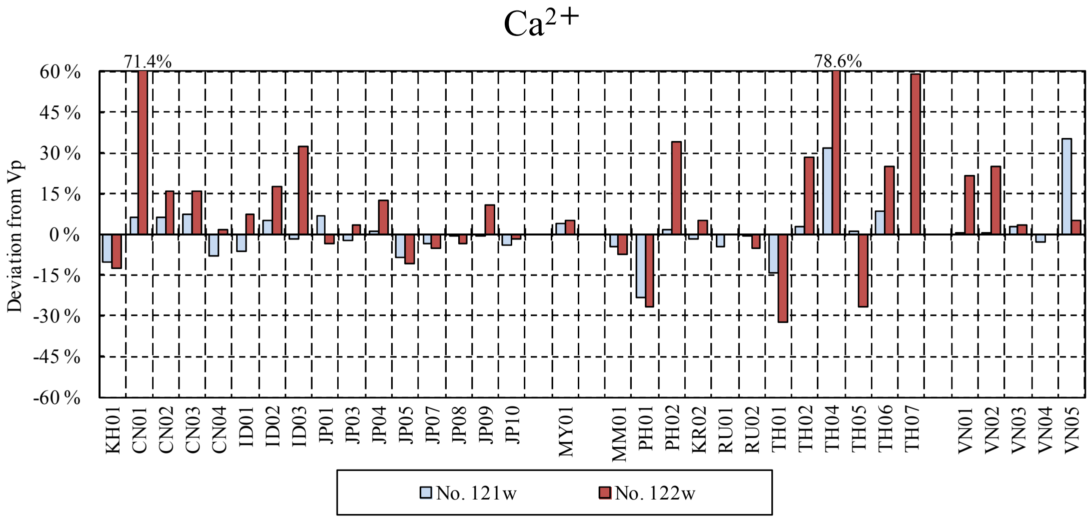
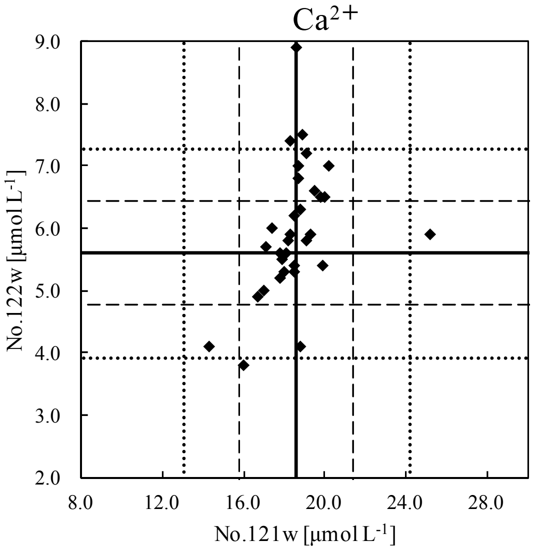


Figure 2.19 Deviation from prepared value for Ca^{2+} (normalized by prepared value)



Two plots are out of scale.
(No. 121w, No. 122w) =
(19.8, 9.6), (24.5, 10.0)

Figure 2.20 Scatter diagram for Ca^{2+}

9) Mg^{2+}

The data of sample No. 121w from 4 laboratories (CN04, PH01, TH01 and TH04) and the data of sample No. 122w from 5 laboratories (CN01, ID03, MM01, PH01 and VN02) exceeded the DQO and marked with flag "E". Additionally, the data of sample No. 122w from 3 laboratories (TH01, TH04 and TH06) exceeded the DQO more than a factor of 2 and were marked with flag "X".

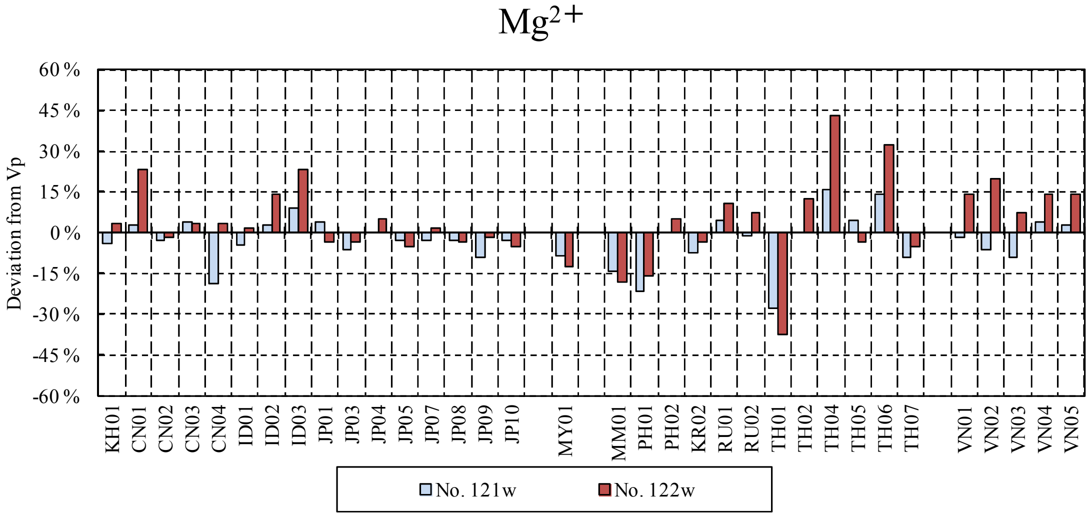


Figure 2.21 Deviation from prepared value for Mg^{2+} (normalized by prepared value)

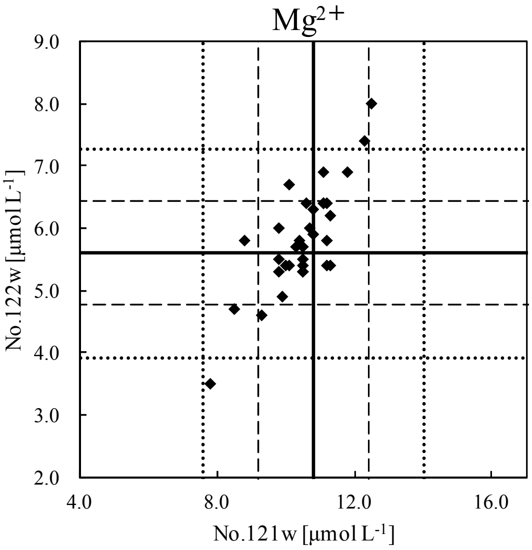


Figure 2.22 Scatter diagram for Mg^{2+}

10) NH_4^+

The data of sample No. 121w from PH01 and the data of sample No. 122w from 8 laboratories (CN04, ID01, JP08, PH01, KR02, VN01, VN02 and VN04) exceeded the DQO and were marked with flag "E". Additionally, the data of sample No. 121w from TH07 and the data of sample No. 122w from 5 laboratories (KH01, MM01, TH04, TH07 and VN03) exceeded the DQO more than a factor of 2 and were marked with flag "X".

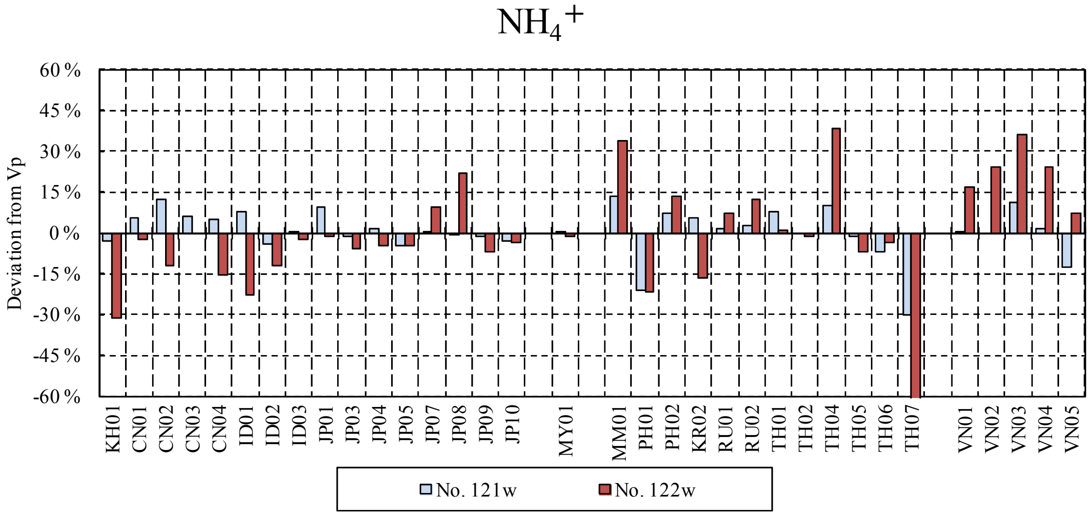
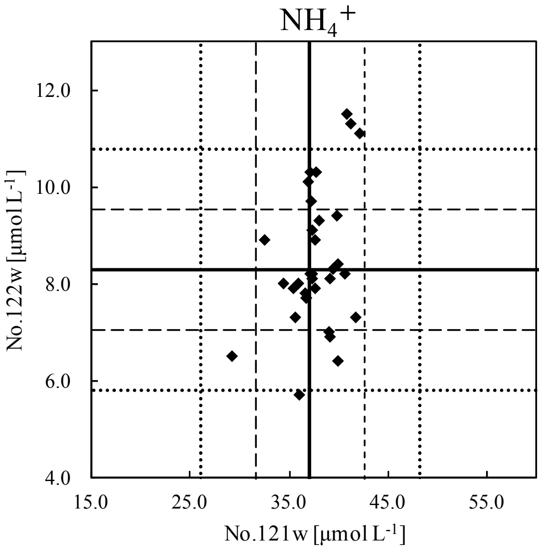


Figure 2.23 Deviation from prepared value for NH_4^+ (normalized by prepared value)



One plot is out of scale.
(No. 121w, No. 122w) =
(25.9, 2.4)

Figure 2.24 Scatter diagram for NH_4^+

11) Scatter diagrams

Most of constituents showed positive correlation between the submitted pairs of results of sample No. 121w and 122w. It suggested that systematic deviation could be the reason for the deviation of results in many of laboratories.

2.3.3 Sample and Analysis Evaluation

The concentrations of the analytical parameters in the samples for this survey were fixed on the basis of the reference to monitoring data on wet deposition in EANET. Two samples were not distinguished as high or low concentration samples when they were distributed to participating laboratories. Ions (including pH as H^+) concentrations of sample No. 121w were higher than those of No. 122w.

The relative standard deviations (R.S.D.) of each parameter for the sample No. 121w and No. 122w were shown in the Figure 2.25. The R.S.D. of K^+ for sample No. 122w was the highest in this survey. The R.S.D. values for sample No. 122w were higher than those for sample No. 121w for all the constituents.

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

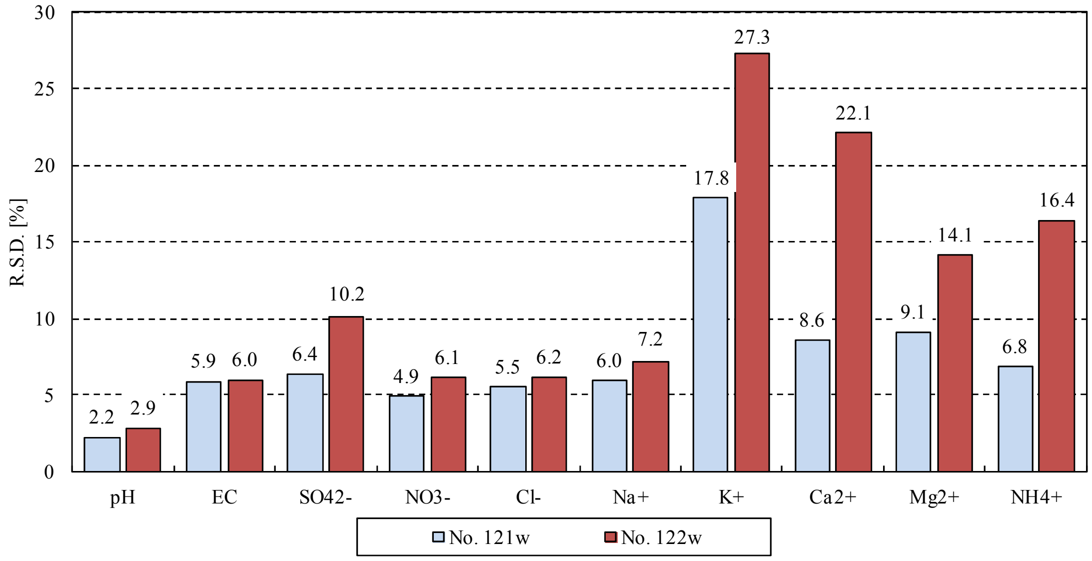


Figure 2.25 Relative standard deviations (R.S.D.) of each constituent

2.3.4 Information on Laboratories

1) Number of analysts and their experience

Number of analysts and years of their experience were shown in Table 2.11 and Table 2.12 respectively. In the Table 2.11, the letters of "A", "B" and "C" mean individuals of analysts in each laboratory who carried out analyses. In 19 laboratories, same analyst carried out the analyses for all parameters. Clear relationship between the number of analysts and flagged data was not suggested.

Table 2.11 Number of analysts

Lab. ID	Total	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	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	2	A	A	B	B	B	B	B	B	B	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	2	A	A	A	A	A	B	B	B	B	B
ID03	1	A	A	A	A	A	A	A	A	A	A
JP01	1	A	A	A	A	A	A	A	A	A	A
JP03	1	A	A	A	A	A	A	A	A	A	A
JP04	1	A	A	A	A	A	A	A	A	A	A
JP05	1	A	A	A	A	A	A	A	A	A	A
JP07	1	A	A	A	A	A	A	A	A	A	A
JP08	1	A	A	A	A	A	A	A	A	A	A
JP09	1	A	A	A	A	A	A	A	A	A	A
JP10	1	A	A	A	A	A	A	A	A	A	A
LA01	1	A	A	A	A	A	--	--	--	--	--
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	2	A	A	B	B	B	B	B	B	B	B
PH02	2	A	A	B	B	B	B	B	B	B	B
KR02	1	A	A	A	A	A	A	A	A	A	A
RU01	3	A	A	A	A	A	B	B	B	B	C
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	2	A	B	B	B	B	B	B	B	B	B
TH04	2	A	A	B	B	B	B	B	B	B	B
TH05	2	A	A	B	B	B	B	B	B	B	B
TH06	1	A	A	A	A	A	A	A	A	A	A
TH07	2	A	A	B	B	B	B	B	B	B	B
TH08	1	A	A	--*	--*	--*	--*	--*	--*	--*	--*
VN01	2	A	A	B	B	B	B	B	B	B	B
VN02	2	A	A	B	B	B	B	B	B	B	B
VN03	3	A	A	B	--	--	C	C	C	C	B
VN04	2	A	A	B	B	B	B	B	B	B	B
VN05	3	A	B	C	C	C	C	C	C	C	C

Note: Light mesh, Analytic data of sample No. 121w or No. 122w was marked with flag "E" or "X";
Dark mesh, Analytic data of both samples were marked with flag "E" or "X";
"---", Not measured *: For TH08, ions were analyzed by TH06.

Total of 158 data out of 347 were analyzed by the analysts whose experience was less than 5 years. The number corresponds to 45.5% of all the submitted data. Clear relationship between the years of experience and flagged data was not suggested.

Table 2.12 Years of experience

Lab. ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	4	4	4	4	4	4	4	4	4	4
CN01	1	1	1	1	1	1	1	1	1	1
CN02	14	14	4	4	4	4	4	4	4	4
CN03	1	1	1	1	1	1	1	1	1	1
CN04	4	4	17	17	17	17	17	17	17	17
ID01	11	11	6	6	6	6	6	6	6	6
ID02	13	13	13	13	13	13	13	13	13	13
ID03	2	2	2	2	2	2	2	2	2	2
JP01	9	9	9	9	9	9	9	9	9	9
JP03	1	1	1	1	1	1	1	1	1	1
JP04	5	5	5	5	5	5	5	5	5	5
JP05	3	3	3	3	3	3	3	3	3	3
JP07	3	3	3	3	3	3	3	3	3	3
JP08	2	2	2	2	2	2	2	2	2	2
JP09	6	6	6	6	6	6	6	6	6	6
JP10	1	1	1	1	1	1	1	1	1	1
LA01	5	5	5	5	5	--	--	--	--	--
MY01	6	6	2	2	2	2	2	2	2	2
MN01	15	15	--	--	--	--	--	--	--	--
MM01	7	7	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
PH01	1	1	5	5	5	15	15	15	15	5
PH02	9	9	5	5	5	5	5	5	5	5
KR02	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
RU01	3	3	3	3	3	5	5	5	5	3
RU02	1.5	1.5	1.5	1.5	1.5	21	21	21	21	1.5
TH01	3	3	3	3	3	3	3	3	3	3
TH02	15	9	9	9	9	15	15	15	15	15
TH04	9	9	6	6	6	6	6	6	6	6
TH05	11	11	9	9	9	9	9	9	9	9
TH06	7	7	7	7	7	7	7	7	7	7
TH07	10	10	10	10	10	10	10	10	10	10
TH08	4	4	--*	--*	--*	--*	--*	--*	--*	--*
VN01	1	1	19	--	--	19	19	19	19	19
VN02	0	0	8	8	8	8	8	8	8	8
VN03	6	6	6			9	9	9	9	7
VN04	10	10	6	6	6	6	6	6	6	6
VN05	3	3	6	6	6	6	6	6	6	6

Note: Light mesh, Analytic data of sample No. 121w or No. 122w was marked with flag "E" or "X";
Dark mesh, Analytic data of both samples were marked with flag "E" or "X";
"---", Not measured *: For TH08, ions were analyzed by TH06.

2) Analytical instruments

As shown in Figure 2.26, most of the participating laboratories used the specified methods described in the "Technical Manual for Wet Deposition Monitoring in East Asia". Laboratory of RU01 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^-. (Titrimetry) The specified methods were shown in Table 2.3.

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

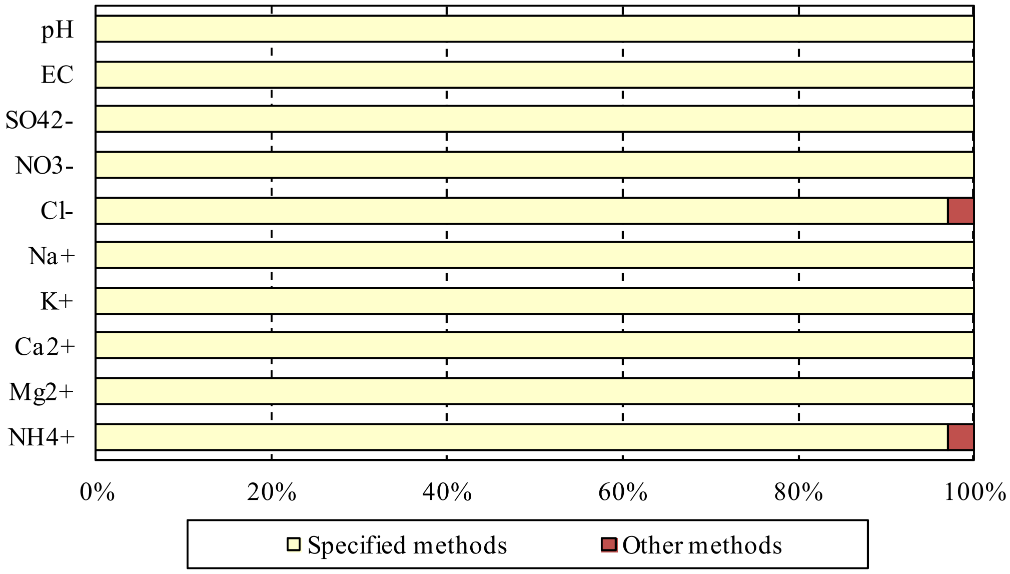


Figure 2.26 Percentage of laboratories that use the specified methods

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

Lab. ID	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	IC	IC	IC	IC	IC	IC	IC	IC
CN01	IC	IC	IC	IC	IC	IC	IC	IC
CN02	IC	IC	IC	IC	IC	IC	IC	IC
CN03	IC	IC	IC	IC	IC	IC	IC	IC
CN04	IC	IC	IC	IC	IC	IC	IC	IC
ID01	IC	IC	IC	IC	IC	IC	IC	IC
ID02	IC	IC	IC	IC	IC	IC	IC	IC
ID03	IC	IC	IC	IC	IC	IC	IC	IC
JP01	IC	IC	IC	IC	IC	IC	IC	IC
JP03	IC	IC	IC	IC	IC	IC	IC	IC
JP04	IC	IC	IC	IC	IC	IC	IC	IC
JP05	IC	IC	IC	IC	IC	IC	IC	IC
JP07	IC	IC	IC	IC	IC	IC	IC	IC
JP08	IC	IC	IC	IC	IC	IC	IC	IC
JP09	IC	IC	IC	IC	IC	IC	IC	IC
JP10	IC	IC	IC	IC	IC	IC	IC	IC
LA01	IC	IC	IC	---	---	---	---	---
MY01	IC	IC	IC	IC	IC	IC	IC	IC
MN01	---	---	---	---	---	---	---	---
MM01	IC	IC	IC	IC	IC	IC	IC	IC
PH01	IC	IC	IC	IC	IC	IC	IC	IC
PH02	IC	IC	IC	IC	IC	IC	IC	IC
KR02	IC	IC	IC	IC	IC	IC	IC	IC
RU01	IC	IC	IC	AES	AES	AAS	AAS	SP-other
RU02	SP	SP	TI	AES	AES	AAS	AAS	SP-IP
TH01	IC	IC	IC	IC	IC	IC	IC	IC
TH02	IC	IC	IC	IC	IC	IC	IC	IC
TH04	IC	IC	IC	IC	IC	IC	IC	IC
TH05	IC	IC	IC	IC	IC	IC	IC	IC
TH06	IC	IC	IC	IC	IC	IC	IC	IC
TH07	IC	IC	IC	IC	IC	IC	IC	IC
TH08	---*	---*	---*	---*	---*	---*	---*	---*
VN01	IC	IC	IC	IC	IC	IC	IC	IC
VN02	IC	IC	IC	IC	IC	IC	IC	IC
VN03	SP	---	---	AAS	AAS	AAS	AAS	SP-IP
VN04	IC	IC	IC	IC	IC	IC	IC	IC
VN05	IC	IC	IC	IC	IC	IC	IC	IC

Note: "---" Not measured *: For TH08, ions were analyzed by TH06.

IC: Ion Chromatography	AAS: Atomic Absorption Spectrometry
AES: Atomic Emission Spectrometry	SP: Spectrophotometry
SP-IP: Spectrophotometry (Indophenol)	SP-other: Spectrophotometry (Other)
TI: Titrometry	

3) Date of Analysis

Figure 2.27 shows the distribution of "Start date" and "Finish date" of analysis in the participating laboratories. In total, 76% of all the submitted data was determined within the year of 2012.

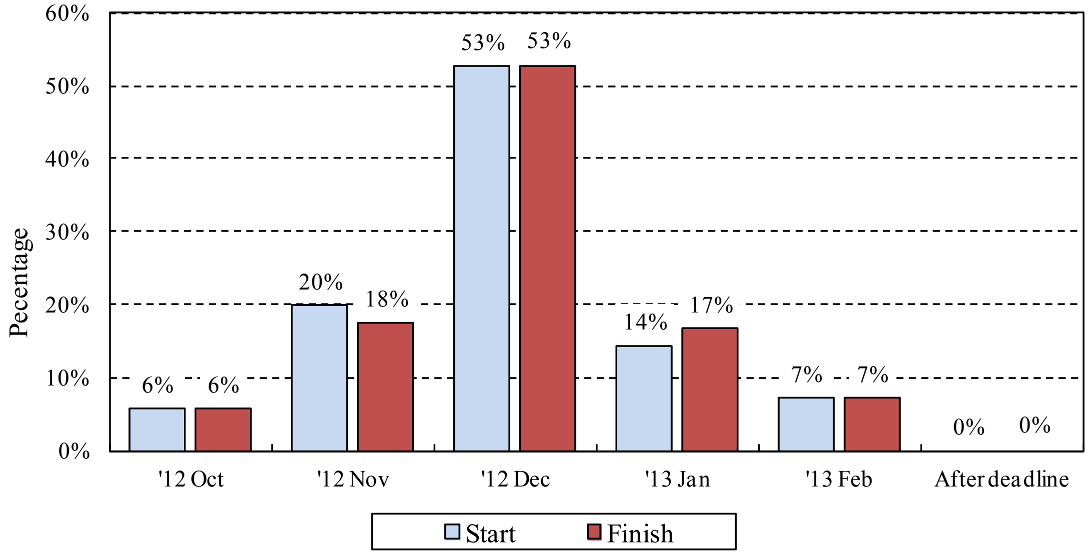


Figure 2.27 Distribution of Start date and Finish date of analysis

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

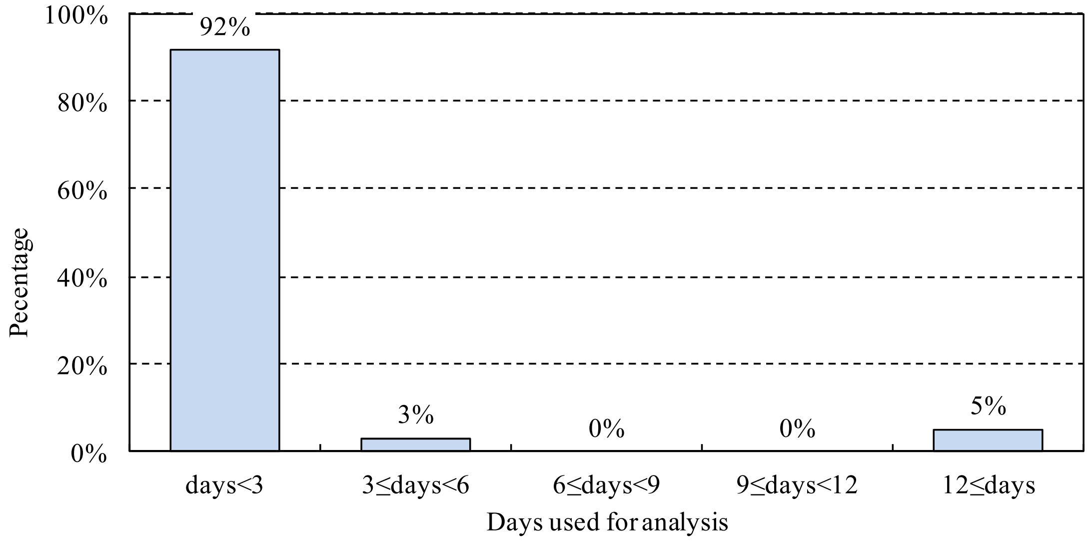


Figure 2.28 Distribution of Days used for analysis

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

2.4 Comparison with past surveys

Since the beginning of EANET, inter-laboratory comparison on wet deposition reached the 15th 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. 121w and sample No. 122w were treated as high and low concentration samples respectively.

The percentages of data within DQO for the sample No. 121w and No. 122w were 90.8% and 78.7% respectively. They were the lowest values among the recent several years' surveys. As shown in section 2.3.1 2), many of laboratories were marked with multiple flags. It could be one reason for higher percentages of flagged data.

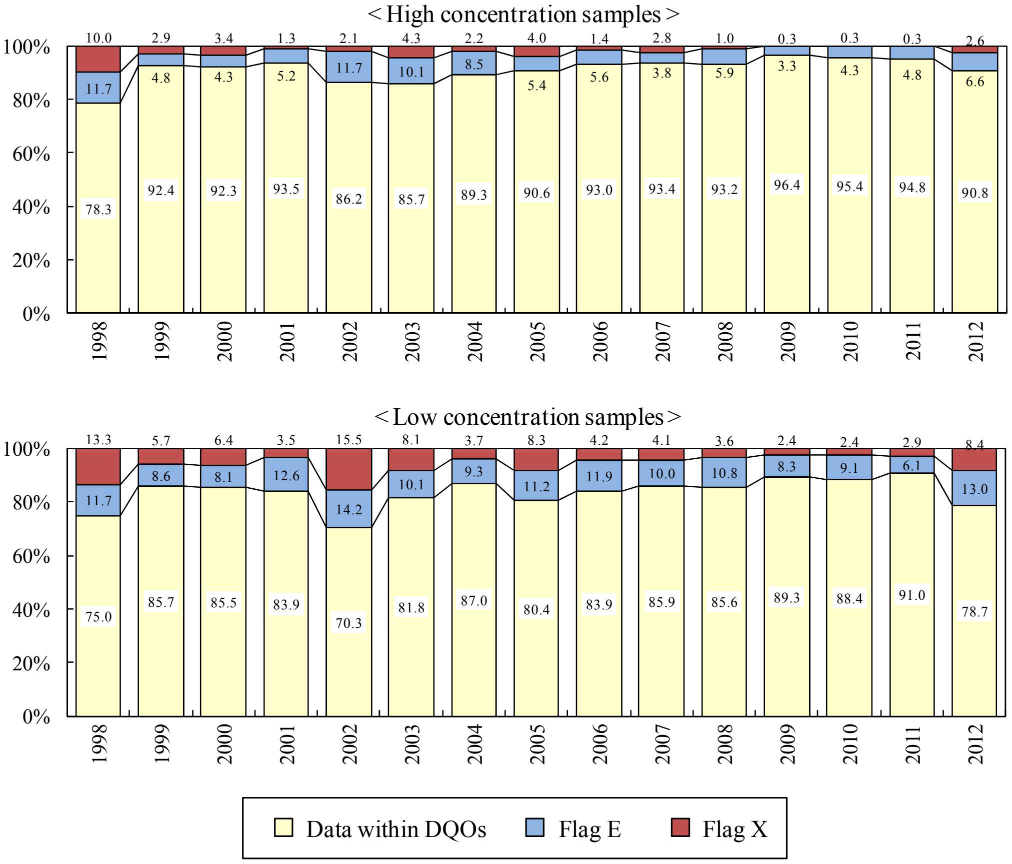


Figure 2.29 Comparison of results from the inter-laboratory comparison projects

Figure 2.30 showed the trend of the prepared values and the percentage of flagged data. The percentages of flagged data were relatively high in cations than anions through the series of surveys. Compared to previous survey, the percentages of flagged data of low concentration samples were remarkably increased from 32.3% to 52.9%, from 16.1% to 44.1% and from 3.2% to 38.2% on K^+, Ca^{2+} and NH_4^+ respectively. It was also suggested that lower ion concentration might be a reason for higher percentages of flagged data.

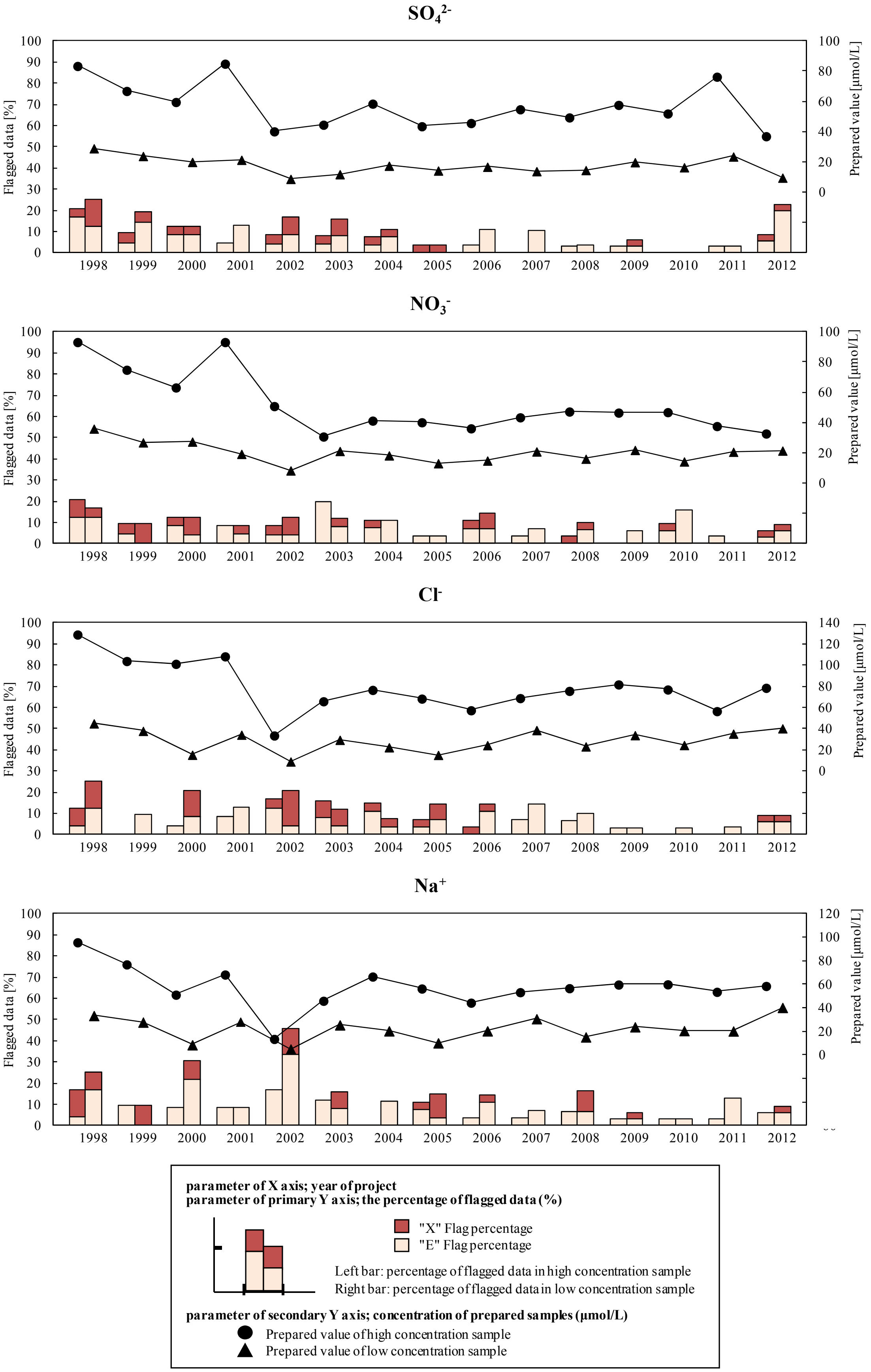


Figure 2.30 Comparison for each parameter in inter-laboratory comparison (ILC) project

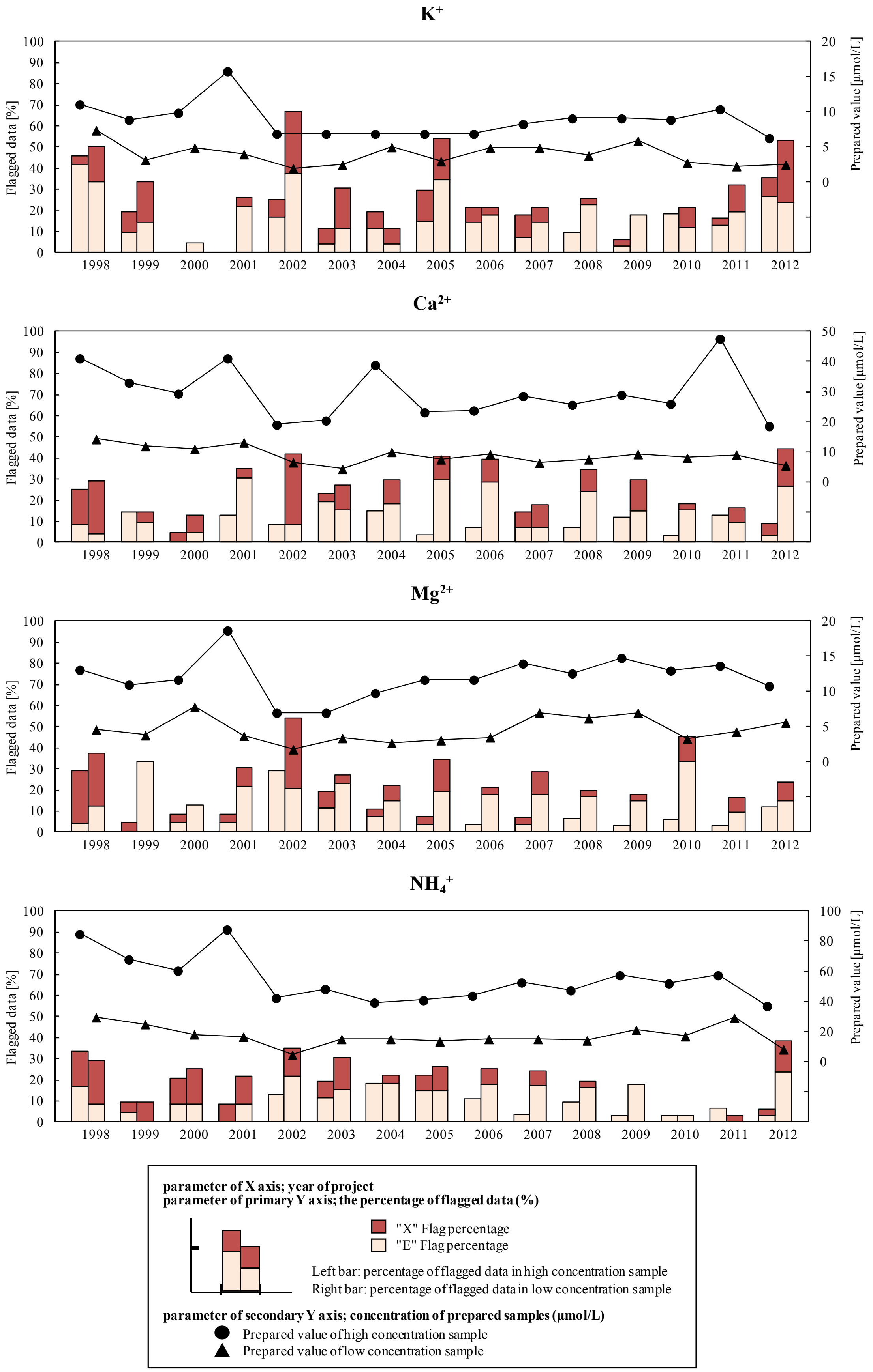


Figure 2.30 Comparison for each parameter in ILC project (continued)

As shown in the figure 2.31, the total number of data in this survey was 694, which was the highest among the series of surveys.

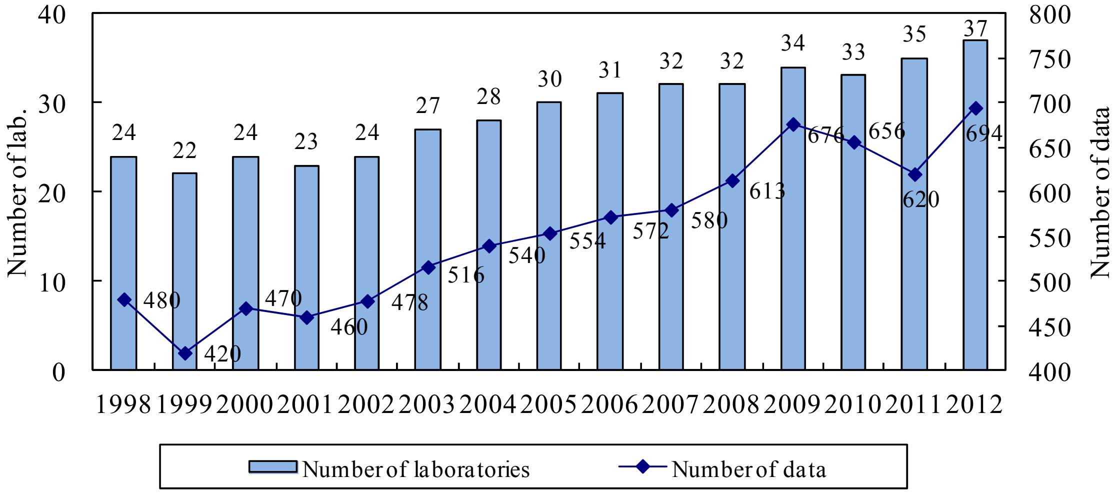


Figure 2.31 The number of participating laboratories and data in the inter-laboratory comparison projects on wet deposition

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

► Low ion concentration could be one reason for poor data quality. Each laboratory was encouraged to grasp the relation between concentration and data qualities in each laboratory.

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.

References

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EANET (2013). *Report of the Inter-laboratory Comparison Project 2011.* Niigata, Japan: Asia Center for Air Pollution Research.

Appendix 2.1 Data precision of submitted data

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

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

In appendix table 2.1.1 and appendix table 2.1.2, data precisions calculated from the submitted results were shown. Sample No. 121 of higher concentration had a tendency to show better R.S.D. than sample No. 122 of lower concentration in each constituent. It was suggested that R.S.D. was greatly affected by sample concentration.

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

Appendix Table 2.1.1 Data precision (R.S.D.) of sample No. 121w

Lab. ID	pH as H^+ %	EC %	SO_4^{2-} %	NO_3^- %	Cl^- %	Na^+ %	K^+ %	Ca^{2+} %	Mg^{2+} %	NH_4^+ %
KH01	3.4	0.7	6.1	6.3	3.3	1.4	8.2	3.9	1.7	2.2
CN01	3.3	0.5	0.5	0.5	0.2	0.2	2.2	0.8	1.4	0.4
CN02	1.7	0.3	0.3	0.2	0.1	0.1	0.0	0.3	0.7	0.3
CN03	1.2	0.2	0.1	0.2	0.1	0.1	0.7	0.6	0.9	0.2
CN04	2.8	0.8	0.4	0.8	0.2	0.3	1.1	0.9	1.6	0.9
ID01	4.9	0.9	2.0	2.5	1.7	0.6	3.3	0.8	1.1	1.6
ID02	15.6	2.6	0.4	0.4	0.2	0.8	0.9	1.0	0.8	0.8
ID03	9.5	2.3	0.8	0.9	2.0	3.8	7.3	3.8	2.8	1.6
JP01	1.2	0.2	0.6	0.5	0.4	1.1	2.3	1.2	2.3	1.3
JP03	1.7	1.0	0.6	0.6	0.8	0.3	1.1	1.2	0.7	1.1
JP04	1.2	0.2	0.1	0.1	0.1	0.6	3.2	2.8	2.2	0.5
JP05	2.3	0.3	0.3	0.3	0.2	0.4	0.8	0.3	0.5	0.2
JP07	1.9	0.3	1.8	0.7	1.6	0.2	0.7	0.3	0.5	0.3
JP08	60.4	0.8	0.2	0.5	0.2	0.5	0.0	0.5	0.3	1.2
JP09	7.0	0.6	4.1	5.1	3.1	2.9	5.3	4.6	4.8	2.3
JP10	2.3	0.5	0.3	0.2	0.1	0.4	6.5	0.6	0.9	0.9
LA01	4.0	0.3	0.5	0.6	0.9	--	--	--	--	--
MY01	2.7	0.4	0.2	0.4	0.3	0.1	1.3	1.6	0.7	0.2
MN01	3.5	0.5	--	--	--	--	--	--	--	--
MM01	14.7	1.3	0.6	1.6	1.2	1.9	7.5	3.8	7.7	2.8
PH01	15.4	0.8	1.2	4.7	1.0	0.3	5.6	1.3	1.4	1.5
PH02	1.2	0.7	1.0	0.4	1.0	0.9	1.2	1.0	0.8	1.0
KR02	2.3	0.3	0.2	0.4	0.4	0.9	4.8	1.3	1.0	0.3
RU01	5.0	0.5	0.4	2.3	0.5	1.0	2.5	0.8	1.9	0.6
RU02	9.4	3.4	3.6	1.9	1.6	3.4	7.1	1.5	2.6	1.1
TH01	11.8	0.5	1.5	1.0	0.8	0.3	2.2	0.8	2.4	0.5
TH02	1.2	0.2	1.2	0.8	1.2	0.4	2.3	1.2	1.2	0.6
TH04	6.2	0.3	0.5	0.6	0.5	0.3	1.9	1.5	2.3	0.6
TH05	3.7	0.3	0.6	1.6	1.0	2.2	6.3	2.2	3.6	2.0
TH06	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TH07	44.9	12.1	6.7	4.3	0.9	1.9	61.7	20.8	16.6	32.6
TH08	3.2	0.4	--	--	--	--	--	--	--	--
VN01	1.5	0.3	0.5	0.5	0.4	1.0	1.7	1.0	1.6	0.8
VN02	1.1	0.2	0.3	0.7	0.2	0.2	1.2	0.4	0.8	0.6
VN03	2.2	0.4	0.6	--	--	0.2	1.7	1.0	2.3	0.2
VN04	1.6	0.2	0.2	0.2	0.1	0.1	0.7	0.3	0.5	0.2
VN05	5.2	2.6	2.3	3.0	1.8	2.1	2.7	3.4	2.5	1.2
Number of data	37	37	35	34	34	34	34	34	34	34
Minimum	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
25% value	1.7	0.3	0.3	0.4	0.2	0.2	1.1	0.7	0.8	0.4
Median	3.2	0.5	0.5	0.6	0.5	0.5	2.2	1.0	1.4	0.8
75% value	6.2	0.8	1.2	1.6	1.2	1.1	5.2	1.5	2.3	1.3
Maximum	60.4	12.1	6.7	6.3	3.3	3.8	61.7	20.8	16.6	32.6

Note: R.S.D. for "pH as H^+" was calculated after pH value was converted to H^+ concentration;
"--", Not measured

Appendix Table 2.1.2 Data precision (R.S.D.) of sample No. 122w

Lab. ID	pH as H^+ %	EC %	SO_4^{2-} %	NO_3^- %	Cl^- %	Na^+ %	K^+ %	Ca^{2+} %	Mg^{2+} %	NH_4^+ %
KH01	13.0	1.8	5.5	5.7	3.0	3.0	10.3	3.5	5.5	3.5
CN01	3.8	1.2	1.6	0.4	0.4	0.3	3.9	1.5	1.3	2.1
CN02	2.7	0.4	0.7	0.2	0.2	0.2	0.0	0.5	0.0	0.0
CN03	1.2	0.4	0.4	0.3	0.2	0.2	1.4	0.9	1.2	0.7
CN04	3.6	1.2	1.7	1.2	0.6	0.6	1.8	2.3	1.2	1.7
ID01	1.1	0.7	5.0	1.3	1.6	1.0	6.7	3.0	1.5	8.9
ID02	9.2	0.8	0.8	0.5	0.7	2.4	4.0	2.8	0.7	0.7
ID03	29.8	4.6	1.2	1.7	0.9	22.1	10.6	7.0	6.9	2.0
JP01	1.7	1.0	0.8	0.6	0.5	0.6	2.1	1.7	1.9	0.9
JP03	2.3	1.3	1.0	1.3	0.8	0.6	3.0	4.3	0.6	8.0
JP04	1.7	0.6	0.5	0.5	0.6	0.9	7.2	3.1	2.9	2.2
JP05	18.6	2.6	0.5	0.2	0.3	0.7	6.9	1.4	1.0	1.9
JP07	2.4	0.9	0.5	0.8	0.3	0.5	3.2	1.5	0.9	1.1
JP08	11.9	1.9	0.7	0.3	0.3	0.5	6.1	0.6	1.2	9.0
JP09	9.6	1.9	3.7	4.2	5.4	2.9	4.5	5.7	4.7	2.0
JP10	1.7	0.4	0.5	0.3	0.1	0.2	6.1	2.9	0.9	0.5
LA01	4.4	0.8	0.1	0.1	0.4	--	--	--	--	--
MY01	7.7	0.0	0.5	0.3	0.2	0.3	2.1	2.5	1.5	0.0
MN01	3.6	0.4	--	--	--	--	--	--	--	--
MM01	10.3	0.6	1.7	2.2	0.7	1.2	12.8	11.9	6.6	6.6
PH01	4.8	1.3	1.3	1.6	1.1	0.8	5.7	3.6	2.4	2.5
PH02	4.9	1.2	2.6	1.0	0.6	0.8	1.8	4.9	1.0	0.8
KR02	2.7	0.4	0.5	0.5	0.5	0.7	8.2	6.5	9.0	1.3
RU01	9.2	0.5	3.5	3.2	1.0	0.6	3.9	1.8	0.0	1.2
RU02	21.9	1.1	2.0	3.0	10.1	1.7	21.5	4.0	2.0	8.4
TH01	11.9	0.0	2.1	1.2	0.7	0.3	2.0	2.7	3.4	1.4
TH02	0.7	0.3	1.2	0.7	0.9	0.2	4.3	0.7	0.0	0.0
TH04	4.0	0.4	0.7	0.3	0.3	0.2	5.3	4.0	3.6	1.2
TH05	21.6	0.4	1.5	1.2	1.2	1.0	4.1	4.9	1.5	3.7
TH06	3.3	0.3	0.5	0.5	0.5	0.8	3.7	2.6	2.7	3.1
TH07	78.5	12.1	16.6	7.5	1.4	14.2	124.4	44.4	19.2	65.0
TH08	1.6	1.1	--	--	--	--	--	--	--	--
VN01	1.4	0.7	0.9	1.6	1.1	0.4	2.7	2.0	0.9	1.9
VN02	8.1	0.4	1.8	0.8	0.4	0.2	5.2	1.9	1.3	1.6
VN03	6.3	1.5	2.0	--	--	0.1	3.7	1.4	0.8	1.2
VN04	2.5	0.4	0.7	0.2	0.2	0.1	2.9	0.9	0.9	0.6
VN05	10.6	1.6	8.9	3.5	0.8	2.8	5.8	1.5	1.6	1.6
Number of data	37	37	35	34	34	34	34	34	34	34
Minimum	0.7	0.0	0.1	0.1	0.1	0.1	0.0	0.5	0.0	0.0
25% value	2.4	0.4	0.6	0.4	0.3	0.3	2.9	1.5	0.9	0.9
Median	4.4	0.8	1.2	0.8	0.6	0.6	4.2	2.6	1.4	1.7
75% value	10.3	1.3	2.0	1.6	1.0	1.0	6.5	4.0	2.9	3.0
Maximum	78.5	12.1	16.6	7.5	10.1	22.1	124.4	44.4	19.2	65.0

Note: R.S.D. for "pH as H^+" was calculated after pH value was converted to H^+ concentration;
"--", Not measured

Appendix 2.2 Analytical results submitted by the laboratories

Appendix Table 2.2.1 Analytical data concerning sample No. 121w

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	4.59	2.59	30.4	25.9	66.8	54.9	5.2	16.7	10.4	36.0
CN01	4.73	3.30	36.0	31.3	77.1	68.9	7.2	19.8	11.1	39.1
CN02	4.57	3.37	40.3	32.4	79.2	61.3	6.4	19.8	10.5	41.7
CN03	4.60	3.30	40.6	31.3	76.9	65.6	6.7	20.0	11.2	39.4
CN04	4.57	3.26	40.8	32.3	79.4	61.8	6.3	17.1	8.8	39.0
ID01	4.79	3.12	36.9	35.2	73.7	56.7	5.7	17.4	10.3	39.9
ID02	4.67	3.03	38.0	32.6	78.8	58.2	6.1	19.5	11.1	35.6
ID03	4.87	2.81	36.5	32.7	78.0	58.5	7.4	18.3	11.8	37.3
JP01	4.65	3.20	36.3	32.0	76.5	61.9	6.4	19.9	11.2	40.6
JP03	4.65	3.18	36.2	32.0	79.2	58.3	5.8	18.2	10.1	36.6
JP04	4.67	3.15	35.8	32.2	77.5	56.6	6.1	18.8	10.8	37.6
JP05	4.54	3.13	36.4	32.0	74.8	56.7	6.6	17.0	10.5	35.4
JP07	4.62	3.28	36.6	33.2	77.2	57.3	5.0	18.0	10.5	37.3
JP08	4.97	3.10	37.4	33.0	78.7	57.5	6.0	18.5	10.5	36.9
JP09	4.68	3.10	36.4	31.2	76.4	59.4	6.1	18.5	9.8	36.7
JP10	4.69	3.11	35.6	31.1	74.2	56.4	6.1	17.9	10.5	35.9
LA01	4.71	2.93	10.7	22.7	51.1	---	---	---	---	---
MY01	4.71	3.17	37.5	31.9	77.8	58.2	5.7	19.3	9.9	37.3
MN01	4.58	3.12	---	---	---	---	---	---	---	---
MM01	4.68	3.52	37.9	31.8	80.5	65.3	5.6	17.8	9.3	42.1
PH01	4.77	2.87	28.7	29.8	59.2	46.1	5.4	14.3	8.5	29.2
PH02	4.67	3.16	37.5	32.5	73.5	59.8	6.2	18.9	10.8	39.8
KR02	4.63	3.13	37.8	30.6	78.4	59.0	5.8	18.3	10.0	39.1
RU01	4.62	3.22	33.9	32.4	78.6	57.5	6.2	17.8	11.3	37.6
RU02	4.67	3.13	36.4	33.5	78.9	58.6	6.2	18.5	10.7	38.0
TH01	4.79	3.10	34.3	29.3	75.9	58.3	5.2	16.0	7.8	39.9
TH02	4.65	3.27	35.8	30.2	73.6	59.3	6.5	19.1	10.8	37.1
TH04	4.71	3.10	36.6	33.2	78.9	60.4	7.4	24.5	12.5	40.8
TH05	4.48	3.22	38.2	31.4	76.0	58.2	5.7	18.8	11.3	36.7
TH06	4.71	3.05	36.9	30.0	79.0	55.7	7.9	20.2	12.3	34.4
TH07	4.97	3.67	35.8	32.8	80.0	66.8	15.2	18.6	9.8	25.9
TH08	4.54	3.10	---	---	---	---	---	---	---	---
VN01	4.69	3.04	37.6	32.8	75.8	62.0	7.7	18.7	10.6	37.2
VN02	4.71	2.91	36.8	32.4	68.4	60.0	10.4	18.7	10.1	37.1
VN03	4.64	3.03	34.2	---	---	53.2	5.3	19.1	9.8	41.2
VN04	4.71	3.02	36.1	31.4	74.7	59.3	9.2	18.1	11.2	37.7
VN05	4.53	3.00	35.1	31.0	76.4	52.7	5.1	25.2	11.1	32.5
Prepared value	**4.60**	**3.25**	**37.1**	**32.9**	**78.7**	**58.7**	**6.3**	**18.6**	**10.8**	**37.1**
Number of data	37	37	34	33	33	33	33	33	34	33
Average	4.68	3.13	36.4	31.7	76.1	59.2	6.4	18.5	10.5	37.7
Minimum	4.48	2.59	28.7	25.9	59.2	52.7	5.0	14.3	7.8	29.2
Maximum	4.97	3.67	40.8	35.2	80.5	68.9	10.4	24.5	12.5	42.1
Standard deviation	0.11	0.18	2.32	1.56	4.21	3.52	1.14	1.59	0.96	2.58

Note: The outliers judged by 3S.D. method were painted with light mesh and were excluded from statistics;
"---", Not measured

Appendix Table 2.2.2 Analytical data concerning sample No. 122w

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	5.15	1.10	7.4	16.7	32.7	38.0	1.7	4.9	5.8	5.7
CN01	5.21	1.39	11.2	21.8	42.4	47.7	3.6	9.6	6.9	8.1
CN02	4.96	1.41	10.9	21.9	42.0	43.0	2.5	6.5	5.5	7.3
CN03	5.08	1.40	11.2	22.1	40.3	45.4	3.6	6.5	5.8	8.3
CN04	5.07	1.28	10.0	21.4	41.2	44.0	2.8	5.7	5.8	7.0
ID01	5.33	1.33	9.0	21.3	38.8	40.9	2.6	6.0	5.7	6.4
ID02	5.05	1.29	10.7	21.9	40.5	42.7	2.8	6.6	6.4	7.3
ID03	5.58	1.37	9.6	21.5	39.5	45.5	3.1	7.4	6.9	8.1
JP01	5.11	1.35	9.6	20.5	38.7	44.3	2.4	5.4	5.4	8.2
JP03	5.10	1.27	10.4	21.9	40.2	40.2	2.2	5.8	5.4	7.8
JP04	5.18	1.28	9.4	21.3	40.0	37.8	2.9	6.3	5.9	7.9
JP05	5.11	1.25	9.6	21.5	40.2	39.2	2.4	5.0	5.3	7.9
JP07	5.08	1.38	10.0	21.9	41.0	39.4	1.6	5.3	5.7	9.1
JP08	5.20	1.26	9.7	21.6	39.7	39.6	2.3	5.4	5.4	10.1
JP09	5.22	1.28	9.7	21.0	39.9	41.4	2.2	6.2	5.5	7.7
JP10	5.14	1.22	9.2	21.2	38.0	38.4	2.3	5.5	5.3	8.0
LA01	5.24	1.18	41.3	35.9	92.9	---	---	---	---	---
MY01	5.12	1.33	9.6	20.7	39.6	39.6	2.4	5.9	4.9	8.2
MN01	5.00	1.29	---	---	---	---	---	---	---	---
MM01	5.20	1.41	9.8	20.7	40.5	45.4	2.1	5.2	4.6	11.1
PH01	5.15	1.25	7.6	18.3	31.0	31.6	2.2	4.1	4.7	6.5
PH02	5.14	1.32	9.6	21.7	38.2	41.8	2.5	7.5	5.9	9.4
KR02	5.03	1.31	9.4	19.9	39.8	40.6	1.9	5.9	5.4	6.9
RU01	5.02	1.38	9.0	23.1	42.1	39.3	2.7	5.6	6.2	8.9
RU02	5.12	1.25	9.2	23.1	41.4	41.2	2.4	5.3	6.0	9.3
TH01	5.05	1.17	7.7	18.7	38.5	39.5	1.7	3.8	3.5	8.4
TH02	5.11	1.37	9.0	19.6	38.1	41.2	2.9	7.2	6.3	8.2
TH04	5.60	1.26	9.5	21.9	40.2	42.9	3.3	10.0	8.0	11.5
TH05	5.00	1.32	9.2	19.9	38.2	37.7	1.7	4.1	5.4	7.7
TH06	5.17	1.31	9.9	20.1	44.9	38.6	2.7	7.0	7.4	8.0
TH07	5.89	1.92	7.5	21.2	40.7	53.3	0.6	8.9	5.3	2.4
TH08	5.15	1.24	---	---	---	---	---	---	---	---
VN01	5.30	1.20	9.8	21.6	40.1	40.5	1.9	6.8	6.4	9.7
VN02	5.39	1.17	9.3	21.4	40.8	39.8	1.9	7.0	6.7	10.3
VN03	5.42	1.22	8.3	---	---	39.5	3.3	5.8	6.0	11.3
VN04	5.35	1.18	8.1	21.9	38.5	41.4	2.1	5.6	6.4	10.3
VN05	5.29	1.20	8.7	20.6	39.1	40.5	4.1	5.9	6.4	8.9
Prepared value	**5.10**	**1.31**	**9.7**	**21.6**	**40.4**	**40.4**	**2.5**	**5.6**	**5.6**	**8.3**
Number of data	36	36	34	33	33	33	34	34	34	33
Average	5.18	1.28	9.4	21.0	39.6	40.9	2.5	6.2	5.8	8.5
Minimum	4.96	1.10	7.4	16.7	31.0	31.6	0.6	3.8	3.5	5.7
Maximum	5.60	1.41	11.2	23.1	44.9	47.7	4.1	10.0	8.0	11.5
Standard deviation	0.15	0.08	0.95	1.29	2.44	2.94	0.67	1.36	0.82	1.39

Note: The outliers judged by 3S.D. method were painted with light mesh and were excluded from statistics;
"---", Not measured

Appendix 2.3 Normalized Data

Appendix Table 2.3.1 Deviation% from prepared values of sample No. 121w

Lab. ID	pH %	EC %	SO_4^{2-} %	NO_3^- %	Cl^- %	Na^+ %	K^+ %	Ca^{2+} %	Mg^{2+} %	NH_4^+ %
KH01	-0.2	-20.3	-18.1	-21.3	-15.1	-6.5	-17.5	-10.2	-3.7	-3.0
CN01	2.8	1.5	-3.0	-4.9	-2.0	17.4	14.3	6.5	2.8	5.4
CN02	-0.7	3.7	8.6	-1.5	0.6	4.4	1.6	6.5	-2.8	12.4
CN03	0.0	1.5	9.4	-4.9	-2.3	11.8	6.3	7.5	3.7	6.2
CN04	-0.7	0.3	10.0	-1.8	0.9	5.3	0.0	-8.1	-18.5	5.1
ID01	4.1	-4.0	-0.5	7.0	-6.4	-3.4	-9.5	-6.5	-4.6	7.5
ID02	1.5	-6.8	2.4	-0.9	0.1	-0.9	-3.2	4.8	2.8	-4.0
ID03	5.9	-13.5	-1.6	-0.6	-0.9	-0.3	17.5	-1.6	9.3	0.5
JP01	1.1	-1.5	-2.2	-2.7	-2.8	5.5	1.6	7.0	3.7	9.4
JP03	1.1	-2.2	-2.4	-2.7	0.6	-0.7	-7.9	-2.2	-6.5	-1.3
JP04	1.5	-3.1	-3.5	-2.1	-1.5	-3.6	-3.2	1.1	0.0	1.3
JP05	-1.3	-3.7	-1.9	-2.7	-5.0	-3.4	4.8	-8.6	-2.8	-4.6
JP07	0.4	0.9	-1.3	0.9	-1.9	-2.4	-20.6	-3.2	-2.8	0.5
JP08	8.0	-4.6	0.8	0.3	0.0	-2.0	-4.8	-0.5	-2.8	-0.5
JP09	1.7	-4.6	-1.9	-5.2	-2.9	1.2	-3.2	-0.5	-9.3	-1.1
JP10	2.0	-4.3	-4.0	-5.5	-5.7	-3.9	-3.2	-3.8	-2.8	-3.2
LA01	2.4	-9.8	-71.2	-31.0	-35.1	---	---	---	---	---
MY01	2.4	-2.5	1.1	-3.0	-1.1	-0.9	-9.5	3.8	-8.3	0.5
MN01	-0.4	-4.0	---	---	---	---	---	---	---	---
MM01	1.7	8.3	2.2	-3.3	2.3	11.2	-11.1	-4.3	-13.9	13.5
PH01	3.7	-11.7	-22.6	-9.4	-24.8	-21.5	-14.3	-23.1	-21.3	-21.3
PH02	1.5	-2.8	1.1	-1.2	-6.6	1.9	-1.6	1.6	0.0	7.3
KR02	0.7	-3.7	1.9	-7.0	-0.4	0.5	-7.9	-1.6	-7.4	5.4
RU01	0.4	-0.9	-8.6	-1.5	-0.1	-2.0	-1.6	-4.3	4.6	1.3
RU02	1.5	-3.7	-1.9	1.8	0.3	-0.2	-1.6	-0.5	-0.9	2.4
TH01	4.1	-4.6	-7.5	-10.9	-3.6	-0.7	-17.5	-14.0	-27.8	7.5
TH02	1.1	0.6	-3.5	-8.2	-6.5	1.0	3.2	2.7	0.0	0.0
TH04	2.4	-4.6	-1.3	0.9	0.3	2.9	17.5	31.7	15.7	10.0
TH05	-2.6	-0.9	3.0	-4.6	-3.4	-0.9	-9.5	1.1	4.6	-1.1
TH06	2.4	-6.2	-0.5	-8.8	0.4	-5.1	25.4	8.6	13.9	-7.3
TH07	8.0	12.9	-3.5	-0.3	1.7	13.8	141.3	0.0	-9.3	-30.2
TH08	-1.3	-4.6	---	---	---	---	---	---	---	---
VN01	2.0	-6.5	1.3	-0.3	-3.7	5.6	22.2	0.5	-1.9	0.3
VN02	2.4	-10.5	-0.8	-1.5	-13.1	2.2	65.1	0.5	-6.5	0.0
VN03	0.9	-6.8	-7.8	---	---	-9.4	-15.9	2.7	-9.3	11.1
VN04	2.4	-7.1	-2.7	-4.6	-5.1	1.0	46.0	-2.7	3.7	1.6
VN05	-1.5	-7.7	-5.4	-5.8	-2.9	-10.2	-19.0	35.5	2.8	-12.4
Number of data	37	37	35	34	34	34	34	34	34	34
Average	1.7	-3.7	-3.9	-4.3	-4.3	0.2	5.4	0.8	-2.8	0.6
Minimum	-2.6	-20.3	-71.2	-31.0	-35.1	-21.5	-20.6	-23.1	-27.8	-30.2
Maximum	8.0	12.9	10.0	7.0	2.3	17.4	141.3	35.5	15.7	13.5

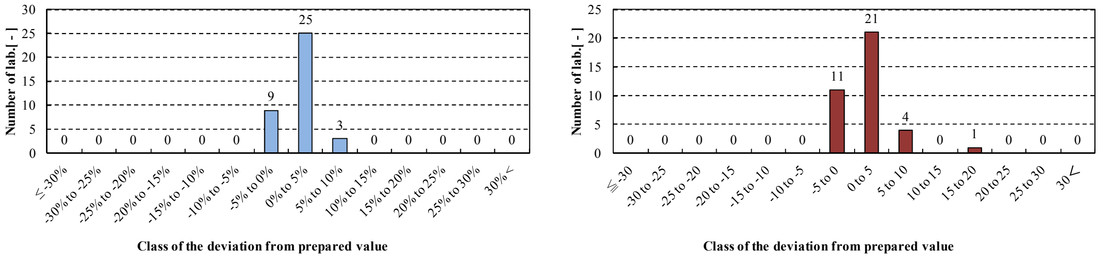
Note: "---", Not measured

Appendix Table 2.3.2 Deviation% from prepared values of sample No. 122w

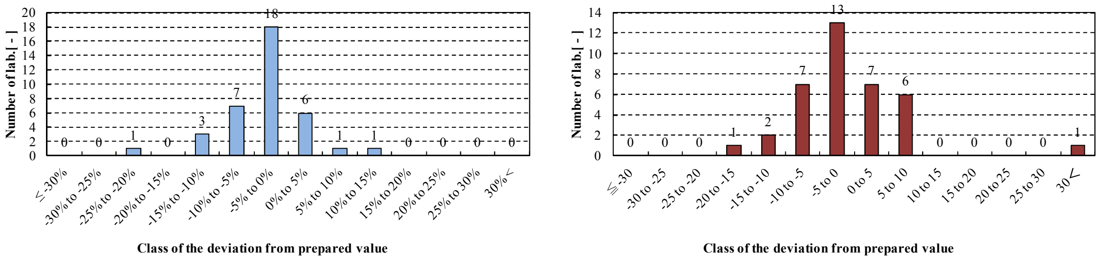
Lab. ID	pH %	EC %	SO_4^{2-} %	NO_3^- %	Cl^- %	Na^+ %	K^+ %	Ca^{2+} %	Mg^{2+} %	NH_4^+ %
KH01	1.0	-16.0	-23.7	-22.7	-19.1	-5.9	-32.0	-12.5	3.6	-31.3
CN01	2.2	6.1	15.5	0.9	5.0	18.1	44.0	71.4	23.2	-2.4
CN02	-2.7	7.6	12.4	1.4	4.0	6.4	0.0	16.1	-1.8	-12.0
CN03	-0.4	6.9	15.5	2.3	-0.2	12.4	44.0	16.1	3.6	0.0
CN04	-0.6	-2.3	3.1	-0.9	2.0	8.9	12.0	1.8	3.6	-15.7
ID01	4.5	1.5	-7.2	-1.4	-4.0	1.2	4.0	7.1	1.8	-22.9
ID02	-1.0	-1.5	10.3	1.4	0.2	5.7	12.0	17.9	14.3	-12.0
ID03	9.4	4.6	-1.0	-0.5	-2.2	12.6	24.0	32.1	23.2	-2.4
JP01	0.2	3.1	-1.0	-5.1	-4.2	9.7	-4.0	-3.6	-3.6	-1.2
JP03	0.0	-3.1	7.2	1.4	-0.5	-0.5	-12.0	3.6	-3.6	-6.0
JP04	1.6	-2.3	-3.1	-1.4	-1.0	-6.4	16.0	12.5	5.4	-4.8
JP05	0.2	-4.6	-1.0	-0.5	-0.5	-3.0	-4.0	-10.7	-5.4	-4.8
JP07	-0.4	5.3	3.1	1.4	1.5	-2.5	-36.0	-5.4	1.8	9.6
JP08	2.0	-3.8	0.0	0.0	-1.7	-2.0	-8.0	-3.6	-3.6	21.7
JP09	2.4	-2.3	0.0	-2.8	-1.2	2.5	-12.0	10.7	-1.8	-7.2
JP10	0.8	-6.9	-5.2	-1.9	-5.9	-5.0	-8.0	-1.8	-5.4	-3.6
LA01	2.7	-9.9	325.8	66.2	130.0	---	---	---	---	---
MY01	0.4	1.5	-1.0	-4.2	-2.0	-2.0	-4.0	5.4	-12.5	-1.2
MN01	-2.0	-1.5	---	---	---	---	---	---	---	---
MM01	2.0	7.6	1.0	-4.2	0.2	12.4	-16.0	-7.1	-17.9	33.7
PH01	1.0	-4.6	-21.6	-15.3	-23.3	-21.8	-12.0	-26.8	-16.1	-21.7
PH02	0.8	0.8	-1.0	0.5	-5.4	3.5	0.0	33.9	5.4	13.3
KR02	-1.4	0.0	-3.1	-7.9	-1.5	0.5	-24.0	5.4	-3.6	-16.9
RU01	-1.6	5.3	-7.2	6.9	4.2	-2.7	8.0	0.0	10.7	7.2
RU02	0.4	-4.6	-5.2	6.9	2.5	2.0	-4.0	-5.4	7.1	12.0
TH01	-1.0	-10.7	-20.6	-13.4	-4.7	-2.2	-32.0	-32.1	-37.5	1.2
TH02	0.2	4.6	-7.2	-9.3	-5.7	2.0	16.0	28.6	12.5	-1.2
TH04	9.8	-3.8	-2.1	1.4	-0.5	6.2	32.0	78.6	42.9	38.6
TH05	-2.0	0.8	-5.2	-7.9	-5.4	-6.7	-32.0	-26.8	-3.6	-7.2
TH06	1.4	0.0	2.1	-6.9	11.1	-4.5	8.0	25.0	32.1	-3.6
TH07	15.5	46.6	-22.7	-1.9	0.7	31.9	-76.0	58.9	-5.4	-71.1
TH08	1.0	-5.3	---	---	---	---	---	---	---	---
VN01	3.9	-8.4	1.0	0.0	-0.7	0.2	-24.0	21.4	14.3	16.9
VN02	5.7	-10.7	-4.1	-0.9	1.0	-1.5	-24.0	25.0	19.6	24.1
VN03	6.3	-6.9	-14.4	---	---	-2.2	32.0	3.6	7.1	36.1
VN04	4.9	-9.9	-16.5	1.4	-4.7	2.5	-16.0	0.0	14.3	24.1
VN05	3.7	-8.4	-10.3	-4.6	-3.2	0.2	64.0	5.4	14.3	7.2
Number of data	37	37	35	34	34	34	34	34	34	34
Average	1.9	-0.7	6.1	-0.6	1.9	2.1	-1.9	10.1	4.1	-0.1
Minimum	-2.7	-16.0	-23.7	-22.7	-23.3	-21.8	-76.0	-32.1	-37.5	-71.1
Maximum	15.5	46.6	325.8	66.2	130.0	31.9	64.0	78.6	42.9	38.6

Note: "---", Not measured

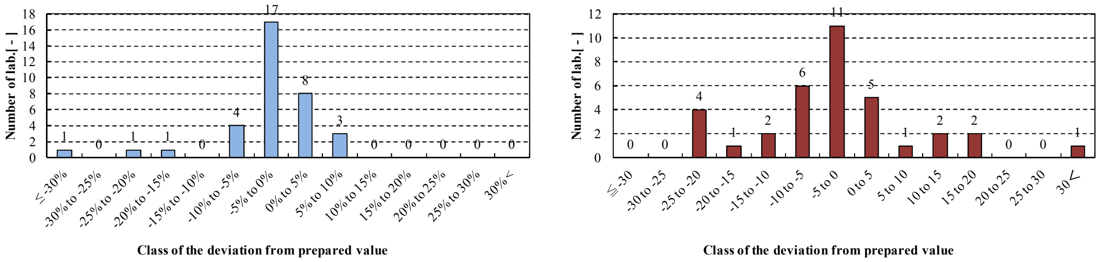
Appendix 2.4 Data Distribution



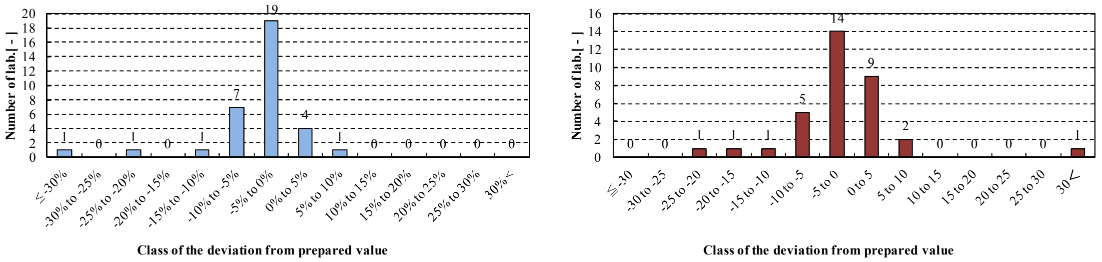
Appendix Figure 2.4.1 Data Distribution for pH (Left: 121w, Right: 122w)



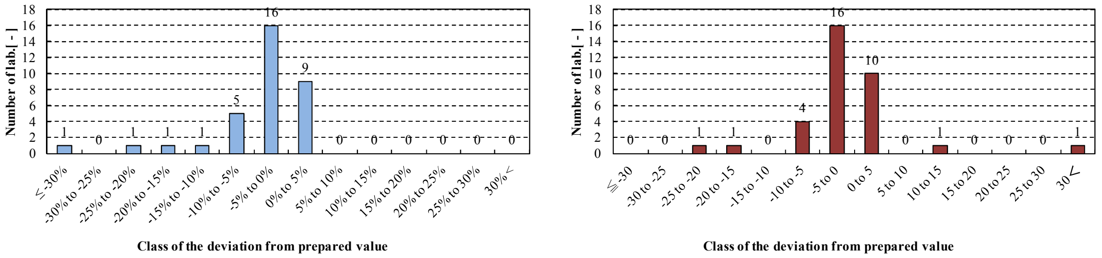
Appendix Figure 2.4.2 Data Distribution for EC (Left: 121w, Right: 122w)



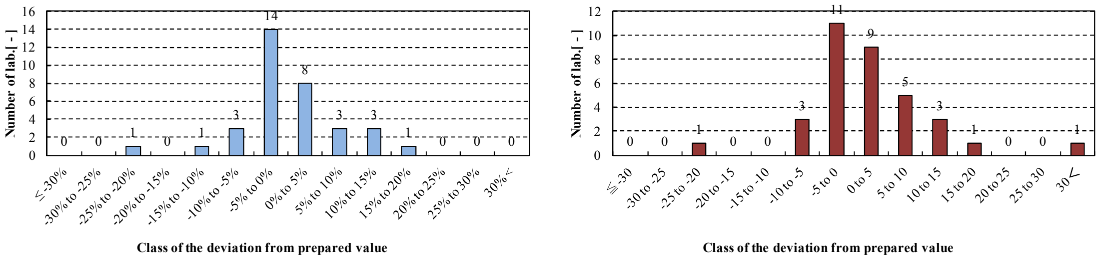
Appendix Figure 2.4.3 Data Distribution for SO_4^{2-} (Left: 121w, Right: 122w)



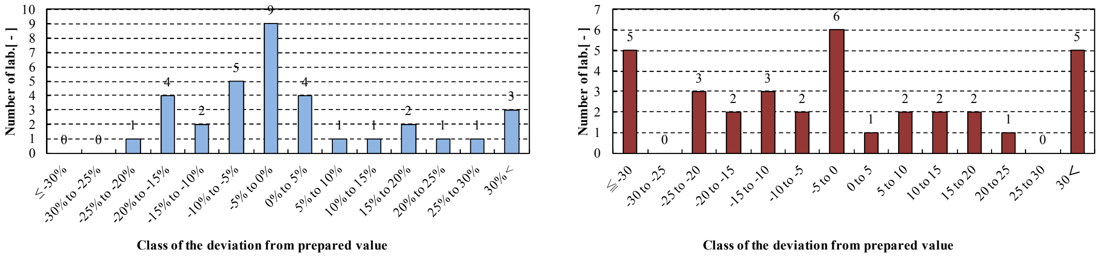
Appendix Figure 2.4.4 Data Distribution for NO_3^- (Left: 121w, Right: 122w)



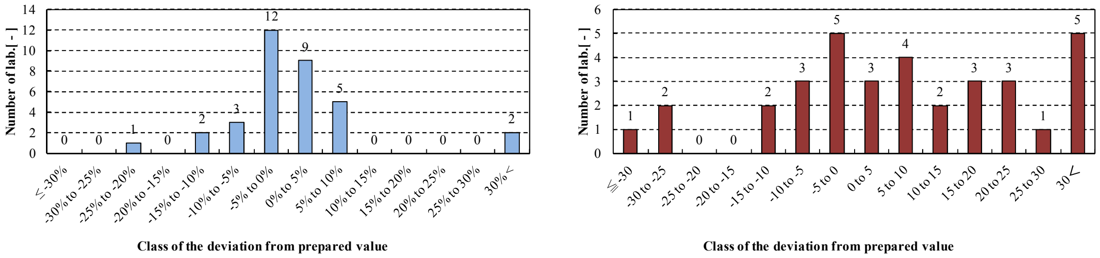
Appendix Figure 2.4.5 Data Distribution for Cl^- (Left: 121w, Right: 122w)



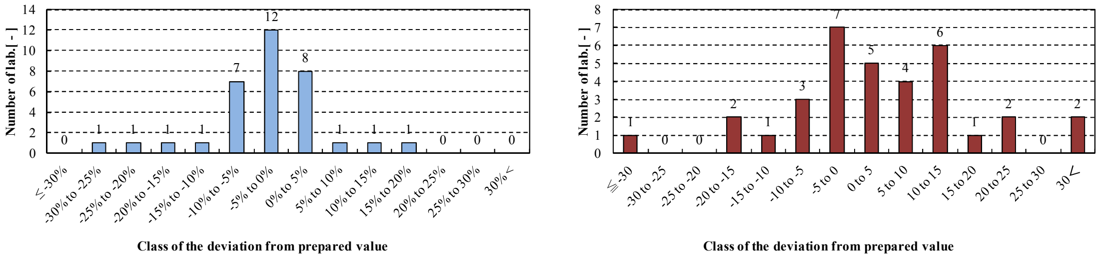
Appendix Figure 2.4.6 Data Distribution for Na^+ (Left: 121w, Right: 122w)



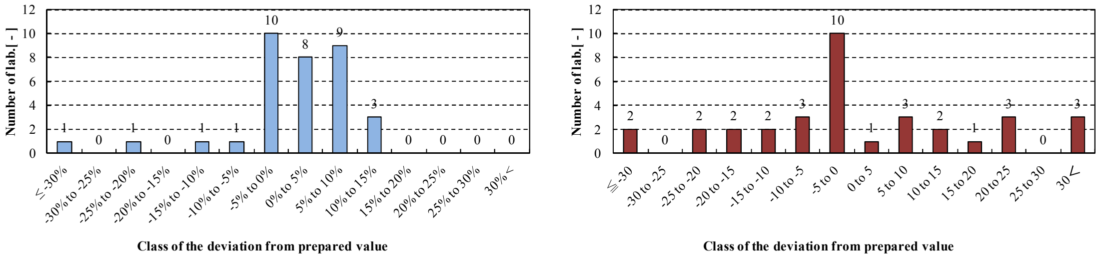
Appendix Figure 2.4.7 Data Distribution for K^+ (Left: 121w, Right: 122w)



Appendix Figure 2.4.8 Data Distribution for Ca^{2+} (Left: 121w, Right: 122w)



Appendix Figure 2.4.9 Data Distribution for Mg^{2+} (Left: 121w, Right: 122w)



Appendix Figure 2.4.10 Data Distribution for NH_4^+ (Left: 121w, Right: 122w)

3. 8th 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 2012. 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 27 laboratories in charge of EANET monitoring in 12 countries of EANET participated in this eighth 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.121d-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.121d-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.122d-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.122d-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.123d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Blank
No.123d-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.121d-1, No.122d-1, No.123d-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.121d-2, No.122d-2, No.123d-2

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

(3) Filtration

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

Note 1) Carry out the 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 4ºC.

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
SO_4^{2-} ,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:

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

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

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

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

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

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

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

$M_{sol,Sample}$: quantity (μg) of each component in the filtrate from sample No.121d-1,No.121d-2,No.122d-1 and No.122d-2;

$M_{sol,Blank}$: the average quantity (μg) in the filtrate from blank sample No.123d-1 and No.123d-2.

3.3 Results

The NC distributed the filter samples to 27 laboratories in the participating countries of EANET, and received their results from 26 laboratories. The results compared to the prepared values are summarized in Table 3.3. The average, minimum, maximum, standard deviation (S.D.) and number of data (N) were calculated from each analyzed ion quantity. Analytical results of Samples No.121d and No.122d 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, five data were rejected.

As shown in Table 3.3, the deviations ($\Delta V/V\mathrm{p}$) for SO_4^{2-} in Sample No. 121d and Sample No.122d were -8.9% and -11.1%. The deviations for Cl^- in Sample No. 121d and Sample No.122d were -9.7% and -14.4%. The deviations for NH_4^+ were within ±5%.

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

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

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

The evaluation of the results on both Samples No.121d and No.122d 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* (*V*p)	Average (*V*a)	Δ*V*/*V*p* (%)	S.D.	Number (N)	Minimum	Maximum
Sample No. 121d								
SO_4^{2-}	(μg)	22	20.0	-8.9	1.43	23	17.4	21.9
Cl^-	(μg)	2.5	2.26	-9.7	0.99	24	0.04	6.02
NH_4^+	(μg)	20	20.3	1.3	2.77	26	14.8	27.8
Sample No. 122d								
SO_4^{2-}	(μg)	170	151	-11.1	11.7	24	123	165
Cl^-	(μg)	11	9.42	-14.4	1.30	24	7.37	14.0
NH_4^+	(μg)	70	67.5	-3.6	6.25	25	49.8	80.2

* Prepared: Prepared values

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

3.3.1 Evaluation of Laboratories' Performance (by sample)

Samples No. 121d-1, No.121d-2

For Sample No.121d, 12 analytical data in 76 results were flagged E, and 9 analytical data were flagged X. The total percentage of flagged samples was 27.9%. (Figure 3.2, Table 3.4 and 3.5).

Table 3.4 Number of flagged data for Sample No.121d

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E*	5	4	3	12
Flag X*	2	5	2	9
Data within DQOs	18	16	21	55
Ratio of Flagged (%)	28.0	36.0	19.2	27.6

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

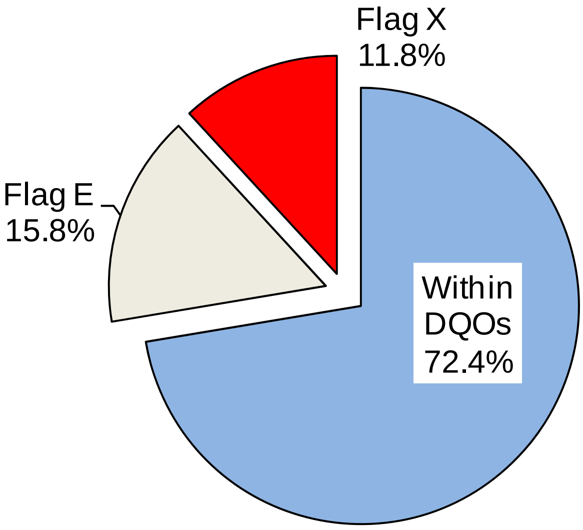


Figure 3.1 Percentage of flagged data for Sample No.121d

Table 3.5 Average analytical results of Sample No.121d

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
KH01	20.0	2.25	19.5
CN02	4.76 X	6.10 X	21.9
ID01	20.1	2.22	20.4
ID03	21.1	2.39	19.4
JP01	19.3	2.06 E	18.3
JP02	21.6	2.36	19.7
JP03	21.9	2.37	20.1
JP04	21.9	2.49	20.0
JP05	21.4	2.55	19.0
JP08	21.9	2.45	16.2 E
JP09	19.5	2.64	17.7
JP10	21.2	2.36	19.8
MY01	17.4 E	2.32	21.7
MM01	18.3 E	1.75 E	14.8 E
PH01	17.5 E	2.25	19.1
PH02	20.2	0.83 X	22.7
KR02	18.5 E	2.49	20.0
RU01	--	--	19.7
TH01	19.7	2.60	21.8

TH02	19.1	1.86 E	20.5
TH04	21.9	1.21 X	21.0
TH05	21.0	2.50	26.7 X
TH06	20.5	2.29	21.0
TH07	3.62 X	0.04 X	27.8 X
VN01	18.7	6.02 X	22.1
VN02	18.4 E	1.87 E	15.6 E

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

*--: not measured

Samples No. 122d-1, No.122d-2

For Sample No.122d, 17 analytical data in 76 results were flagged E and 5 analytical data were flagged X. The total percentage of flagged samples was 28.9%. (Figure 3.3, Table 3.6 and 3.7).

Table 3.6 Number of flagged data for Sample No.122d

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E*	6	9	2	17
Flag X*	1	3	1	5
Data within DQOs	18	13	23	54
Ratio of Flagged (%)	28.0	48.0	11.5	28.9

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

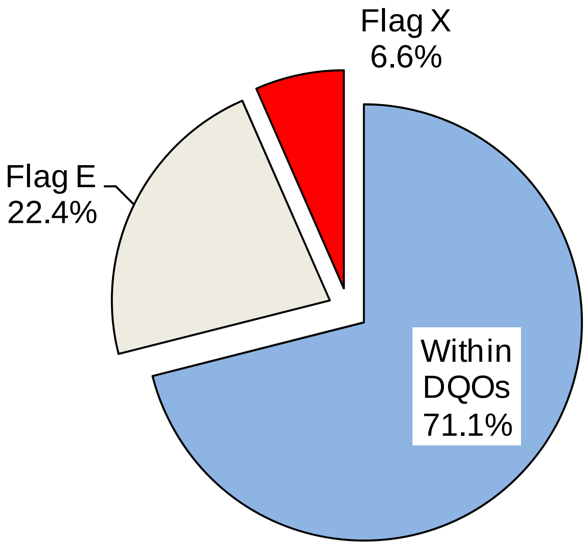


Figure 3.2 Percentage of flagged data for Sample No.122d

Table 3.7 Average analytical results of Sample No.122d

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
KH01	153	8.36 E	68.4
CN02	82.1 X	14.5 X	78.2
ID01	162	9.58	67.4
ID03	150	8.94 E	71.0
JP01	165	9.39	68.0
JP02	161	10.3	66.8
JP03	157	9.52	67.7
JP04	165	10.7	68.8
JP05	153	9.82	65.3
JP08	159	10.1	49.8 E
JP09	156	10.1	61.7
JP10	153	9.86	68.3
MY01	152	10.1	75.1
MM01	133 E	8.16 E	62.6
PH01	159	8.41 E	66.4
PH02	143 E	7.37 X	66.0
KR02	160	10.1	63.5

RU01	--	--	67.3
TH01	157	9.20 E	73.8
TH02	134 E	7.48 X	68.1
TH04	159	9.43	67.0
TH05	151	9.10 E	80.2
TH06	158	9.49	66.3
TH07	129 E	7.99 E	92.9 X
VN01	134 E	14.0 E	73.6
VN02	123 E	8.48 E	55.2 E

*Flag E: 15% < | Deviation | ≤ 30%
*Flag X: 30% < | Deviation |
*--: not measured

Blank Sample (No.123d)

Each quantity of SO_4^{2-}, Cl^-, and NH_4^+ was determined for blank sample No.123d-1 and No.123d-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.123d (blank)

Lab. Code	SO_4^{2-} (µg)	Cl^- (µg)	NH_4^+ (µg)
KH01	2.33	1.04	0.00
CN02	0.00	0.22	0.00
ID01	0.25	0.50	0.10
ID03	0.32	0.85	0.81
JP01	0.19	0.34	0.22
JP02	0.07	0.39	0.17
JP03	0.00	1.14	0.27
JP04	0.41	0.37	0.09
JP05	1.51	0.78	0.30
JP08	0.00	0.66	0.16
JP09	0.00	0.97	0.26

JP10	0.13	0.30	0.30
MY01	0.13	0.45	0.13
MM01	0.55	1.87	6.21
PH01	5.64	3.68	1.00
PH02	9.94	2.80	0.97
KR02	0.38	1.85	4.14
RU01	--	--	1.28
TH01	0.29	1.31	0.39
TH02	0.54	0.44	0.33
TH04	1.48	0.00	0.23
TH05	3.07	1.44	0.00
TH06	0.27	0.27	0.34
TH07	0.00	0.00	0.18
VN01	0.86	0.67	0.00
VN02	5.00	0.00	1.20
Average	1.33	0.89	0.73
Median	0.32	0.66	0.27
Minimum	0.00	0.00	0.00
Maximum	9.94	3.68	6.21
Standard deviation	2.30	0.87	1.36

*--: not measured

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

	Sample No.121d			Sample No.122d		
Lab. Code	SO_4^{2-}	Cl^-	NH_4^+	SO_4^{2-}	Cl^-	NH_4^+
KH01	10.4	31.6	0.0	1.5	11.1	0.0
CN02	0.0	3.4	0.0	0.0	1.5	0.0
ID01	1.2	18.5	0.5	0.2	5.0	0.1
ID03	1.5	26.3	4.0	0.2	8.7	1.1
JP01	1.0	14.2	1.2	0.1	3.5	0.3
JP02	0.3	14.1	0.9	0.0	3.6	0.3
JP03	0.0	32.5	1.3	0.0	10.7	0.4

JP04	1.8	13.1	0.5	0.2	3.4	0.1
JP05	6.6	23.5	1.6	1.0	7.4	0.5
JP08	0.0	21.3	1.0	0.0	6.2	0.3
JP09	0.0	26.7	1.5	0.0	8.7	0.4
JP10	0.6	11.3	1.5	0.1	3.0	0.4
MY01	0.7	16.3	0.6	0.1	4.3	0.2
MM01	2.9	51.7	29.6	0.4	18.7	9.0
PH01	24.3	62.1	5.0	3.4	30.4	1.5
PH02	33.0	77.2	4.1	6.5	27.5	1.4
KR02	2.0	42.6	17.1	0.2	15.5	6.1
RU01	--	--	6.1	--	--	1.9
TH01	1.4	33.6	1.8	0.2	12.5	0.5
TH02	2.7	19.2	1.6	0.4	5.6	0.5
TH04	6.4	0.0	1.1	0.9	0.0	0.3
TH05	12.8	36.5	0.0	2.0	13.6	0.0
TH06	1.3	10.6	1.6	0.2	2.8	0.5
TH07	0.0	0.0	0.6	0.0	0.0	0.2
VN01	4.4	10.0	0.0	0.6	4.6	0.0
VN02	21.4	0.0	7.1	3.9	0.0	2.1

▨ : Data flagged E
■ : Data flagged X
-- : Not measured

3.3.2 Comparison of Laboratories' Performance (by Analyte)

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

SO_4^{2-} (Sulfate)

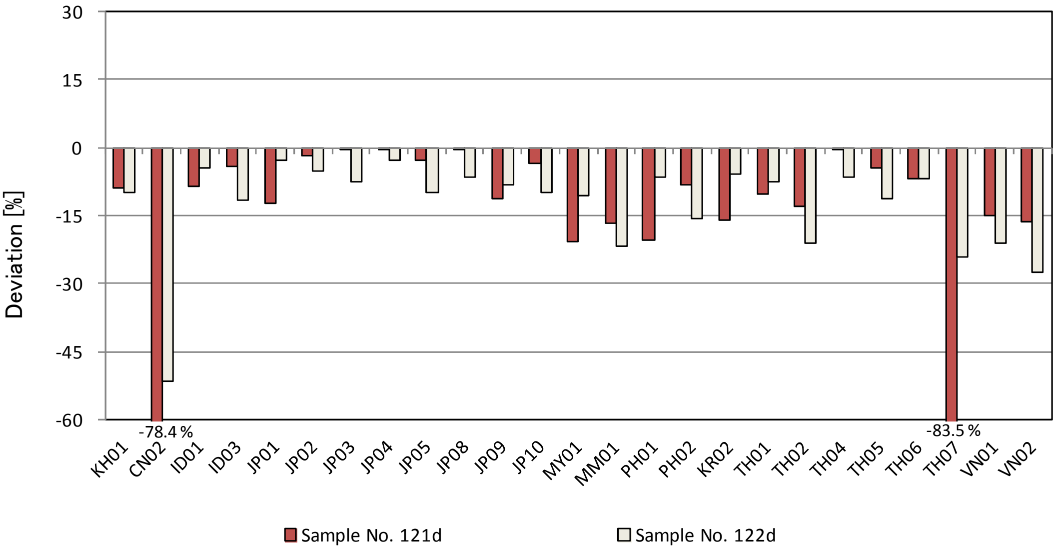


Figure 3.3 Deviation for SO_4^{2-}

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

Table 3.10.1 Analytical method of SO_4^{2-}

Analytical Method	
Ion Chromatography	25/25

Table 3.10.2 Flagged data of SO_4^{2-}

Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.121d	5	2	28.0
Sample No.122d	6	1	28.0

All participating laboratories used Ion Chromatography for the determination of SO_4^{2-}.
E flag appeared at 5 laboratories and X flag appeared at 2 laboratories for Sample No.121d. E flag appeared at 6 laboratories and X flag appeared at 1 laboratory for Sample No.122d. Four laboratories were flagged E or X for both samples.

Cl^- (Chloride)

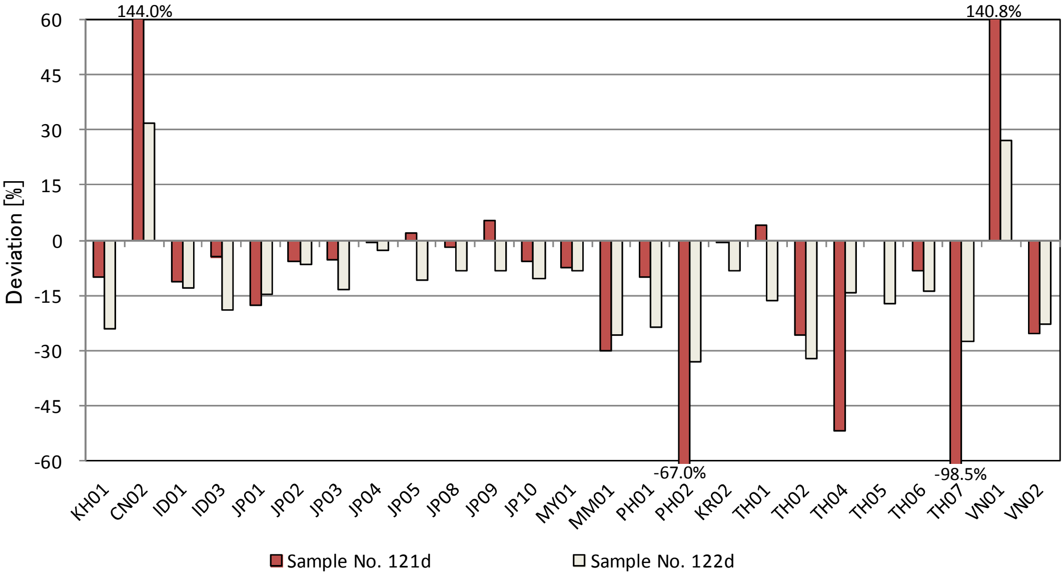


Figure 3.4 Deviation for Cl^-

Table 3.11.1 Analytical method of Cl^-

Analytical Method	
Ion Chromatography	25/25

Table 3.11.2 Flagged data of Cl^-

Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.121d	4	5	36.0
Sample No.122d	9	3	48.0

As with the analysis of Cl^-, all laboratories used Ion Chromatography for the determination of Cl^-. E flag appeared at 4 laboratories and X flag appeared at 5 laboratories for Sample No.121d. E flag appeared at 9 laboratories and X flag appeared at 3 laboratories for Sample No. 122d. Seven laboratories were flagged E or X for both samples.

NH_4^+ (Ammonium)

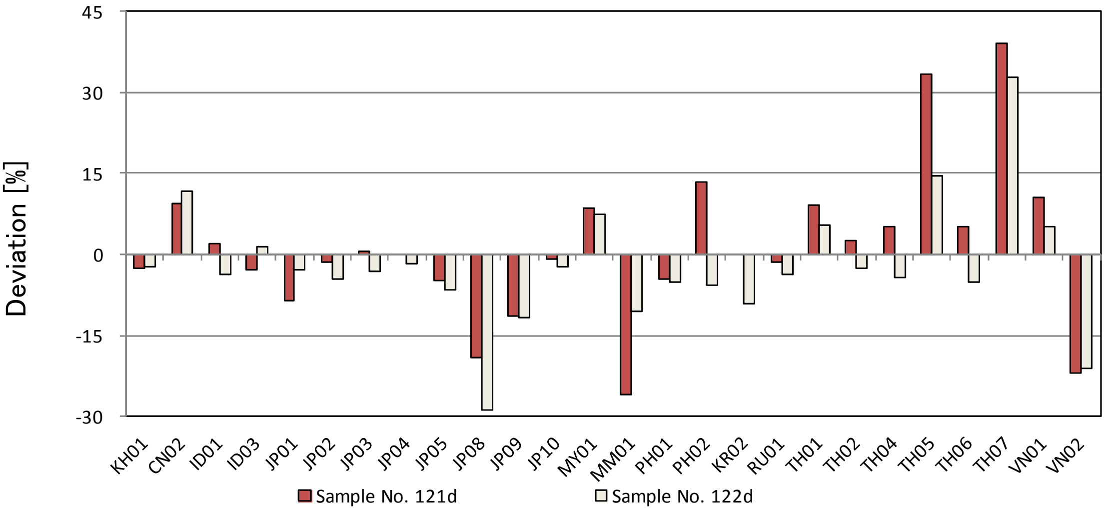


Figure 3.5 Deviation for NH_4^+

Table 3.12.1 Analytical method of NH_4^+

Analytical Method	
Ion Chromatography	25/26
Spectrophotometry (Nessler)	1/26

Table 3.12.2 Flagged data of NH_4^+

Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.121d	3	2	19.2
Sample No.122d	2	1	11.5

Twenty-five laboratories used Ion Chromatography and one laboratory used Spectrophotometry (Nessler). E flag appeared at 3 laboratories and X flag appeared at 2 laboratories for Sample No.121d. E flag appeared at 2 laboratories and X flag appeared at 1 laboratory for Sample No. 122d. Three laboratories were flagged E or X for both samples.

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-five laboratories used ion chromatography and one laboratory used Spectrophotometry (Nessler) .

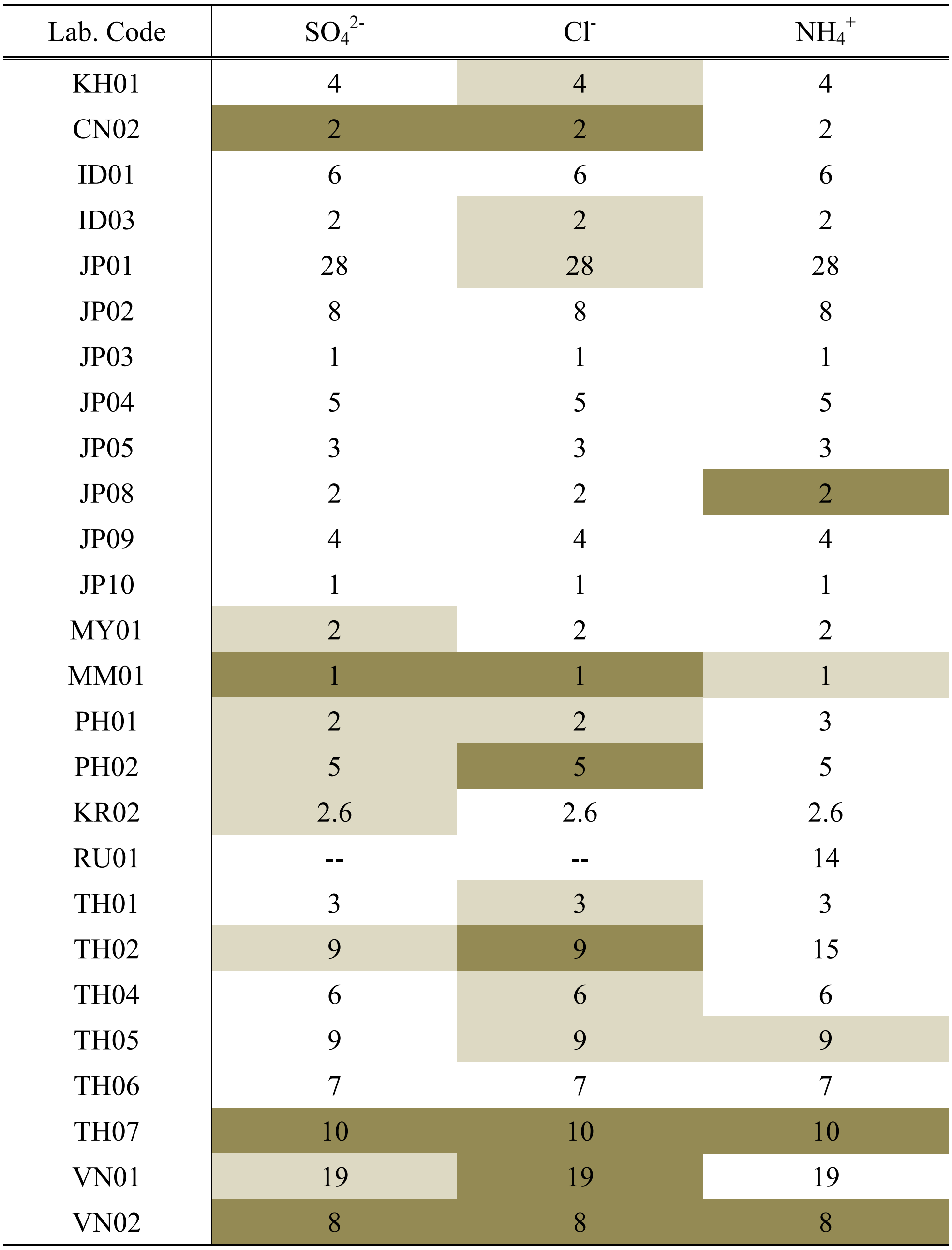
Table 3.13 Analytical methods used for sample analysis

Lab. Code	SO_4^{2-},Cl^-	NH_4^+
KH01	Ion Chromatography	
CN02	Ion Chromatography	
ID01	Ion Chromatography	
ID03	Ion Chromatography	
JP01	Ion Chromatography	
JP02	Ion Chromatography	
JP03	Ion Chromatography	
JP04	Ion Chromatography	
JP05	Ion Chromatography	
JP08	Ion Chromatography	
JP09	Ion Chromatography	
JP10	Ion Chromatography	
MY01	Ion Chromatography	
MM01	Ion Chromatography	
PH01	Ion Chromatography	
PH02	Ion Chromatography	
KR02	Ion Chromatography	
RU01	(not measured)	Spectrophotometry (Nessler)
TH01	Ion Chromatography	
TH02	Ion Chromatography	
TH04	Ion Chromatography	
TH05	Ion Chromatography	
TH06	Ion Chromatography	
TH07	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.121d or 122d. Data in dark gray color cells indicate flagged data in both Sample No.121d and No.122d.

Table 3.14 Years of staff experience (unit: year)



Lab. Code	SO_4^{2-}	Cl^-	NH_4^+
KH01	4	4	4
CN02	2	2	2
ID01	6	6	6
ID03	2	2	2
JP01	28	28	28
JP02	8	8	8
JP03	1	1	1
JP04	5	5	5
JP05	3	3	3
JP08	2	2	2
JP09	4	4	4
JP10	1	1	1
MY01	2	2	2
MM01	1	1	1
PH01	2	2	3
PH02	5	5	5
KR02	2.6	2.6	2.6
RU01	--	--	14
TH01	3	3	3
TH02	9	9	15
TH04	6	6	6
TH05	9	9	9
TH06	7	7	7
TH07	10	10	10
VN01	19	19	19
VN02	8	8	8

░ : One datum (either sample) is flagged.

▓ : Two data (both samples) are flagged.

-- : Not measured

Flagged Data

In the results of Sample No.121d and 122d, the total number of flagged data was 43 (E: 29, X: 14) in the whole values (152). The number of flagged data in each laboratory is shown in Figure 3.8. Nine laboratories met DQOs (34.6%).

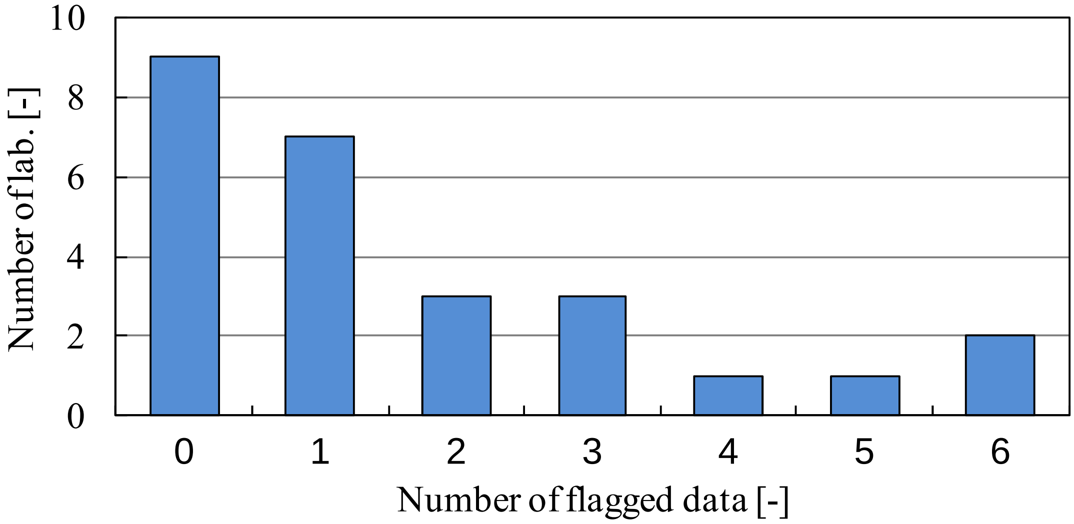


Figure 3.6 Number of flagged data and laboratories

Calibration standard solution

Table 3.15 shows the lowest and highest concentrations of their calibration standard solutions (SO_4^{2-}, Cl^-, NH_4^+) used in each laboratory, and also shows their concentrations of the prepared values in µmol 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	0.0	52.0	0.0	141.3	0.0	277.2
CN02	0.0	102.0	0.0	112.7	0.0	285.7
ID01	0.0	104.2	0.0	84.5	0.0	166.7
ID03	0.0	104.2	0.0	112.7	0.0	110.9
JP01	0.0	104.5	0.0	282.4	0.0	278.0
JP02	0.0	104.1	0.0	282.1	0.0	332.6
JP03	0.0	104.1	0.0	56.4	0.0	221.7
JP04	0.0	104.1	0.0	141.0	0.0	277.2
JP05	0.0	104.1	0.0	141.0	0.0	277.2
JP08	0.0	83.4	0.0	225.9	0.0	222.4
JP09	0.0	104.1	0.0	282.1	0.0	554.4
JP10	0.0	104.1	0.0	28.2	0.0	277.2
MY01	0.0	93.9	0.0	254.2	0.0	277.3
MM01	0.0	78.8	0.0	42.3	0.0	162.9
PH01	0.0	208.2	0.0	564.2	0.0	1108.6
PH02	0.0	104.1	0.0	282.1	0.0	554.3
KR02	0.0	104.1	0.0	282.1	0.0	277.2
RU01	--	--	--	--	0.0	222.2
TH01	0.0	104.2	0.0	282.1	0.0	277.2
TH02	0.2	104.1	0.6	282.1	1.1	277.2
TH04	0.0	104.1	0.0	28.2	0.0	332.6
TH05	0.0	83.3	0.0	56.4	0.0	221.7
TH06	0.0	93.7	0.0	253.9	0.0	221.7
TH07	0.0	104.1	0.0	141.0	0.0	166.3
VN01	0.0	104.1	0.0	141.0	0.0	277.2
VN02	0.0	109.3	0.0	84.6	0.0	99.8
*Sample No. 121d	11.5		3.53		55.4	
*Sample No. 122d	88.5		15.5		194	

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

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

*--: not measured

*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.

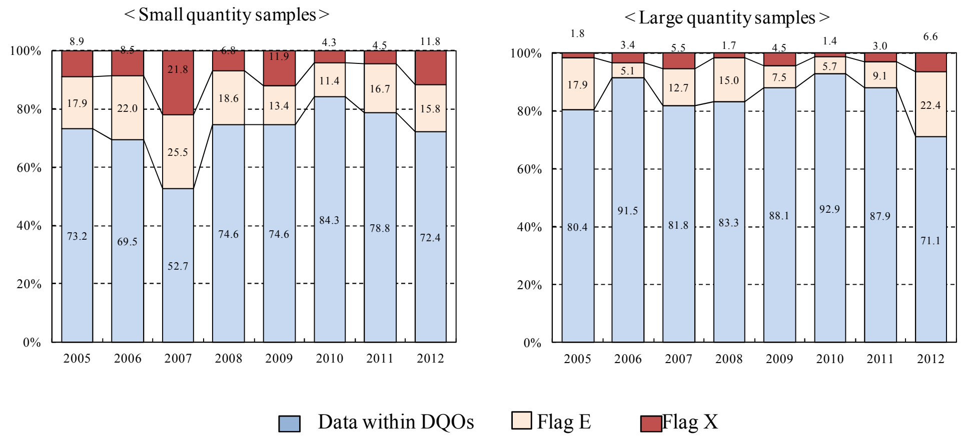


Figure 3.7 Comparison of DQOs' results for the past years

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

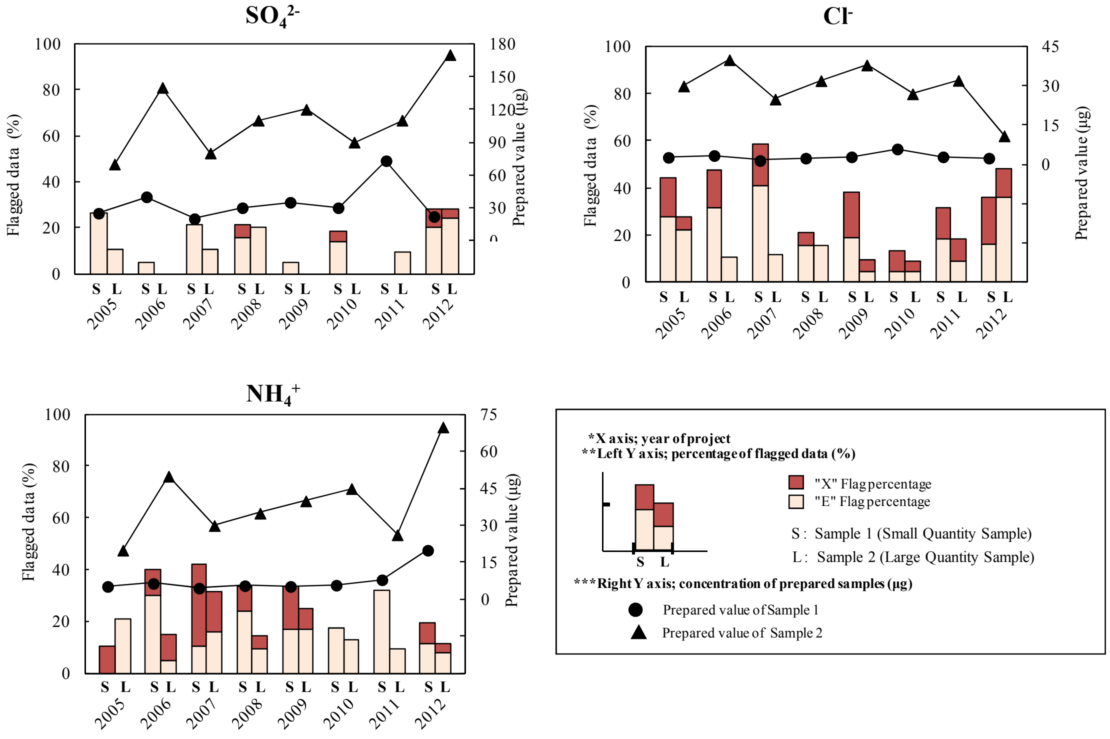


Figure 3.8 Comparison for each parameter in inter-laboratory comparison project

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4. 14th 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 14th project, Network Center (NC) provided two soil samples (No.121 and No.122) 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

Seventeen laboratories of 8 countries participated in the 14th 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.121: Cambisols
Sample No.122: Cambisols

Soils for Sample No.121 and No.122 were collected in Japanese cedar (*Cryptomeria japonica*) plantation established about 50 years ago in Toyama prefecture, Japan. Both soils were collected from B-horizon composed chiefly of soil minerals. The soils were air-dried, sieved to separate the fine earth fraction (< 2 mm) and mixed well by the following procedures; 1) the bulk sample was divided into two parts, 2) each part was mixed well, 3) the parts were joined and mixed well and 4) the sample was divided again. This procedure was repeated 15 times to ensure a completely homogeneous bulk sample. Finally, portions of 400 - 500 g were weighed out, packed in 500 ml plastic bottles, and then, sterilized using radioisotope (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.121 and 122
a) Moisture Content	wt %	M
b) pH (H_2O)		M
c) pH (KCl)		M
d) Exchangeable Ca^{2+}	$cmol_c$ kg^{-1}	M
e) Exchangeable Mg^{2+}	$cmol_c$ kg^{-1}	M
f) Exchangeable K^+	$cmol_c$ kg^{-1}	M
g) Exchangeable Na^+	$cmol_c$ kg^{-1}	M
h) Exchangeable acidity	$cmol_c$ kg^{-1}	M
i) Exchangeable Al^{3+}	$cmol_c$ kg^{-1}	M
j) Exchangeable H^+	$cmol_c$ kg^{-1}	M

M: Mandatory items

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

4.2.4 Analytical Methodologies

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

4.2.4.1 Standardization of methods

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

(1) **Atomic absorption spectrometry (AAS)** method should be used basically for analysis of Ex-Ca, Mg, K and Na. (If it is impossible to use AAS, Flame (emission) photometry method is allowable for Ex-K and Na).
(2) **Titration method** should be used for analysis of Ex-acidity, Al and H.
(3) **Calibration curve method** should be used for determination of Ex-Ca, Mg, K and Na.
(4) The Samples should be extracted and diluted with **1M CH_3COONH_4 (pH 7.0)** for analysis of Ex-Ca, Mg, K and Na. Then, 1M CH_3COONH_4 (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 CH_3COONH_4 (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. ($SrCl_2$ solution eliminates the interference of the sample.) And then make to volume with 1M CH_3COONH_4 (pH 7.0). This solution is named " Prepared sample".
(3) Prepare three "prepared samples".
(4) Prepare each standard solution with diluting 1M CH_3COONH_4 (pH 7.0) solution.
(5) Add 100g-Sr/L solution to each standard solution to be the same concentration $SrCl_2$ as the sample.
(6) Analyze the standard solution and the prepared samples by AAS.

(7) Store the calibration curves certainly and report them together with reporting formats.

(8) **Repeat the procedure 1) - 7) twice.**

(9) Calculation of content in the soil

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

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

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

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

Ex-Na ($\mathrm{cmol_c\ kg^{-1}}$ 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:

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

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

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

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. On the 14th inter-laboratory project, pH, cation exchangeable capacity and exchangeable acidity were clearly different between both samples, respectively. pH, exchangeable Ca and Mg were higher in No.121 than in No.122, whereas exchangeable acidity, Al and H were much lower in No.121 than in No.122. We observed the large variations in the analyzed data (CVs) of exchangeable acidity in No.121 (e.g. 210% and 127% in Ex-acidity and H). Meanwhile, in both samples, CVs were moderate for exchangeable cations (25 - 86%) and enough small for pH (1.8 - 3.1%).

Table 4.2 Statistical summary

Statistics	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol$_c$ kg^{-1}						
	No. 121								
Number of Laboratories	17	17	14	14	13	13	17	17	17
Total average	5.6	4.5	5.5	0.7	0.2	0.1	0.7	0.1	0.5
Median	5.5	4.5	6.0	0.8	0.2	0.1	0.3	0.1	0.2
Maximum	5.7	4.7	7.6	1.0	0.4	0.4	5.9	0.7	5.4
Minimum	5.3	4.5	0.8	0.3	0.1	0.0	0.1	0.0	0.0
Standard deviation	0.1	0.1	1.8	0.2	0.1	0.1	1.4	0.2	1.3
CV (%)^{*1}	2.3	1.8	32.9	25.3	40.4	67.3	210.6	126.9	251.8
	No. 122								
Number of Laboratories	17	17	14	14	13	13	17	17	17
Total average	4.5	3.8	1.04	0.31	0.16	0.12	11.60	9.89	2.10
Median	4.5	3.8	0.89	0.30	0.17	0.11	10.68	9.52	1.06
Maximum	4.7	4.0	3.57	0.47	0.28	0.32	31.37	15.43	15.86
Minimum	4.2	3.6	0.03	0.12	0.04	0.05	3.08	6.96	0.67
Standard deviation	0.1	0.1	0.90	0.08	0.06	0.07	5.56	1.91	3.59
CV (%)^{*1}	3.2	3.1	86.4	26.3	37	62	47.9	19.4	171

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.121 and 122 analyzed by 17 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 plots showed several “non-parametrical” outliers in each property. Those outliers might be due to wrong calculation, procedure, irregular contamination, and so on because the values were 5-20 times higher or lower than average. Therefore, in following section, we removed these outliers by parametrically statistical method to calculate the good reference more close to true value.

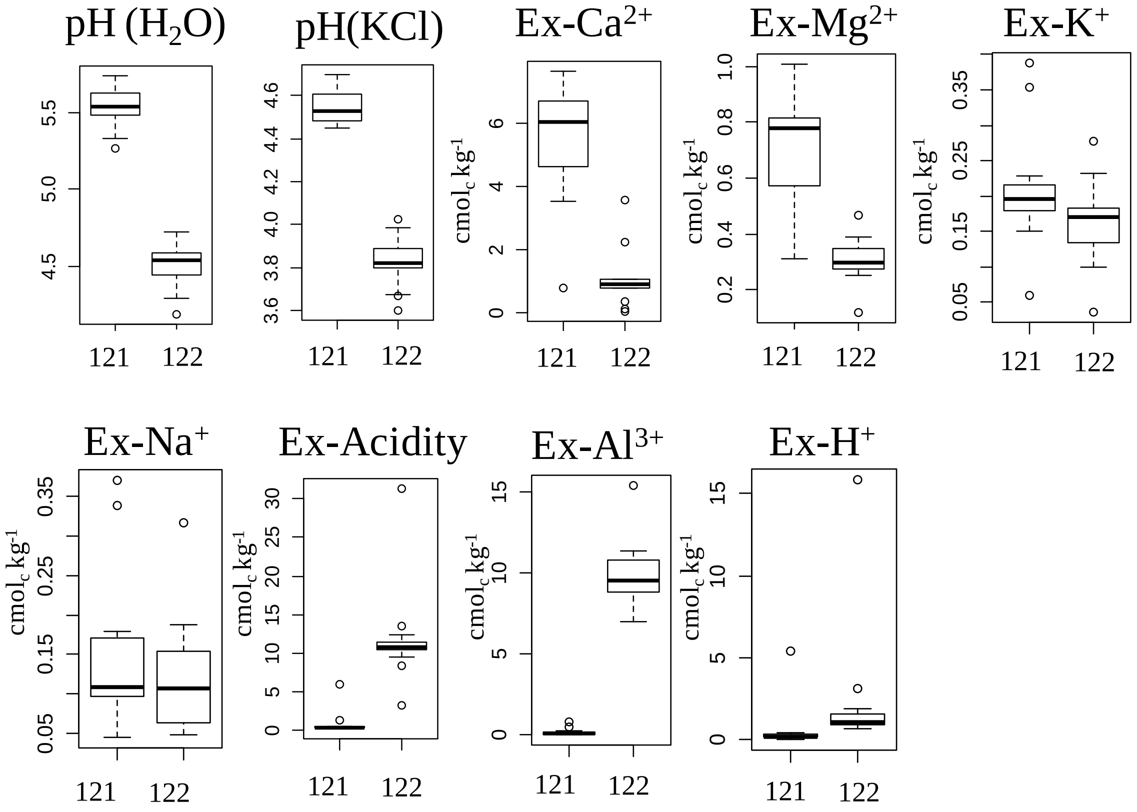

Figure 4.1 Data variability of No.121 and No.122

Table 4.3 Data verification by Cochran-Grubbs methods

No.121

Country	Lab.	Repeat analysis	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
					cmol$_c$ kg^{-1}						
China	CN01	1st	5.7	4.6	0.8 g	0.3	0.2	0.0	0.1	0.0	0.2
		2nd	5.7	4.7	0.8 g	0.3	0.2	0.0	0.1	0.0	0.2
	CN02	1st	5.7	4.6	4.0	0.6	0.2	0.1	0.3 c	0.1	0.2 **c**
		2nd	5.7	4.6	4.0	0.6	0.1	0.1	0.3 c	0.1	0.2 **c**
	CN03	1st	5.6	4.7	4.6	0.5	0.2	0.1	1.2 g	0.7 g	0.4 **c**
		2nd	5.6	4.7	4.6	0.5	0.2	0.1	1.2 g	0.8 g	0.5 **c**
	CN04	1st	5.7	4.5	6.3	0.8	0.2	0.2 c	0.2	0.1	0.1 **c**
		2nd	5.7	4.5	6.4	0.8	0.2	0.2 c	0.2	0.1	0.1 **c**
Indonesia	ID01	1st	5.5	4.5	5.4	0.8	0.2	0.1	0.3	0.1	0.1
		2nd	5.5	4.5	5.4	0.8	0.2	0.0	0.3	0.1	0.1
	ID04	1st	5.4 **c**	4.5	5.7	1.0 **c**	0.1	0.1	0.2	0.1	0.2
		2nd	5.3 **c**	4.5	5.7	1.1 **c**	0.1	0.1	0.2	0.1	0.2
Mongolia	MN01	1st	5.4	4.7					0.4	0.0	0.4 **g**
		2nd	5.4	4.7					0.4	0.0	0.4 **g**
Malaysia	MY04	1st	5.5	4.4	7.6	0.9	0.2 **c**	0.3	5.3 **c**	0.4 **c**	4.9 **c**
		2nd	5.5	4.5	7.7	0.9	0.1 **c**	0.4	6.5 **c**	0.5 **c**	5.9 **c**
Phillipin	PH03	1st	5.5	4.5	7.0 **c**	0.8	0.2	0.1	0.3	0.1	0.2 **c**
		2nd	5.5	4.5	6.4 **c**	0.8	0.2	0.1	0.3	0.1	0.2 **c**
	PH03*	1st	5.6 **c**	4.5	7.3	0.7	0.2	0.1	0.2	0.0	0.2
		2nd	5.5 **c**	4.5	7.3	0.7	0.2	0.1	0.2	0.0	0.2
Russia	RU01	1st	5.7	4.6	6.8	0.8	0.2	0.2	0.2	0.1	0.1
		2nd	5.7	4.6	6.8	0.8	0.2	0.2	0.2	0.1	0.1
Thailand	TH01	1st	5.6	4.5	5.5	0.8	0.4	0.1	0.3	0.2	0.0
		2nd	5.6	4.5	5.9	0.8	0.4	0.1	0.3	0.2	0.0
	TH06	1st	5.5	4.6	6.9	0.5	0.4	0.4	0.2	0.2	0.1
		2nd	5.5	4.6	6.5	0.6	0.4	0.4	0.2	0.2	0.0
Vietnum	VN01	1st	5.6	4.5	6.4	0.9	0.2	0.1	0.3	0.1	0.2
		2nd	5.6	4.4	6.4	0.9	0.2	0.1	0.3	0.1	0.2
	VN02	1st	5.3	4.5					0.3	0.0	0.3 **c**
		2nd	5.3	4.5					0.3	0.0	0.3 **c**
	VN03	1st	5.5	4.5					0.3	0.2	0.1
		2nd	5.5	4.5					0.3	0.2	0.1
	VN04	1st	5.6	4.5	3.4	0.6			0.3	0.0	0.3 **c**
		2nd	5.6	4.5	3.6	0.7			0.3	0.0	0.3 **c**

Note; The outliers judged by Cochran and Grubbs methods were marked with **c** and **g**, respectively.

*Additional dataset submitted by PH03

No.122

Country	Lab.	Repeat analysis	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
					cmol$_c$ kg^{-1}						
China	CN01	1st	4.7	4.0	0.0	0.1 **g**	0.1	0.0 **g**	3.1 **g**	7.0	3.1 **g**
		2nd	4.7	4.0	0.0	0.1 **g**	0.1	0.0 **g**	3.1 **g**	7.0	3.1 **g**
	CN02	1st	4.7	3.9	0.8	0.3	0.1	0.1	10.8 **c**	9.7 **c**	1.1
		2nd	4.7	3.9	0.8	0.3	0.1	0.1	10.3 **c**	9.3 **c**	1.0
	CN03	1st	4.7	4.0	1.0	0.3	0.1	0.2	9.6	8.3	1.3
		2nd	4.7	4.0	1.0	0.3	0.1	0.2	9.5	8.2	1.3
	CN04	1st	4.6	3.8	1.1	0.3	0.2	0.2	10.5 **c**	9.0 **c**	1.5
		2nd	4.6	3.8	1.0	0.3	0.2	0.2	10.2 **c**	8.6 **c**	1.6
Indonesia	ID01	1st	4.4	3.7	1.0	0.3	0.2	0.1	11.0	10.0	1.0
		2nd	4.4	3.7	1.0	0.3	0.2	0.1	10.9	9.9	1.0
	ID04	1st	4.4	3.9 **c**	0.8	0.4	0.0	0.1	9.5	8.7	0.8
		2nd	4.4	3.9 **c**	0.9	0.4	0.0	0.1	9.5	8.8	0.8
Mongolia	MN01	1st	4.6	4.0					10.7	9.9	0.8
		2nd	4.6	4.0					10.7	9.9	0.8
Malaysia	MY04	1st	4.6	3.8	2.1 **c**	0.3	0.2	0.3 **g**	34.1 **c**	16.8 **c**	17.2 **c**
		2nd	4.6	3.8	2.3 **c**	0.4	0.2	0.3 **g**	28.6 **c**	14.0 **c**	14.5 **c**
Phillipin	PH03	1st	4.5	3.8	0.8	0.3	0.2	0.1	10.6	9.4	1.2
		2nd	4.5	3.8	0.8	0.2	0.2	0.1	10.4	9.3	1.2
	PH03*	1st	4.5 **c**	3.6	3.5 **c**	0.2	0.2	0.1	10.4	9.4	1.1
		2nd	4.4 **c**	3.6	3.7 **c**	0.3	0.2	0.1	10.4	9.4	1.1
Russia	RU01	1st	4.2	3.9	1.0	0.3	0.2	0.1	8.3	7.3	1.0
		2nd	4.2	4.0	1.0	0.3	0.2	0.1	8.3	7.3	1.0
Thailand	TH01	1st	4.5	3.8 **c**	0.8	0.3	0.3 **c**	0.1	11.5 **c**	11.0 **c**	1.3 **c**
		2nd	4.5	3.8 **c**	0.8	0.3	0.3 **c**	0.1	10.8 **c**	10.3 **c**	1.0 **c**
	TH06	1st	4.5	3.9	0.9	0.3	0.2	0.2	11.4	10.7	0.7
		2nd	4.6	3.9	0.9	0.3	0.2	0.2	11.5	10.8	0.7
Vietnum	VN01	1st	4.5	3.8	0.1	0.4	0.2	0.1	11.1	9.5	1.6
		2nd	4.5	3.8	0.1	0.4	0.2	0.1	11.2	9.5	1.6
	VN02	1st	4.3	3.7					12.4	11.2	0.9
		2nd	4.3	3.7					12.4	11.2	0.9
	VN03	1st	4.6	3.8					13.6	11.4	1.9
		2nd	4.6	3.8					13.4	11.3	1.9
	VN04	1st	4.5	3.7	0.3	0.5 **g**			12.3	11.1	0.9
		2nd	4.5	3.7	0.3	0.5 **g**			12.3	11.0	0.8

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. “PH03” in Ex-Ca, “MY04” in Ex-acidity of No.121. Then, the rest of data were tested by Grubbs method (examination of the average value of each laboratory). In this method, the laboratory which has remarkably large or small average was judged as outliers. Cochran-Grubbs method detected the several outliers for each parameter. As a result of removing outliers, the “verified” dataset consisting of 15-17 laboratories in pH, 12-13 laboratories in base cations and 10-15 laboratories in acid cations and exchangeable acidity 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.121 and No.122 were shown in Table 4.4. Although chemical properties in both soils were not largely changed by verification, the data variability of exchangeable acidity decreased from entire dataset. The variation included an error produced by same person (repetition), different person (within-laboratory) or different laboratories (inter-laboratory). We separated this variation in next section to detect the source of it.

Table 4.4 Statistical summary of the "verified" dataset*2

Statistics	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			$cmol_c\ kg^{-1}$						
	No. 121								
Number of Laboratories	15	17	12	13	12	12	14	15	10
Total average	5.6	4.5	5.85	0.69	0.21	0.15	0.26	0.09	0.14
Median	5.6	4.5	6.04	0.78	0.20	0.11	0.26	0.10	0.15
Maximum	5.7	4.7	7.64	0.90	0.39	0.37	0.40	0.22	0.24
Minimum	5.3	4.5	3.52	0.31	0.06	0.05	0.12	0.00	0.02
Standard deviation	0.1	0.1	1.28	0.17	0.09	0.10	0.08	0.08	0.07
CV (%)*1	2.2	1.8	21.9	24.2	41.7	71.2	29.5	84.3	50.4
	No. 122								
Number of Laboratories	16	15	13	12	12	12	12	13	14
Total average	4.5	3.8	0.84	0.31	0.15	0.13	10.89	9.52	1.12
Median	4.5	3.8	0.87	0.30	0.17	0.12	10.81	9.52	1.00
Maximum	4.7	4.0	2.22	0.39	0.23	0.32	13.49	11.36	1.89
Minimum	4.2	3.6	0.03	0.25	0.04	0.06	8.30	6.96	0.67
Standard deviation	0.1	0.1	0.54	0.05	0.05	0.07	1.42	1.42	0.36
CV (%)*1	3.2	3.3	64.3	15.0	33.4	59.3	13.0	14.9	32.1

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-Na. The result suggests that triplicate analyses were carried out under the same condition. In general, the participating laboratories could analyze the parameters with their own standard procedures and stable instruments.

2) Within-laboratory precision

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

3) Inter-laboratories precision

The CVs in the inter-laboratories precision were less than 5% in pH (H_2O) and pH (KCl). However, the CVs of exchangeable bases and acidity ranged 13 to 84%. We discussed the possible factor of the relatively high CVs in inter-laboratory precision, in the following section.

4) Calculation of permissible tolerance

The repeatability limit and within-laboratory reproducibility limit might be enough small to use as a reference value for the repeat analysis on the instrumental analysis in the respective laboratories. For assessment of temporal pH change of monitoring data at each site, participating laboratories can detect the significant change more than 0.1 pH units. Meanwhile, the result about reproducibility limit (inter-laboratories reproducibility limit) suggested that participating laboratories can detect the significant difference between the monitoring sites if the differences are more than about 0.3-0.4 for pH, 1.0 – 3.6 $\mathrm{cmol_c\ kg^{-1}}$ in Ex-Ca, 0.1 – 0.5 $\mathrm{cmol_c\ kg^{-1}}$ in Ex-Mg and 0.2 – 4.0 $\mathrm{cmol_c\ kg^{-1}}$ in Ex-acidity.

Table 4.5 Analysis of variance for “verified” dataset

Statistics	No. 121								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	15	17	12	13	12	12	14	15	9
Total sum of square	250992	214550	177262	2936	227	110	488	66	48
ST/lmd	2789	2103	2462	38	3	2	6	1	1
Number of Data	90	102	72	78	72	72	84	90	54
Total sum	501.0	463.2	421.03	54.18	15.07	10.51	22.08	8.10	6.96
Total average	5.6	4.5	5.85	0.69	0.21	0.15	0.26	0.09	0.13
Sum of square inter-laboratories (S_R)	1.3	0.6	108.61	2.03	0.50	0.71	0.47	0.48	0.20
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.34	0.01	0.00	0.00	0.00	0.00	0.00
Sum of square repeatablility (S_r)	0.1	0.0	3.00	0.04	0.00	0.18	0.01	0.01	0.01
Total sum of square (S_T)	1.4	0.7	111.94	2.07	0.50	0.89	0.48	0.49	0.21
Inter-laboratories degree of freedom (ϕ_R)	14	16	11	12	11	11	13	14	8
Within-laboratory degree of freedom (ϕ_{RW})	15	17	12	13	12	12	14	15	9
Repeatability degree of freedom (ϕ_r)	60	68	48	52	48	48	56	60	36
Total degree of freedom (ϕ_T)	89	101	71	77	71	71	83	89	53
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.09	0.04	9.873	0.169	0.046	0.065	0.036	0.035	0.025
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.028	0.001	0.000	0.000	0.000	0.000	0.000
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.063	0.001	0.000	0.004	0.000	0.000	0.000
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.02	0.01	1.641	0.028	0.008	0.011	0.006	0.006	0.004
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	-0.011	0.000	0.000	-0.001	0.000	0.000	0.000
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.063	0.001	0.000	0.004	0.000	0.000	0.000
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.1	0.1	1.28	0.17	0.09	0.10	0.08	0.08	0.07
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.10	0.01	0.00	0.01	0.01	0.00	0.00
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.25	0.03	0.01	0.06	0.02	0.01	0.01
Inter-laboratories precision CV (%)	2.2	1.8	21.94	24.17	41.68	71.18	29.53	84.32	50.48
Within-laboratory precision CV (%)	0.2	0.3	1.66	1.99	1.72	6.95	2.33	5.55	0.73
Repeatability precision CV (%)	0.6	0.4	4.28	3.78	3.14	41.48	5.78	12.92	10.49
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.35	0.22	3.592	0.470	0.244	0.291	0.217	0.213	0.182
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.03	0.03	0.271	0.039	0.010	0.028	0.017	0.014	0.003
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.11	0.06	0.825	0.087	0.022	0.200	0.050	0.038	0.045

Statistics	No. 122								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	16	15	12	12	12	11	12	13	14
Total sum of square	188353	118728	2743	501	123	52	614861	550909	8790
ST/lmd	1962	1319	38	7	2	1	8540	7063	105
Number of Data	96	90	72	72	72	66	72	78	84
Total sum	434.0	344.6	52.38	22.39	11.07	7.18	784.13	742.23	93.76
Total average	4.5	3.8	0.73	0.31	0.15	0.11	10.89	9.52	1.12
Sum of square inter-laboratories (S_R)	1.9	1.3	8.80	0.14	0.17	0.13	132.77	145.20	9.99
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.02	0.01	0.00	0.00	0.07	0.06	0.04
Sum of square repeatablility (S_r)	0.1	0.0	0.15	0.01	0.00	0.01	0.16	0.22	0.41
Total sum of square (S_T)	2.0	1.3	8.97	0.17	0.18	0.15	133.00	145.47	10.44
Inter-laboratories degree of freedom (ϕ_R)	15	14	11	11	11	10	11	12	13
Within-laboratory degree of freedom (ϕ_{RW})	16	15	12	12	12	11	12	13	14
Repeatability degree of freedom (ϕ_r)	64	60	48	48	48	44	48	52	56
Total degree of freedom (ϕ_T)	95	89	71	71	71	65	71	77	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.13	0.09	0.800	0.013	0.016	0.013	12.070	12.100	0.768
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.002	0.001	0.000	0.000	0.006	0.005	0.003
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.003	0.000	0.000	0.000	0.003	0.004	0.007
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.02	0.02	0.133	0.002	0.003	0.002	2.011	2.016	0.128
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	0.000	0.000	0.000	0.000	0.001	0.000	-0.001
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.003	0.000	0.000	0.000	0.003	0.004	0.007
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.1	0.1	0.37	0.05	0.05	0.05	1.42	1.42	0.36
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.02	0.02	0.00	0.01	0.05	0.04	0.03
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.06	0.02	0.01	0.02	0.06	0.06	0.09
Inter-laboratories precision CV (%)	3.2	3.3	50.21	14.99	33.41	42.83	13.02	14.92	32.06
Within-laboratory precision CV (%)	0.3	0.1	3.43	5.24	2.24	7.67	0.42	0.41	2.90
Repeatability precision CV (%)	0.9	0.3	7.64	5.27	4.69	15.77	0.52	0.68	7.65
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.41	0.35	1.023	0.131	0.144	0.131	3.971	3.976	1.002
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.03	0.01	0.070	0.046	0.010	0.023	0.128	0.110	0.091
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.13	0.04	0.183	0.054	0.024	0.057	0.188	0.212	0.282

4.3.5 Inter-laboratory variations in each parameter

To assess the precision in each laboratories and properties, we showed scatter plots between No.121 and No.122 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 Grubbs method (as mentioned above) were denoted by §. The plot did not include extreme outliers for eye-friendly.

1) pH

Linear correlation between No.121 and No.122 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.121 and No.122. No laboratories were judged by outliers using Grubbs method for pH(H_2O) and pH(KCl).

2) Base cations

The plots of exchangeable base cations (Figure 4.4 to 4.7) also suggested the systematic errors of the inter-laboratory variation. The error might be caused by the condition of ammonium acetate (extraction liquid), standard solution or dilution rate. 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. More than half laboratories were included in the range of 20% of verified mean for Ex-Ca, Ex-Mg and Ex-K in both samples.

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). 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). In Ex-acidity, Al and H, 2-3 outliers have been detected in Grubbs method.

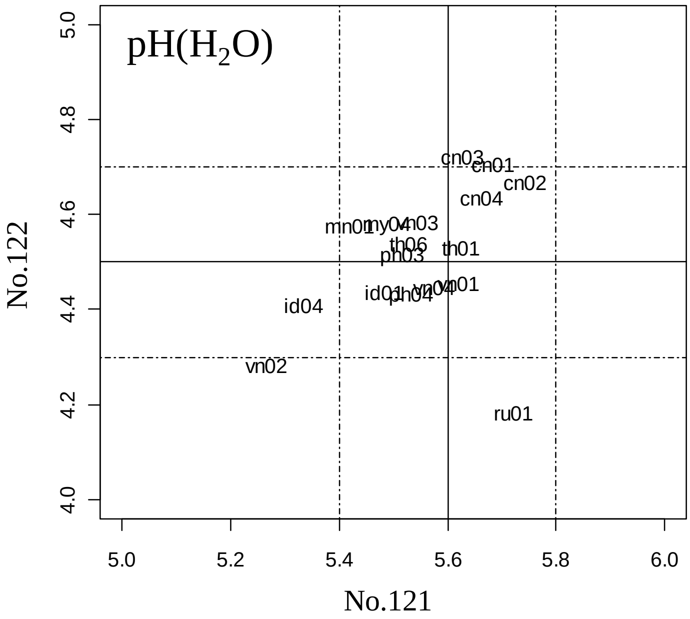

Figure 4.2 Scatter diagram of pH (H_2O) between No.121 and No.122 (Solid lines show mean of verified datasets and dashed lines show 0.2 pH units from the mean.)

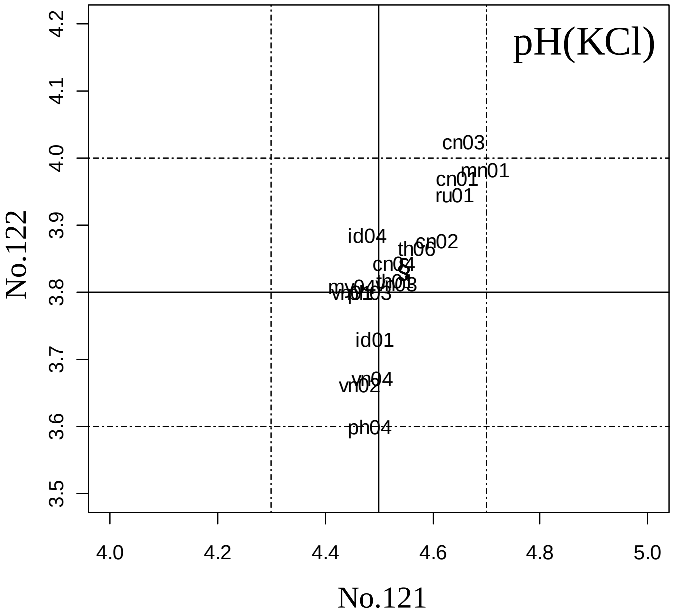

Figure 4.3 Scatter diagram of pH (KCl) between No.121 and No.122 (Solid lines show mean of verified datasets and dashed lines show 0.2 pH units from the mean.)

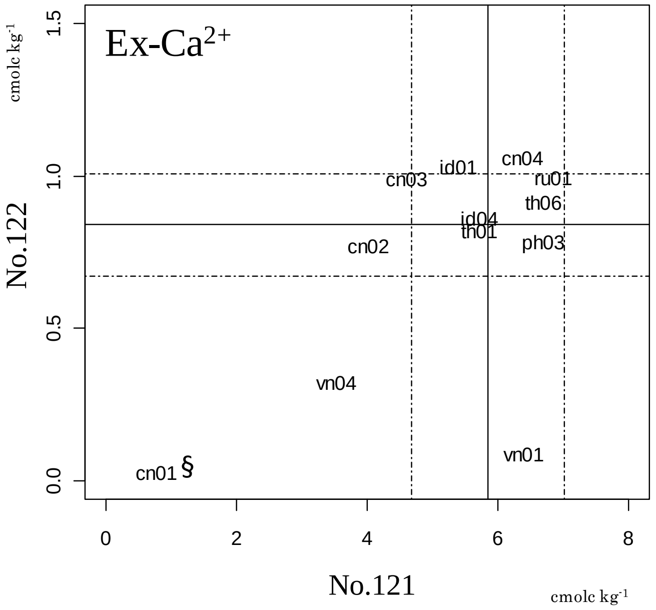

Figure 4.4 Scatter plot of Ex-Ca between No.121 and No.122 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Grubbs method were denoted by §.)

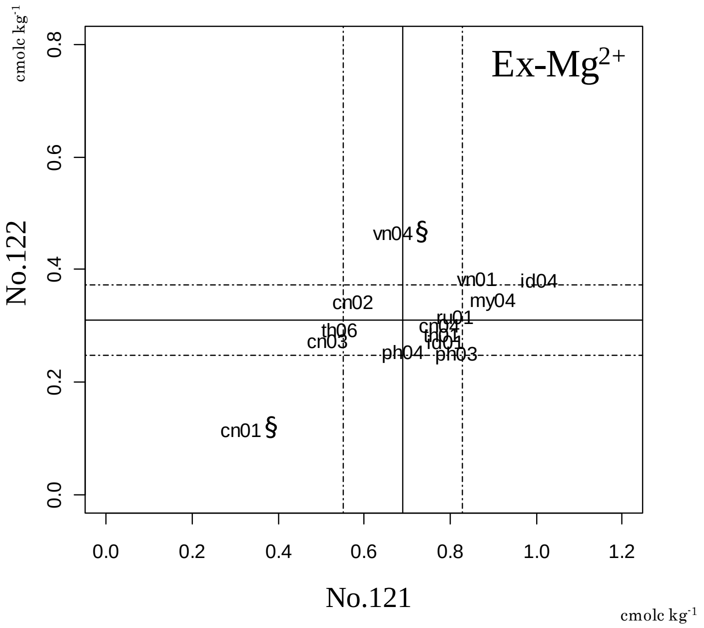

Figure 4.5 Scatter plot of Ex-Mg between No.121 and No.122 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Grubbs method were denoted by §.)

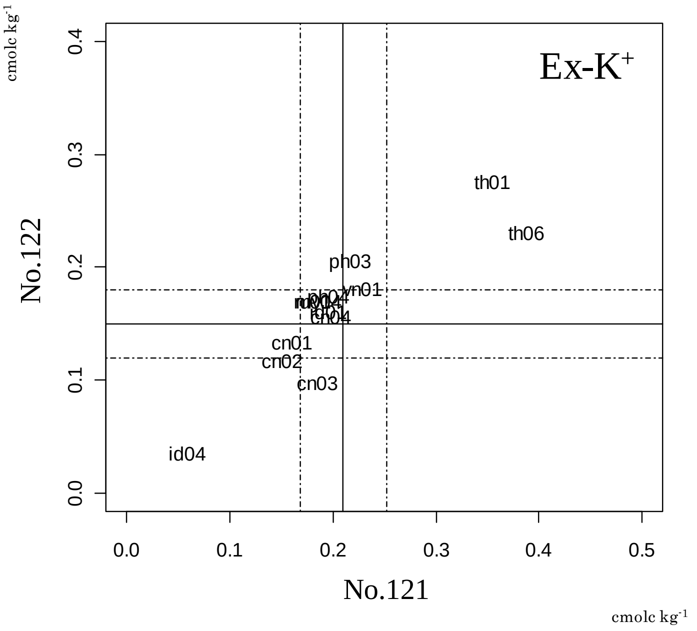

Figure 4.6 Scatter plot of Ex-K between No.121 and No.122 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean.)

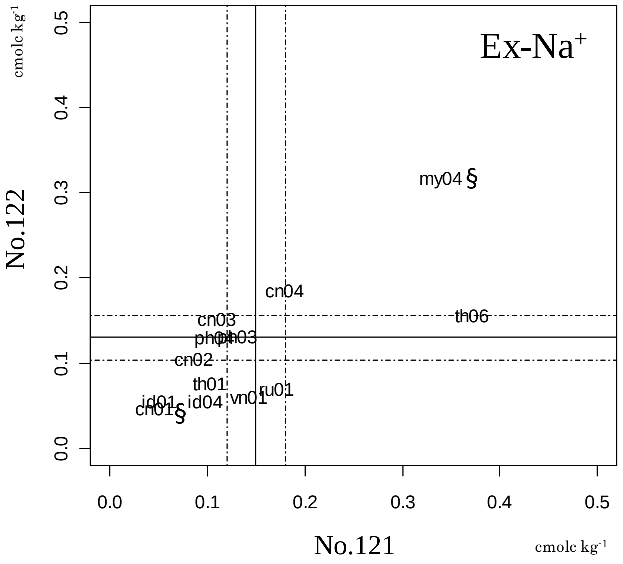

Figure 4.7 Scatter plot of Ex-Na between No.121 and No.122 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Grubbs method were denoted by §.)

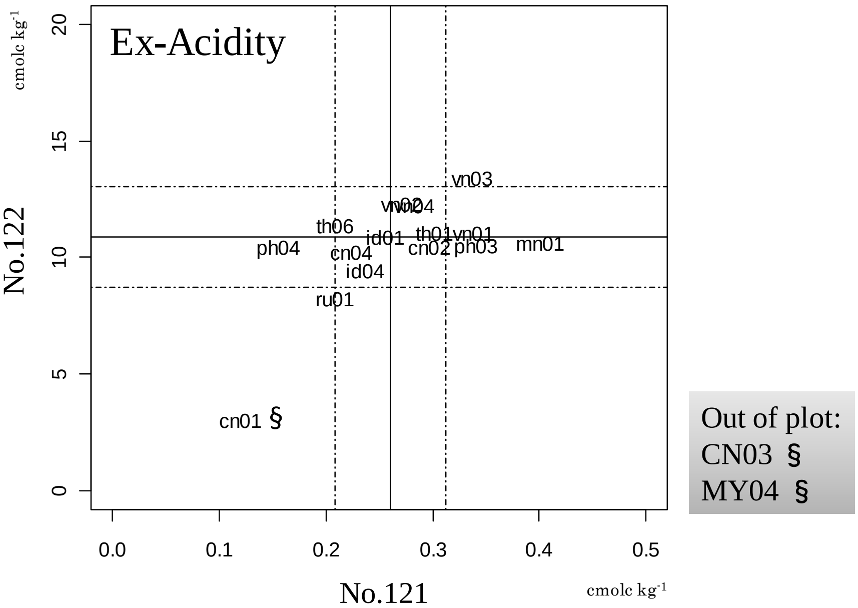

Figure 4.8 Scatter plot of Ex-acidity between No.121 and No.122 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cohcran and Grubbs method were denoted by §.)

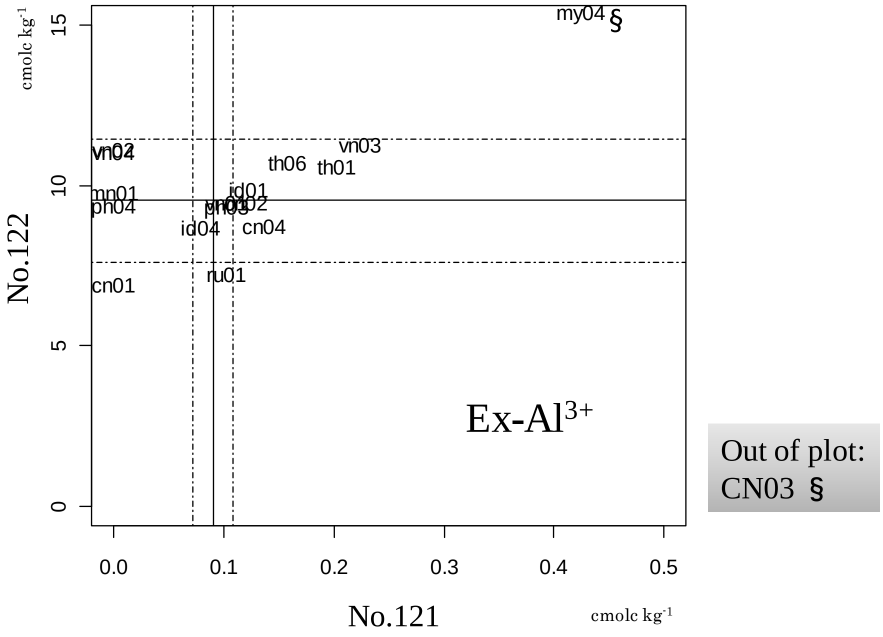

Figure 4.9 Scatter plot of Ex-Al between No.121 and No.122 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cohcran and Grubbs method were denoted by §.)

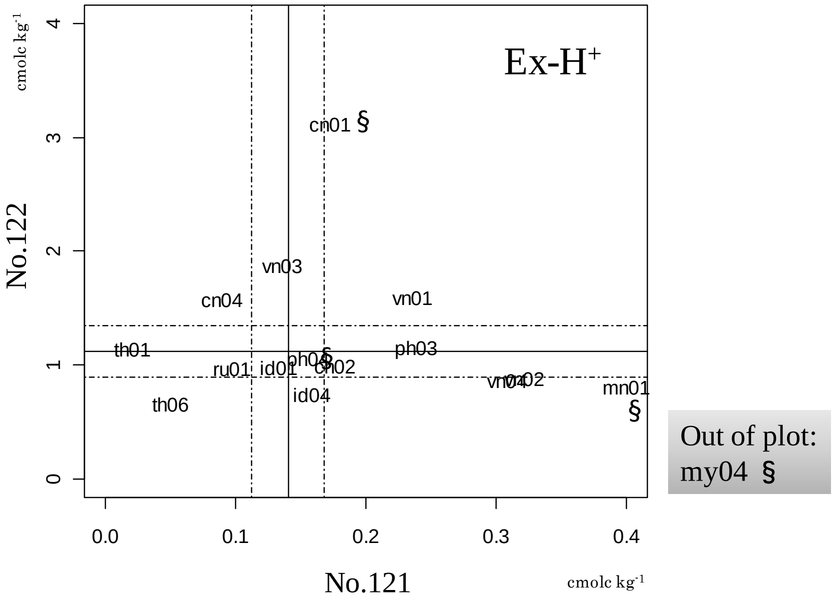

Figure 4.10 Scatter plot of Ex-H between No.121 and No.122 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean. Outliers selected by Cohcran and Grubbs method were denoted by §.)

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 2 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 3 to 27.

Seven laboratories used percolation tube procedures for extraction of exchangeable base cations, while Buchner funnel procedures, centrifuge procedures and automatic extractor procedures were used in 2, 3 and 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. 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 32 days. It was suggested that repeat analyses would be carried out with several-day interval (three days or more) in order to estimate actual within-laboratory reproducibility, as a supplementary instruction for the project, based on the discussion at SAC3 (The third session of the Scientific Advisory Committee on EANET). Mostly half of the laboratories followed the recommendation, although a few laboratories might conduct the instrumental analysis of both samples in a same day.

Table 4.6 Number and experience of analyst

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience		Number of analyst	Years of experience		
		Chemical	Soil		Chemical	Soil	
CN01	3	5	3	3	5	3	s
CN02	1	14	14	1	23	23	d
CN03	1	17	14	1	17	14	s
CN04	1	27	9	1	6	4	d
ID01	1	8	5	1	8	5	s
ID04	1	30	28	1	14	12	d
MN01	-	-	-	1	19	19	-
MY04	2	5	5	2	5	5	s
PH03	1	8	2	1	36	36	d
PH04	1	8	2	1	36	36	d
RU01	1	27	14	1	12	9	d
TH01	1	8	7	1	19	3	d
TH06	2	7	3	2	7	3	s
VN01	1	20	15	1	20	15	s
VN02	-	-	-	1	8	4	-
VN03	-	-	-	1	6	6	-
VN04	1	11	9	1	9	8	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	Ex-Acidity, Al and H		
													method	Size of burette (ml)	
		Instrument	Years*1	Instrument	Years		Instrument	Years	Instrument	Years				Capacity	Minimum graduate
CN01	No.111	AAS	6	AAS	6	Sr	AAS	6	AAS	6	na	Centrifuge	Titration	25	0.1
	No.112	AAS	6	AAS	6	Sr	AAS	6	AAS	6	na			25	0.1
CN02	No.111	AAS	14	AAS	14	Sr	AAS	14	AAS	14	Sr	Percolation tube	Titration	50	0.1
	No.112	AAS	14	AAS	14	Sr	AAS	14	AAS	14	Sr			50	0.1
CN03	No.111	AAS	4	AAS	3	Sr	AAS	3	AAS	3	Sr	Automatic extractor	Titration	5	1/800
	No.112	AAS	4	AAS	3	Sr	AAS	3	AAS	3	Sr			5	1/800
CN04	No.111	AAS	7	AAS	7	Sr	AAS	7	AAS	7	Sr	Automatic extractor	Titration	25	0.1
	No.112	AAS	7	AAS	7	Sr	AAS	7	AAS	7	Sr			25	0.1
ID01	No.111	AAS	7	AAS	7	Sr	AAS	7	AAS	7	Sr	Centrifuge	Titration	50	0.05
	No.112	AAS	7	AAS	7	Sr	AAS	7	AAS	7	Sr			50	0.05
ID04	No.111	AAS	15	AAS	15	+	AAS	15	AAS	15	+	Percolation tube	Titration	50	0.02
	No.112	AAS	15	AAS	15	+	AAS	15	AAS	15	+			50	0.02
MN01	No.111												Titration	25	0.1
	No.112													25	0.1
MY04	No.111	AAS	8	AAS	8	na	AAS	8	AAS	8	na	Centrifuge	Titration	50	0
	No.112	AAS	8	AAS	8	na	AAS	8	AAS	8	na			50	0
PH03	No.111	AAS	3	AAS	3	Sr	AAS	3	AAS	3	na	Buchner funnel	Titration	50	0.01
	No.112	AAS	3	AAS	3	Sr	AAS	3	AAS	3	na			50	0.01
PH04	No.111	AAS	3		3	Sr	AAS	3	AAS	3			Titration	50	0.01
	No.112	AAS	3		3	Sr	AAS	3	AAS	3				50	0.01
RU01	No.111	AAS	27	AAS	27	La	FEP	27	FEP	27	La	Percolation tube	Titration	25	0.1
	No.112	AAS	27	AAS	27	La	FEP	27	FEP	27	La			25	0.1
TH01	No.111	ICP	5	ICP	5	na	ICP	5	ICP	5	na	Percolation tube	Titration	25	0.05
	No.112	ICP	5	ICP	5	na	ICP	5	ICP	5	na			25	0.05
TH06	No.111	AAS	5	AAS	5	Sr	FEP	5	FEP	5	Sr	Percolation tube	Titration	25	0.05
	No.112	AAS	5	AAS	5	Sr	FEP	5	FEP	5	Sr			25	0.05
VN01	No.111	AAS	6	AAS	6	na	AAS	6	AAS	6	na	Buchner funnel	Titration	10	0.05
	No.112	AAS	6	AAS	6	na	AAS	6	AAS	6	na			10	0.05
VN02	No.111												Titration	10	0.05
	No.112													10	0.05
VN03	No.111											Percolation tube	Titration	10	0.02
	No.112													10	0.02
VN04	No.111	AAS	8	AAS	9	na						Percolation tube	Titration	10	0.05
	No.112	AAS	8	AAS	9	na								10	0.05

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			Days			Days	
CN01	1st	2013/1/15	1	1	2013/3/4	3	5	2013/3/4	3	5	2013/3/7	2	2
	2nd	2013/1/16	1		2013/3/9	3		2013/3/9	3		2013/3/9	2	
CN02	1st	2013/2/24	1	2	2013/1/11	2	7	2013/1/11	2	7	2013/2/1	5	27
	2nd	2013/2/26	1		2013/1/18	2		2013/1/18	2		2013/2/28	4	
CN03	1st	2012/12/8	6	7	2012/12/8	6	7	2012/12/3	1	12	2012/12/8	6	7
	2nd	2012/12/15	6		2012/12/15	6		2012/12/15	6		2012/12/15	6	
CN04	1st	2013/2/3	2	17	2013/2/3	2	23	2013/2/3	2	23	2013/1/15	4	32
	2nd	2013/2/20	2		2013/2/26	7		2013/2/26	7		2013/2/16	2	
ID01	1st	2013/1/2	1	7	2013/1/18	1	3	2013/1/18	1	3	2013/1/4	1	7
	2nd	2013/1/9	1		2013/1/21	1		2013/1/21	1		2013/1/11	1	
ID04	1st	2012/12/10	8	7	2012/12/10	8	7	2012/12/10	8	7	2012/12/10	8	7
	2nd	2012/12/17	8		2012/12/17	8		2012/12/17	8		2012/12/17	8	
MN01	1st	2013/1/24	1	0	-			-			2013/1/25	1	0
	2nd	2013/1/24	1								2013/1/25	1	
MY04	1st	2013/2/15	1	0	2013/2/17	1	2	2013/2/17	1	2	2013/3/20	2	2
	2nd	2013/2/15	1		2013/2/19	1		2013/2/19	1		2013/3/22	2	
PH03	1st	2013/5/8	1	7	2013/5/10	1	0	2013/5/14	1	0	2013/5/9	1	7
	2nd	2013/5/15	1		2013/5/10	1		2013/5/14	1		2013/5/16	1	
PH04	1st	2013/5/8	1	7	2013/5/10	1	7	2013/5/10	1	7	2013/5/9	1	7
	2nd	2013/5/15	1		2013/5/17	1		2013/5/17	1		2013/5/16	1	
RU01	1st	2013/1/28	1	14	2013/1/30	3	13	2013/1/30	3	13	2013/1/31	3	7
	2nd	2013/2/11	1		2013/2/12	2		2013/2/12	2		2013/2/7	2	
TH01	1st	2013/4/5	1	0	2013/4/19	2	13	2013/4/19	2	13	2013/4/4	1	5
	2nd	2013/4/5	1		2013/5/2	2		2013/5/2	2		2013/4/9	1	
TH06	1st	2013/3/13	1	7	2013/3/19	2	7	2013/3/19	2	7	2013/3/14	1	7
	2nd	2013/3/20	1		2013/3/26	2		2013/3/26	2		2013/3/21	1	
VN01	1st	2012/12/11	1	3	2012/12/11	1	3	2012/12/11	1	3	2012/12/11	1	3
	2nd	2012/12/14	1		2012/12/14	1		2012/12/14	1		2012/12/14	1	
VN02	1st	2012/3/12	1	0	-			-			2012/4/12	32	0
	2nd	2012/3/12	1								2012/4/12	1	
VN03	1st	2012/12/12	1	0	-			-			2012/12/12	1	0
	2nd	2012/12/12	1								2012/12/12	1	
VN04	1st	2012/12/13	1	0	2012/12/11	2	0	-			2012/12/11	1	0
	2nd	2012/12/13	1		2012/12/11	2					2012/12/11	1	

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 2012 (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 2012). 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.

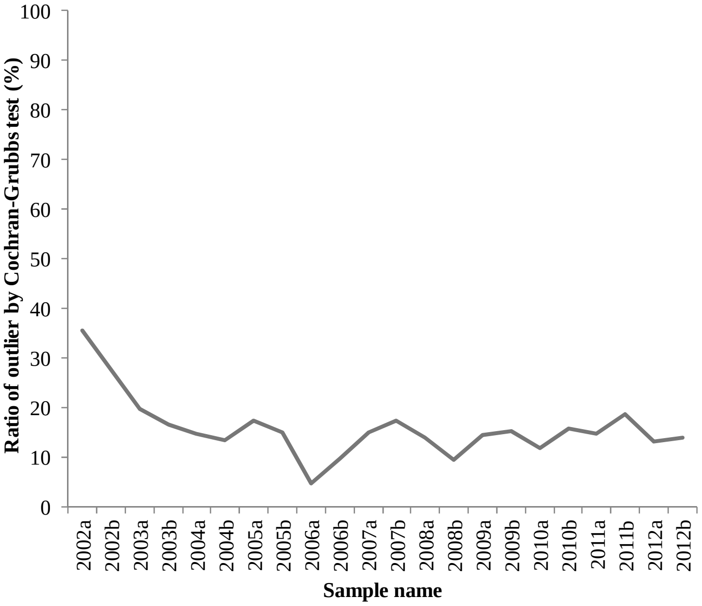

Figure 4.11 Change of the outlier ratio in all properties and laboratories from 2002 to 2010 (*N* of outliers / *N* of all data)

4.5 Recommendations

Reducing the outliers (about 15% 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 regent 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.121)

Lab.	$pH(H_2O)$			pH(KCl)			Ex-Ca ($cmol_c$ kg^{-1})			Ex-Mg ($cmol_c$ kg^{-1})			Ex-K ($cmol_c$ kg^{-1})			Ex-Na ($cmol_c$ kg^{-1})			Ex-acidity ($cmol_c$ kg^{-1})			Ex-Al ($cmol_c$ kg^{-1})			Ex-H ($cmol_c$ kg^{-1})		
	Lab. Ave.	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	5.7	5.7 (0.0)	5.7	4.7	4.6 (0.0)	4.6	0.78	0.78 (0.01)	0.79	0.31	0.31 (0.00)	0.31	0.16	0.16 (0.00)	0.16	0.05	0.04 (0.00)	0.04	0.1	0.1 (0.01)	0.1	0.0	0.0 (0.00)	0.0	0.2	0.2 (0.01)	0.2
			5.7			4.6			0.78			0.31			0.16			0.04			0.1			0.0			0.2
			5.7			4.6			0.76			0.31			0.16			0.04			0.1			0.0			0.2
		5.7 (0.0)	5.7		4.7 (0.0)	4.7		0.78 (0.02)	0.80		0.31 (0.00)	0.32		0.16 (0.01)	0.16		0.05 (0.00)	0.05		0.1 (0.00)	0.1		0.0 (0.00)	0.0		0.2 (0.00)	0.2
			5.7			4.7			0.78			0.31			0.17			0.05			0.1			0.0			0.2
			5.7			4.7			0.76			0.31			0.15			0.04			0.1			0.0			0.2
CN02	5.7	5.7 (0.0)	5.8	4.6	4.6 (0.0)	4.6	4.02	4.04 (0.02)	4.01	0.57	0.57 (0.02)	0.56	0.15	0.15 (0.01)	0.17	0.09	0.09 (0.00)	0.09	0.3	0.3 (0.05)	0.3	0.1	0.1 (0.01)	0.1	0.2	0.2 (0.04)	0.1
			5.7			4.6			4.06			0.57			0.16			0.09			0.2			0.1			0.1
			5.7			4.6			4.05			0.59			0.14			0.09			0.3			0.1			0.2
		5.7 (0.0)	5.8		4.6 (0.0)	4.6		4.00 (0.09)	3.91		0.57 (0.01)	0.57		0.15 (0.00)	0.14		0.08 (0.01)	0.08		0.3 (0.02)	0.3		0.1 (0.01)	0.1		0.2 (0.04)	0.2
			5.7			4.6			4.07			0.58			0.15			0.08			0.3			0.1			0.2
			5.7			4.6			4.02			0.57			0.15			0.09			0.3			0.1			0.2
CN03	5.6	5.6 (0.0)	5.6	4.7	4.7 (0.0)	4.7	4.61	4.61 (0.02)	4.61	0.52	0.51 (0.01)	0.51	0.19	0.19 (0.00)	0.18	0.11	0.11 (0.00)	0.11	1.2	1.2 (0.02)	1.2	0.8	0.7 (0.04)	0.7	0.5	0.4 (0.02)	0.5
			5.6			4.7			4.62			0.50			0.19			0.11			1.2			0.8			0.4
			5.6			4.7			4.59			0.52			0.19			0.11			1.2			0.7			0.5
		5.6 (0.0)	5.6		4.7 (0.0)	4.7		4.61 (0.02)	4.61		0.52 (0.01)	0.51		0.18 (0.00)	0.18		0.11 (0.00)	0.11		1.2 (0.02)	1.2		0.8 (0.02)	0.7		0.5 (0.00)	0.5
			5.6			4.7			4.59			0.52			0.18			0.11			1.2			0.8			0.5
			5.6			4.7			4.63			0.53			0.19			0.11			1.2			0.7			0.5
CN04	5.7	5.7 (0.0)	5.6	4.5	4.5 (0.0)	4.5	6.38	6.33 (0.28)	6.05	0.78	0.76 (0.06)	0.69	0.20	0.19 (0.01)	0.18	0.18	0.15 (0.04)	0.15	0.2	0.2 (0.02)	0.2	0.1	0.1 (0.03)	0.1	0.1	0.1 (0.04)	0.1
			5.7			4.5			6.33			0.78			0.21			0.20			0.2			0.1			0.1
			5.7			4.5			6.61			0.81			0.19			0.11			0.2			0.2			0.1
		5.7 (0.0)	5.7		4.5 (0.0)	4.5		6.43 (0.26)	6.73		0.79 (0.02)	0.82		0.20 (0.00)	0.21		0.21 (0.03)	0.24		0.2 (0.01)	0.2		0.1 (0.02)	0.1		0.1 (0.02)	0.1
			5.7			4.5			6.22			0.77			0.20			0.20			0.2			0.2			0.1
			5.7			4.5			6.35			0.79			0.20			0.18			0.2			0.1			0.1
ID01	5.5	5.5 (0.0)	5.5	4.5	4.5 (0.0)	4.5	5.40	5.43 (0.18)	5.39	0.79	0.78 (0.01)	0.78	0.20	0.20 (0.00)	0.20	0.05	0.05 (0.00)	0.06	0.3	0.3 (0.00)	0.3	0.1	0.1 (0.00)	0.1	0.1	0.1 (0.00)	0.1
			5.5			4.5			5.62			0.79			0.20			0.05			0.3			0.1			0.1
			5.5			4.5			5.27			0.78			0.19			0.05			0.3			0.1			0.1
		5.5 (0.0)	5.5		4.5 (0.0)	4.5		5.36 (0.07)	5.28		0.80 (0.03)	0.81		0.20 (0.00)	0.19		0.05 (0.00)	0.05		0.3 (0.00)	0.3		0.1 (0.00)	0.1		0.1 (0.00)	0.1
			5.5			4.5			5.39			0.81			0.19			0.05			0.3			0.1			0.1
			5.5			4.5			5.41			0.76			0.20			0.05			0.3			0.1			0.1
ID04	5.4	5.4 (0.0)	5.4	4.5	4.5 (0.0)	4.5	5.71	5.71 (0.16)	5.77	1.01	0.95 (0.03)	0.92	0.06	0.06 (0.00)	0.06	0.10	0.09 (0.01)	0.09	0.2	0.2 (0.01)	0.2	0.1	0.1 (0.01)	0.1	0.2	0.2 (0.02)	0.1
			5.4			4.5			5.84			0.99			0.05			0.09			0.2			0.1			0.2
			5.3			4.5			5.53			0.95			0.06			0.10			0.2			0.1			0.2
		5.3 (0.0)	5.3		4.5 (0.0)	4.5		5.70 (0.16)	5.83		1.06 (0.02)	1.06		0.06 (0.01)	0.07		0.10 (0.01)	0.10		0.2 (0.01)	0.2		0.1 (0.00)	0.1		0.2 (0.01)	0.2
			5.3			4.5			5.74			1.08			0.06			0.12			0.2			0.1			0.2
			5.3			4.4			5.52			1.04			0.06			0.09			0.2			0.1			0.1
MN01	5.4	5.4 (0.0)	5.5	4.7	4.7 (0.0)	4.8		-			-			-			-		0.4	0.4 (0.00)	0.4	0.0	0.0 (0.00)	0.0	0.4	0.4 (0.00)	0.4
			5.4			4.7															0.4			0.0			0.4
			5.4			4.7															0.4			0.0			0.4
		5.4 (0.0)	5.4		4.7 (0.0)	4.7														0.4 (0.00)	0.4		0.0 (0.00)	0.0		0.4 (0.00)	0.4
			5.5			4.7															0.4			0.0			0.4
			5.4			4.7															0.4			0.0			0.4
MY04	5.5	5.5 (0.0)	5.5	4.5	4.4 (0.0)	4.4	7.65	7.63 (0.08)	7.54	0.90	0.91 (0.01)	0.90	0.19	0.22 (0.01)	0.22	0.34	0.32 (0.19)	0.23	5.9	5.3 (1.15)	4.2	0.4	0.4 (0.00)	0.4	5.4	4.9 (1.15)	3.8
			5.5			4.4			7.67			0.92			0.22			0.20			5.2			0.4			4.7
			5.5			4.4			7.67			0.90			0.23			0.54			6.5			0.4			6.1
		5.5 (0.0)	5.4		4.5 (0.0)	4.5		7.66 (0.20)	7.70		0.89 (0.01)	0.89		0.15 (0.12)	0.01		0.35 (0.22)	0.61		6.5 (0.75)	5.6		0.5 (0.25)	0.4		5.9 (0.70)	5.2
			5.5			4.5			7.44			0.89			0.21			0.20			6.8			0.8			5.9
			5.5			4.5			7.84			0.90			0.23			0.26			7.0			0.4			6.6

Appendix Table 4.1 continued

Lab.	pH(H_2O)			pH(KCl)			Ex-Ca (cmol$_c$ kg^{-1})			Ex-Mg (cmol$_c$ kg^{-1})			Ex-K (cmol$_c$ kg^{-1})			Ex-Na (cmol$_c$ kg^{-1})			Ex-acidity (cmol$_c$ kg^{-1})			Ex-Al (cmol$_c$ kg^{-1})			Ex-H (cmol$_c$ kg^{-1})		
	Lab. Ave.	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
PH03	5.5	5.5 (0.1)	5.5	4.5	4.5 (0.1)	4.4	6.70	6.99 (0.14)	6.83	0.82	0.81 (0.08)	0.73	0.22	0.22 (0.00)	0.22	0.14	0.13 (0.02)	0.15	0.3	0.3 (0.01)	0.3	0.1	0.1 (0.03)	0.1	0.2	0.3 (0.02)	0.2
			5.6			4.5			7.10			0.81			0.21			0.12			0.3			0.1			0.3
			5.5			4.5			7.05			0.88			0.22			0.11			0.3			0.1			0.3
		5.5 (0.0)	5.5		4.5 (0.0)	4.5		6.40 (0.17)	6.46		0.82 (0.05)	0.88		0.22 (0.01)	0.21		0.14 (0.02)	0.13		0.3 (0.02)	0.3		0.1 (0.01)	0.1		0.2 (0.02)	0.2
			5.5			4.5			6.21			0.82			0.21			0.16			0.4			0.1			0.3
			5.5			4.5			6.53			0.78			0.22			0.11			0.3			0.1			0.2
PH03*	5.6	5.6 (0.1)	5.6	4.5	4.5 (0.1)	4.4	7.27	7.26 (0.73)	6.88	0.69	0.69 (0.02)	0.72	0.20	0.20 (0.00)	0.20	0.11	0.11 (0.01)	0.12	0.2	0.2 (0.01)	0.2	0.0	0.0 (0.00)	0.0	0.2	0.2 (0.01)	0.2
			5.6			4.5			6.80			0.69			0.20			0.11			0.2			0.0			0.2
			5.5			4.5			8.10			0.68			0.20			0.10			0.1			0.0			0.1
		5.5 (0.0)	5.5		4.5 (0.0)	4.5		7.28 (0.81)	6.89		0.68 (0.01)	0.68		0.19 (0.00)	0.19		0.11 (0.01)	0.11		0.2 (0.01)	0.2		0.0 (0.00)	0.0		0.2 (0.01)	0.2
			5.5			4.5			6.74			0.69			0.19			0.10			0.2			0.0			0.2
			5.5			4.5			8.21			0.68			0.19			0.10			0.1			0.0			0.1
RU01	5.7	5.7 (0.0)	5.7	4.6	4.6 (0.0)	4.6	6.84	6.84 (0.05)	6.85	0.82	0.79 (0.00)	0.78	0.18	0.18 (0.00)	0.18	0.17	0.16 (0.04)	0.19	0.2	0.2 (0.00)	0.2	0.1	0.1 (0.00)	0.1	0.1	0.1 (0.00)	0.1
			5.7			4.6			6.88			0.79			0.18			0.17			0.2			0.1			0.1
			5.7			4.6			6.79			0.79			0.18			0.11			0.2			0.1			0.1
		5.7 (0.0)	5.7		4.6 (0.0)	4.6		6.84 (0.01)	6.84		0.84 (0.00)	0.84		0.18 (0.00)	0.18		0.18 (0.02)	0.18		0.2 (0.02)	0.2		0.1 (0.00)	0.1		0.1 (0.00)	0.1
			5.8			4.6			6.82			0.84			0.18			0.20			0.2			0.1			0.1
			5.7			4.7			6.85			0.84			0.18			0.17			0.2			0.1			0.1
TH01	5.6	5.6 (0.0)	5.6	4.5	4.5 (0.0)	4.5	5.71	5.54 (0.02)	5.56	0.78	0.78 (0.01)	0.77	0.36	0.36 (0.00)	0.36	0.11	0.11 (0.01)	0.10	0.3	0.3 (0.03)	0.3	0.2	0.2 (0.00)	0.2	0.0	0.0 (0.00)	0.0
			5.6			4.5			5.53			0.77			0.36			0.12			0.3			0.2			0.0
			5.6			4.5			5.53			0.79			0.35			0.10			0.3			0.2			0.0
		5.6 (0.0)	5.6		4.5 (0.0)	4.5		5.87 (0.03)	5.90		0.78 (0.01)	0.78		0.35 (0.01)	0.36		0.10 (0.01)	0.10		0.3 (0.03)	0.3		0.2 (0.00)	0.2		0.0 (0.00)	0.0
			5.6			4.5			5.84			0.78			0.35			0.09			0.3			0.2			0.0
			5.6			4.5			5.87			0.79			0.35			0.10			0.3			0.2			0.0
TH06	5.5	5.5 (0.0)	5.5	4.6	4.6 (0.0)	4.6	6.70	6.85 (0.07)	6.93	0.54	0.53 (0.05)	0.50	0.39	0.39 (0.01)	0.38	0.37	0.36 (0.01)	0.37	0.2	0.2 (0.03)	0.2	0.2	0.2 (0.00)	0.2	0.1	0.1 (0.03)	0.0
			5.5			4.6			6.82			0.52			0.39			0.36			0.2			0.2			0.1
			5.5			4.6			6.80			0.58			0.41			0.36			0.2			0.2			0.0
		5.5 (0.0)	5.5		4.6 (0.0)	4.6		6.55 (0.07)	6.47		0.55 (0.00)	0.56		0.38 (0.01)	0.39		0.38 (0.02)	0.40		0.2 (0.00)	0.2		0.2 (0.02)	0.1		0.1 (0.02)	0.1
			5.5			4.6			6.61			0.55			0.37			0.35			0.2			0.2			0.0
			5.5			4.6			6.56			0.55			0.40			0.39			0.2			0.2			0.0
VN01	5.6	5.6 (0.0)	5.7	4.5	4.5 (0.0)	4.4	6.39	6.40 (0.07)	6.49	0.87	0.86 (0.00)	0.86	0.23	0.23 (0.00)	0.23	0.14	0.14 (0.01)	0.15	0.3	0.3 (0.00)	0.3	0.1	0.1 (0.00)	0.1	0.2	0.2 (0.00)	0.2
			5.6			4.5			6.36			0.86			0.23			0.14			0.3			0.1			0.2
			5.6			4.5			6.37			0.86			0.23			0.13			0.3			0.1			0.2
		5.6 (0.0)	5.7		4.4 (0.0)	4.5		6.38 (0.02)	6.39		0.87 (0.01)	0.88		0.23 (0.00)	0.23		0.14 (0.00)	0.14		0.3 (0.00)	0.3		0.1 (0.00)	0.1		0.2 (0.00)	0.2
			5.6			4.5			6.39			0.87			0.23			0.14			0.3			0.1			0.2
			5.6			4.4			6.36			0.86			0.23			0.14			0.3			0.1			0.2
VN02	5.3	5.3 (0.0)	5.3	4.5	4.5 (0.0)	4.5		-			-			-			-		0.3	0.3 (0.00)	0.3	0.0	0.0 (0.00)	0.0	0.3	0.3 (0.00)	0.3
			5.3			4.5															0.3			0.0			0.3
			5.3			4.5															0.3			0.0			0.3
		5.3 (0.0)	5.3		4.5 (0.0)	4.5														0.3 (0.00)	0.3		0.0 (0.00)	0.0		0.3 (0.06)	0.3
			5.3			4.5															0.3			0.0			0.4
			5.3			4.5															0.3			0.0			0.3
VN03	5.5	5.5 (0.1)	5.5	4.5	4.5 (0.0)	4.5		-			-			-			-		0.3	0.3 (0.01)	0.3	0.2	0.2 (0.02)	0.2	0.1	0.1 (0.02)	0.1
			5.6			4.5															0.3			0.2			0.2
			5.6			4.5															0.3			0.2			0.1
		5.5 (0.1)	5.5		4.5 (0.0)	4.5														0.3 (0.01)	0.3		0.2 (0.02)	0.2		0.1 (0.02)	0.1
			5.6			4.5															0.3			0.2			0.1
			5.6			4.5															0.3			0.2			0.2
VN04	5.6	5.6 (0.1)	5.6	4.5	4.5 (0.0)	4.5	3.52	3.42 (0.01)	3.43	0.67	0.64 (0.02)	0.62		-			-		0.3	0.3 (0.03)	0.3	0.0	0.0 (0.00)	0.0	0.3	0.3 (0.12)	0.4
			5.5			4.5			3.43			0.66									0.3			0.0			0.2
			5.6			4.5			3.41			0.63									0.3			0.0			0.2
		5.6 (0.0)	5.6		4.5 (0.0)	4.5		3.61 (0.05)	3.59		0.69 (0.01)	0.69								0.3 (0.03)	0.3		0.0 (0.00)	0.0		0.3 (0.12)	0.4
			5.6			4.5			3.57			0.70									0.3			0.0			0.4
			5.6			4.5			3.66			0.69									0.3			0.0			0.2

Appendix Table 4.2 Results submitted by the laboratories (sample No. 122)

Lab.	pH(H_2O)			pH(KCl)			Ex-Ca ($\mathrm{cmol_c\ kg^{-1}}$)			Ex-Mg ($\mathrm{cmol_c\ kg^{-1}}$)			Ex-K ($\mathrm{cmol_c\ kg^{-1}}$)			Ex-Na ($\mathrm{cmol_c\ kg^{-1}}$)			Ex-acidity ($\mathrm{cmol_c\ kg^{-1}}$)			Ex-Al ($\mathrm{cmol_c\ kg^{-1}}$)			Ex-H ($\mathrm{cmol_c\ kg^{-1}}$)		
	Lab. Ave.	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	4.7	4.7 (0.0)	4.7	4.0	4.0 (0.0)	4.0	0.03	0.03 (0.00)	0.03	0.12	0.12 (0.00)	0.12	0.14	0.14 (0.00)	0.14	0.05	0.05 (0.00)	0.05	3.1	3.1 (0.04)	3.0	7.0	7.0 (0.01)	7.0	3.1	3.1 (0.12)	3.0
			4.7			4.0			0.04			0.12			0.14			0.05			3.1			7.0			3.3
			4.7			4.0			0.03			0.12			0.14			0.05			3.1			7.0			3.1
		4.7 (0.0)	4.7		4.0 (0.0)	4.0		0.03 (0.00)	0.03		0.12 (0.00)	0.12		0.13 (0.01)	0.13		0.05 (0.01)	0.04		3.1 (0.02)	3.1		7.0 (0.03)	7.0		3.1 (0.05)	3.1
			4.7			4.0			0.03			0.12			0.12			0.05			3.1			7.0			3.2
			4.7			4.0			0.03			0.12			0.13			0.05			3.1			6.9			3.1
CN02	4.7	4.7 (0.0)	4.7	3.9	3.9 (0.0)	3.9	0.78	0.79 (0.01)	0.79	0.35	0.35 (0.03)	0.34	0.12	0.12 (0.02)	0.12	0.11	0.12 (0.00)	0.12	10.5	10.8 (0.05)	10.8	9.5	9.7 (0.09)	9.8	1.0	1.1 (0.14)	1.0
			4.7			3.9			0.78			0.32			0.10			0.11			10.8			9.6			1.2
			4.7			3.9			0.80			0.38			0.15			0.12			10.7			9.7			1.0
		4.7 (0.0)	4.7		3.9 (0.0)	3.9		0.77 (0.03)	0.74		0.35 (0.02)	0.33		0.11 (0.01)	0.10		0.10 (0.00)	0.10		10.3 (0.10)	10.4		9.3 (0.08)	9.3		1.0 (0.10)	1.0
			4.7			3.9			0.76			0.34			0.12			0.10			10.2			9.3			0.8
			4.7			3.9			0.80			0.36			0.12			0.09			10.2			9.2			1.0
CN03	4.7	4.7 (0.0)	4.7	4.0	4.0 (0.0)	4.0	1.00	0.99 (0.02)	0.97	0.28	0.28 (0.00)	0.28	0.10	0.10 (0.00)	0.10	0.15	0.15 (0.00)	0.15	9.6	9.6 (0.05)	9.6	8.3	8.3 (0.03)	8.3	1.3	1.3 (0.03)	1.3
			4.7			4.0			1.01			0.28			0.10			0.16			9.5			8.3			1.3
			4.7			4.0			0.99			0.28			0.10			0.15			9.5			8.3			1.3
		4.7 (0.0)	4.7		4.0 (0.0)	4.0		1.00 (0.01)	1.01		0.28 (0.00)	0.27		0.10 (0.00)	0.10		0.15 (0.00)	0.16		9.6 (0.00)	9.5		8.2 (0.03)	8.2		1.3 (0.03)	1.3
			4.7			4.0			1.00			0.28			0.10			0.15			9.5			8.2			1.3
			4.7			4.0			0.99			0.28			0.10			0.15			9.5			8.3			1.3
CN04	4.6	4.6 (0.0)	4.6	3.8	3.8 (0.0)	3.9	1.07	1.11 (0.05)	1.16	0.30	0.30 (0.01)	0.31	0.16	0.16 (0.00)	0.15	0.19	0.17 (0.04)	0.17	10.3	10.5 (0.22)	10.3	8.8	9.0 (0.20)	9.1	1.6	1.5 (0.28)	1.2
			4.6			3.9			1.09			0.30			0.16			0.21			10.7			9.2			1.6
			4.6			3.8			1.08			0.31			0.15			0.14			10.6			8.8			1.8
		4.6 (0.0)	4.7		3.8 (0.0)	3.8		1.02 (0.11)	0.93		0.30 (0.01)	0.30		0.16 (0.01)	0.16		0.20 (0.06)	0.22		10.2 (0.12)	10.3		8.6 (0.02)	8.6		1.6 (0.10)	1.8
			4.6			3.8			0.99			0.30			0.15			0.13			10.1			8.6			1.6
			4.6			3.9			1.15			0.32			0.17			0.26			10.1			8.6			1.6
ID01	4.4	4.4 (0.0)	4.4	3.7	3.7 (0.0)	3.7	1.04	1.03 (0.05)	1.00	0.28	0.28 (0.01)	0.29	0.16	0.16 (0.00)	0.16	0.06	0.06 (0.00)	0.07	10.9	11.0 (0.07)	10.9	9.9	10.0 (0.05)	9.9	1.0	1.0 (0.01)	1.0
			4.4			3.7			1.09			0.28			0.16			0.06			11.0			10.0			1.0
			4.4			3.7			1.00			0.27			0.17			0.06			11.0			10.0			1.0
		4.4 (0.0)	4.5		3.7 (0.0)	3.7		1.05 (0.06)	0.99		0.27 (0.00)	0.27		0.16 (0.00)	0.16		0.05 (0.00)	0.05		10.9 (0.00)	10.9		9.9 (0.05)	9.9		1.0 (0.05)	1.0
			4.4			3.7			1.05			0.28			0.16			0.05			10.9			9.9			1.0
			4.4			3.7			1.10			0.27			0.17			0.05			10.9			10.0			0.9
ID04	4.4	4.4 (0.0)	4.4	3.9	3.9 (0.0)	3.9	0.87	0.83 (0.06)	0.90	0.39	0.37 (0.02)	0.38	0.04	0.03 (0.01)	0.04	0.06	0.06 (0.00)	0.06	9.5	9.5 (0.01)	9.5	8.8	8.7 (0.03)	8.7	0.8	0.8 (0.02)	0.8
			4.4			3.9			0.82			0.38			0.03			0.05			9.5			8.8			0.7
			4.4			3.9			0.78			0.35			0.04			0.06			9.5			8.8			0.8
		4.4 (0.1)	4.5		3.9 (0.0)	3.9		0.90 (0.04)	0.92		0.40 (0.02)	0.39		0.04 (0.00)	0.03		0.06 (0.00)	0.06		9.5 (0.01)	9.5		8.8 (0.00)	8.8		0.8 (0.01)	0.8
			4.3			3.9			0.86			0.39			0.04			0.05			9.5			8.8			0.8
			4.5			3.9			0.94			0.42			0.04			0.06			9.5			8.8			0.7
MN01	4.6	4.6 (0.0)	4.6	4.0	4.0 (0.0)	4.0		-			-			-			-		10.7	10.7 (0.00)	10.7	9.9	9.9 (0.00)	9.9	0.8	0.8 (0.00)	0.8
			4.6			4.0															10.7			9.9			0.8
			4.6			4.0															10.7			9.9			0.8
		4.6 (0.0)	4.6		4.0 (0.0)	4.0														10.7 (0.00)	10.7		9.9 (0.00)	9.9		0.8 (0.00)	0.8
			4.6			4.0															10.7			9.9			0.8
			4.6			4.0															10.7			9.9			0.8
MY04	4.6	4.6 (0.1)	4.6	3.8	3.8 (0.0)	3.8	2.22	2.10 (0.08)	2.17	0.35	0.32 (0.01)	0.33	0.17	0.17 (0.00)	0.17	0.32	0.33 (0.15)	0.31	31.4	34.1 (1.01)	35.1	15.4	16.8 (1.22)	16.9	15.9	17.2 (1.89)	18.2
			4.6			3.8			2.01			0.33			0.17			0.49			33.1			18.0			15.0
			4.5			3.8			2.11			0.31			0.17			0.18			34.0			15.6			18.4
		4.6 (0.0)	4.6		3.8 (0.0)	3.8		2.34 (0.17)	2.51		0.37 (0.03)	0.38		0.17 (0.01)	0.16		0.31 (0.06)	0.24		28.7 (2.38)	27.7		14.0 (0.13)	14.2		14.5 (2.39)	13.4
			4.6			3.8			2.17			0.35			0.18			0.33			26.9			13.9			12.9
			4.6			3.8			2.33			0.40			0.18			0.35			31.4			14.0			17.3

Appendix Table 4.2 continued

Lab.	pH(H_2O)			pH(KCl)			Ex-Ca (cmol$_c$ kg^{-1})			Ex-Mg (cmol$_c$ kg^{-1})			Ex-K (cmol$_c$ kg^{-1})			Ex-Na (cmol$_c$ kg^{-1})			Ex-acidity (cmol$_c$ kg^{-1})			Ex-Al (cmol$_c$ kg^{-1})			Ex-H (cmol$_c$ kg^{-1})		
	Lab. Ave.	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
PH03	4.5	4.5 (0.1)	4.6	3.8	3.8 (0.0)	3.8	0.78	0.77 (0.18)	0.79	0.25	0.26 (0.04)	0.24	0.21	0.21 (0.01)	0.21	0.13	0.13 (0.00)	0.13	10.5	10.6 (0.06)	10.6	9.3	9.4 (0.06)	9.4	1.2	1.2 (0.01)	1.2
			4.5			3.8			0.59			0.24			0.21			0.13			10.6			9.4			1.2
			4.5			3.8			0.94			0.31			0.19			0.14			10.5			9.3			1.1
		4.5 (0.0)	4.5		3.8 (0.0)	3.8		0.79 (0.12)	0.81		0.24 (0.02)	0.21		0.20 (0.01)	0.20		0.13 (0.01)	0.12		10.4 (0.13)	10.5		9.3 (0.14)	9.3		1.2 (0.01)	1.1
			4.5			3.8			0.67			0.25			0.21			0.13			10.5			9.4			1.2
			4.5			3.8			0.90			0.26			0.21			0.14			10.3			9.1			1.2
PH03*	4.5	4.5 (0.1)	4.5	3.6	3.6 (0.0)	3.6	3.57	3.48 (0.17)	3.68	0.26	0.24 (0.01)	0.23	0.17	0.17 (0.01)	0.18	0.13	0.13 (0.01)	0.14	10.4	10.4 (0.02)	10.4	9.4	9.4 (0.09)	9.3	1.1	1.1 (0.07)	1.1
			4.5			3.6			3.36			0.25			0.18			0.13			10.5			9.5			1.0
			4.4			3.6			3.41			0.24			0.17			0.12			10.4			9.4			1.1
		4.4 (0.0)	4.4		3.6 (0.0)	3.6		3.66 (0.19)	3.72		0.27 (0.02)	0.25		0.17 (0.01)	0.17		0.13 (0.01)	0.14		10.4 (0.01)	10.4		9.4 (0.08)	9.3		1.1 (0.07)	1.1
			4.4			3.6			3.81			0.29			0.18			0.12			10.4			9.4			1.0
			4.4			3.6			3.44			0.27			0.16			0.13			10.4			9.4			1.1
RU01	4.2	4.2 (0.0)	4.2	4.0	3.9 (0.0)	4.0	1.01	1.00 (0.02)	1.01	0.32	0.32 (0.02)	0.34	0.17	0.17 (0.00)	0.17	0.07	0.07 (0.02)	0.08	8.3	8.3 (0.05)	8.2	7.3	7.3 (0.07)	7.3	1.0	1.0 (0.11)	0.9
			4.2			4.0			1.00			0.31			0.17			0.09			8.3			7.3			1.0
			4.2			3.9			0.98			0.31			0.17			0.05			8.3			7.2			1.1
		4.2 (0.0)	4.2		4.0 (0.0)	4.0		1.01 (0.03)	1.04		0.32 (0.01)	0.32		0.17 (0.00)	0.17		0.07 (0.01)	0.07		8.3 (0.03)	8.3		7.3 (0.07)	7.3		1.0 (0.00)	1.0
			4.2			4.0			0.98			0.31			0.17			0.06			8.3			7.3			1.0
			4.2			4.0			0.99			0.31			0.17			0.09			8.3			7.2			1.0
TH01	4.5	4.5 (0.0)	4.5	3.8	3.8 (0.0)	3.9	0.83	0.81 (0.02)	0.79	0.29	0.30 (0.01)	0.30	0.28	0.29 (0.01)	0.28	0.08	0.08 (0.01)	0.08	11.2	11.5 (0.12)	11.6	10.7	11.0 (0.21)	11.0	1.2	1.3 (0.12)	1.2
			4.6			3.9			0.82			0.31			0.30			0.09			11.4			11.2			1.2
			4.6			3.8			0.82			0.31			0.28			0.07			11.4			10.8			1.4
		4.5 (0.0)	4.5		3.8 (0.0)	3.8		0.84 (0.01)	0.85		0.27 (0.01)	0.28		0.27 (0.00)	0.26		0.08 (0.00)	0.08		10.8 (0.25)	11.1		10.4 (0.21)	10.3		1.0 (0.38)	1.3
			4.5			3.8			0.83			0.26			0.27			0.08			10.7			10.6			0.6
			4.5			3.8			0.84			0.28			0.27			0.07			10.7			10.1			1.2
TH06	4.6	4.5 (0.0)	4.5	3.9	3.9 (0.0)	3.9	0.92	0.91 (0.01)	0.90	0.30	0.30 (0.00)	0.30	0.23	0.23 (0.00)	0.23	0.16	0.16 (0.01)	0.16	11.5	11.4 (0.03)	11.4	10.8	10.8 (0.03)	10.7	0.7	0.7 (0.01)	0.7
			4.5			3.9			0.92			0.30			0.23			0.17			11.4			10.8			0.7
			4.5			3.9			0.91			0.30			0.23			0.16			11.4			10.8			0.7
		4.6 (0.0)	4.6		3.9 (0.0)	3.9		0.92 (0.01)	0.92		0.29 (0.00)	0.29		0.23 (0.00)	0.23		0.15 (0.00)	0.15		11.5 (0.06)	11.6		10.8 (0.03)	10.8		0.7 (0.04)	0.7
			4.6			3.9			0.91			0.29			0.23			0.15			11.4			10.8			0.6
			4.6			3.9			0.94			0.29			0.24			0.16			11.4			10.8			0.6
VN01	4.5	4.5 (0.0)	4.5	3.8	3.8 (0.0)	3.8	0.10	0.10 (0.01)	0.09	0.39	0.39 (0.02)	0.39	0.18	0.18 (0.01)	0.19	0.06	0.06 (0.00)	0.06	11.1	11.1 (0.17)	10.9	9.5	9.5 (0.10)	9.4	1.6	1.6 (0.11)	1.5
			4.5			3.8			0.09			0.37			0.18			0.06			11.3			9.5			1.7
			4.5			3.8			0.10			0.41			0.19			0.07			11.1			9.6			1.6
		4.5 (0.0)	4.5		3.8 (0.0)	3.8		0.09 (0.00)	0.10		0.39 (0.01)	0.39		0.18 (0.00)	0.18		0.06 (0.00)	0.06		11.2 (0.08)	11.2		9.5 (0.03)	9.5		1.6 (0.10)	1.7
			4.4			3.8			0.09			0.39			0.18			0.06			11.1			9.5			1.6
			4.5			3.8			0.09			0.38			0.19			0.07			11.1			9.6			1.6
VN02	4.3	4.3 (0.0)	4.3	3.7	3.7 (0.0)	3.7		-			-			-			-		12.4	12.4 (0.03)	12.3	11.2	11.2 (0.06)	11.1	0.9	0.9 (0.06)	1.0
			4.3			3.7															12.4			11.2			0.8
			4.3			3.7															12.3			11.1			1.0
		4.3 (0.0)	4.3		3.7 (0.0)	3.7														12.4 (0.03)	12.4		11.2 (0.06)	11.2		0.9 (0.06)	0.8
			4.3			3.7															12.3			11.1			0.8
			4.3			3.7															12.4			11.1			1.0
VN03	4.6	4.6 (0.1)	4.7	3.8	3.8 (0.0)	3.8		-			-			-			-		13.5	13.6 (0.01)	13.6	11.4	11.4 (0.00)	11.4	1.9	1.9 (0.04)	1.9
			4.6			3.8															13.5			11.4			2.0
			4.5			3.8															13.6			11.4			1.9
		4.6 (0.1)	4.7		3.8 (0.0)	3.8														13.4 (0.01)	13.4		11.3 (0.00)	11.3		1.9 (0.05)	1.8
			4.6			3.8															13.4			11.3			1.8
			4.5			3.8															13.4			11.3			1.9
VN04	4.5	4.5 (0.1)	4.5	3.7	3.7 (0.0)	3.6	0.33	0.32 (0.00)	0.32	0.47	0.46 (0.00)	0.45		-			-		12.3	12.3 (0.03)	12.3	11.1	11.1 (0.13)	11.0	0.9	0.9 (0.00)	0.9
			4.5			3.7			0.32			0.46									12.3			11.2			0.9
			4.4			3.7			0.32			0.46									12.3			11.2			0.9
		4.5 (0.0)	4.4		3.7 (0.0)	3.7		0.34 (0.01)	0.34		0.48 (0.01)	0.49								12.3 (0.03)	12.3		11.1 (0.13)	11.0		0.8 (0.13)	0.9
			4.5			3.7			0.33			0.47									12.3			11.0			0.7
			4.5			3.7			0.35			0.48									12.3			11.2			0.9

5. 13th INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENT

5.1 Introduction

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

5.2 Procedures

5.2.1 Participating Laboratories

In the 13th Project, the NC shipped an artificial inland water sample on October 3, 2012 to 23 laboratories involved in the EANET activities, and most of them submitted their analytical data to the NC by February 28, 2013. Participating laboratories and their identification codes are listed in Table 1.1. For this attempt, the laboratory LA01 submitted the data of 6 parameters (pH, EC, alkalinity, and all of the anions), and the laboratory MN01 submitted the data of 3 parameters (pH, EC and alkalinity). Furthermore, 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 specified in the technical documents in EANET to the analysis. The methods and procedures applied were 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)”. Moreover, the latest version of the manual 2010 came to be available nowadays.

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 (2000)

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 (μeq L^{-1}) is calculated by sum up the concentration of anions (C: μmol L^{-1}) and alkalinity (ALK: μeq L^{-1}). Alkalinity considered to be corresponded to bicarbonate ions (HCO_3^-).

$\boldsymbol{A}$ (μeq L^{-1}) $=\Sigma n\, C_{Ai}$ (μmol L^{-1}) $= C(SO_4^{2-}) + C(NO_3^-) + C(Cl^-) + (ALK)$

C_{Ai}: electric charge of ion and concentration (μmol L^{-1}) of anion “i”.

(2) Total cation (C) equivalent concentration (μeq L^{-1}) is calculated by sum up the concentration of all cations (C: μmol L^{-1}).

$$\boldsymbol{C}\ (\mu\text{eq/L}) = \Sigma n\, C_{Ci}\ (\mu\text{mol/L}) = 10^{(6-\text{pH})} + C(NH_4^+) + C(Na^+) + C(K^+) + C(Ca^{2+}) + C(Mg^{2+})$$

C_{Ci}: electric charge of ion and concentration (μmol L^{-1}) of cation “i”.

(3) Calculation of ion balance (R_1)

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

(4) R_1, which is calculated using the above equation, should be compared with 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

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

$$\Lambda\text{calc (mS m}^{-1}) = \{349.7 \times 10^{(3-\mathrm{pH})} + 80.0 \times C(SO_4^{2-}) + 71.5 \times C(NO_3^-) + 76.3 \times C(Cl^-) + 73.5 \times C(NH_4^+) + 50.1 \times C(Na^+) + 73.5 \times C(K^+) + 59.8 \times C(Ca^{2+}) + 53.3 \times C(Mg^{2+}) + 44.5 \times (ALK)\}/10000$$

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

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

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

Table 5.6 Allowable ranges for R_2 in different concentration ranges

Λmeas[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 deviated from the average three times greater than standard deviation (S.D.) is not included for the calculation in Table 5.7. Average of submitted data agreed well with the prepared value/concentration within a range of ±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	7.05	6.99	0.14	22	6.71	7.20
EC (mS m^{-1})	6.66	6.29	0.25	21	5.88	7.17
Alkalinity (meq L^{-1})	0.132	0.145	0.02	21	0.117	0.184
SO_4^{2-} (mg L^{-1})	9.09	8.93	0.59	21	7.33	9.98
NO_3^- (mg L^{-1})	2.72	2.64	0.14	19	2.19	2.91
Cl^- (mg L^{-1})	5.73	5.54	0.34	21	4.87	6.32
Na^+ (mg L^{-1})	3.13	3.12	0.10	20	2.94	3.33
K^+ (mg L^{-1})	1.89	1.86	0.11	20	1.66	2.15
Ca^{2+} (mg L^{-1})	3.49	3.48	0.24	20	3.05	4.14
Mg^{2+} (mg L^{-1})	1.86	1.85	0.08	20	1.65	1.99
NH_4^+ (mg L^{-1})	0.27	0.25	0.05	20	0.10	0.33

(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 ± 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 (± 15% − ± 30%) and the flag "X" is put to the data that exceed DQO more than a factor of 2 (< −30% or > 30%). Data set for each laboratory was evaluated by the data checking procedures described in chapter 5.2.4 of this report. The results were evaluated following the two aspects: i) comparison of individual parameters, and ii) comparison of conditions in each participating laboratory. Evaluation of data for each constituent is presented in "5.3.2 Evaluation of laboratories' performance (by analytical parameters) ", and evaluation of data by laboratory conditions such as analytical methods used for the project, experience of personnel, and other analytical conditions is described in “5.3.4 Information on laboratories”.

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

Table 5.8 Number of flagged data

Flag*	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total	Ratio
E	0	0	2	1	2	0	0	0	1	0	7	13	5.7%
X	0	1	4	0	0	0	0	0	0	0	2	7	3.1%
Data within DQOs	22	21	16	20	18	21	20	20	19	20	11	208	91.2%
Flagged(%)	0.0	4.5	27.3	4.8	10.0	0.0	0.0	0.0	5.0	0.0	45.0	8.8	

*E: Value exceeded the DQO within a factor of 2 (± 15% − ± 30%)

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

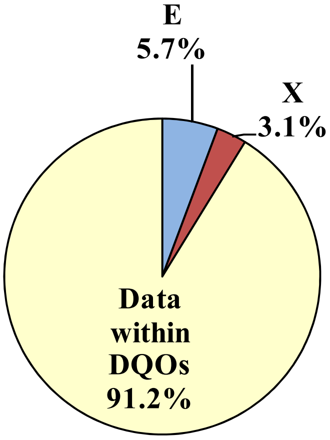


Figure 5.1 Percentage of flagged data

The data flagged by "E", which exceeded the DQOs within a factor of 2, shared 5.7% of all the reported data of samples. Furthermore, the data flagged by "X", which exceeded the DQOs more than a factor of 2, shared 3.1% of all the reported data of samples. Concerning the respective parameters, the percentage of flagged NH_4^+ was comparatively high, 45%.

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	7	32%
1	12	55%
2	2	9%
3	0	0%
4	1	5%
5	0	0%
6	0	0%
7	0	0%
8	0	0%
9	0	0%
Total	22	100%

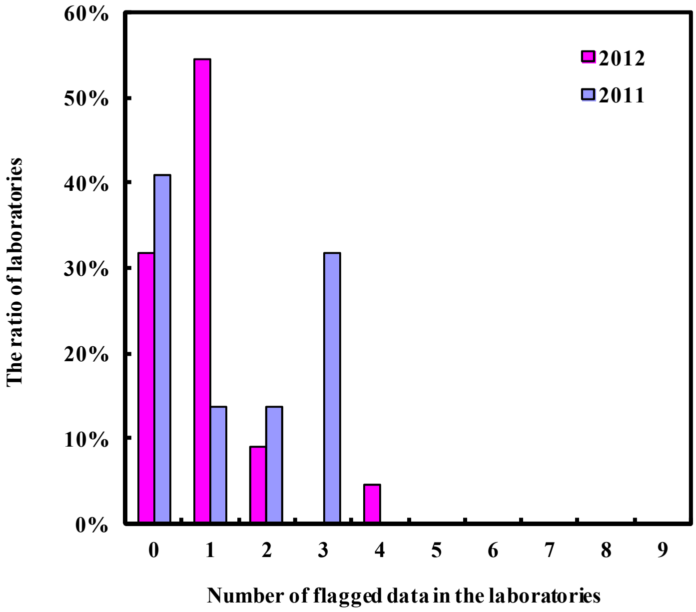


Figure 5.2 Distribution of laboratories with the number of flagged data

The percentage of the laboratories without flagged data was 32% in this attempt, while that in the last attempt (2011) was 41%. The maximum number of flagged data was four, which was submitted by one laboratory. Furthermore, the number of flagged data was one, which was submitted by 12 laboratories (correspond to 55%) as the largest ratio.

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

Table 5.10 Analytical Results of Sample No.121i (artificial inland aquatic environment sample : EANET in 2012)

Lab. ID	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	R1	R2
	-	mS m^{-1}	meq L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	-	-
KH01	6.93	5.88	0.021 X	7.33 E	2.19 E	4.87	3.14	1.81	3.47	1.80	0.20 E	19.60 I	-2.85
CN01	6.94	6.30	0.145	9.30	2.69	5.75	3.16	1.89	3.54	1.86	0.32 E	-1.00	3.74
CN02	6.95	6.36	0.132	9.32	2.69	5.76	3.16	1.86	3.61	1.82	0.23	-0.33	2.58
CN03	7.08	6.37	0.141	9.33	2.70	5.75	3.33	2.06	3.67	1.88	0.22 E	0.58	3.68
CN04	7.08	6.38	0.136	9.09	2.67	5.75	3.25	1.92	3.70	1.82	0.21 E	0.59	2.63
ID01	7.20	6.35	0.151	9.98	2.56	5.04	3.05	1.66	3.57	1.85	0.33 E	-1.74	2.70
ID05	6.82	6.33	0.145	7.94	2.82	5.00	3.05	1.78	3.05	1.71	0.10 X	-2.07	-2.06
JP04	7.16	6.39	0.142	8.63	2.67	5.39	3.03	1.83	3.51	1.89	0.27	0.73	1.06
JP05	7.15	6.20	0.134	8.50	2.49	5.55	3.06	1.81	3.55	1.85	0.23 E	1.40	2.13
LA01	6.83	5.89	0.184 X	9.88	2.91	6.32						-	-
MY01	7.19	6.23	0.146	9.01	2.64	5.64	3.12	1.86	3.26	1.75	0.26	-2.98	2.51
MN01	6.89	6.25	0.117									-	-
PH01	7.08	7.17	0.129	8.43	2.53	5.43	3.09	1.89	3.59	1.85	0.26	2.92	-5.27
PH02	7.18	6.28	0.140	9.31	2.71	5.33	3.20	1.91	3.46	1.90	0.28	0.43	2.99
RU01	6.81	6.31	0.124	8.74	2.61	6.06	3.01	1.82	3.05	1.82	0.31	-2.23	1.07
RU02	7.02	6.31	0.130	8.62	1.95 E	5.62	2.94	1.97	3.44	1.96	0.16 X	2.00	0.83
TH01	7.06	62.6 X	0.150	9.11	2.62	5.56	3.14	1.92	3.64	1.93	0.27	0.18	-80.48 C
TH02	6.71	6.32	0.126	9.27	2.62	5.62	3.08	1.83	4.14 E	1.89	0.23 E	3.37	3.63
VN01	6.99	6.39	0.160 E	8.88	2.67	5.69	3.11	1.81	3.32	1.96	0.25	-2.45	2.32
VN02	6.96	6.17	0.175 X	8.94	2.69	5.56	3.18	1.72	3.45	1.99	0.28	-2.57	4.94
VN03	6.87	6.13	0.180 X	9.09		5.30	2.98	1.78	3.27	1.65	0.30	-	-
VN04	6.95	6.17	0.163 E	8.89	2.64	5.33	3.26	2.15	3.31	1.79	0.28	-1.55	3.87
Expected value	7.05	6.66	0.132	9.09	2.72	5.73	3.13	1.89	3.49	1.86	0.27	-	-

E: Value exceeded the DQO within a factor of 2 (± 15% − ± 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 from 5.3 to 5.13 for each analytical parameter. The results received from each laboratory are normalized by the prepared values to evaluate deviation from the prepared values.

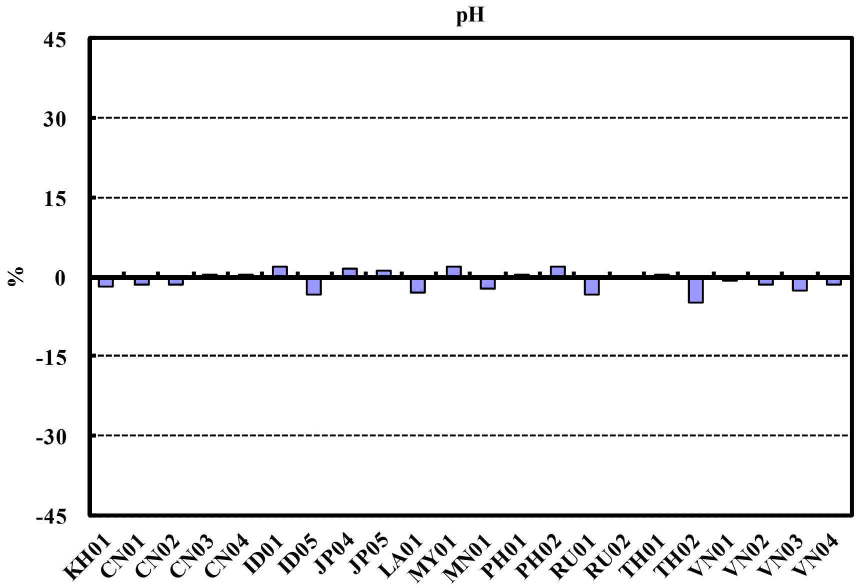


Figure 5.3 Distribution of results for pH (normalized by the prepared value)

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

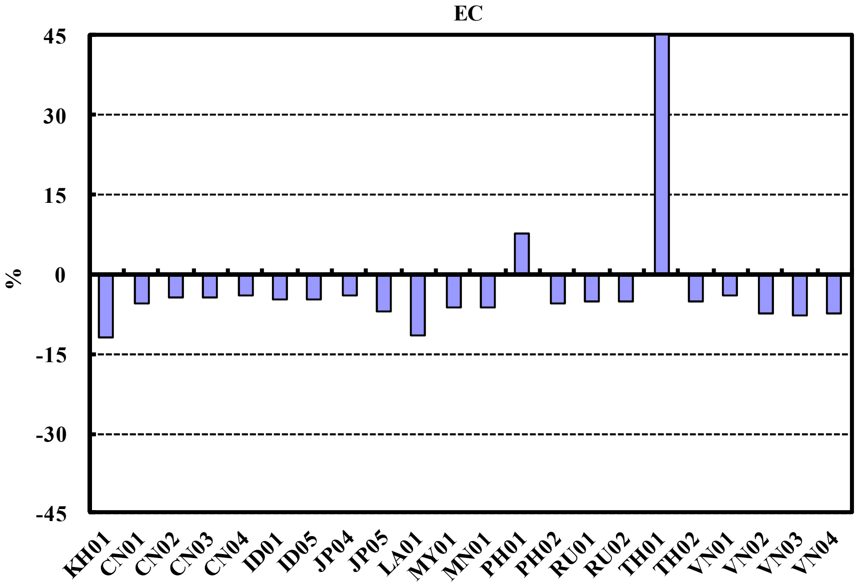


Figure 5.4 Distribution of results for EC (normalized by the prepared value)

Except for TH01, all the submitted data of EC were within DQO, 15%. Almost all of them were lower than the prepared value and their differences between laboratories were small, although the data of TH01 exceeds DQOs extremely.

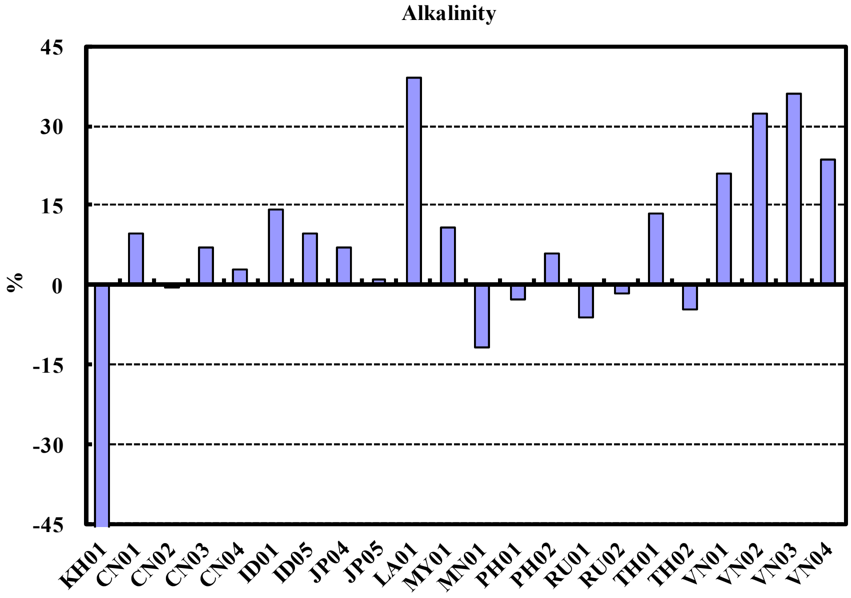


Figure 5.5 Distribution of results for alkalinity (normalized by prepared concentration)

Data from six laboratories were flagged, and four of them were deviated more than 30%. In particular, the data submitted by laboratory KH01 was significantly deviated from the prepared value.

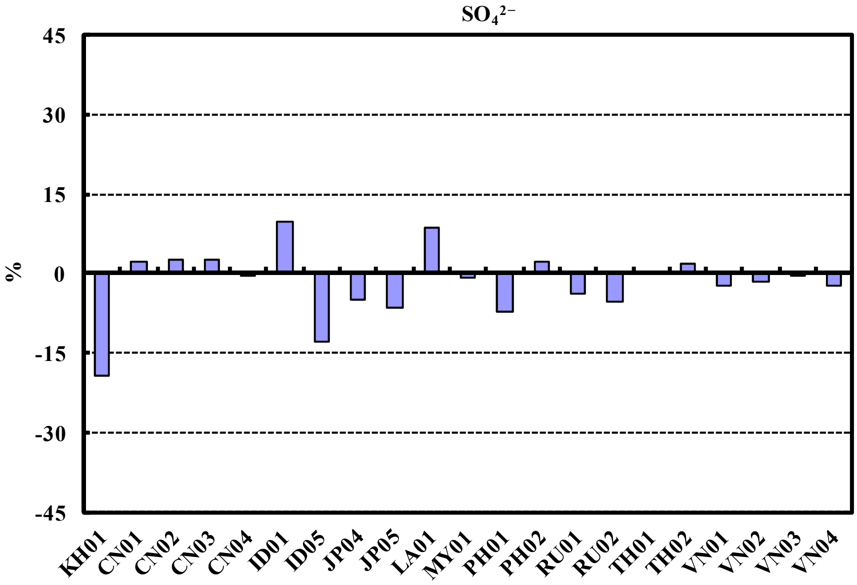


Figure 5.6 Distribution of results for SO_4^{2-} (normalized by prepared concentration)

One data was flagged, and that stayed within 30%. Most of the participating laboratories used ion chromatography for the determination of SO_4^{2-}, and also the flagged data was obtained through this method.

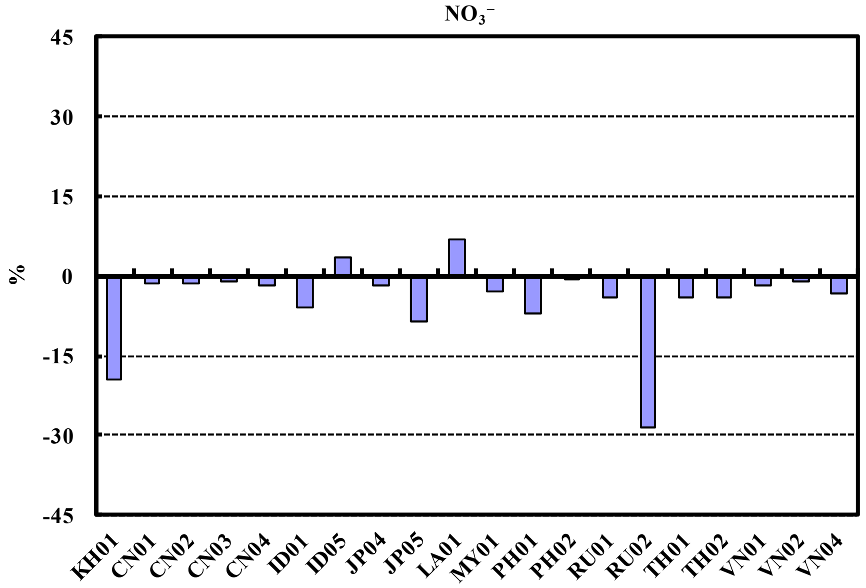


Figure 5.7 Distribution of results for NO_3^- (normalized by prepared concentration)

Data from two laboratories were flagged, and both of them were within 30% deviated from the prepared value. Most of the participating laboratories used ion chromatography for the determination of NO_3^-, while two laboratories used spectrophotometry. Flagged data were found in the data obtained through each method.

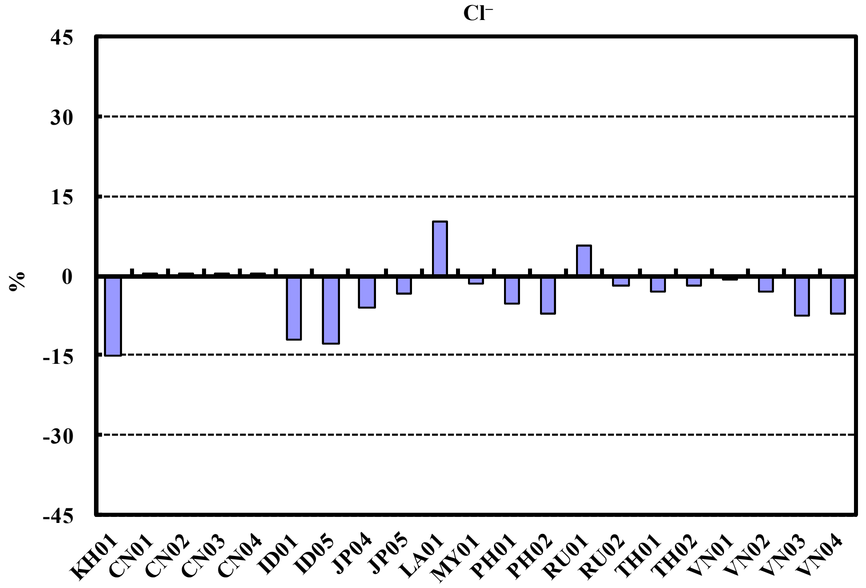


Figure 5.8 Distribution of results for Cl^- (normalized by prepared concentration)

All of the submitted data of Cl^{-} were within DQOs, including the data of KH01 narrowly. Many of them were lower than the prepared value. Most of the participating laboratories used ion chromatography for the determination, while three laboratories used the titration method.

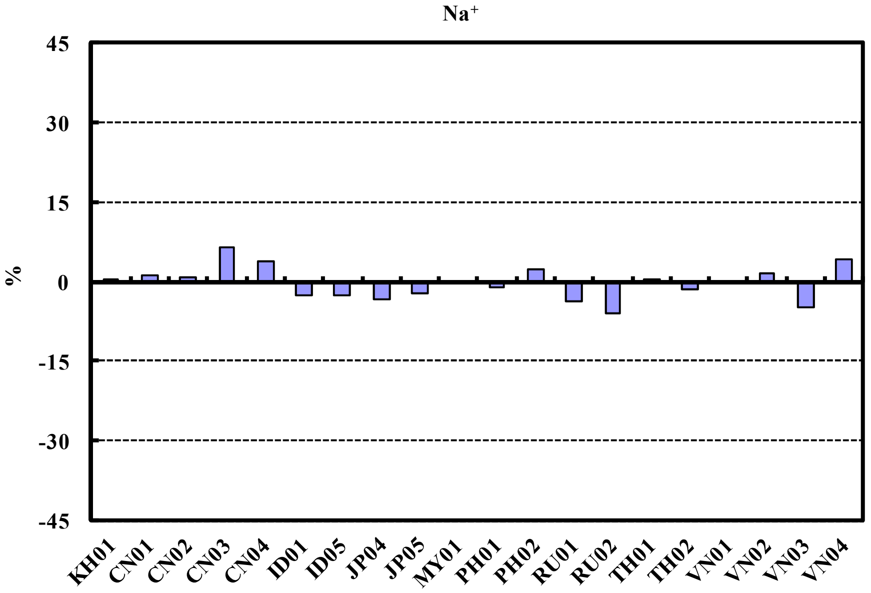


Figure 5.9 Distribution of results for Na^{+} (normalized by prepared concentration)

All of the submitted data of Na^{+} were within DQOs, and their differences were small relatively. Most of the participating laboratories used ion chromatography for the determination, while four laboratories used atomic absorption spectrometry / flame (emission) photometry.

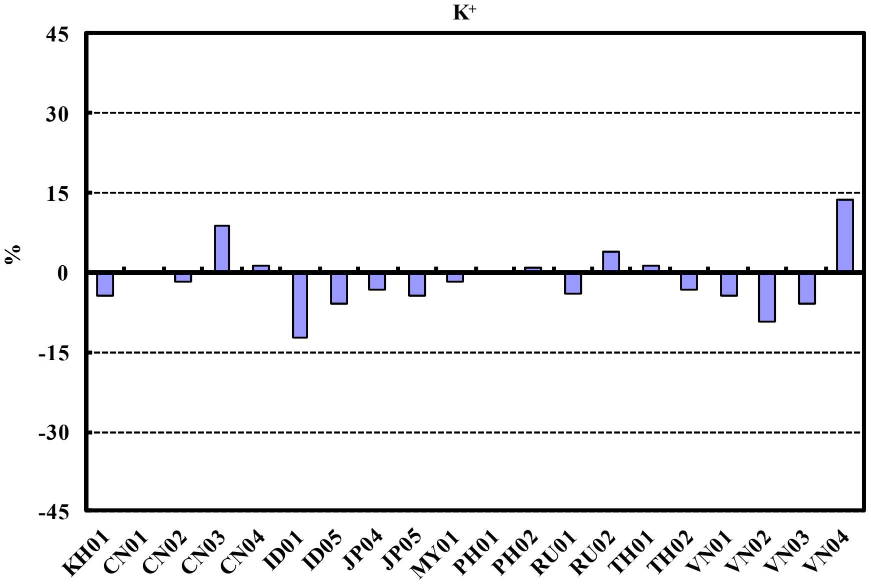


Figure 5.10 Distribution of results for K^{+} (normalized by prepared concentration)

All of the submitted data of K^+ were within DQOs. Most of the participating laboratories used ion chromatography for the determination, while four laboratories used atomic absorption spectrometry / flame (emission) photometry.

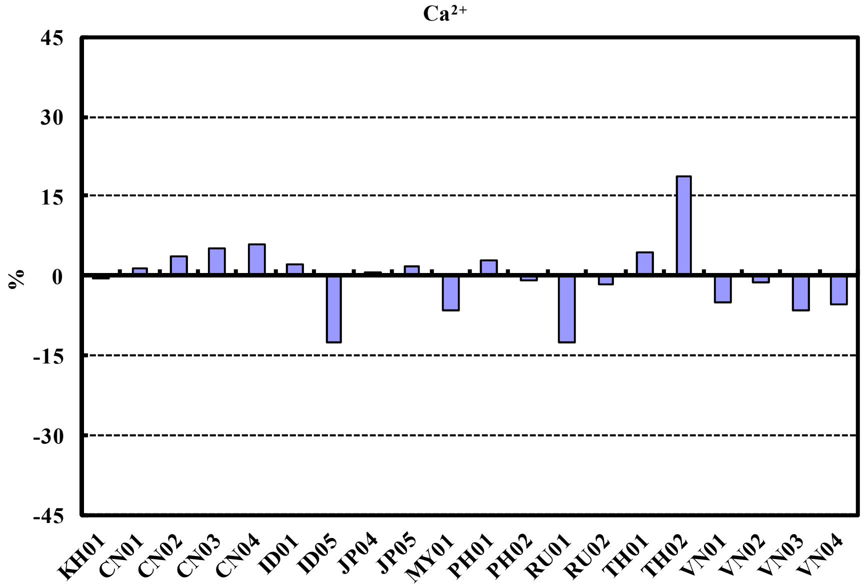


Figure 5.11 Distribution of results for Ca^{2+} (normalized by prepared concentration)

One data was flagged, and that stayed within 30%. Most of the participating laboratories used ion chromatography for the determination of Ca^{2+}, and also the flagged data was obtained through this method.

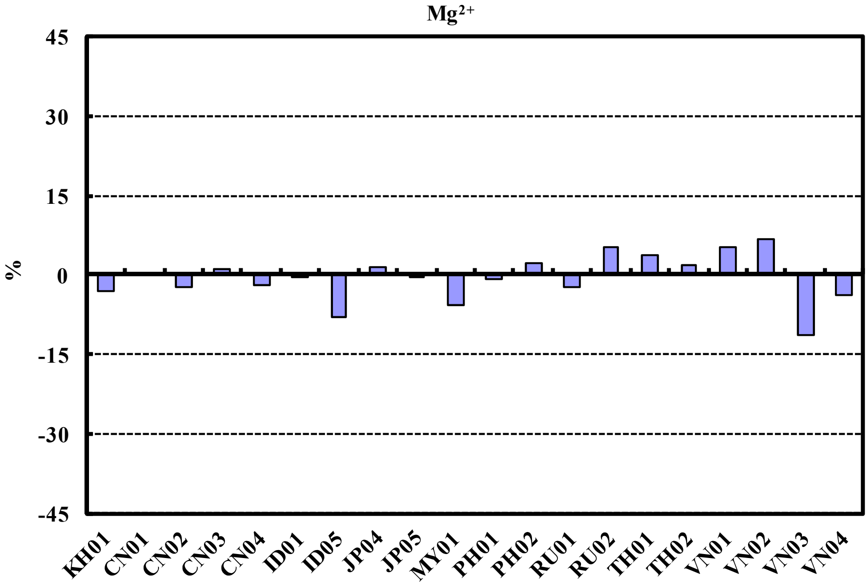


Figure 5.12 Distribution of results for Mg^{2+} (normalized by prepared concentration)

All of the submitted data of Mg^{2+} were within DQOs. Most of the participating laboratories used ion chromatography for the determination, while four laboratories used atomic absorption spectrometry / flame (emission) photometry.

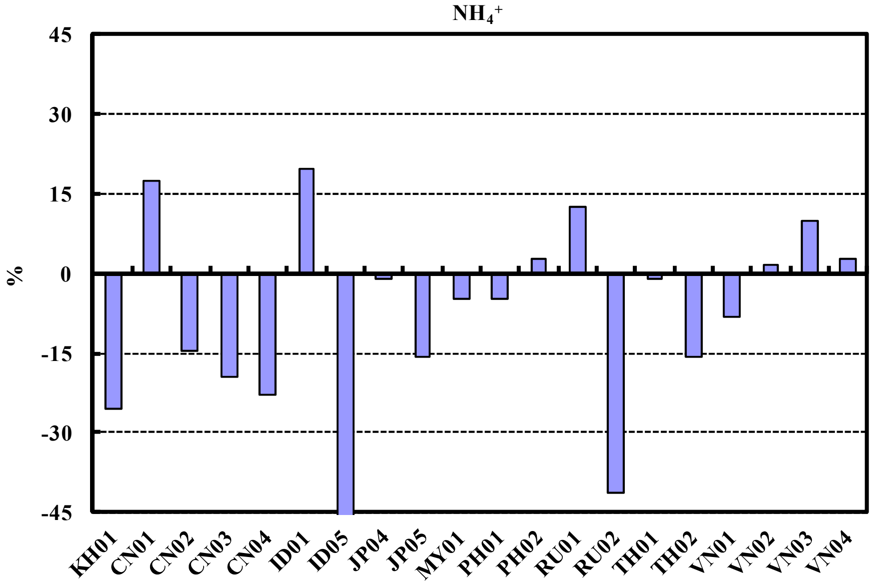


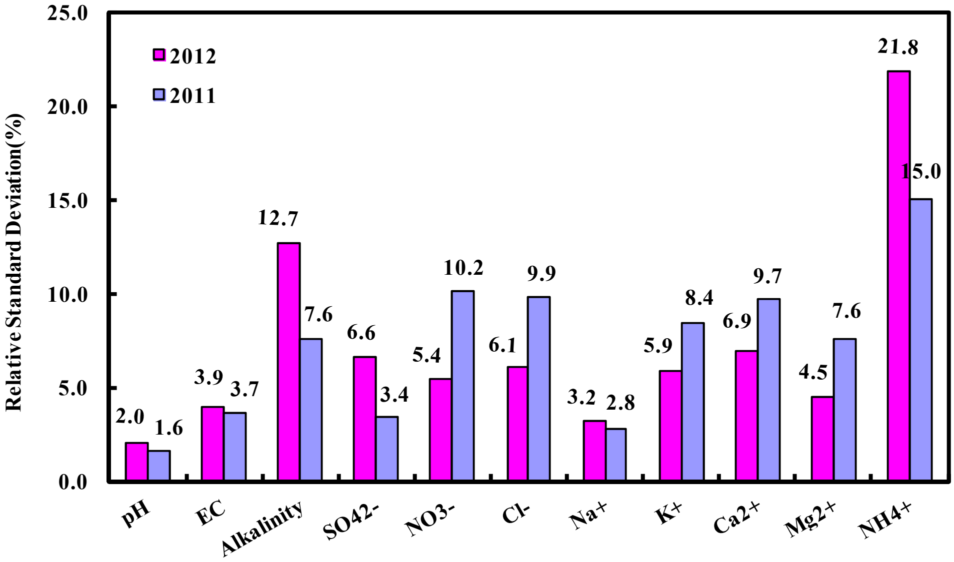
Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

Data from nine laboratories were flagged, and two of them were deviated more than 30%. Among 20 participating laboratories, 16 laboratories used ion chromatography, 3 laboratories used spectrophotometry (Indophenol) and 1 laboratory used spectrophotometry (other method) for the determination of NH_4^+. Flagged data were found through every method. However, in particular, two flagged data exceeding 30% were obtained through both spectrophotometry methods.

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 2003-2011. It may be necessary to pay more attention to the accuracy of NH_4^+ analysis in the inland water sample in each laboratory.

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 (2011).



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

Figure 5.14 Relative standard deviation of each constituent

The relative standard deviation (RSD) of NH_4^+ results from laboratories had tendency to be larger than the other parameters comparatively as similar to that of the last attempt. Although the values in many parameters decreased, those in some parameters increased remarkably in this attempt. In particular, it was clear concerning NO_3^- and Cl^-, the RSDs of these parameters were from 10.2% to 5.4%, and from 9.9% to 6.1%, respectively. On the other hand, as to Alkalinity and NH_4^+, the RSDs increased from 7.6% to 12.7%, and from 15.0% to 21.8%, respectively. The RSD of NH_4^+ 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 Figure 5.15, and the codes used for the various analytical methods are shown in Table 5.11 and 5.12.

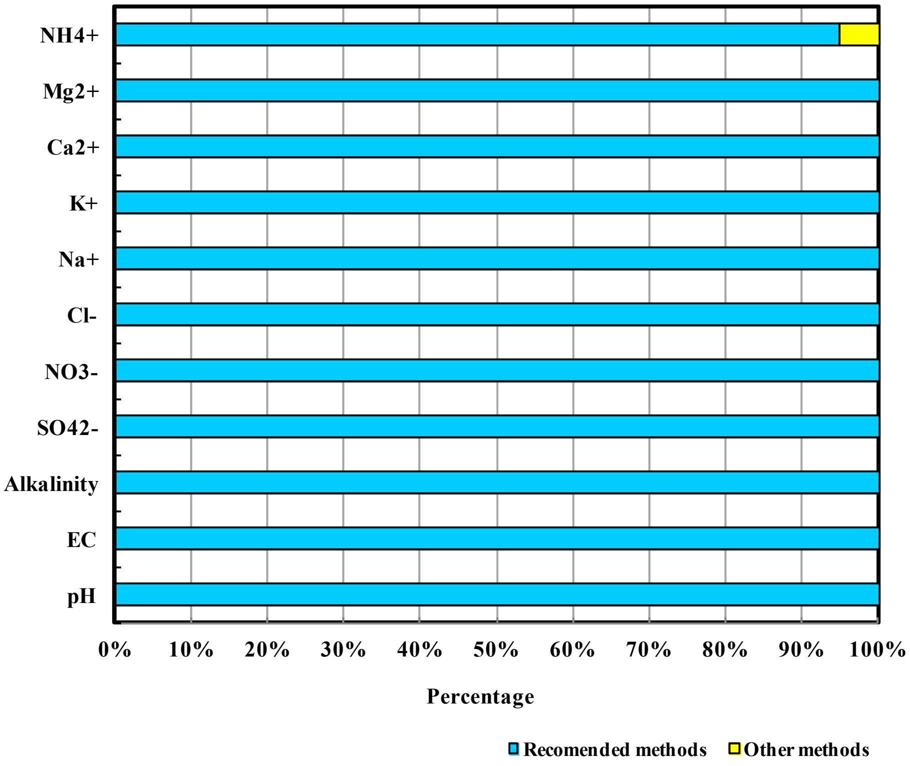


Figure 5.15 Percentage of laboratories using the recommended methods

Table 5.11 List of methods

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

Table 5.12 Analytical methods

Code	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	22										
1		22(1)									
2			22(6)			3					
3							4	4	4	4	
4				18(1)	18(1)	18	16	16	16(1)	16	16(7)
5											
6											
7				3	2(1)						1(1)
8											3(1)
9											
10											
11											
Flagged E	0	0	2	1	2	0	0	0	1	0	7
Flagged X	0	1	4	0	0	0	0	0	0	0	2

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 NH_4^+. One laboratory used spectrophotometry without indophenol blue for NH_4^+ analysis. This data was flagged as one of the two data exceeding DQO, 30%.

For the determination of anions/cations, most of the participating laboratories used ion chromatography, while some of them used other methods. Either data of all anions/cations obtained through ion chromatography included some flagged data. As a conclusion, there was no clear relationship between analytical methods and appearance of flagged data.

Staff (numbers and years of experience)

Number of staff in charge of measurement in each laboratory is shown in Table 5.13.

Table 5.13 Staff in charge of measurement

Lab.ID	Total	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	1	A	A	-	A	A	-	A	-	-	-	-
CN01	1	A	A	A	A	A	A	A	A	A	A	A
CN02	3	A	A	B	C	C	C	C	C	C	C	C
CN03	2	A	A	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	B	A	B	C	D	E	E	D	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
LA01	1	A	A	A	A	A	A					
MY01	3	A	A	A	B	B	B	C	C	C	C	C
MN01	2	A	A	B								
PH01	3	A	A	B	C	C	C	C	C	C	C	C
PH02	3	A	A	B	C	C	C	C	C	C	C	C
RU01	4	A	A	B	C	C	C	D	D	D	D	A
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	A	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

Unit : year

Lab.ID	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	7	7	-	7	7	7	7	7	7	7	7
CN01	5	5	5	5	5	5	5	5	5	5	5
CN02	22	22	7	7	7	7	7	7	7	7	7
CN03	1	1	1	1	1	1	1	1	1	1	1
CN04	6	6	6	27	27	27	27	27	27	27	27
ID01	15	15	15	15	15	15	15	15	15	15	15
ID05	6	6	6	6	6	2	4	4	4	4	29
JP04	1	1	1	1	1	1	1	1	1	1	1
JP05	4	4	4	4	4	4	4	4	4	4	4
LA01	6	6	6	6	6	6					
MY01	6	6	6	2	2	2	8	8	8	8	8
MN01	19	19	14								
PH01	3	3	7	5	5	5	15	15	15	15	5
PH02	22	22	8	21	21	21	21	21	21	21	21
RU01	19	19	10	17	17	17	27	27	27	27	19
RU02	52	52	52	18	18	52	21	21	21	21	18
TH01	7	7	7	15	15	15	15	15	15	15	15
TH02	15	9	15	9	9	9	15	15	15	15	15
VN01	1	1	20	20	20	20	20	20	20	20	20
VN02	6	6	8	20	20	20	20	20	20	20	20
VN03	6	6	6	6		6	9	9	9	9	6
VN04	10	10	9	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 13 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.

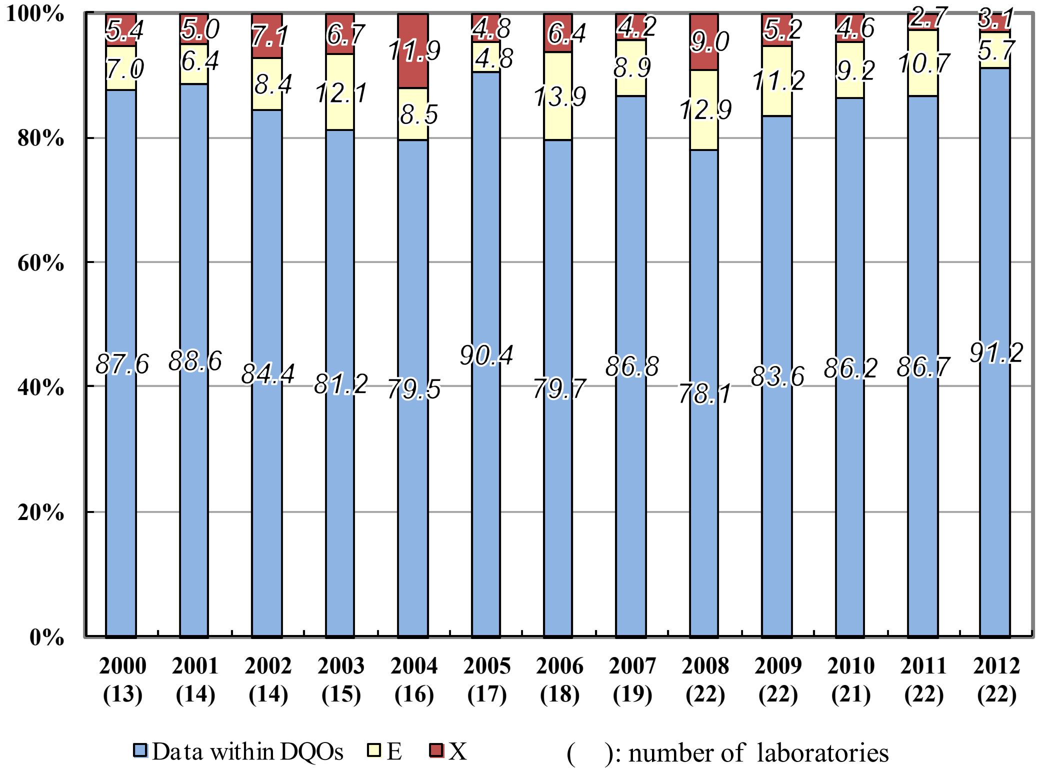


Figure 5. 16 Comparison of the results from the inter-laboratory comparison projects

The number of participating laboratories was not really changed since 2008. The percentage of data that satisfied the DQOs kept on increasing, and that value was the highest up to the present eventually. On the other hand, the percentage of flagged data exceeding the DQOs more than a factor of 2 showed the second lowest value following the last attempt.

The values/concentrations for each parameter from the 1st to 13th project were compared with the percentage of flagged data in Figure 5.17.

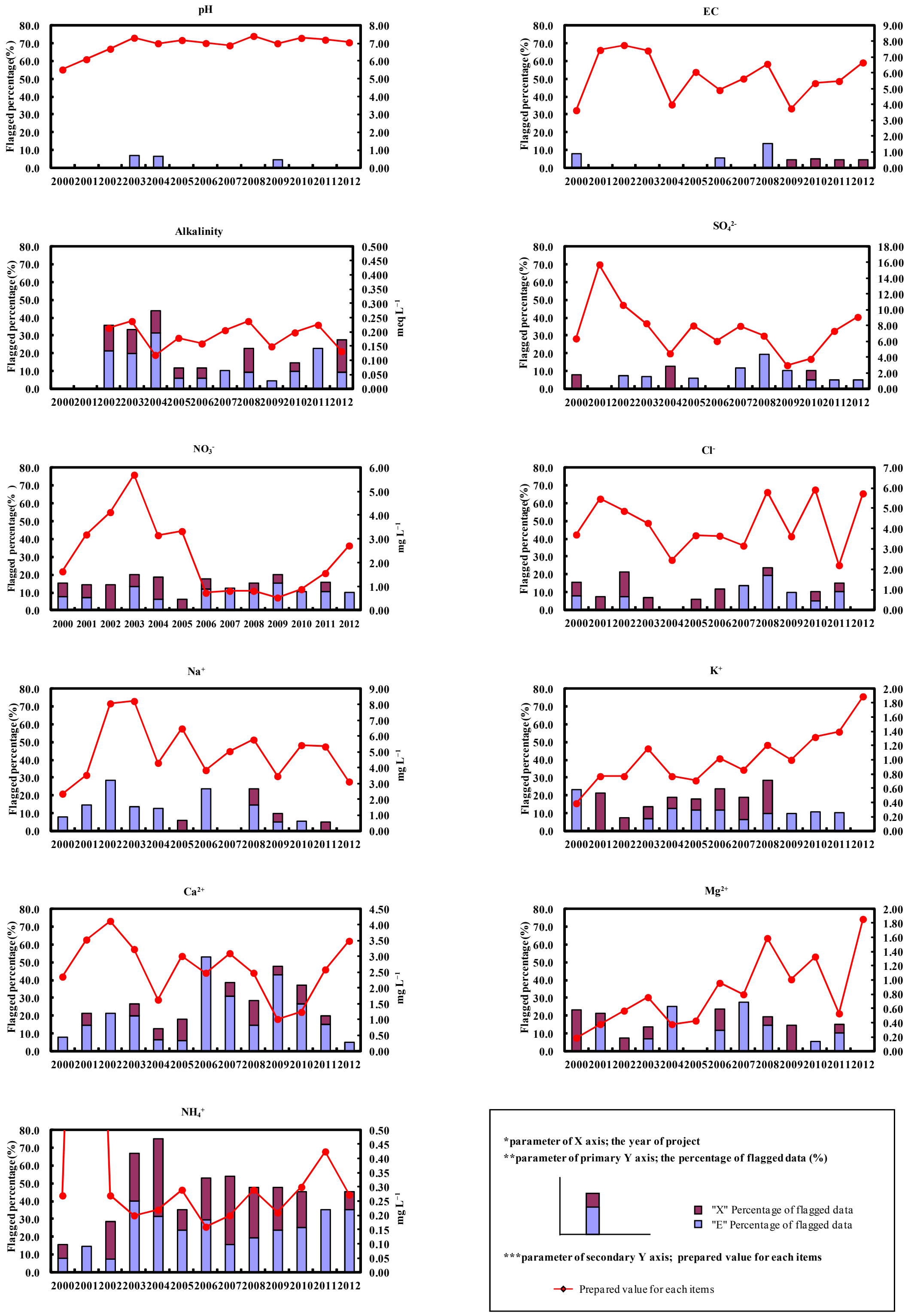


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects

The percentage of flagged data of NH_4^+ had maintained high level since 2003 when its concentration was prepared low. The prepared value of NH_4^+ was lower than that in the last attempt, however, on the same degree of that in 2008 or 2010 in recent years. In comparison with the percentage of flagged data with "X" in 2008 or 2010, that decreased obviously in this attempt. It might reveal that the accuracy of NH_4^+ analysis in each laboratory is to be in the process of improvement.

There was no flagged data for Cl^-, Na^+, K^+ and Mg^{2+} in this attempt. As for K^+ and Mg^{2+}, they were prepared as the highest values since the attempt began. In contrast, with regard to the values of Cl^- and Na^+, there were some records on the same degree of these values in past years. Thus, relationship between the concentration and the percentage of flagged data was not clear yet.

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. 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 $0.15 \mathrm{mS\ m^{-1}}$ is acceptable for measurements, analyses, dilution of precipitation samples and cleaning.

3) Certified materials and certified samples

- The measurements are evaluated by comparison of measured results of samples and certified materials.
- In order to assure the reliability of measurements, the certified solutions and materials should be used as much as possible.

4) Pretreatment of samples at analytical laboratory

- Conductivity and pH should be measured as soon as possible after sample receiving, and checking agreement of samples and sample list.
- Effort should be made to start analysis of the other parameters within a week of sample arrival in the laboratory and to complete the data sets by measuring EC, pH and all other chemical parameters.

5) Calibration of analytical instruments

- Each of the analytical instruments must be calibrated when they are used, and they should be adjusted as appropriate.

5.5.2 Evaluation of reliability

1) Sensitivity fluctuation of analytical instruments

When numerous samples are measured, measurements should only be continued after confirming that the sensitivity fluctuation is within the prescribed range.

For example, in ion chromatography

- ►A new calibration should be performed before the measurements are reached to over 30 samples.
- ►Reference materials should be measured after the calibration. It should also be done once or twice before the next calibration.
- ►Control charts should be applied for the measurement of the reference materials.
- ►Standard solutions and reference solutions must be prepared from different stock solutions in order to be independent.
- ►If the results of the control solutions are outside of 3 standard deviations, or out of 15 % from the expected value, the reasons should be found and corrections should be made, and reference solution should be measured again.
- ►If the retention time changes slowly while the separator column is deteriorating, then adequate actions should be taken as appropriate. If it changes significantly in a relatively short time, the reasons should be found and removed, then the reference material must be measured again.

5.5.3 Data control

1) Data checks by the analytical laboratories

- ►When the sensitivity of instruments is not stable, when the results of duplicate analyses or re-measurements are significantly different, or when the percentage of a theoretical value to that for determined data in ion balances and electrical conductivity is significantly different from 1.0, measurement should be repeated since reliability is low.
- ►When samples seem to be obviously contaminated, these data should be treated as unrecorded data.
- ►Abnormal or unrecorded data can corrupt research results. So, careful checks are needed to avoid data of questionable quality. When abnormal or unrecorded data is detected, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

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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	6.93	5.88	0.021	7.33	2.19	4.87	3.14	1.81	3.47	1.80	0.20
CN01	6.94	6.30	0.145	9.30	2.69	5.75	3.16	1.89	3.54	1.86	0.32
CN02	6.95	6.36	0.132	9.32	2.69	5.76	3.16	1.86	3.61	1.82	0.23
CN03	7.08	6.37	0.141	9.33	2.70	5.75	3.33	2.06	3.67	1.88	0.22
CN04	7.08	6.38	0.136	9.09	2.67	5.75	3.25	1.92	3.70	1.82	0.21
ID01	7.20	6.35	0.151	9.98	2.56	5.04	3.05	1.66	3.57	1.85	0.33
ID05	6.82	6.33	0.145	7.94	2.82	5.00	3.05	1.78	3.05	1.71	0.10
JP04	7.16	6.39	0.142	8.63	2.67	5.39	3.03	1.83	3.51	1.89	0.27
JP05	7.15	6.20	0.134	8.50	2.49	5.55	3.06	1.81	3.55	1.85	0.23
LA01	6.83	5.89	0.184	9.88	2.91	6.32					
MY01	7.19	6.23	0.146	9.01	2.64	5.64	3.12	1.86	3.26	1.75	0.26
MN01	6.89	6.25	0.117								
PH01	7.08	7.17	0.129	8.43	2.53	5.43	3.09	1.89	3.59	1.85	0.26
PH02	7.18	6.28	0.140	9.31	2.71	5.33	3.20	1.91	3.46	1.90	0.28
RU01	6.81	6.31	0.124	8.74	2.61	6.06	3.01	1.82	3.05	1.82	0.31
RU02	7.02	6.31	0.130	8.62	1.95	5.62	2.94	1.97	3.44	1.96	0.16
TH01	7.06	62.6	0.150	9.11	2.62	5.56	3.14	1.92	3.64	1.93	0.27
TH02	6.71	6.32	0.126	9.27	2.62	5.62	3.08	1.83	4.14	1.89	0.23
VN01	6.99	6.39	0.160	8.88	2.67	5.69	3.11	1.81	3.32	1.96	0.25
VN02	6.96	6.17	0.175	8.94	2.69	5.56	3.18	1.72	3.45	1.99	0.28
VN03	6.87	6.13	0.180	9.09		5.30	2.98	1.78	3.27	1.65	0.30
VN04	6.95	6.17	0.163	8.89	2.64	5.33	3.26	2.15	3.31	1.79	0.28
Expected value	7.05	6.66	0.132	9.09	2.72	5.73	3.13	1.89	3.49	1.86	0.27
Number of data	22	22	22	21	20	21	20	20	20	20	20
Average	6.99	8.85	0.140	8.93	2.60	5.54	3.12	1.86	3.48	1.85	0.25
Minimum	6.71	5.88	0.021	7.33	1.95	4.87	2.94	1.66	3.05	1.65	0.10
Maximum	7.20	62.6	0.184	9.98	2.91	6.32	3.33	2.15	4.14	1.99	0.33

blank: not analyzed

Appendix Table 5.2 Data normalized by the prepared value

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

Lab. ID	pH (%)	EC (%)	Alkalinity (%)	SO_4^{2-} (%)	NO_3^- (%)	Cl^- (%)	Na^+ (%)	K^+ (%)	Ca^{2+} (%)	Mg^{2+} (%)	NH_4^+ (%)
KH01	-1.7	-11.7	-84.1	-19.4	-19.6	-15.0	0.3	-4.4	-0.6	-3.2	-25.5
CN01	-1.6	-5.3	9.7	2.3	-1.3	0.3	1.2	-0.3	1.5	0.1	17.3
CN02	-1.5	-4.4	-0.4	2.5	-1.4	0.5	1.0	-1.6	3.5	-2.1	-14.5
CN03	0.4	-4.3	6.9	2.6	-0.9	0.3	6.6	8.8	5.2	1.1	-19.4
CN04	0.4	-4.2	2.9	0.0	-2.0	0.3	3.9	1.3	6.0	-1.9	-23.0
ID01	2.1	-4.6	14.2	9.8	-6.0	-12.1	-2.5	-12.3	2.2	-0.3	19.7
ID05	-3.3	-4.9	9.7	-12.7	3.5	-12.8	-2.5	-6.0	-12.6	-8.0	-63.4
JP04	1.6	-4.0	7.2	-5.0	-2.0	-6.0	-3.2	-3.3	0.6	1.7	-1.1
JP05	1.3	-6.9	1.1	-6.5	-8.6	-3.2	-2.0	-4.2	1.7	-0.5	-15.7
LA01	-3.1	-11.5	39.2	8.7	6.7	10.3					
MY01	1.9	-6.4	10.7	-0.9	-3.1	-1.6	-0.2	-1.6	-6.6	-5.7	-4.7
MN01	-2.3	-6.1	-11.8								
PH01	0.4	7.7	-2.7	-7.3	-7.0	-5.2	-1.2	-0.3	2.9	-0.7	-4.7
PH02	1.8	-5.6	5.9	2.4	-0.7	-7.0	2.4	0.7	-1.0	2.2	2.6
RU01	-3.4	-5.2	-6.2	-3.9	-4.2	5.8	-3.8	-4.0	-12.5	-2.1	12.4
RU02	-0.5	-5.3	-1.7	-5.2	-28.4	-2.0	-6.0	4.1	-1.4	5.3	-41.4
TH01	0.1	840	13.5	0.2	-4.0	-3.1	0.3	1.4	4.3	3.6	-1.1
TH02	-4.8	-5.1	-4.7	2.0	-4.0	-2.0	-1.6	-3.3	18.6	1.9	-15.7
VN01	-0.9	-4.0	21.0	-2.3	-2.0	-0.7	-0.4	-4.4	-4.9	5.3	-8.4
VN02	-1.4	-7.4	32.4	-1.7	-1.1	-3.1	1.6	-9.3	-1.1	6.9	1.4
VN03	-2.6	-7.9	36.2	0.0		-7.5	-4.7	-6.0	-6.3	-11.2	9.9
VN04	-1.5	-7.4	23.5	-2.2	-3.2	-7.1	4.3	13.6	-5.2	-3.7	2.6
Minimum	-4.8	-11.7	-84.1	-19.4	-28.4	-15.0	-6.0	-12.3	-12.6	-11.2	-63.4
Maximum	2.1	840	39.2	9.8	6.7	10.3	6.6	13.6	18.6	6.9	19.7
Average	-0.8	33.0	5.6	-1.7	-4.5	-3.4	-0.3	-1.5	-0.3	-0.6	-8.6

blank: not analyzed

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