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

Report of the Inter-laboratory
Comparison Project 2002 on Inland Aquatic
Environment

3rd Attempt

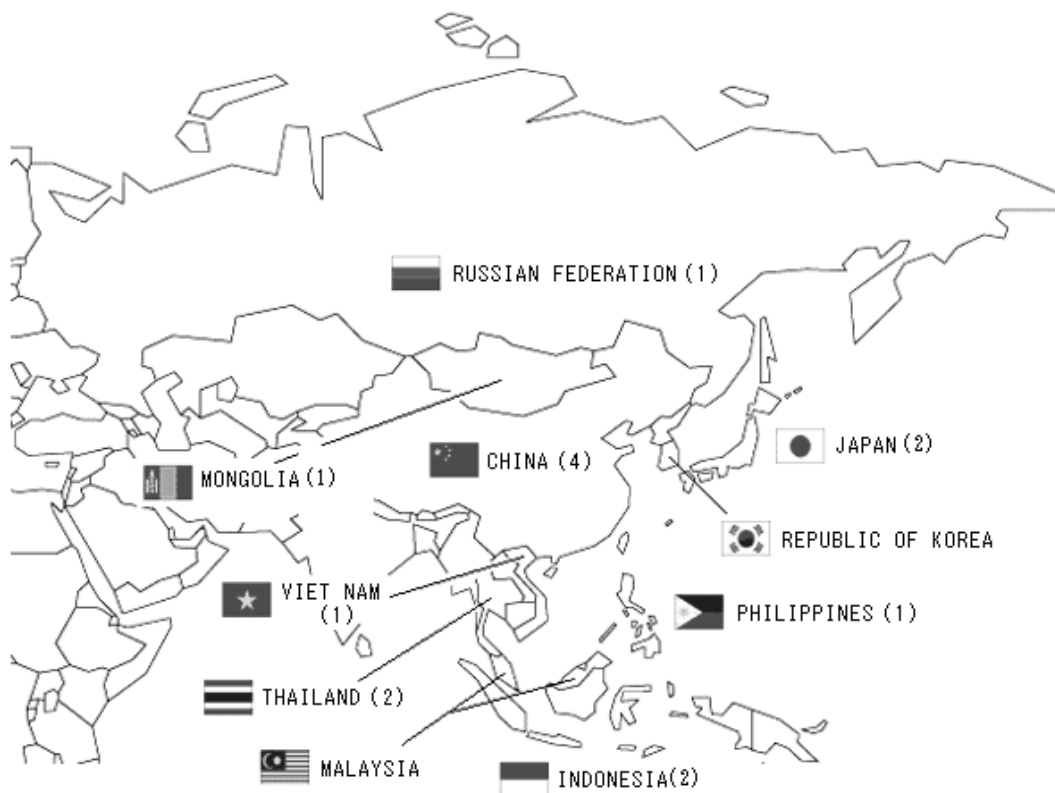November 2003

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, alkalinity 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. Since 2002 Artificial Inland Aquatic Environment samples include alkalinity (HCO_3^-).

RUSSIAN FEDERATION (1)

JAPAN (2)

CHINA (4)

MONGOLIA (1)

REPUBLIC OF KOREA

VIET NAM (1)

PHILIPPINES (1)

THAILAND (2)

MALAYSIA

INDONESIA(2)

* 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 2002 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 eleven parameters of the samples: pH, Electric Conductivity (EC), alkalinity, concentrations of sulfate, nitrate, chloride, sodium-ion, potassium-ion, calcium-ion, magnesium-ion, and ammonium-ion (except one laboratory). 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
Alkalinity	milli equivalent/liter	meq/L
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^+	2 – 20 mg/L
EC	1.5 – 15 mS/m	K^+	0.2 – 2.0 mg/L
Alkalinity	0.05 – 0.5 meq/L	Ca^{2+}	1 – 10 mg/L
SO_4^{2-}	2 – 20 mg/L	Mg^{2+}	0.1 – 1.0 mg/L
NO_3^-	1 – 10 mg/L	NH_4^+	0.05 – 0.5 mg/L
Cl^-	1 – 10 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
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)

2.5 Data Checking Procedures

a) Calculation of ion balance（R_1）

(1) Total anion (A) equivalent concentration (ueq L^{-1}) is calculated by summing the concentrations of all anions (C: umol L^{-1}) and alkalinity (ALK: ueq L^{-1}).   Alkalinity considered to be corresponded to bicarbonate ions (HCO_3^-).

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

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

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

$$C \text{ (ueq } L^{-1}) = \Sigma n \, C_{Ci} \text{ (umol } L^{-1}) = 10^{(6-pH)} + C \, (NH_4^+) + C \, (Na^+) + C \, (K^+)$$
$$+ 2C \, (Ca^{2+}) + 2C \, (Mg^{2+})$$

n, C_{Ci}: electric charge of ion and concentration (umol 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) [ueq / 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）should be calculated as follows;

$$\Lambda \text{calc} (\mu \text{ S cm}^{-1}) = 349.7 \times 10^{(3\text{-pH})} + \{80.0 \times 2C \text{ (SO}_4{}^{2-}) + 71.5 \text{ C (NO}_3{}^-)$$
$$+76.3 \text{ C (Cl}^-) + 73.5 \text{ C (NH}_4{}^+) + 50.1 \text{ C (Na}^+) + 73.5 \times C \text{ (K}^+)$$
$$+ 59.8 \times 2C \text{ (Ca}^{2+}) + 53.3 \times 2C \text{ (Mg}^{2+}) + 44.5 \times \text{(ALK)}\}/1000$$

C: Molar concentrations（μ mol L^{-1}）of ions in the parenthesis; each constant value is ionic equivalent conductance at 25°C. Alkalinity considered to be corresponded to bicarbonate ions (HCO$_3{}^-$).

(2) Ratio (R$_2$) of calculations (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[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)"

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, averages of submitted data were fairly well agreed with the prepared value/concentration within a range of $\pm$10% except Alkalinity and NH_4^+.

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		6.69	6.97	0.27	14	6.41	7.28
EC	(mS/m)	7.76	7.26	0.27	14	6.91	7.95
Alkalinity	(meq/L)	0.214	0.19	0.03	13	0.134	0.238
SO_4^{2-}	(mg/L)	10.61	10.81	1.01	14	9.77	13.66
NO_3^-	(mg/L)	4.13	4.04	0.21	12	2.07	12.33
Cl^-	(mg/L)	4.87	4.55	0.95	14	1.83	6.43
Na^+	(mg/L)	8.07	7.65	0.67	14	6.59	8.40
K^+	(mg/L)	0.77	0.75	0.03	13	0.72	1.80
Ca^{2+}	(mg/L)	4.12	4.19	0.51	14	3.10	4.85
Mg^{2+}	(mg/L)	0.57	0.56	0.04	13	0.50	0.98
NH_4^+	(mg/L)	0.27	0.31	0.09	14	0.20	0.49

(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 $\pm$15% by the QA/QC program of the EANET. In this report, analytical data on artificial inland aquatic environmental samples were compared with the prepared value/concentration and evaluated by the DQO value: the flag "E" was put to the data that exceed DQO by a factor of 2 ($\pm$15%~$\pm$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 was evaluated by the data checking procedures described in chapter 2.5 on 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, thirteen analytical data out of 154 exceeded the DQOs by a factor of 2 and flagged by "E".　Eleven analytical data out of 154 exceeded the DQOs more than a factor of 2 and flagged by "X".　Data flagged by "E" and "X" were 24 out of 154 shared about 15.6 percents of all reported data of samples.

Table 8　　Number of flagged data

Flag[*]	pH	EC	alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total
E	0	0	3	1	0	1	4	0	3	0	1	13
X	0	0	2	0	2	2	0	1	0	1	3	11
Data within DQOs	14	14	9	13	12	11	10	13	11	13	10	130
Flagged(%)	0.0	0.0	35.7	7.1	14.3	21.4	28.6	7.1	21.4	7.1	28.6	15.6

*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%)
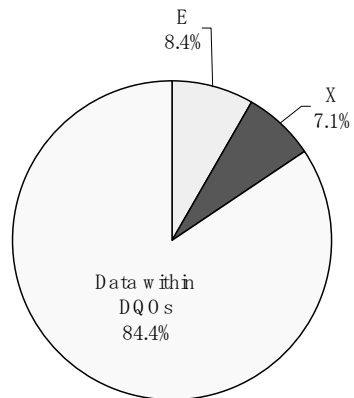

Fig.2　　Percentage of flagged data

Table 9 Analytical Results of Sample No.021 (artificial inland aquatic environment sample : EANET in 2002)

Lab. ID	pH	EC	alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	R1	R2
	–	(mS/m)	(meq/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	–	–
cn01	7.21	7.14	0.20	10.10	4.01	4.60	8.13	0.74	4.52	0.56	0.28	4.4	3.4
cn02	7.12	7.25	0.20	10.09	4.15	4.40	8.16	0.75	4.28	0.56	0.28	3.9	2.1
cn03	7.17	7.10	E 0.17	10.03	3.97	4.59	8.12	0.73	4.67	0.61	0.28	7.9	3.1
cn04	6.98	7.11	0.22	10.11	3.98	4.62	8.02	0.76	4.52	0.56	0.28	2.1	4.2
id01	7.28	7.28	0.24	9.77	3.70	E 4.13	E 6.59	0.76	4.14	0.55	X 0.49	-2.7	-0.1
id02	6.60	7.30	0.21	11.22	X 2.07	X 6.43	E 6.62	0.79	E 3.10	X 0.98	X 0.45	-7.1	1.7
jp01	6.73	7.24	X 0.13	10.40	3.99	4.57	7.49	0.77	3.88	0.53	0.27	4.7	-1.3
jp02	7.21	7.07	0.22	10.60	3.85	4.85	8.40	0.76	E 3.25	0.56	0.26	-2.3	3.1
mn01	7.18	7.31	E 0.18	10.89	4.20	4.23	8.26	0.81	4.15	0.59	X 0.46	5.4	2.3
ph01	6.88	6.91	0.21	10.54	4.11	4.89	E 6.81	0.73	4.67	0.50	0.27	-2.4	4.5
ru01	6.96	7.26	E 0.17	11.49	4.58	5.07	7.69	0.72	4.06	0.55	0.30	-0.4	2.7
th01	6.68	7.02		10.61	4.03	4.82	E 6.74	0.73	E 4.85	0.62	0.24	I 18.9	-2.3
th02	7.14	7.69	X 0.14	E 13.66	3.95	4.62	8.08	0.74	4.17	0.51	E 0.20	1.1	0.7
vn01	6.41	7.95	0.22	11.83	X 12.33	X 1.83	7.96	X 1.80	4.47	0.62	0.28	-2.7	3.9
Expected value	6.69	7.76	0.21	10.61	4.13	4.87	8.07	0.77	4.12	0.57	0.27	-	-
Number of data	14	14	13	14	14	14	14	14	14	14	14	-	-
Average	6.97	7.26	0.19	10.81	4.49	4.55	7.65	0.83	4.19	0.59	0.31	-	-
Minimum	6.41	6.91	0.13	9.77	2.07	1.83	6.59	0.72	3.10	0.50	0.20	-7.1	-2.3
Maximum	7.28	7.95	0.24	13.66	12.33	6.43	8.40	1.80	4.85	0.98	0.49	18.9	4.5
Standard deviation	0.27	0.27	0.03	1.01	2.32	0.95	0.67	0.28	0.51	0.12	0.09	-	-

E:Value exceeded the DQO(±15) by a factor of 2   I:Poor ion balance (R1)
X:Value exceeded the DQO(±15) more than a factor of 2   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.
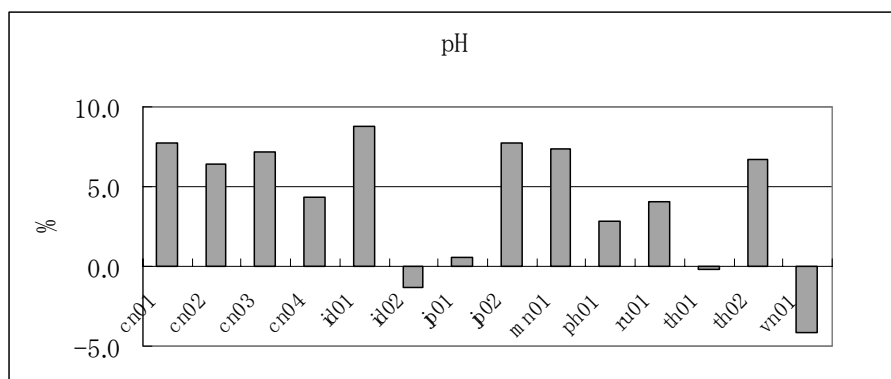

Fig.3　Distribution of pH data normalized by prepared value

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 upper data than prepared value.
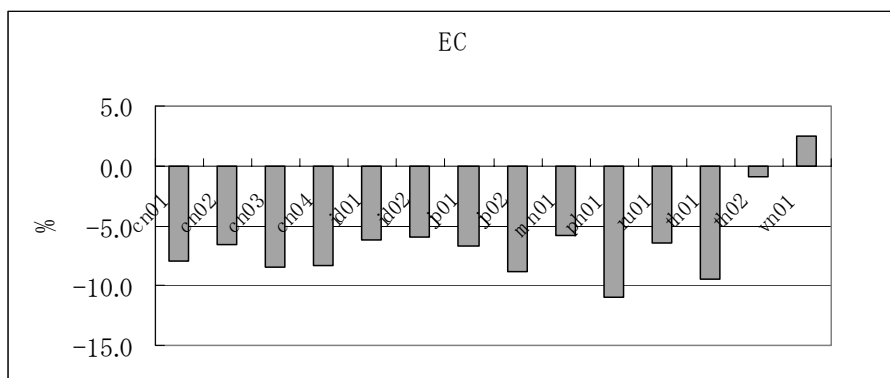
Fig.4   Distribution of EC data normalized by prepared value

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.   Most of obtained data were agreed with prepared value.   Most of the laboratories reported lower data than prepared value.
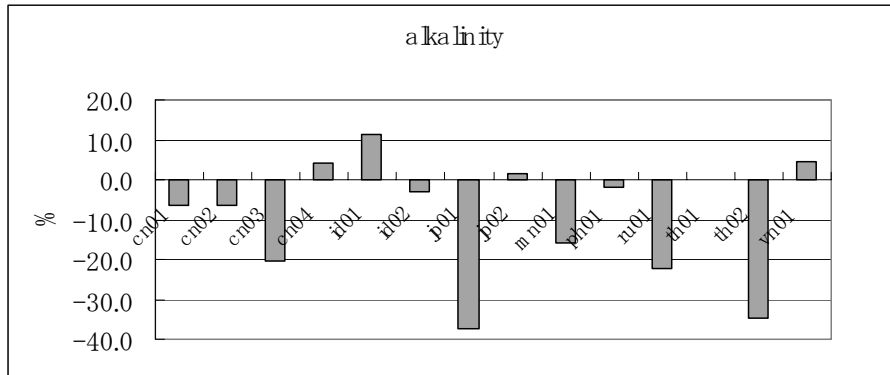
Fig.5   Distribution of Alkalinity data normalized by prepared concentration

Table 12   Analytical method and flagged data of Alkalinity

Analytical Method

Titration	12/14
Other	2/14

Flagged data

	E	X	Flagged (%)
Sample	3	2	0.4

Most of participating laboratories except two used titration for the determination of Alkalinity.   Lab.ru01 used other method (HPLC) without titration.   Lab.th01 did not measure Alkalinity because it is not their normal work.   Since 2002 Artificial Inland Aquatic Environment samples include alkalinity (HCO_3^-).

Fig.6 Distribution of SO$_4^{2-}$ data normalized by prepared concentration

Table 13 Analytical method and flagged data of SO$_4^{2-}$

Analytical Method

Ion chromatography	12/14
spectrophotometry	2/14

Flagged data

	E	X	Flagged (%)
Sample	1	0	0.1

Most of participating laboratories except two used ion chromatography for the determination of SO$_4^2$. Lab.id02 & vn01 used other method (spectrophotometry) without ion chromatography.

Fig.7   Distribution of NO$_3^-$ data normalized by prepared concentration

Table 14   Analytical method and flagged data of NO$_3^-$

Analytical Method

Ion chromatography	11/14
spectrophotometry	3/14

Flagged data

	E	X	Flagged (%)
Sample	0	2	0.1

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.id02 and vn01 obtained with spectrophotometry were all flagged.   There seems to be some problem of the used method in this case, but it was not able to specify the cause.
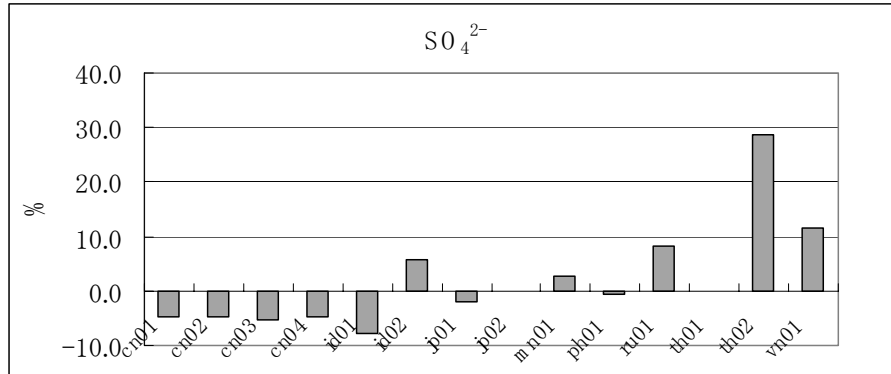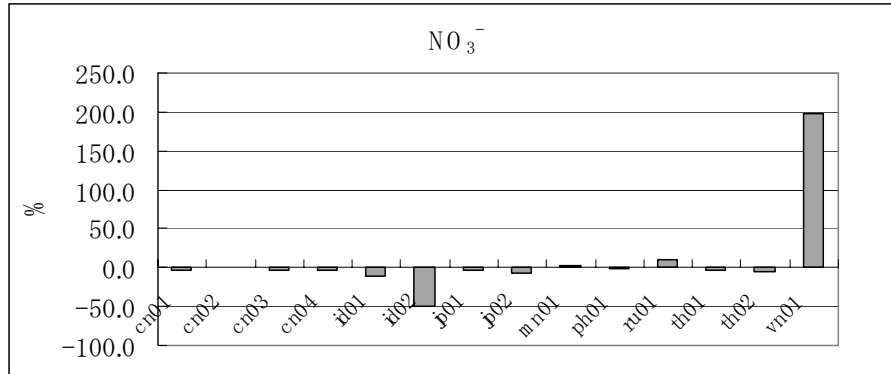
Fig.8   Distribution of Cl⁻ data normalized by prepared concentration

Table 15   Analytical method and flagged data of Cl⁻

Analytical Method

Ion chromatography	12/14
Titration method	2/14

Flagged data

	E	X	Flagged (%)
Sample	1	2	0.2

Same as SO_4^{2-} and NO_3^-, most of participating laboratories used ion chromatography for the determination of Cl⁻.   Two laboratories used titration method.   Data from Lab.id02 and vn01 obtained with titration were all flagged.   There seems to be some problem of the used method in this case, but it was not able to specify the cause.
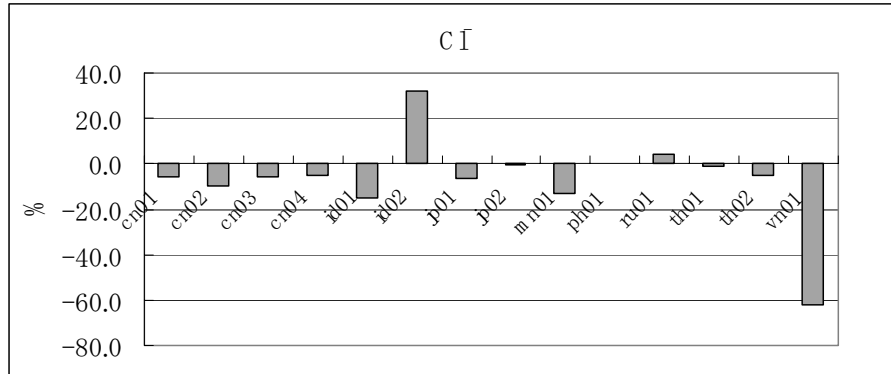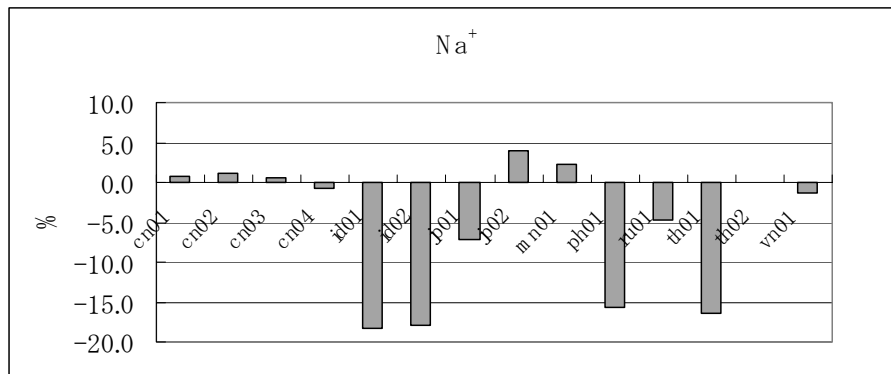
Fig.9 Distribution of Na⁺ data normalized by prepared concentration

Table 16   Analytical method and flagged data of Na⁺

Analytical Method

Ion chromatography	10/14
Atomic absorption / Flame (emission) photometry	4/14

Flagged data

	E	X	Flagged (%)
Sample	4	0	0.3

Among 14 participating laboratories, 10 laboratories used ion chromatography, 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Na⁺. Data from Lab.id01, id02 & ph01 obtained with AAS method are significantly deviated from prepared value.

Fig.10   Distribution of K$^+$ data normalized by prepared concentration

Table 17   Analytical method and flagged data of K$^+$

Analytical Method

Ion chromatography	10/14
Atomic absorption / Flame (emission) photometry	4/14

Flagged data

	E	X	Flagged (%)
Sample	0	1	0.1

Same as Na$^+$, 10 laboratories used ion chromatography, 4 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.   Data from Lab.vn01 obtained with ion chromatography are significantly deviated from prepared value.

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

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

Analytical Method

Ion chromatography	10/14
Atomic absorption / Flame (emission) photometry	3/14
Titration	1/14

Flagged data

	E	X	Flagged (%)
Sample	3	0	0.2

Among 14 participating laboratories, 10 laboratories used ion chromatography, 3 laboratories used atomic absorption/flame (emission) photometry for the determination of Ca^{2+}. 1 laboratory (Lab.id02) determined the concentration of Ca^{2+} by titration.   Data from Lab.jp02 & th01 (ion chromatography), Lab.id02 (titration) are significantly deviated from prepared value.
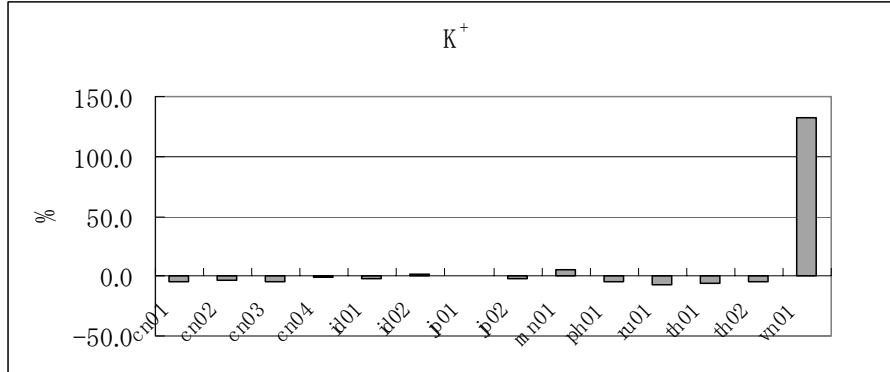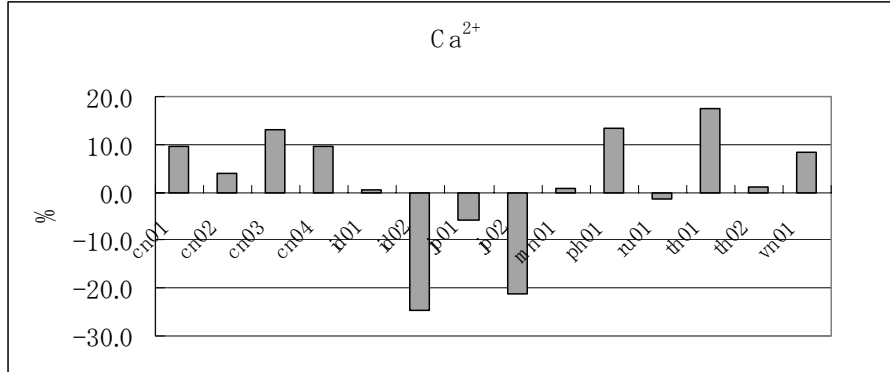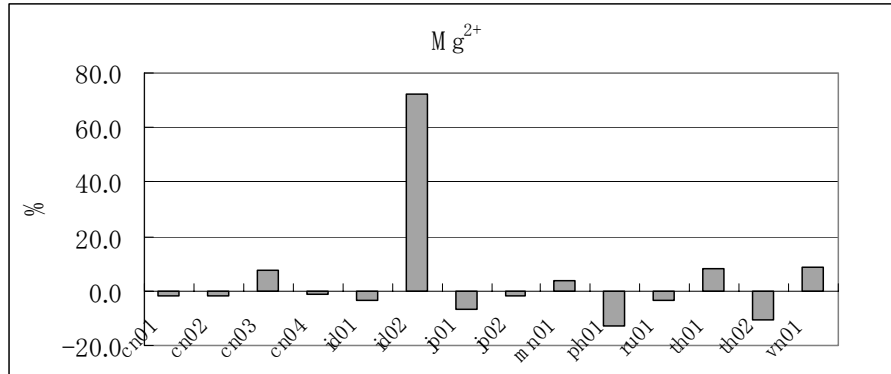
Fig.12 Distribution of Mg²⁺ data normalized by prepared concentration

Table 19 Analytical method and flagged data of Mg²⁺

Analytical Method

Ion chromatography	10/14
Atomic absorption / Flame (emission) photometry	3/14
Titration (Calculation)	1/14

Flagged data

	E	X	Flagged (%)
Sample	0	1	0.1

Among 14 participating laboratories, 10 laboratories used ion chromatography, 3 laboratories used atomic absorption/flame (emission) photometry for the determination of Mg²⁺. 1 laboratory (Lab.id02) determined the concentration of Mg²⁺ by calculation. Data from Lab.id02 obtained with calculation method are significantly deviated from prepared value.
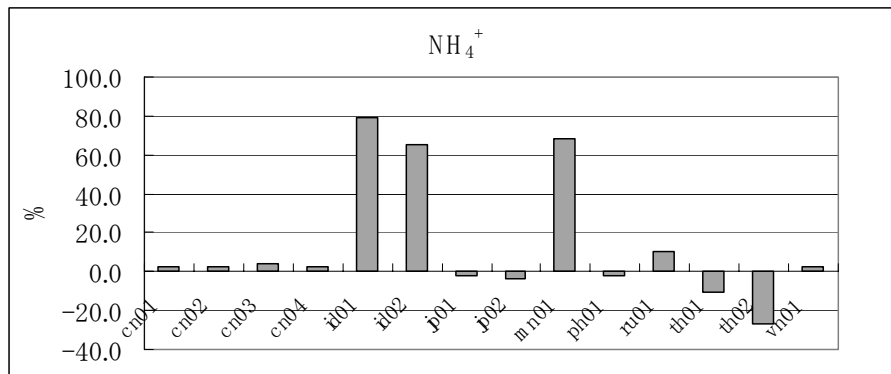
Fig.13   Distribution of NH$_4^+$ data normalized by prepared concentration

Table 20   Analytical method and flagged data of NH$_4^+$

Analytical Method

Ion chromatography	7/14
Spectrophotometry (Indophenol)	3/14
Spectrophotometry (Other method)	4/14

Flagged data

	E	X	Flagged (%)
Sample	1	3	0.3

    Among 14 participating laboratories, 7 laboratories used ion chromatography, 3 laboratories used spectrophotometry (Indophenol) and 4 laboratories used spectrophotometry (other method) for the determination of NH$_4^+$.   Data from Lab.mn01 & th02 obtained with ion chromatography are significantly deviated from prepared value.   Data from Lab.id01 & id02 obtained with spectrophotometry are also significantly deviated from prepared value.

Overall Evaluation

Obtained data on pH and EC were less varied compared with other ion constituents. Most of obtained data on pH was slightly upper than prepared value and EC was slightly lower than one. The cause of this discrepancy is not clear by the results of this project. Analytical data of ion constituents were varied particularly for ions (NO_3^-, K^+, NH_4^+, Cl^-) as shown in Fig.14. Concerning NO_3^-, K^+, Cl^-, the cause of large deviation of analytical data seems that the data from one laboratory are significantly deviated from prepared value. However it was not able to specify the causes of these deviations based on the limited information obtained from this project. Quality of data is expected to be improved in the future by accumulation of experience on this project and QA/QC activities in each laboratories.
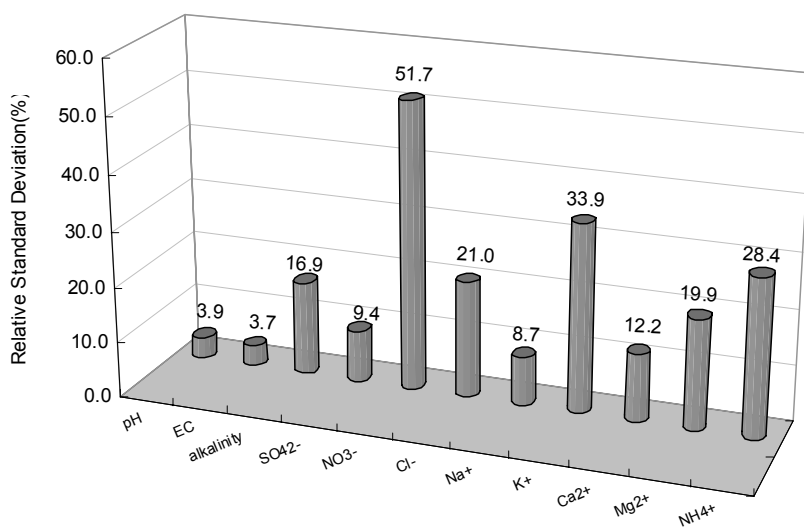
(Relative standard deviation (%) = Standard deviation / Average * 100, Reported data after outliers were removed)

Fig.14　　Relative standard deviation of each constituent

3.3 Circumstance of Sample Analysis

Methods Used

As shown in Fig.15, most of the participating laboratories used recommended methods of EANET, particularly for pH, EC and SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+ analysis. The codes for the various analytical methods used in this project are shown in Table 21 and 22. For Ca^{2+}, Mg^{2+} analysis, one laboratory used titration (calculation) method. For alkalinity analysis, one laboratory used HPLC method. There are some flagged data in these results of using the non- recommended methods.
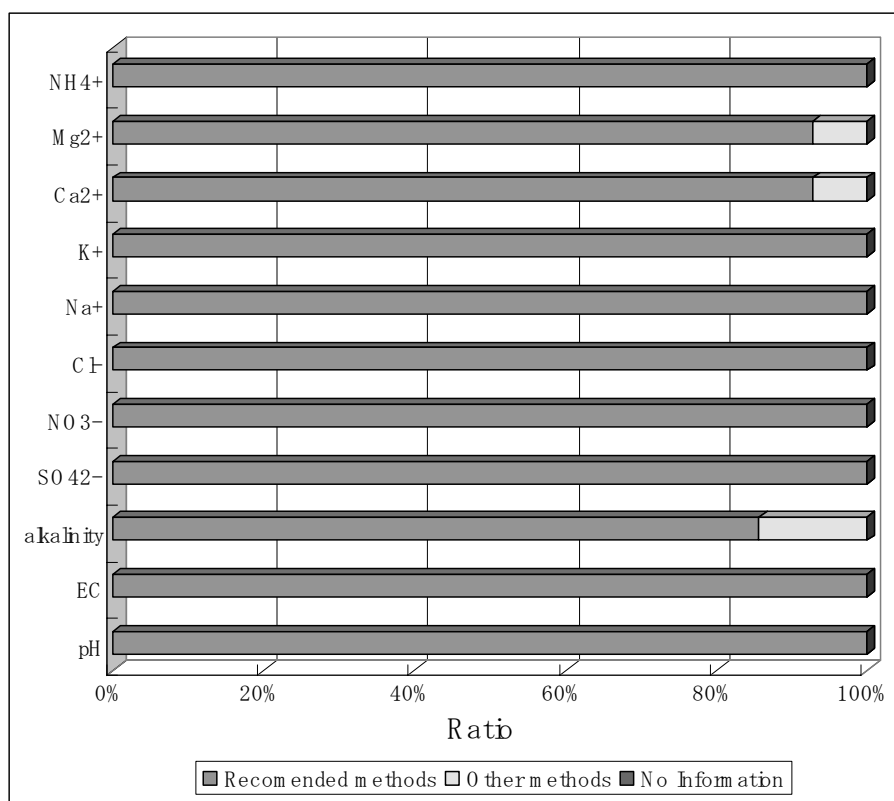
Fig.15   Ratio of recommended methods used in the project

Table 21   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 22   Analytical Method

Code	pH	EC	alkalinity	SO42-	NO3-	Cl-	Na+	K+	Ca2+	Mg2+	NH4+
0	14										
1		14									
2			12(4)			2(2)			1(1)		
3							4(3)	4	3	3	
4				12(1)	11	12(1)	10(1)	10(1)	10(2)	10	7(2)
5											
6										1(1)	
7				2	3(2)						7(2)
8											
9											
X			1 1)								
?											
Flagged E											
Flagged X											

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 shown in Table 23. Only one person carried out sample analysis in 3 laboratories. In other laboratories, 2 - 4 persons carried out them, and usually their responsibilities were separated according to the methods such as anions and cations, or pH, EC and ionic items. In case more than 2 persons carried out this project, anions and cations were separately analyzed by different persons.

Table 23   Staff in charge of measurement

Lab.ID	Total	pH	EC	alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
cn01	1	A	A	A	A	A	A	A	A	A	A	A
cn02	4	A	A	A	B	B	B	C	C	C	C	D
cn03	2	A	A	A	B	B	B	B	B	B	B	B
cn04	1	A	A	A	A	A	A	A	A	A	A	A
id01	4	A	A	A	A	A	A	B	C	B	B	D
id02	2	A	A	B	A	A	A	B	B	B	B	B
jp01	1	A	A	A	A	A	A	A	A	A	A	A
jp02	2	A	A	A	A	B	A	A	A	A	A	B
mn01	2	A	B	B	A	A	A	B	B	B	B	B
ph01	4	A	A	A	B	B	B	C	C	C	C	D
ru01	3	A	A	B	B	B	B	C	C	C	C	A
th01	2	A	B	A	A	A	A	B	B	B	B	B
th02	2	A	A	A	B	B	B	B	B	B	B	B
vn01	2	A	A	B	B	B	B	A	A	A	A	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 so many flagged data exactly in the case of less experience.   Clear evidence for data quality improvement was not found in terms of "years of experience of the staff".

Table 24   Years of experience

Unit: year

Lab.ID	pH	EC	alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
cn01	11	11	11	11	11	11	11	11	11	11	11
cn02	15	15	14	11	11	11	2	2	2	2	2
cn03	4	4	4	4	4	4	4	4	4	4	4
cn04	7	7	7	7	7	7	7	7	7	7	7
id01	1	1	1	1	1	1	1	1	1	1	1
id02	1	1	11	1	1	1	11	11	11	11	11
jp01	4	4	4	4	4	4	4	4	4	4	4
jp02	2	2	2	2	6	2	2	2	2	2	6
mn01	5	5	5	5	5	5	5	5	5	5	5
ph01	3	3	3	2	2	2	3	3	3	3	1
ru01	24	24	7	7	7	7	16	16	16	16	24
th01	0	0	-	0	0	0	0	0	0	0	0
th02	5	5	5	5	5	5	5	5	5	5	5
vn01	16	16	7	7	7	7	16	16	16	16	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 25.

Table 25   Number of flagged data in each laboratory.

Number of flagged data	Number of laboratories	Share
0	3	21%
1	5	36%
2	2	14%
3	3	21%
4	0	0%
5	0	0%
6	1	7%

Number of excellent laboratories without flagged data was only 3, which was equivalent to 21% of the whole participating laboratories.   These results are not so good compared with last year. Especially there are many flagged data of alkalinity.   It needs to confirm an analytical method of alkalinity in detail.   One laboratory had 6 flagged data.   This cause seems that they don't have ion chromatography, and concerning Ca^{2+} and Mg^{2+}, they use titration (calculation) method.
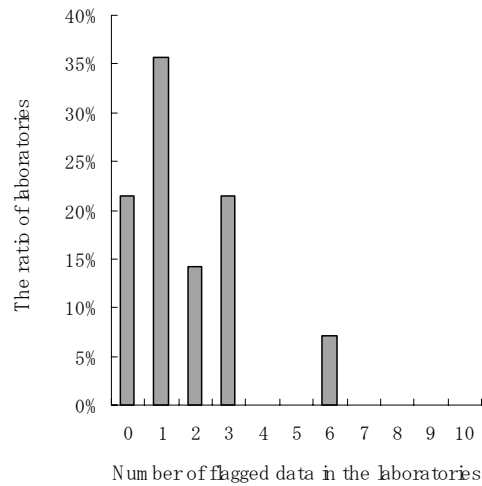

Fig.16 The distribution of laboratories with the number of flagged data

4. COMPARISON OF 1st, 2nd AND 3rd INTER-LABORATORY SURVEY

The inter-laboratory comparison projects were carried out two times, in 2000 and 2001. Their results of the number of flagged data are shown in Fig.17. For the first project (2000), the rate of data that satisfied the required data quality objectives (DQOs) was about 87.6% and for the second project (2001), it was about 88.6%. The data quality of the 3rd project seemed to be not improved by accumulating experiences. However this cause seems that the condition of equipment or apparatus became bad or it is difficult to obtain a standard solution for the equipment or apparatus. The other hand, for the low concentration constituents, contamination from used instrument, measurement apparatus and so on might be considered. It is also important to secure the reduction of background noise and to keep the linearity of calibration curve in analytical process.
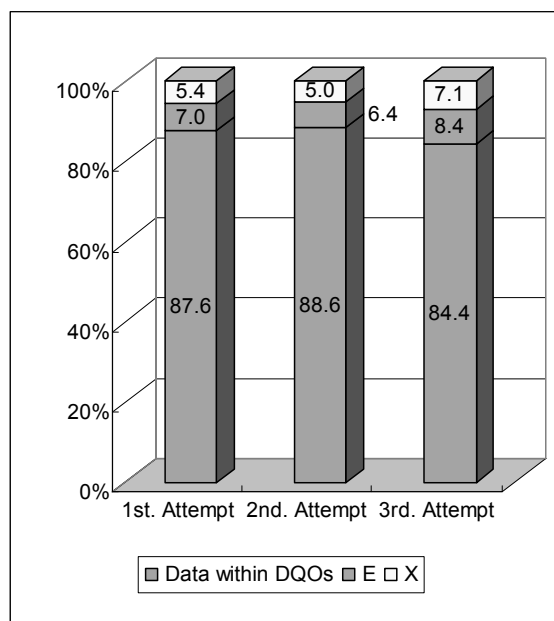

Fig. 17   Comparison of 1st ,2nd and 3rd inter-laboratory comparison project

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 and 2nd attempt, November 2002.

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APPENDIX 2 Original Data

Lab. ID	pH –	EC (mS/m)	alkalinity (meq/L)	SO$_4^{2-}$ (mg/L)	NO$_3^-$ (mg/L)	Cl$^-$ (mg/L)	Na$^+$ (mg/L)	K$^+$ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH$_4^+$ (mg/L)
cn01	7.21	7.14	0.20	10.10	4.01	4.60	8.13	0.74	4.52	0.56	0.28
cn02	7.12	7.25	0.20	10.09	4.15	4.40	8.16	0.75	4.28	0.56	0.28
cn03	7.17	7.10	0.17	10.03	3.97	4.59	8.12	0.73	4.67	0.61	0.28
cn04	6.98	7.11	0.22	10.11	3.98	4.62	8.02	0.76	4.52	0.56	0.28
id01	7.28	7.28	0.24	9.77	3.70	4.13	6.59	0.76	4.14	0.55	0.49
id02	6.60	7.30	0.21	11.22	2.07	6.43	6.62	0.79	3.10	0.98	0.45
jp01	6.73	7.24	0.13	10.40	3.99	4.57	7.49	0.77	3.88	0.53	0.27
jp02	7.21	7.07	0.22	10.60	3.85	4.85	8.40	0.76	3.25	0.56	0.26
mn01	7.18	7.31	0.18	10.89	4.20	4.23	8.26	0.81	4.15	0.59	0.46
ph01	6.88	6.91	0.21	10.54	4.11	4.89	6.81	0.73	4.67	0.50	0.27
ru01	6.96	7.26	0.17	11.49	4.58	5.07	7.69	0.72	4.06	0.55	0.30
th01	6.68	7.02		10.61	4.03	4.82	6.74	0.73	4.85	0.62	0.24
th02	7.14	7.69	0.14	13.66	3.95	4.62	8.08	0.74	4.17	0.51	0.20
vn01	6.41	7.95	0.22	11.83	12.33	1.83	7.96	1.80	4.47	0.62	0.28
Expected value	6.69	7.76	0.21	10.61	4.13	4.87	8.07	0.77	4.12	0.57	0.27
Number of data	14	14	13	14	14	14	14	14	14	14	14
Average	6.97	7.26	0.19	10.81	4.49	4.55	7.65	0.83	4.19	0.59	0.31
Minimum	6.41	6.91	0.13	9.77	2.07	1.83	6.59	0.72	3.10	0.50	0.20
Maximum	7.28	7.95	0.24	13.66	12.33	6.43	8.40	1.80	4.85	0.98	0.49
Standard deviation	0.27	0.27	0.03	1.01	2.32	0.95	0.67	0.28	0.51	0.12	0.09

blank : not analyzed

Lab. ID	pH –	EC (mS/m)	alkalinity (meq/L)	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)
cn01	7.21	7.14	0.20	105.14	64.67	129.76	353.63	18.93	112.77	23.04	15.52
cn02	7.12	7.25	0.20	105.04	66.92	124.12	354.94	19.18	106.79	23.04	15.52
cn03	7.17	7.10	0.17	104.39	64.09	129.53	353.24	18.75	116.39	25.13	15.74
cn04	6.98	7.11	0.22	105.25	64.18	130.32	348.63	19.49	112.82	23.08	15.52
id01	7.28	7.28	0.24	101.71	59.67	116.50	286.65	19.44	103.29	22.62	27.16
id02	6.60	7.30	0.21	116.80	33.38	181.38	287.95	20.21	77.35	40.31	24.95
jp01	6.73	7.24	0.13	108.27	64.34	128.91	325.79	19.72	96.81	21.80	14.86
jp02	7.21	7.07	0.22	110.35	62.09	136.81	365.38	19.44	81.09	23.04	14.52
mn01	7.18	7.31	0.18	113.37	67.73	119.32	359.29	20.72	103.54	24.27	25.50
ph01	6.88	6.91	0.21	109.72	66.28	137.94	296.22	18.72	116.52	20.36	14.86
ru01	6.96	7.26	0.17	119.61	73.86	143.02	334.49	18.41	101.30	22.58	16.63
th01	6.68	7.02		110.43	64.94	136.02	293.26	18.57	120.98	25.38	13.47
th02	7.14	7.69	0.14	142.20	63.70	130.32	351.46	18.93	104.04	20.98	11.09
vn01	6.41	7.95	0.22	123.15	198.84	51.62	346.24	46.04	111.53	25.50	15.52
Expected value	6.69	7.76	0.21	110.40	66.57	137.40	351.15	19.77	102.84	23.41	15.13
Number of data	14	14	13	14	14	14	14	14	14	14	14
Average	6.97	7.26	0.19	112.53	72.48	128.26	332.66	21.18	104.66	24.37	17.20
Minimum	6.41	6.91	0.13	101.71	33.38	51.62	286.65	18.41	77.35	20.36	11.09
Maximum	7.28	7.95	0.24	142.20	198.84	181.38	365.38	46.04	120.98	40.31	27.16
Standard deviation	0.27	0.27	0.03	10.54	37.48	26.87	29.06	7.18	12.73	4.84	4.89

blank : not analyzed

APPENDIX 3　Normalized values by prepared value

Table Original data / Expected Value * 100 (%)

Lab. ID	pH	EC	alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
cn01	107.8	92.0	93.5	95.2	97.1	94.4	100.7	95.7	109.7	98.4	102.6
cn02	106.4	93.5	93.5	95.1	100.5	90.3	101.1	97.0	103.8	98.4	102.6
cn03	107.2	91.5	79.4	94.6	96.3	94.3	100.6	94.8	113.2	107.4	104.0
cn04	104.3	91.7	104.2	95.3	96.4	94.8	99.3	98.6	109.7	98.6	102.6
id01	108.8	93.9	111.2	92.1	89.6	84.8	81.6	98.3	100.4	96.7	179.5
id02	98.7	94.1	97.0	105.8	50.1	132.0	82.0	102.2	75.2	172.2	164.8
jp01	100.6	93.3	62.6	98.1	96.7	93.8	92.8	99.7	94.1	93.1	98.2
jp02	107.8	91.1	101.4	100.0	93.3	99.6	104.1	98.3	78.8	98.4	96.0
mn01	107.3	94.2	84.1	102.7	101.7	86.8	102.3	104.8	100.7	103.7	168.5
ph01	102.8	89.1	98.1	99.4	99.6	100.4	84.4	94.7	113.3	87.0	98.2
ru01	104.0	93.6	77.6	108.3	110.9	104.1	95.3	93.1	98.5	96.5	109.9
th01	99.9	90.5		100.0	97.6	99.0	83.5	93.9	117.6	108.4	89.0
th02	106.7	99.1	65.4	128.8	95.7	94.8	100.1	95.7	101.2	89.6	73.3
vn01	95.8	102.5	104.7	111.6	298.7	37.6	98.6	232.9	108.4	109.0	102.6
Minimum	95.8	89.1	62.6	92.1	50.1	37.6	81.6	93.1	75.2	87.0	73.3
Maximum	108.8	102.5	111.2	128.8	298.7	132.0	104.1	232.9	117.6	172.2	179.5
Average	104.2	93.6	90.2	101.9	108.9	93.3	94.7	107.1	101.8	104.1	113.7

blank : not analyzed