The Network Center for
The Acid Deposition Monitoring Network in East Asia

Report of the Inter-laboratory Comparison Project 2001 on Inland Aquatic Environment

2nd Attempt

November 2002

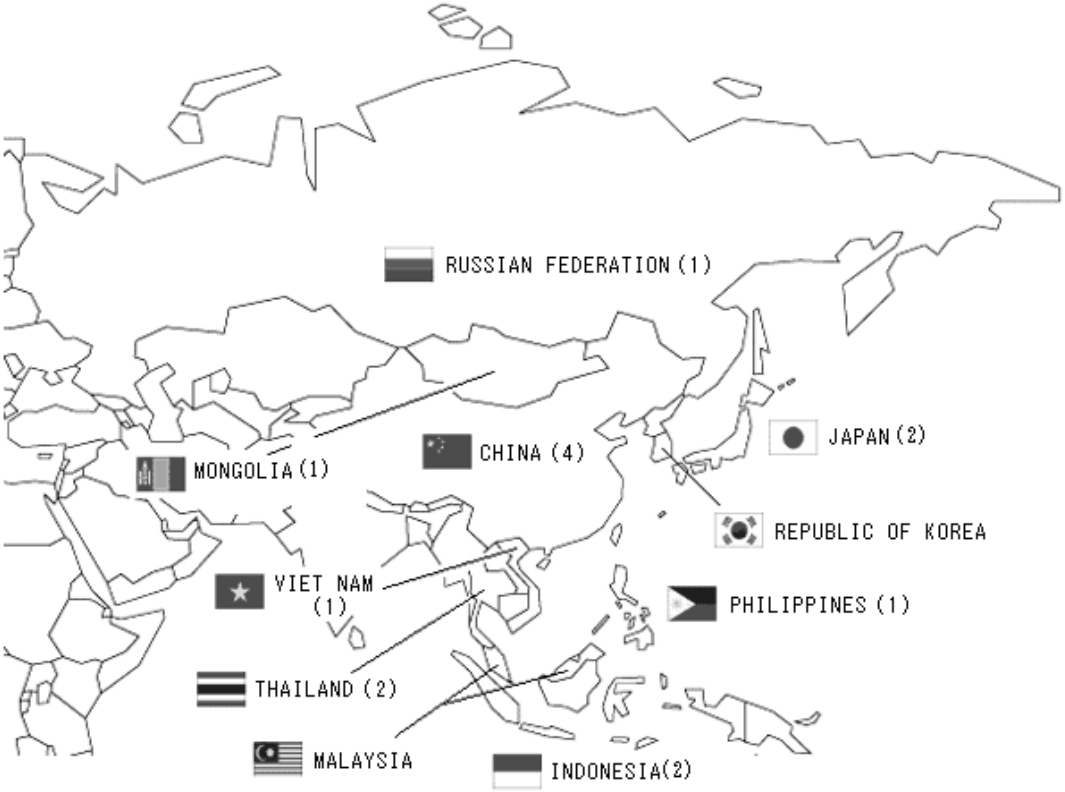
Acid Deposition and Oxidant Research Center

Contents

1. INTRODUCTION

This inter-laboratory comparison project (round robin analysis survey of uniformly prepared artificial Inland Aquatic Environment samples) was conducted among the analytical laboratories of the Acid Deposition Monitoring Network in East Asia (EANET), based on the Quality Assurance / Quality Control (QA/QC) Program of EANET. The purposes of this project are, through the evaluation of analytical results, analytical equipment and its operating condition and other practical problems, (i) to recognize the analytical precision and accuracy of the data in each participating laboratory, and give an opportunity to improve the quality of the analysis on Inland Aquatic Environment, and (ii) to improve a reliability of analytical data through the assessment of suitable analytical methods and techniques.

Artificial Inland Aquatic Environment samples, which contain major ions, were prepared and distributed by the Network Center (NC). All of the participating laboratories submitted their analytical data to NC. Obtained data for pH, EC, and concentrations of SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+ were compared with prepared values and statistically treated. List of the participating laboratories, individual analytical data with their laboratory's short name, and various statistical values are included in this report.



* Figure in parenthesis shows the number of laboratories for each country (14 laboratories from 8 countries)

Fig.1 Laboratories participated in the Inter-comparison project 2001 of the EANET

2. PROCEDURE

2.1 Participating Laboratories

Laboratories in charge of chemical analysis of the participating countries of EANET are listed in APPENDIX 1. The Network Center (NC) shipped artificial inland aquatic environment samples to all of these 14 laboratories, and all laboratories submitted their analytical data to NC. The names and contact addresses of the participating laboratories are presented in APPENDIX 1.

2.2 Dispatched Artificial Inland Aquatic Environment Samples

Artificial inland aquatic environment samples are distributed to the laboratories. The information on the analytical precision and accuracy on individual parameters can be obtained.

Table 1 Outline of artificial inland aquatic environment sample

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

2.3 Analytical Parameters

All participating laboratories were expected to measure and submit the data with the units listed in Table 2 on ten parameters of the samples: pH, Electric Conductivity (EC), concentrations of sulfate, nitrate, chloride, sodium-ion, potassium-ion, calcium-ion, magnesium-ion, and ammonium-ion. It was informed to the participating laboratories that concentration of each parameter was within range described in Table 3.

Table 2 Reporting units of analyze

Analyze	Reporting Units	
PH	pH Unites	-
EC	milli siemens/meter	mS/m
SO_4^{2-}	milligram/liter	mg/L
NO_3^-	milligram/liter	mg/L
Cl^-	milligram/liter	mg/L
Na^+	milligram/liter	mg/L
K^+	milligram/liter	mg/L
Ca^{2+}	milligram/liter	mg/L
Mg^{2+}	milligram/liter	mg/L
NH_4^+	milligram/liter	mg/L

Table 3 Concentration range of artificial inland aquatic environment sample

Parameter	Range	Parameter	Range
pH	5.5– 8.5	Na^+	0.5 – 5.0 mg/L
EC	1.5 – 15 mS/m	K^+	0.1 – 1.0 mg/L
SO_4^{2-}	2 – 20 mg/L	Ca^{2+}	0.5 – 5.0 mg/L
NO_3^-	1 – 10 mg/L	Mg^{2+}	0.05 – 0.5 mg/L
Cl^-	1 – 10 mg/L	NH_4^+	0.5 – 5.0 mg/L

2.4 Analytical Method

Participating laboratories were expected to use analytical methods and data checking procedures that are specified in the “Technical Manual for Monitoring on Inland Aquatic Environment in East Asia (2000)” and “the QA/QC Program for Monitoring on Inland Aquatic Environment in East Asia (2000)”. Analytical methods specified in the manual are described in Table 4.

Table 4 Analytical methods specified in the manual

Parameter	Analytical method
pH	Glass electrode
EC	Conductivity cell
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)

2.5 Data Checking Procedures

a) Calculation of ion balance (R_1)

(1) Total anion (A) equivalent concentration (μeq L^{-1}) is calculated by summing the concentrations of all anions (C: μmol L^{-1}).

$A\ (\mu eq\ L^{-1}) = \Sigma n\ C_{Ai}\ (\mu mol\ L^{-1}) = 2C\ (SO_4^{2-}) + C\ (NO_3^-) + C\ (Cl^-)$

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

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

$C\ (\mu eq\ L^{-1}) = \Sigma n\ C_{Ci}\ (\mu mol\ L^{-1}) = 10^{(6-pH)} + C\ (NH_4^+) + C\ (Na^+) + C\ (K^+) + 2C\ (Ca^{2+}) + 2C\ (Mg^{2+})$

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

(3) Calculation of ion balance (R_1)

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

(4) R_1, which is calculated using the above equation, should be compared with standard values in Table 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 Allowable ranges for R_1 in different concentration ranges

(C+A) [μeq / L]	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) should be calculated as follows;

$$\Lambda\text{calc } (\mu S\ cm^{-1}) = 349.7\times 10^{(3-pH)} + \{80.0\times 2C\ (SO_4^{2-}) + 71.5\ C\ (NO_3^-) + 76.3\ C\ (Cl^-) + 73.5\ C\ (NH_4^+) + 50.1\ C\ (Na^+) + 73.5\times C\ (K^+) + 59.8\times 2C\ (Ca^{2+}) + 53.3\times\ 2C\ (Mg^{2+})\}/1000$$

C: Molar concentrations (μmol L^{-1}) of ions in the parenthesis; each constant value is ionic equivalent conductance at 25°C.

(2) Ratio (R_2) of calculations (Λcalc) to measurements(Λmeas) in electric conductivity should be 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, should be compared with standard values in Table 6. Re-measurement, check with standard solutions, and/or inspection of calibration curves are necessary, when R_2 is not within the range.

Table 6 Allowable ranges for R_2 in different concentration ranges

Λmeas[mSm^{-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)”

3. RESULTS

3.1 Outline of Results

The Network Center shipped artificial inland aquatic environment samples to 14 laboratories in the participating countries of EANET, and received the data on analytical results from all laboratories. Obtained data are summarized in Table 7. Statistics that were calculated for each constituent of the artificial Inland Aquatic Environment samples were: Average, Standard deviation (S.D.), Number of data (N), Minimum (Min.), and Maximum (Max.). For the calculation, outlying data that apart from the average greater than a factor of 3 of S.D. were not included. As shown in Table.7, average of submitted data were fairly well agreed with the prepared value/concentration within a range of ±10%.

Table 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	6.10	5.55	0.19	14	5.40	6.05
EC(mS/m)	7.45	7.10	0.19	14	6.76	7.45
SO_4^{2-}(mgl/L)	15.74	15.68	0.93	14	13.70	17.86
NO_3^-(mg/L)	3.19	3.05	0.21	13	2.57	3.49
Cl^-(mg/L)	5.47	5.38	0.19	13	5.14	5.81
Na^+(mg/L)	3.54	3.40	0.23	14	2.88	3.63
K^+(mgl/L)	0.77	0.78	0.16	14	0.34	1.04
Ca^{2+}(mg/L)	3.53	3.58	0.40	14	2.93	4.61
Mg^{2+}(mgl/L)	0.38	0.39	0.06	14	0.28	0.56
NH_4^+(mg/L)	2.73	2.79	0.32	14	2.11	3.44

(note) Prepared : Value or concentration, which was calculated from the amount of chemicals, used for the preparation of samples.

The Data Quality Objectives (DQOs) of data obtained during the preparatory-phase activities of EANET was specified for every constituent as ±15% by the QA/QC program of the EANET. In this report, analytical data on artificial inland aquatic environmental samples were compared with the prepared value/concentration and evaluated by the DQO value: the flag "E" was put to the data that exceed DQO by a factor of 2 (±15%~±30%), and the flag "X" was put to the data that exceed DQO more than a factor of 2 (<-30% or >30%). A set of data for each sample were evaluated by the data checking procedures described in chapter 2.5 of this report. The flag “I” was put for poor ion balance data sets, and the flag “C” was put for poor conductivity agreement data sets.

The results were evaluated following the two aspects: i) comparison of individual parameters, and ii) comparison of circumstance of analysis in each participating laboratory. Evaluation of data for each constituent is shown in “3.2 Analytical Parameter”, and evaluation of data by circumstances of analysis such as analytical method used, experience of personnel, and other analytical condition is described in “3.3 Circumstance of Sample Analysis ”.

As shown in Table.8, 9 and Fig.2, nine analytical data out of 140 exceeded the DQOs by a factor of 2 and flagged by "E". Seven analytical data out of 140 exceeded the DQOs more than a factor of 2 and flagged by "X. Data flagged by "E" and "X" were 16 out of 140 shared about 11.4 percents of all reported data of samples.

Table 8 Number of flagged data

Flag*	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca2+	Mg^{2+}	NH_4^+	Total
E	0	0	0	1	0	2	0	2	2	2	9
X	0	0	0	1	1	0	3	1	1	0	7
Data within DQOs	14	14	14	12	13	12	11	11	11	12	124
Flagged(%)	0.0	0.0	0.0	14.3	7.1	14.3	21.4	21.4	21.4	14.3	11.4

*E : Value Exceeded the DQO by a factor of 2 of the DQO (±15%~±30%)

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

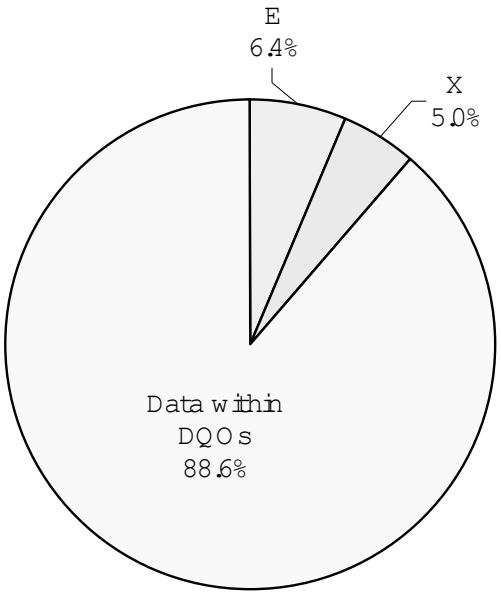


Fig.2 Percentage of flagged data

Table 9 Analytical Results of Sample

Lab.ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	R1	R2
	-	(mS/m)	(mgl/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	-	-
cn01	5.42	7.06	15.79	2.83	5.38	E 2.88	X 1.04	3.37	E 0.28	3.10	-0.7	2.8
cn02	5.40	7.22	15.22	2.89	5.21	E 2.96	0.75	3.61	0.40	2.97	1.8	1.1
cn03	5.49	6.99	15.60	3.09	5.25	3.44	0.76	3.60	0.38	2.76	1.3	3.2
cn04	5.44	6.76	15.48	3.08	5.24	3.41	0.76	3.59	0.37	2.81	1.6	4.9
id01	5.52	7.15	15.13	3.49	5.64	3.26	0.82	3.39	0.38	E 2.11	-4.7	0.0
id02	6.05	7.20	13.70	3.04	X 8.79	3.54	X 0.34	3.80	E 0.44	E 3.44	-0.2	6.0
jp01	5.51	6.98	15.50	3.07	5.45	3.62	0.71	E 4.12	0.41	2.55	3.1	4.2
jp02	5.55	6.91	15.30	E 2.57	5.35	3.50	0.85	3.43	0.37	2.38	-0.1	1.9
mn01	5.44	7.07	16.74	3.17	5.51	3.50	0.83	3.46	0.37	2.68	-2.4	4.1
ph01	5.92	6.91	16.10	3.15	5.44	3.46	0.75	3.45	0.36	2.74	-1.4	3.8
ru01	5.41	7.17	15.37	3.12	5.24	3.57	X 1.02	3.42	0.40	2.80	2.4	2.2
th01	5.51	7.42	16.25	3.16	5.31	3.63	0.81	X 4.61	X 0.56	2.73	6.1	3.8
th02	5.47	7.14	15.50	2.94	5.14	3.43	0.76	3.32	0.36	2.85	1.0	1.4
vn01	5.52	7.45	17.86	X 1.12	5.81	3.38	0.72	E 2.93	E 0.46	3.10	-2.7	1.5
Prepared value	6.10	7.45	15.74	3.19	5.47	3.54	0.77	3.53	0.38	2.73		
Number of data	14	14	14	14	14	14	14	14	14	14		
Average	5.55	7.10	15.68	2.91	5.63	3.40	0.78	3.58	0.39	2.79		
Minimum	5.40	6.76	13.70	1.12	5.14	2.88	0.34	2.93	0.28	2.11		
Maximum	6.05	7.45	17.86	3.49	8.79	3.63	1.04	4.61	0.56	3.44		
Standard deviation	0.19	0.19	0.93	0.55	0.93	0.23	0.16	0.40	0.06	0.32		

E:Value exceeded the DQO(±15) by a factor of
X:Value exceeded the DQO(±15) more than a factor of
I:Poor ion balance (R1
C:Poor conductivity agreement (R2

3.2 Analytical Parameter

The general overviews of data were presented below in Figures and Tables for each analytical parameter. The results received from each laboratory were normalized by prepared values to evaluate a deviation. The numbers of flagged data were shown in table for each analytical parameter.

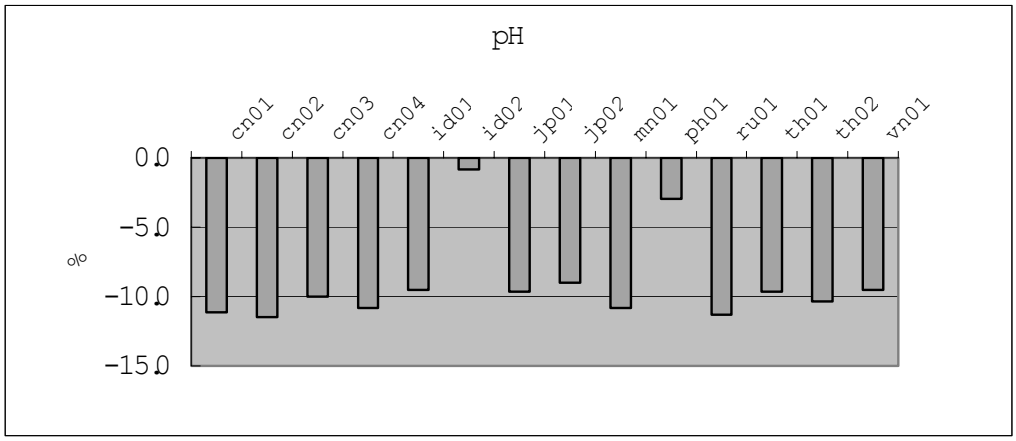


Fig.3 Distribution of pH data normalized by prepared value

Table 10 Analytical method and flagged data of pH

Analytical Method

pH meter and electrode	14/14
Other method	0/14

Flagged data

	E	X	Flagged (%)
Sample	0	0	0.0

All participating laboratories used pH meter with glass electrode for measurement of pH.

Most of obtained data were fairly agreed with prepared value. Most of the laboratories reported lower data than prepared concentration.

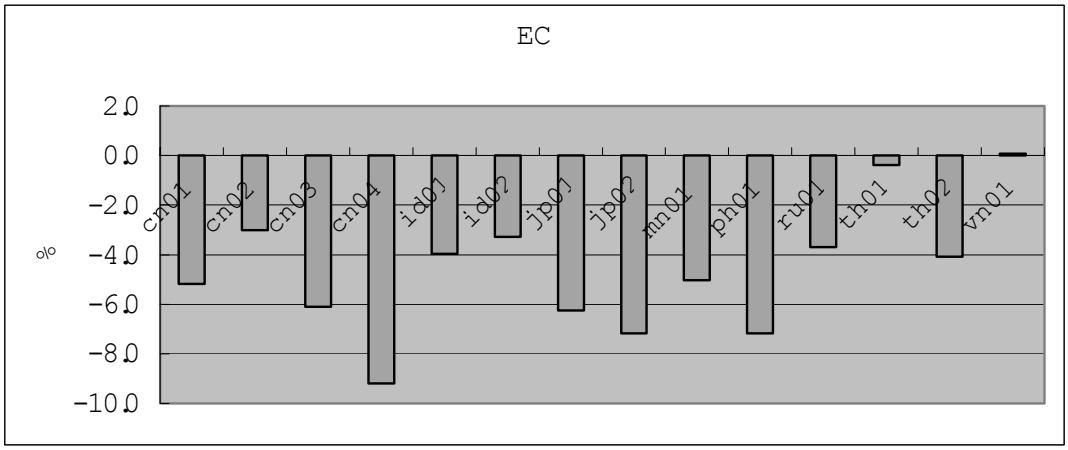


Fig.4 Distribution of EC data normalized by prepared value

Table 11 Analytical method and flagged data of EC

Analytical Method

Conductivity meter and cell	14/14
Other method	0/14

Flagged data

	E	X	Flagged (%)
Sample	0	0	0.0

All participating laboratories used conductivity cell for the measurement of EC. Obtained data were almost agreed with the prepared value. All of the laboratories reported lower data than prepared concentration.

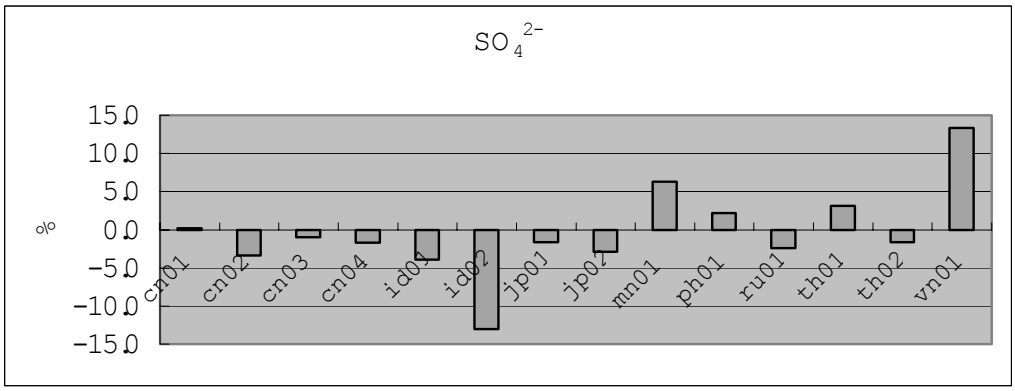


Fig.5 Distribution of SO_4^{2-} data normalized by prepared concentration

Table 12 Analytical method and flagged data of SO_4^{2-}

Analytical Method

Ion chromatography	12/14
spectrophotometry	2/14

Flagged data

	E	X	Flagged (%)
Sample	0	0	0.0

All of the participating laboratories except two used ion chromatography for the determination of SO_4^2. Lab.id02 & vn01 used other method (spectrophotometry) without ion chromatography. These obtained data were slightly higher or lower than other laboratories.

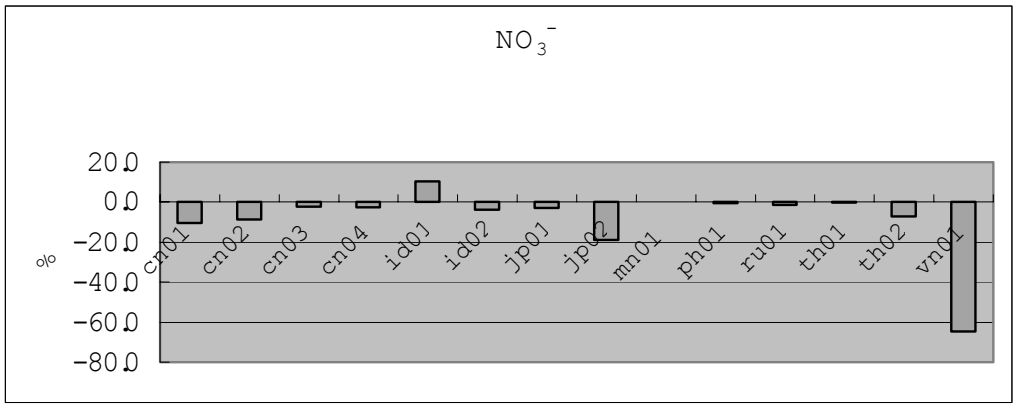


Fig.6 Distribution of NO_3^- data normalized by prepared concentration

Table 13 Analytical method and flagged data of NO_3^-

Analytical Method

Ion chromatography	11/14
spectrophotometry	3/14

Flagged data

	E	X	Flagged (%)
Sample	1	1	14.3

Same as SO_4^{2-}, most of participating laboratories used ion chromatography for the determination of NO_3^-. Three laboratories used spectrophotometry. Data from Lab.jp02 and vn01 obtained with spectrophotometry were all flagged. Perhaps there is a problem of the used method in this case.

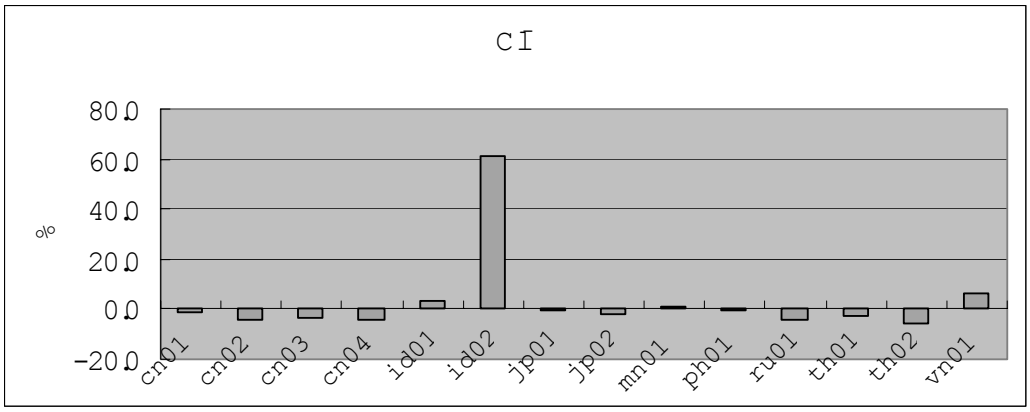


Fig.7 Distribution of Cl^- data normalized by prepared concentration

Table 14 Analytical method and flagged data of Cl^-

Analytical Method

Ion chromatography	12/14
titration method	2/14

Flagged data

	E	X	Flagged (%)
Sample	0	1	7.1

Same as SO_4^{2-} and NO_3^-, most laboratories used ion chromatography for the determination of Cl^-. Lab.id02 & vn01 used a titration method, and Lab.id02 submitted data significantly deviated from the prepared concentration.

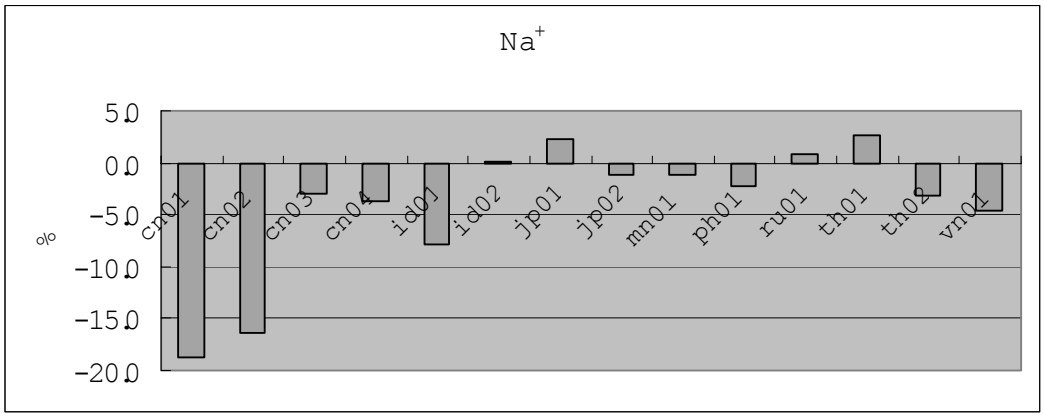


Fig.8 Distribution of Na^+ data normalized by prepared concentration

Table 15 Analytical method and flagged data of Na^+

Analytical Method

Ion chromatography	8/14
Atomic absorption / Flame (emission) photometry	6/14

Flagged data

	E	X	Flagged (%)
Sample	2	0	14.3

Among 14 participating laboratories, 8 laboratories used ion chromatography, 6 laboratories used atomic absorption/flame (emission) photometry. Lab.cn01 & cn02 submitted data significantly deviated from the prepared concentration. Most of the laboratories reported lower data than prepared concentration.

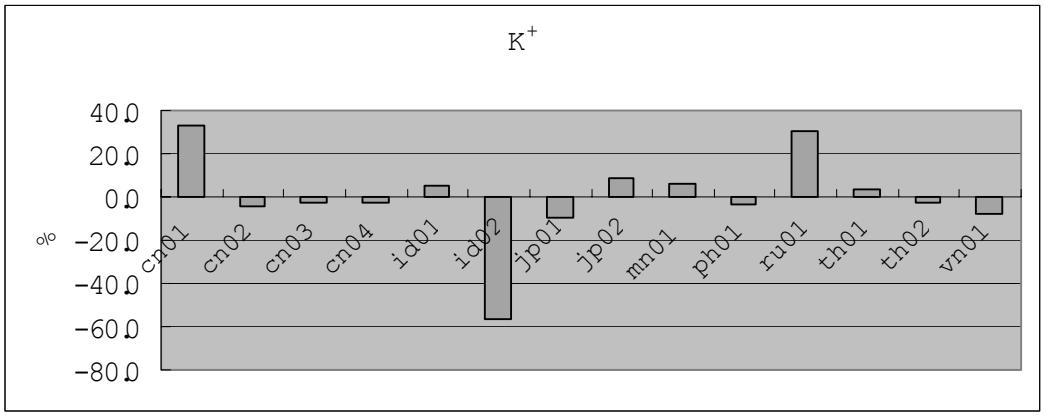


Fig.9 Distribution of K^+ data normalized by prepared concentration

Table 16 Analytical method and flagged data of K^+

Analytical Method

Ion chromatography	8/14
Atomic absorption / Flame (emission) photometry	6/14

Flagged data

	E	X	Flagged (%)
Sample	0	3	21.4

Same as Na^+, 8 laboratories used ion chromatography, 6 laboratories used atomic absorption/flame (emission) photometry for the determination of K^+. There was no clear difference among the data obtained by these two analytical methods. Lab.cn01 (ion chromatography) and Lab.id02 & ru01 (Flame (emission) photometry) submitted data significantly deviated from the prepared concentration.

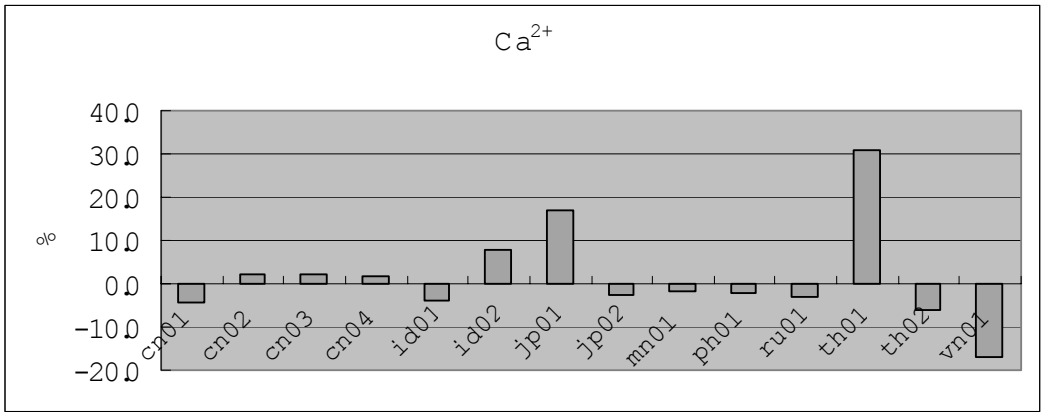


Fig.10 Distribution of Ca^{2+} data normalized by prepared concentration

Table 17 Analytical method and flagged data of Ca^{2+}

Analytical Method

Ion chromatography	8/14
Atomic absorption / Flame (emission) photometry	4/14
Titration	2/14

Flagged data

	E	X	Flagged (%)
Sample	2	1	21.4

Among 14 participating laboratories, ion chromatography is used in 8 laboratories, while 4 laboratories used atomic absorption/flame (emission) photometry. The two laboratories (Lab.id02 & vn01) determined the concentration of Ca^{2+} by titration.

Lab.jp01 & th01 (ion chromatography), Lab.vn01 (titration) submitted data significantly deviated from the prepared concentration.

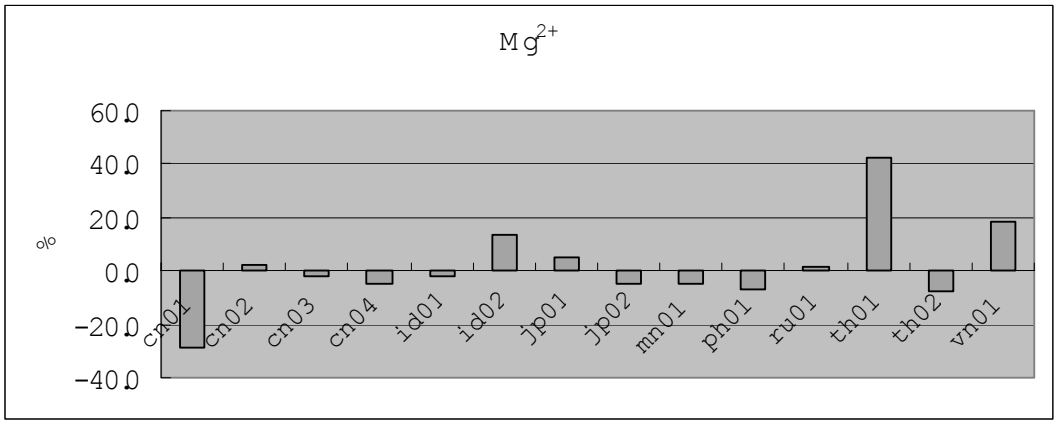


Fig.11 Distribution of Mg^{2+} data normalized by prepared concentration

Table 18 Analytical method and flagged data of Mg^{2+}

Analytical Method

Ion chromatography	8/14
Atomic absorption / Flame (emission) photometry	4/14
Titration (Calculation)	2/14

Flagged data

	E	X	Flagged (%)
Sample	0	3	23.1

Among 14 participating laboratories, 8 laboratories used ion chromatography, while 4 laboratories used atomic absorption/flame (emission) photometry. The two laboratories (Lab.id02 & vn01) determined the concentration of Mg^{2+} by calculation. Lab.cn01 & th01 (ion chromatography), and Lab.vn01(titration (calculation)) submitted data significantly deviated from the prepared concentration.

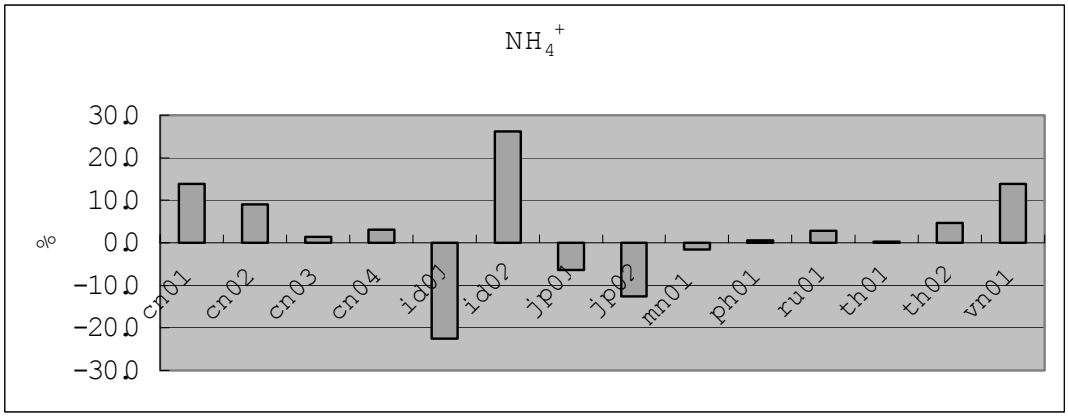


Fig.12 Distribution of NH_4^+ data normalized by prepared concentration

Table 19 Analytical method and flagged data of NH_4^+

Analytical Method

Ion chromatography	8/14
Spectrophotometry (Indophenol)	3/14
Spectrophotometry (Other method)	3/14

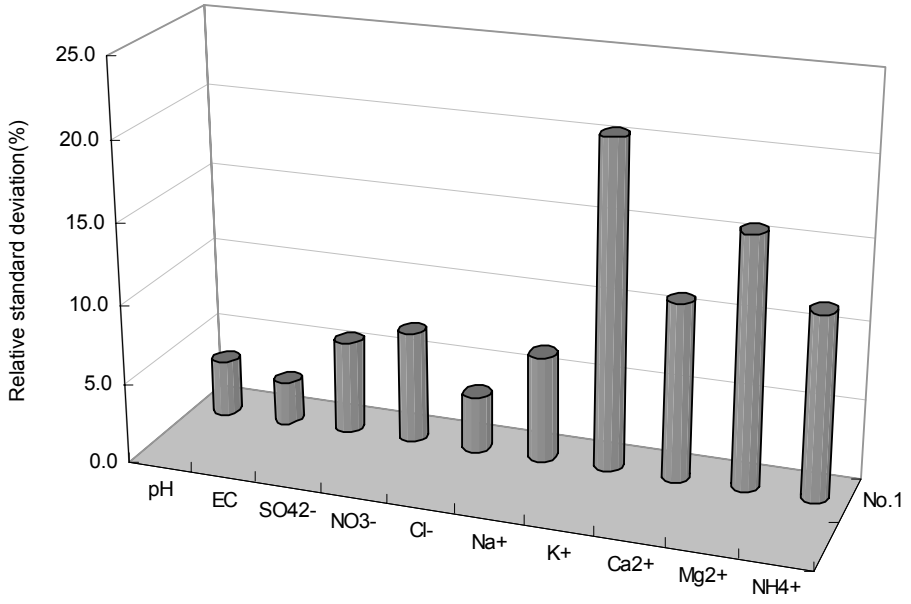
Flagged data

	E	X	Flagged (%)
Sample	2	0	14.3

Most participating laboratories used recommended analytical method of EANET for the determination of NH_4^+: 8 laboratories used ion chromatography, 3 laboratories used Spectrophotometry (Indophenol) and 3 laboratories used Spectrophotometry (Other method). The data of two laboratories (Lab.id01(ion chromatography), and id02(Other method)) were flagged.

Overall Evaluation

Data on pH and EC were less varied compared with other ionic constituents. Measured data on pH & EC were slightly lower than the prepared value. Cause of this discrepancy is not clear by the results of this round robin project. Analytical data of ionic constituents were varied particularly for ions (K^+, Mg^{2+},$NH_4^+$and Ca^{2-})as described in Fig.13. The cause of large deviation of analytical data for some ions (K^+ and Mg^{2+}) was supposed to be the difficulty of analysis on lower concentration constituents. Possible causes of these deviations were not clear by limited information obtained by this project. Quality of data is expected to be improved in the future by accumulation of experience on round robin analysis survey and QA/QC activities in each laboratories.



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

Fig.13 Relative standard deviation of each constituent

3.3 Circumstance of Sample Analysis

Methods Used

As shown in Fig.14, most of participating laboratories used recommended methods of EANET, particularly for pH and EC, SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+ measurements. The codes for the various analytical methods used in this project are shown in Table 20,21. For Ca^{2+}, Mg^{2+} analysis, two laboratories used titration (EDTA) method. Three laboratories used other spectrophotometry method for NH_4^+ analysis. There are some flagged data in these results of using the non-recommended methods.

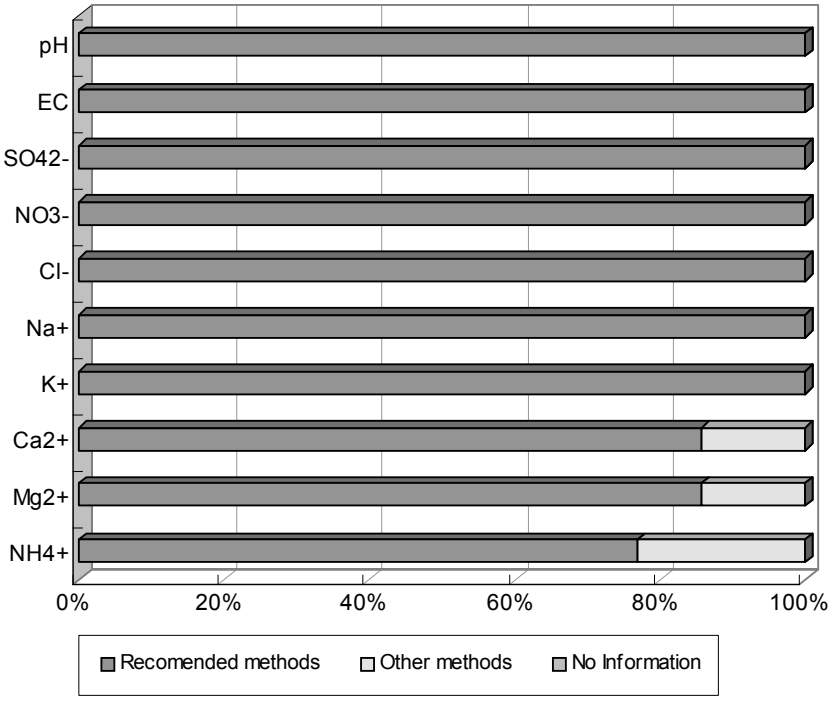


Fig.14 Ratio of recommended methods used in the project

Table 20 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	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
9	Graphite Furnace Atomic Absorption spectrometry (GFAA)
X	Other method
?	No information

Table 21 Analytical Method

Method	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	14									
1		14								
2					2(1)			2(1)	2(1)	
3						6(1)	6(2)	4	4	
4			12	11	12	8(1)	8(1)	8(2)	8(2)	8(1)
5										
6										
7			2	3(2)						3
8										
9										
X										3(1)
?										
Flagged E	0	0	0	1	0	2	0	2	2	2
Flagged X	0	0	0	1	1	0	3	1	1	0

Reverse mesh is recommended method of EANET

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

Number of Staff in Charge of Measurement

Number of staff in charge of measurement on Inland Aquatic Environment samples is described in Table 22. Only one person carried out measurement of sample in 5 laboratories. In other laboratories, 2 or 3 persons carried out measurement, and usually their responsibilities were separated according to the methods used for analysis such as anions and cations or pH, EC and ionic items. In most cases that more than one person carried out the analysis of the round robin sample, anions and cations were separately analyzed by different persons.

Table 22 Staff in charge of measurement

Lab.ID	Total	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
cn01	1	A	A	A	A	A	A	A	A	A	A
cn02	4	A	A	B	B	B	C	C	C	C	D
cn03	2	A	A	B	B	B	B	B	B	B	B
cn04	1	A	A	A	A	A	A	A	A	A	A
id01	3	A	A	B	B	B	C	C	A	A	B
id02	1	A	A	A	A	A	A	A	A	A	A
jp01	1	A	A	A	A	A	A	A	A	A	A
jp02	1	A	A	A	A	A	A	A	A	A	A
mn01	2	A	B	B	B	B	A	A	A	A	A
ph01	5	A	A	B	B	B	C,D	C,D	C,D	C,D	E
ru01	3	A	A	B	B	B	C	C	C	C	A
th01	2	A	A	B	B	B	A	A	A	A	A
th02	2	A	A	B	B	B	B	B	B	B	B
vn01	2	A	A	B	B	B	A	A	B	B	B

"-": No information, "A", "B", "C", "D" and "E" represent individuals of staff in each laboratory who are in charge of measurement. Reverse mesh: "E" or "X" in sample flagged Data.

Years of Experience

According to information obtained through this project, there are not many flagged data exactly in the case of less experience. Clear evidence of data quality improvement was not found in terms of “years of experience of the staff”. 72% data of the participating laboratories had one or no flag.

Table 23 Years of experience

Unit: year

Lab.ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
cn01	10	10	10	10	10	10	10	10	10	10
cn02	5	5	10	10	10	2	2	2	2	6
cn03	3	3	3	3	3	3	3	3	3	3
cn04	6	6	6	6	6	6	6	6	6	6
id01	1	1	1	1	1	1	1	1	1	1
id02	10	10	10	10	10	10	10	10	10	10
jp01	3	3	3	3	3	3	3	3	3	3
jp02	1	1	1	5	1	1	1	1	1	5
mn01	4	4	4	4	4	4	4	4	4	4
ph01	2	2	1	1	1	2	2	2	2	4
ru01	23	23	25	25	25	2	2	2	2	23
th01	1	1	1	1	1	1	1	1	1	1
th02	5	5	4	4	4	4	4	4	4	4
vn01	16	16	7	7	7	16	16	7	7	7

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

1 year means experienced with one year or less.

Number of Flagged Data in Laboratories

The attribution of flagged data in each laboratory is as shown in Table 24.

Table 24 Number of flagged data in each laboratory.

Number of flagged data	Number of laboratories	Share
0	5	36%
1	5	36%
2	1	7%
3	3	21%

Number of excellent laboratories without flagged data was 5, which was equivalent to 1/3 of the whole participating laboratories. Moreover, there are 11 laboratories (79% of whole) that submitted two or less flagged data, which seemed to be managed comparatively well.

On the other hand, three laboratories with three flagged data particularly needs improvement.

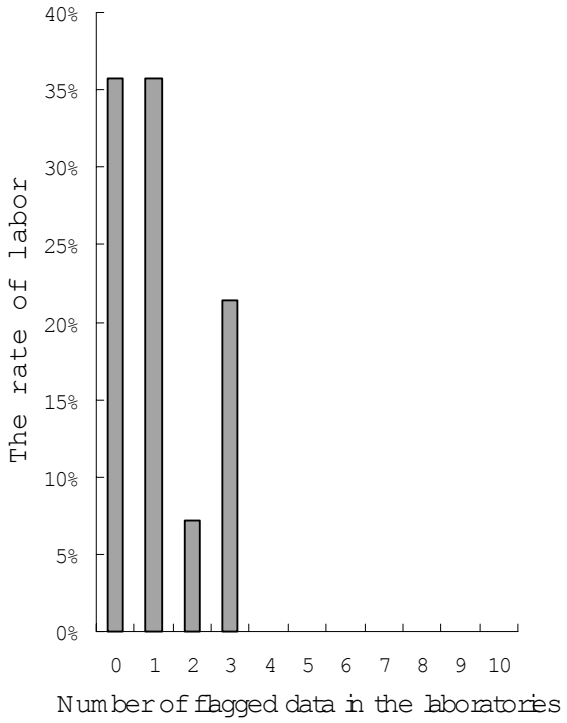


Fig.15 The distribution of laboratories with the number of flagged data

4 COMPARISON OF 1st AND 2nd INTER-LABORATORY SURVEY

The inter-laboratory comparison surveys were carried out two times, so far, their results of the number of flagged data are shown in Fig.16. For the first survey (2000), the rate of data that satisfied the required data quality objectives (DQOs) was about 87.6%. The data quality of the 2nd survey seemed to be just improved by accumulating experiences. However, there seem to be room to be improved taking account the laboratories, which have inadequate using condition of equipment or apparatus. Especially, for the low concentration constituents, contamination from used instrument, measurement apparatus and so on might be considered and should be reduced to improve the data quality. It is also important to secure the reduction of background noise and to keep the linearity of calibration curve in analytical process.

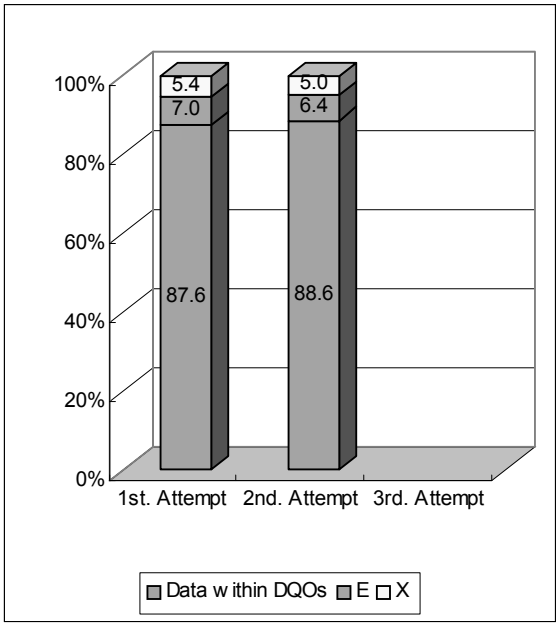


Fig. 16 Comparison of 1st, 2nd inter-laboratory comparison project

5. REFERENCES

1) Technical Manuals for Monitoring on Inland Aquatic Environment in East Asia: Adopted at The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, March 2000.

2) Quality Assurance / Quality Control (QA/QC) Program for Monitoring on Inland Aquatic Environment in East Asia: Adopted at The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, March 2000.

3) Report on the Inter-laboratory Comparison Project 2000 on Inland Aquatic Environment, 1St attempt, November 2001.

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APPENDIX 2 Original Data

Lab.ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
	-	(mS/m)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
cn01	5.42	7.06	15.79	2.83	5.38	2.88	1.04	3.37	0.28	3.10
cn02	5.40	7.22	15.22	2.89	5.21	2.96	0.75	3.61	0.40	2.97
cn03	5.49	6.99	15.60	3.09	5.25	3.44	0.76	3.60	0.38	2.76
cn04	5.44	6.76	15.48	3.08	5.24	3.41	0.76	3.59	0.37	2.81
id01	5.52	7.15	15.13	3.49	5.64	3.26	0.82	3.39	0.38	2.11
id02	6.05	7.20	13.70	3.04	8.79	3.54	0.34	3.80	0.44	3.44
jp01	5.51	6.98	15.50	3.07	5.45	3.62	0.71	4.12	0.41	2.55
jp02	5.55	6.91	15.30	2.57	5.35	3.50	0.85	3.43	0.37	2.38
mn01	5.44	7.07	16.74	3.17	5.51	3.50	0.83	3.46	0.37	2.68
ph01	5.92	6.91	16.10	3.15	5.44	3.46	0.75	3.45	0.36	2.74
ru01	5.41	7.17	15.37	3.12	5.24	3.57	1.02	3.42	0.40	2.80
th01	5.51	7.42	16.25	3.16	5.31	3.63	0.81	4.61	0.56	2.73
th02	5.47	7.14	15.50	2.94	5.14	3.43	0.76	3.32	0.36	2.85
vn01	5.52	7.45	17.86	1.12	5.81	3.38	0.72	2.93	0.46	3.10
Prepared value	6.10	7.45	15.74	3.19	5.47	3.54	0.77	3.53	0.38	2.73
Number of data	14	14	14	14	14	14	14	14	14	14
Average	5.55	7.10	15.68	2.91	5.63	3.40	0.78	3.58	0.39	2.79
Minimum	5.40	6.76	13.70	1.12	5.14	2.88	0.34	2.93	0.28	2.11
Maximum	6.05	7.45	17.86	3.49	8.79	3.63	1.04	4.61	0.56	3.44
Standard deviation	0.19	0.19	0.93	0.55	0.93	0.23	0.16	0.40	0.06	0.32

E:Value exceeded the DQO(±15) by a factor of 2
X:Value exceeded the DQO(±15) more than a factor of 2

Lab.ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
	-	(mS/m)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)
cn01	5.42	7.06	164.38	45.64	151.76	125.27	26.60	84.08	11.44	171.84
cn02	5.40	7.22	158.44	46.61	146.97	128.75	19.18	90.07	16.33	164.63
cn03	5.49	6.99	162.39	49.86	148.10	149.54	19.49	89.75	15.63	153.05
cn04	5.44	6.76	161.15	49.67	147.81	148.33	19.44	89.57	15.22	155.77
id01	5.52	7.15	157.51	56.28	159.10	141.80	20.97	84.58	15.63	116.96
id02	6.05	7.20	142.63	49.09	247.95	154.15	8.77	94.79	18.18	190.63
jp01	5.51	6.98	161.36	49.51	153.74	157.46	18.16	102.79	16.87	141.35
jp02	5.55	6.91	159.28	41.44	150.92	152.24	21.66	85.58	15.22	131.93
mn01	5.44	7.07	174.27	51.12	155.43	152.24	21.23	86.33	15.22	148.56
ph01	5.92	6.91	167.60	50.80	153.46	150.50	19.28	86.08	14.89	151.89
ru01	5.41	7.17	160.00	50.31	147.81	155.28	26.09	85.33	16.25	155.21
th01	5.51	7.42	169.18	50.88	149.65	157.98	20.69	115.09	22.83	151.50
th02	5.47	7.14	161.36	47.41	144.99	149.20	19.44	82.83	14.81	157.98
vn01	5.52	7.45	185.93	18.06	163.89	147.02	18.41	73.10	18.92	171.84
Prepared value	6.10	7.45	163.80	51.40	154.40	154.00	19.80	88.10	15.60	151.40
Number of data	14	14	14	14	14	14	14	14	14	14
Average	5.55	7.10	163.25	46.91	158.68	147.84	19.96	89.28	16.25	154.51
Minimum	5.40	6.76	142.63	18.06	144.99	125.27	8.77	73.10	11.44	116.96
Maximum	6.05	7.45	185.93	56.28	247.95	157.98	26.60	115.09	22.83	190.63
Standard deviation	0.19	0.19	9.65	8.94	26.20	9.81	4.12	9.93	2.57	17.91

E:Value exceeded the DQO(±15) by a factor of 2
X:Value exceeded the DQO(±15) more than a factor of 2

APPENDIX 3 Normalized values by prepared value

Original data / Expected Value * 100 (%)

Lab. ID	pH (%)	EC (%)	SO42- (%)	NO3- (%)	Cl- (%)	Na+ (%)	K+ (%)	Ca2+ (%)	Mg2+ (%)	NH4+ (%)
cn01	88.9	94.8	100.2	89.5	98.5	81.3	133.0	95.5	71.5	113.8
cn02	88.5	97.0	96.6	91.4	95.4	83.6	95.9	102.4	102.1	109.0
cn03	90.0	93.9	99.0	97.8	96.2	97.1	97.4	102.0	97.7	101.4
cn04	89.2	90.8	98.3	97.4	96.0	96.3	97.2	101.8	95.1	103.2
id01	90.5	96.0	96.0	110.4	103.3	92.1	104.9	96.1	97.7	77.5
id02	99.2	96.7	87.0	96.3	161.0	100.1	43.9	107.7	113.6	126.2
jp01	90.3	93.8	98.4	97.1	99.8	102.2	90.8	116.8	105.4	93.6
jp02	91.0	92.8	97.1	81.3	98.0	98.9	108.3	97.3	95.1	87.4
mn01	89.2	95.0	106.3	100.2	100.9	98.9	106.1	98.1	95.1	98.4
ph01	97.0	92.8	102.2	99.6	99.6	97.7	96.4	97.8	93.1	100.6
ru01	88.7	96.3	97.6	98.6	96.0	100.8	130.4	97.0	101.6	102.8
th01	90.3	99.6	103.2	99.8	97.2	102.6	103.5	130.8	142.7	100.3
th02	89.7	95.9	98.4	93.0	94.1	96.9	97.2	94.1	92.6	104.6
vn01	90.5	100.1	113.4	35.4	106.4	95.5	92.1	83.1	118.3	113.8
Minimum	88.5	90.8	87.0	35.4	94.1	81.3	43.9	83.1	71.5	77.5
Maximum	99.2	100.1	113.4	110.4	161.0	102.6	133.0	130.8	142.7	126.2
Average	90.9	95.4	99.5	92.0	103.0	96.0	99.8	101.5	101.5	102.3