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

Report of the Inter-laboratory Comparison Project 2003 on Inland Aquatic Environment

4th Attempt

November 2004

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. HCO_3^- has been contained in artificial inland aquatic environment samples since 2002 to determine Alkalinity.
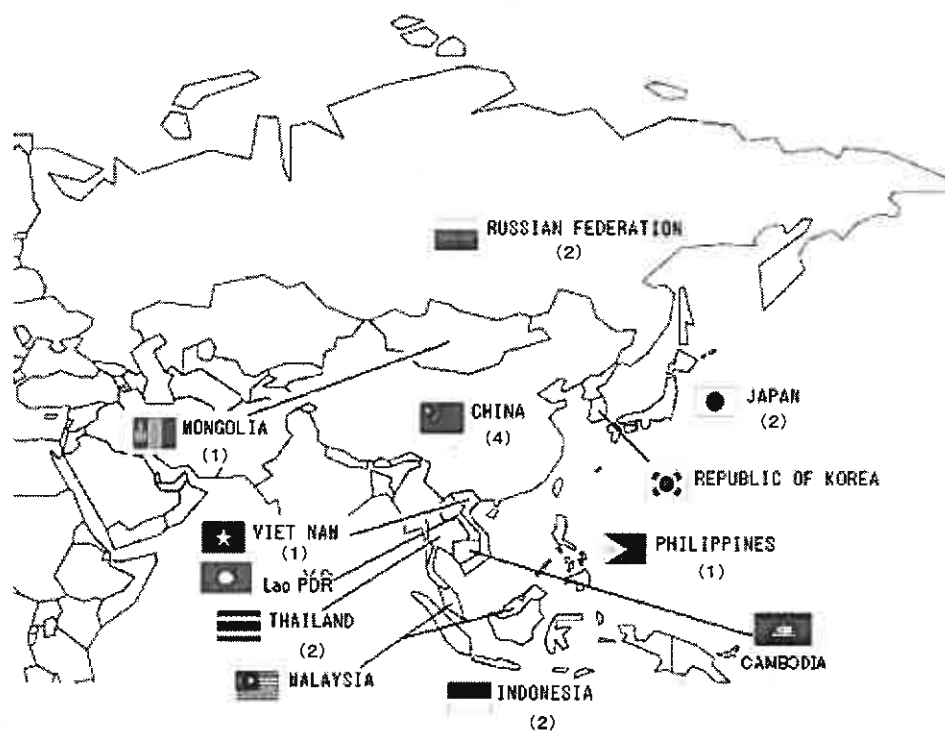
* Figure in parenthesis shows the number of laboratories for each country (15 laboratories from 8 countries)

Fig. 1 Laboratories participated in the inter-laboratory comparison project 2003 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 15 laboratories, and all laboratories submitted their analytical data to NC. The contact addresses of the participating laboratories are presented in APPENDIX 1.

2.2 Dispatched Artificial Inland Aquatic Environment Samples

Artificial inland aquatic environment samples were distributed to each laboratories by net work center in December 2003 with expected submission of results by March 15, 2004.

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-propyl ene 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 SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+. 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 units	-
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 (μeq/L) is calculated by sum up the concentration of anions (C: μmol/L) and Alkalinity (ALK: μeq/L).   Alkalinity considered to be corresponded to bicarbonate ions (HCO_3^-).

$\quad$ A (μeq/L) = Σn C_{Ai} (μmol/L) = 2C (SO_4^{2-}) + C (NO_3^-) + C (Cl^-) + (ALK)

$\quad$ C_{Ai}: electric charge of ion and concentration (μmol/L) of anion "i".

(2) Total cation (C) equivalent concentration (μeq/L) is calculated by sum up the concentration of all cations (C: μmol/L).

$\quad$ C (μeq/L) = Σn C_{Ci} (μmol/L) = $10^{(6-pH)}$ + C (NH_4^+) + C (Na^+) + C (K^+)
$$+ 2C\ (Ca^{2+}) + 2C\ (Mg^{2+})$$

$\quad$ C_{Ci}: electric charge of ion and concentration (μmol/L) of cation "i".

(3) Calculation of ion balance (R_1)

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

(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;

Λcalc (mS/m) = {349.7×10$^{(6-pH)}$ + 80.0×2C (SO$_4^{2-}$) + 71.5×C (NO$_3^-$)

+76.3×C (Cl$^-$) + 73.5×C (NH$_4^+$) + 50.1×C (Na$^+$) + 73.5×C (K$^+$)

+ 59.8×2C (Ca^{2+}) + 53.3×2C (Mg^{2+}) + 44.5×(ALK)}/10000

C: Molar concentrations (μmol/L) 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 should be calculated as follows;

R$_2$ = 100 × (Λcalc-Λmeas)/(Λcalc +Λmeas)

(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]	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 15 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 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

Constituents		Prepared	Average	S.D	N	Min.	Max.
pH		7.31	7.11	0.33	15	6.07	7.30
EC	(mS/m)	7.41	7.12	0.22	15	6.78	7.53
Alkalinity	(meq/L)	0.238	0.239	0.04	15	0.165	0.341
SO_4^{2-}	(mg/L)	8.29	8.35	0.69	15	6.25	9.32
NO_3^-	(mg/L)	5.70	5.50	0.66	15	3.90	6.43
Cl^-	(mg/L)	4.28	4.25	0.47	15	3.69	5.70
Na^+	(mg/L)	8.22	8.14	0.61	15	6.88	9.32
K^+	(mg/L)	1.16	1.23	0.25	15	1.10	2.10
Ca^{2+}	(mg/L)	3.23	3.17	0.59	15	2.02	3.69
Mg^{2+}	(mg/L)	0.76	0.83	0.12	15	0.71	1.23
NH_4^+	(mg/L)	0.20	0.20	0.08	15	0.09	0.40

(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 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 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 presented 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, twenty analytical data out of 165 exceeded the DQOs by a factor of 2 and flagged by "E". Eleven analytical data out of 165 exceeded the DQOs more than a factor of 2 and flagged by "X. Data flagged by "E" and "X" were 31 out of 165 and shared about 18.8% 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	1	0	3	1	2	0	2	1	3	1	6	20
X	0	0	2	0	1	1	0	1	1	1	4	11
Data within DQOs	14	15	10	14	12	14	13	13	11	13	5	134
Flagged(%)	6.7	0.0	33.3	6.7	20.0	6.7	13.3	13.3	26.7	13.3	66.7	18.8

*E : Value Exceeded the DQO by a factor of 2 of the DQO ($\pm 15\% \sim \pm 30\%$)
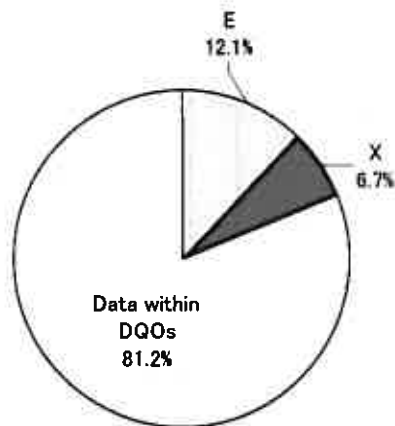*X : Value Exceeded the DQO more than a factor of 2 of the DQO (<-30% or >30%)

Fig. 2   Percentage of flagged data

Table 9 Analytical Results of Sample No.031 (artificial inland aquatic environment sample : EANET in 2003)

Lab. ID	pH	EC (mS/m)	Alkalinity (meq/L)	SO₄²⁻ (mg/L)	NO₃⁻ (mg/L)	Cl⁻ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	NH₄⁺ (mg/L)	R1	R2
cn01	7.25	6.99	0.25	8.02	5.77	4.37	8.53	1.19	3.69	0.87	X 0.11	2.3	4.6
cn02	7.29	6.96	0.24	9.32	6.43	4.53	9.32	1.16	3.65	E 0.89	X 0.09	2.4	7.5
cn03	7.29	6.89	0.24	8.19	5.75	4.20	8.37	1.11	3.64	0.81	X 0.09	1.9	4.3
cn04	7.27	6.96	0.25	8.09	5.67	4.22	8.33	1.14	3.69	0.82	0.20	2.3	4.2
id01	7.21	7.05	0.24	8.45	5.53	4.34	8.33	1.19	3.57	0.78	0.19	1.3	3.6
id02	6.73	7.17	X 0.34	E 6.25	E 4.68	X 5.70	8.57	E 1.36	X 2.02	X 1.23	E 0.26	-6.3	3.6
jp01	7.29	7.34	0.20	8.47	5.76	4.24	6.88	1.11	3.24	0.78	E 0.24	-2.3	-2.3
jp02	7.28	7.53	0.24	8.67	5.56	3.95	8.33	1.13	E 2.45	0.72	0.20	-2.7	-2.7
mn01	7.24	7.13	E 0.18	8.40	5.80	4.40	7.90	1.20	3.10	0.80	X 0.40	3.9	0.5
ph01	6.90	7.09	0.22	8.83	6.14	4.23	E 6.94	1.15	E 2.37	0.86	0.18	-7.6	-1.1
ru01	7.24	7.32	0.24	8.41	5.68	3.69	E 8.18	1.11	E 2.27	0.78	E 0.26	-2.9	-2.0
ru02	7.30	6.91	E 0.28	9.20	X 3.90	3.90	8.00	1.10	3.40	0.78	E 0.14	-2.1	3.6
th01	7.04	7.14	X 0.17	8.41	5.65	4.23	8.29	1.17	3.50	0.80	0.19	7.6	-5.0
th02	7.27	6.78	0.24	8.17	5.67	4.03	8.37	1.21	3.57	0.86	E 0.25	3.3	5.4
vn01	E 6.07	7.51	E 0.27	8.44	E 4.44	3.77	7.78	X 2.10	3.38	0.71	E 0.24	0.4	-0.2
Expected value	7.31	7.41	0.24	8.29	5.70	4.28	8.22	1.16	3.23	0.76	0.20	-	-
Number of data	15	15	15	15	15	15	15	15	15	15	15	-	-
Average	7.11	7.12	0.24	8.35	5.50	4.25	8.14	1.23	3.17	0.83	0.20	-	-
Minimum	6.07	6.78	0.17	6.25	3.90	3.69	6.88	1.10	2.02	0.71	0.09	-7.1	-2.3
Maximum	7.30	7.53	0.34	9.32	6.43	5.70	9.32	2.10	3.69	1.23	0.40	18.9	4.5
Standard deviation	0.33	0.22	0.04	0.69	0.66	0.47	0.61	0.25	0.59	0.12	0.08	-	-

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

I:Poor ion balance (R1)
C:Poor Conductivity agreement (R2)

3.2 Analytical Parameters

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.
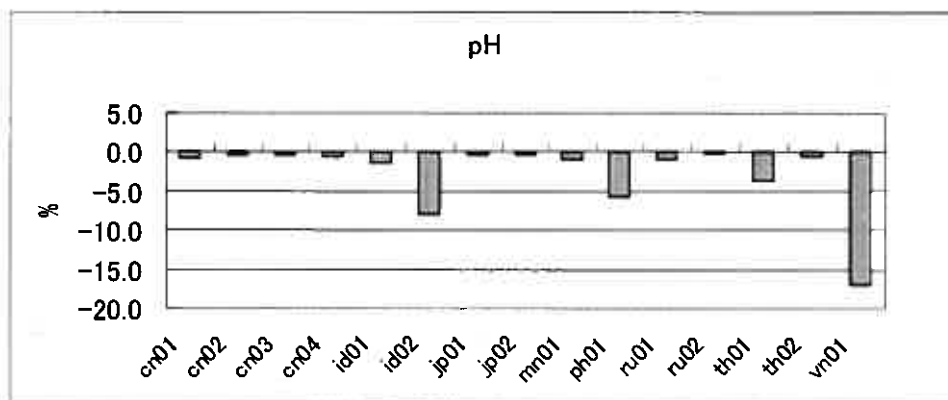

Fig.3   Distribution of pH data normalized by prepared value

Table 10   Analytical method and flagged data of pH

Analytical Method

pH meter and electrode	15/15

Flagged data

	E	X	Flagged (%)
Sample	1	0	6.7

All participating laboratories used pH meter with glass electrode for measurement of pH. Obtained data were almost agreed with the prepared value. However, Lab.vn01 submitted the data flagged by "E".   All participating laboratories reported lower than prepared value.
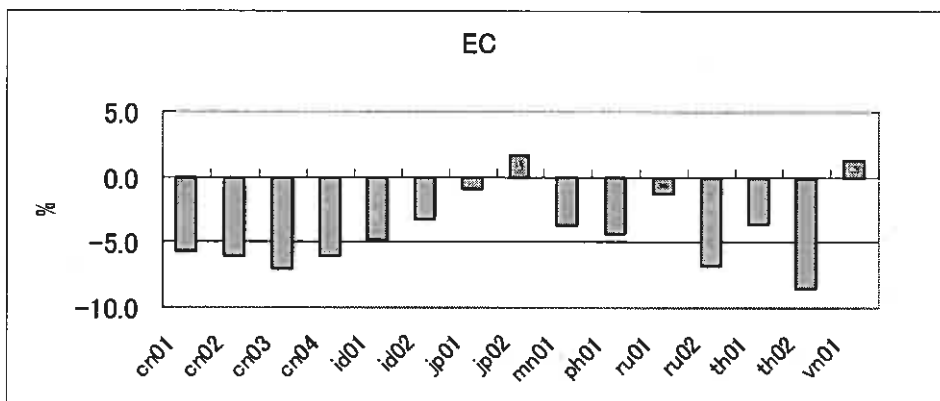
Fig.4   Distribution of EC data normalized by prepared value

Table 11   Analytical method and flagged data of EC

Analytical Method

Conductivity meter and cell	15/15

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 than prepared value.
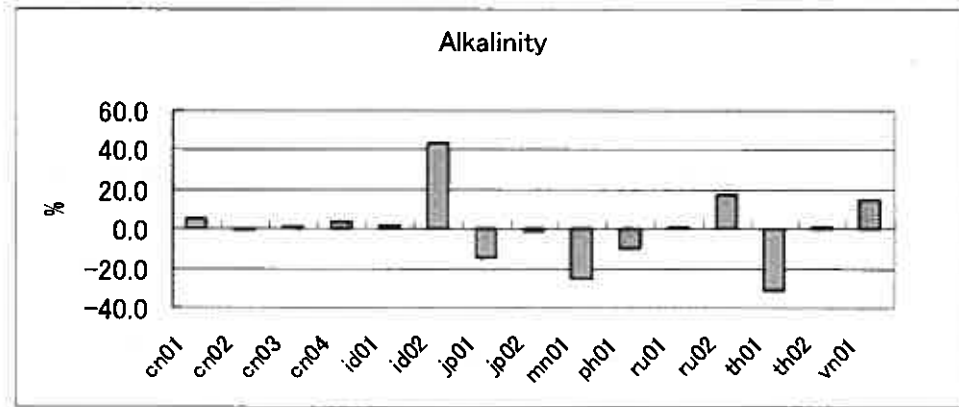
Fig.5   Distribution of Alkalinity data normalized by prepared concentration

Table 12   Analytical method and flagged data of Alkalinity

Analytical Method

Titration	15/15

Flagged data

	E	X	Flagged (%)
Sample	3	2	33.3

All participating laboratories used titration for the determination of Alkalinity.

Data from 5 laboratories were flagged. Especially data from Lab.id02 and th01 were significantly deviated from prepared value.
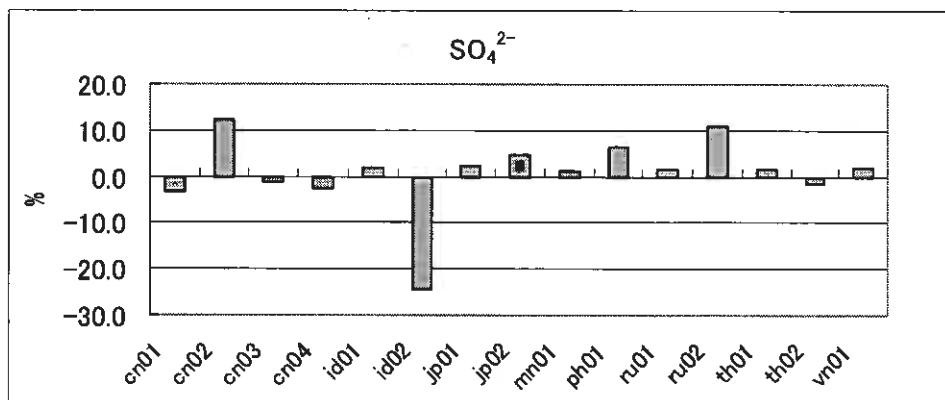
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Fig.6   Distribution of SO$_4^{2-}$ data normalized by prepared concentration

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

Analytical Method

Ion chromatography	13/15
spectrophotometry	2/15

Flagged data

	E	X	Flagged (%)
Sample	1	0	6.7

Most of participating laboratories except for two used ion chromatography for the determination of SO$_4^{2-}$.   Lab.ru02 and id02 used other method (spectrophotometry) instead of ion chromatography. Data from Lab.id02 were flagged.
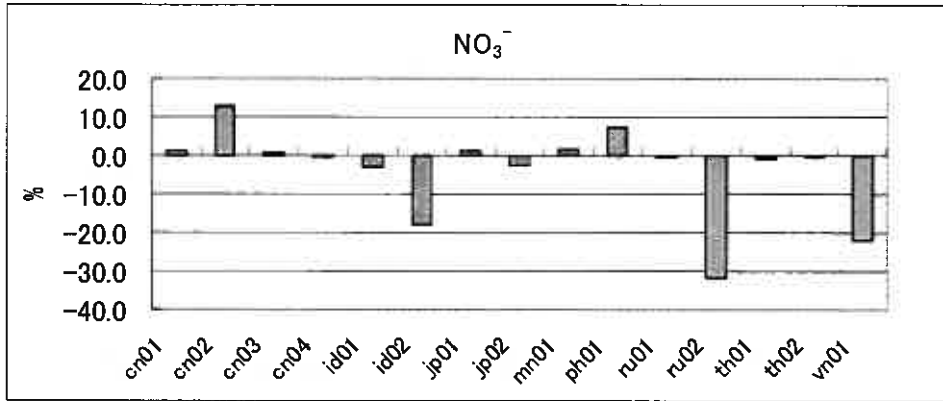
Fig.7 Distribution of NO₃⁻ data normalized by prepared concentration

Table 14 Analytical method and flagged data of NO₃⁻

Analytical Method

Ion chromatography	12/15
spectrophotometry	2/15
Other method	1/15

Flagged data

	E	X	Flagged (%)
Sample	2	1	20.0

Same as SO_4^{2-}, most of participating laboratories used ion chromatography for the determination of NO_3^-. Two laboratories used spectrophotometry. Lab.ru02 used other method (ion-selected electrode). Data from Lab.id02 and vn01, which were obtained by spectrophotometry, were all flagged. Data from Lab.ru02, which were obtained by ion-selected electrode, were flagged too. There seems to be some problem of the used method in this case, but it was not able to specify the cause.
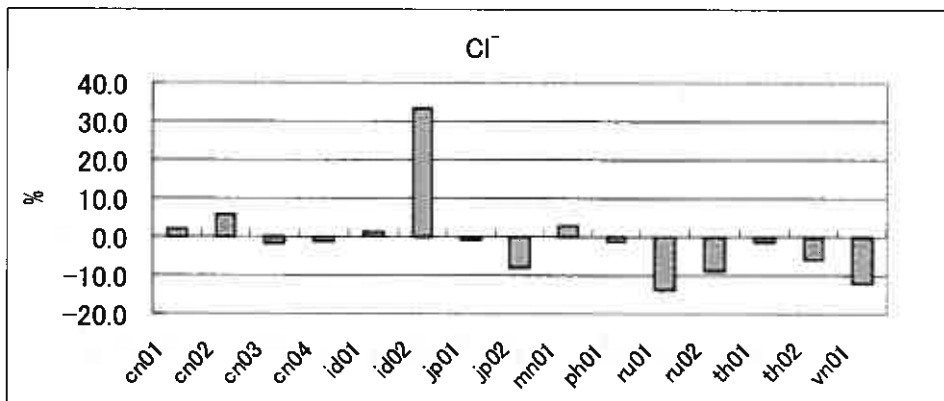
Fig.8   Distribution of Cl⁻ data normalized by prepared concentration

Table 15   Analytical method and flagged data of Cl⁻

Analytical Method

Ion chromatography	13/15
Titration method	2/15

Flagged data

	E	X	Flagged (%)
Sample	0	1	6.7

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 obtained with titration were flagged. There seems to be some problem of the used method in this case, but it was not able to specify the cause.
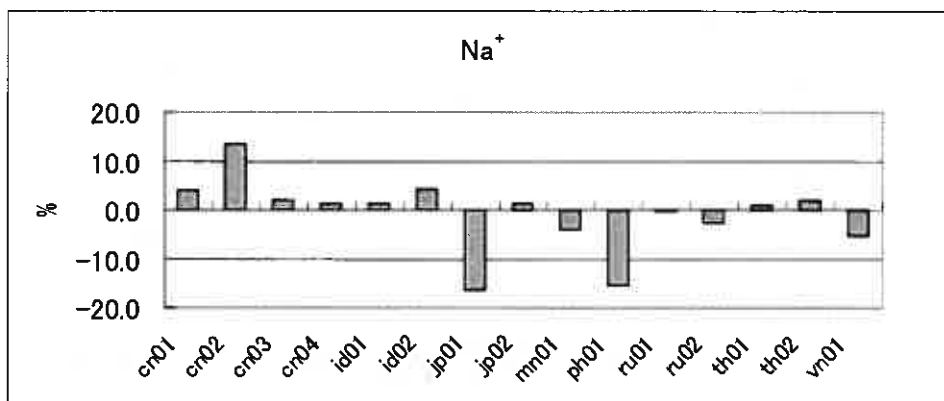
Fig.9   Distribution of Na⁺ data normalized by prepared concentration

Table 16   Analytical method and flagged data of Na⁺

Analytical Method

Ion chromatography	11/15
Atomic absorption / Flame (emission) photometry	4/15

Flagged data

	E	X	Flagged (%)
Sample	2	0	13.3

Among 15 participating laboratories, 11 laboratories used ion chromatography, while 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Na⁺. Data from Lab.jp01 and ph01 were flagged .

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

Table 17   Analytical method and flagged data of K⁺

Analytical Method

Ion chromatography	11/15
Atomic absorption / Flame (emission) photometry	4/15

Flagged data

	E	X	Flagged (%)
Sample	1	1	13.3

Same as Na⁺, 11 laboratories used ion chromatography, and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of K⁺. Data from 2 laboratories were flagged. Especially data from Lab.vn01 were 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	11/15
Atomic absorption / Flame (emission) photometry	3/15
Titration	1/15

Flagged data

	E	X	Flagged (%)
Sample	3	1	26.7

Among 15 participating laboratories, 11 laboratories used ion chromatography and 3 laboratories used atomic absorption/flame (emission) photometry for the determination of Ca^{2+}. One laboratory (Lab.id02) determined the concentration of Ca^{2+} by titration. Data from Lab.jp02 (ion chromatography), Lab.id02 (titration) and Lab.ph01 and ru02 (atomic absorption/flame) significantly deviated from prepared value.
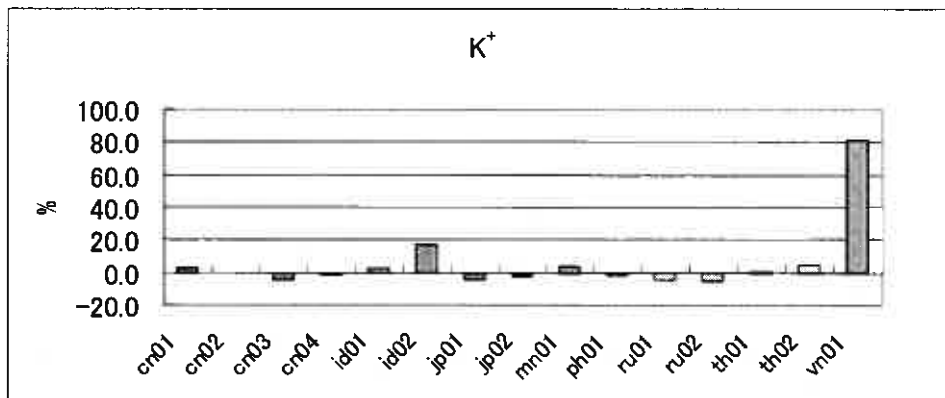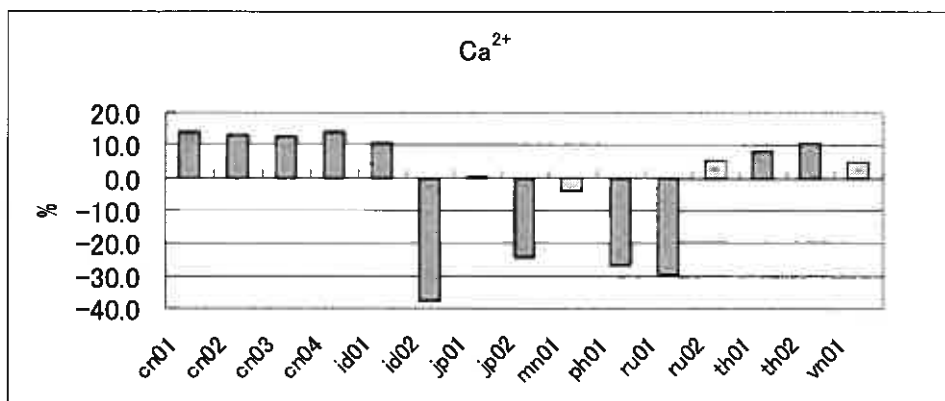
Fig.12   Distribution of Mg²⁺ data normalized by prepared concentration

Table 19   Analytical method and flagged data of Mg²⁺

Analytical Method

Ion chromatography	10/15
Atomic absorption / Flame (emission) photometry	4/15
Titration (Calculation)	1/15

Flagged data

	E	X	Flagged (%)
Sample	1	1	13.3

Among 15 participating laboratories, 10 laboratories used ion chromatography and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Mg^{2+}. One laboratory (Lab.id02) determined the concentration of Mg^{2+} by calculation.   Data from Lab.id02 and cn02 obtained with calculation method were significantly deviated from prepared value.
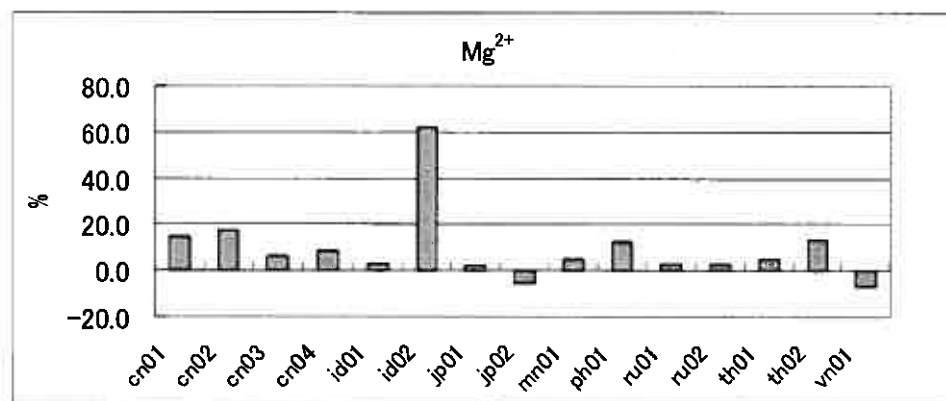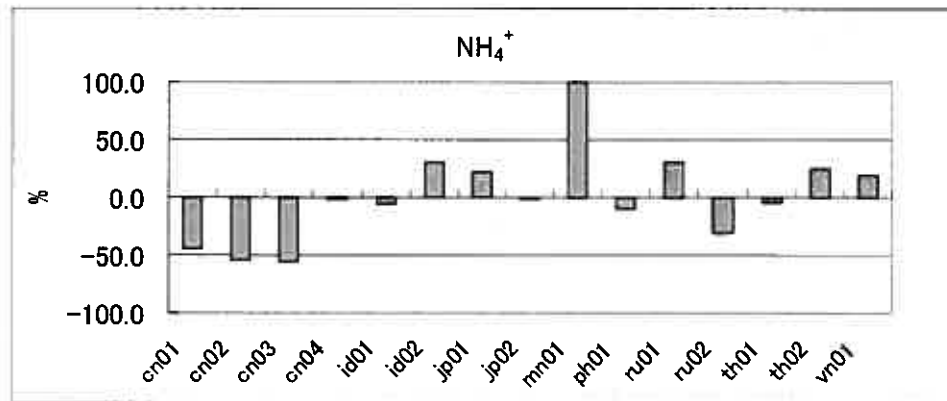
Fig.13   Distribution of NH₄⁺ data normalized by prepared concentration

Table 20   Analytical method and flagged data of NH₄⁺

Analytical Method

Ion chromatography	9/15
Spectrophotometry (Indophenol)	3/15
Spectrophotometry (Other method)	3/15

Flagged data

	E	X	Flagged (%)
Sample	6	4	66.7

Among 15 participating laboratories, 9 laboratories used ion chromatography, 3 laboratories used spectrophotometry(Indophenol) and 3 laboratories used spectrophotometry(other method) for the determination of NH₄⁺. The percentage of flagged was 66.7% and these results were worst among the all ion constituents.

Overall Evaluation

Obtained data on pH and EC were less varied in comparison with other ionic constituents. Most of obtained data on pH and EC were slightly lower than prepared value. The cause of this is not clear from the results of this project. Analytical data of ionic constituents were varied significantly for ions (K^+, NH_4^+) as shown in Fig.14. Concerning K^+ the cause of large deviation of analytical data seems to be a result from one laboratory were significantly deviated from prepared value. However it was not able to specify the causes of these deviations with the limited information obtained from this project. Quality of data is expected to be improved in the future by accumulation of experience on inter-laboratory comparison projects and QA/QC activities in each laboratories.
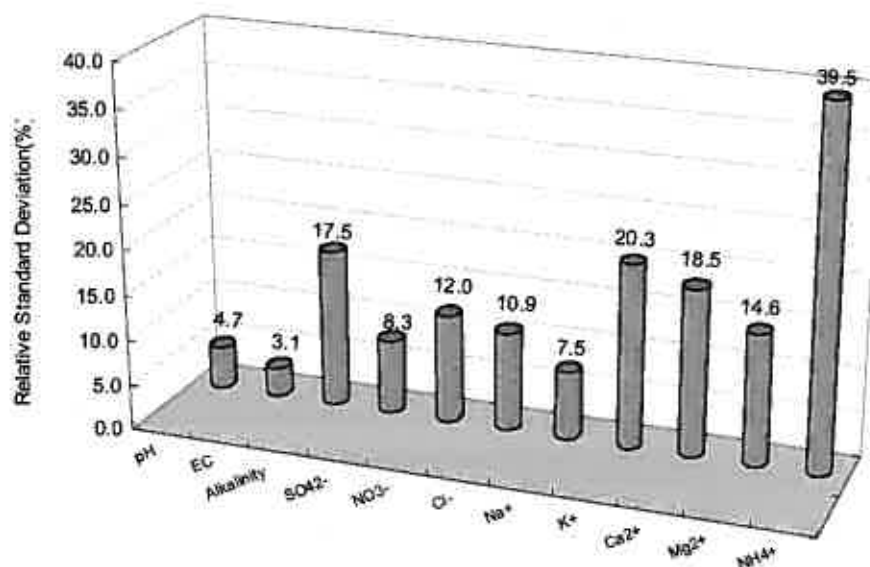
Fig.14   Relative standard deviation of each constituent

3.3 Circumstance of Sample Analysis

Methods Used

As shown in Fig. 15, most of the participating laboratories used recommended methods of EANET, particularly to be analyze for the pH, EC, Alkalinity and SO_4^{2-}, Cl^-, Na^+, K^+. 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 NO_3^- analysis, one laboratory used ion-selected electrode. For NH_4^+ analysis, three laboratories used spectrophotometry instead of indophenol blue. 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

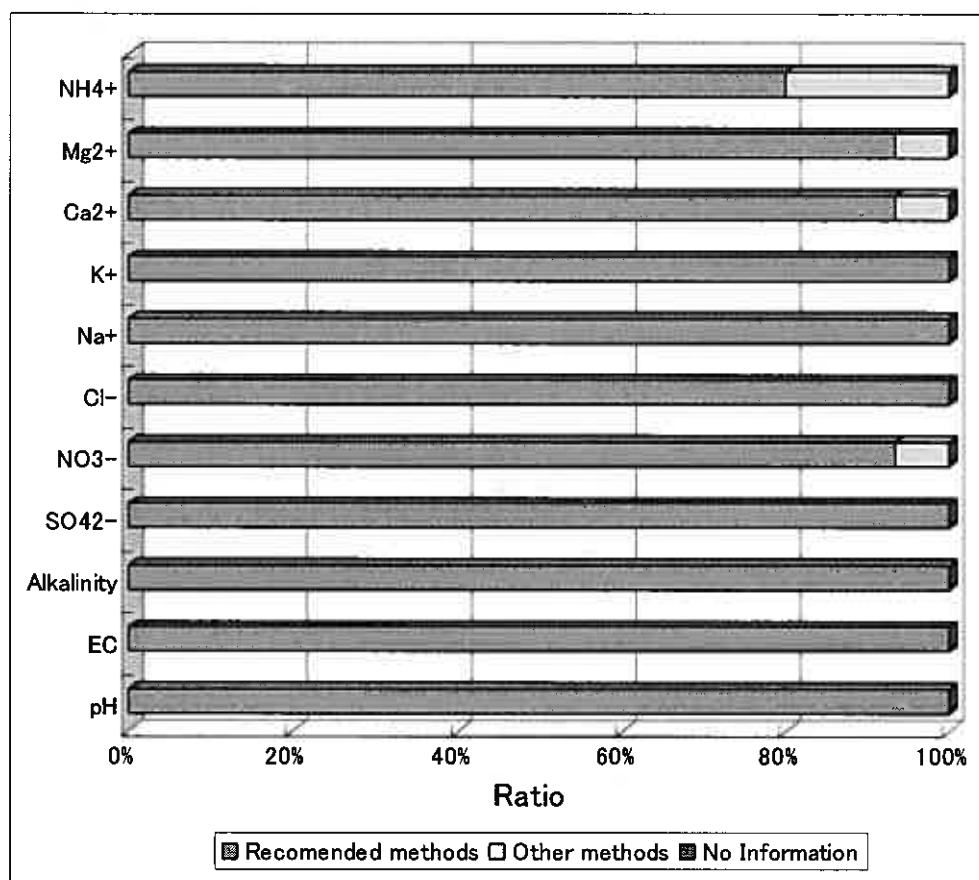| Code	Method
0	pH meter with electrode
1	Conductivity cell
2	Titration
3	Atomic absorption / Flame (emission) photometry
4	Ion chromatography
5	Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP - AES)
6	Calculation
7	Spectrophotometry
8	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
9	Graphite Furnace Atomic Absorption spectrometry (GFAA)
X	Other method
?	No information

Table 22　Analytical Method

Code	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	15(1)										
1		15									
2			15(5)			2(1)			1(1)		
3							4(1)	4(1)	3(2)	4	
4				13(1)	12(2)	13	11(1)	11(1)	11(1)	10(1)	9(6)
5											
6										1(1)	
7				2	2						3(2)
8											
9											
X					1(1)						3(2)
?											
Flagged E	1	0	3	1	2	0	2	1	3	1	6
Flagged X	0	0	2	0	1	1	0	1	1	1	4

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 presented in Table 23. Only one person carried out sample analysis in 4 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	B	C	C	C	D	D	D	D	D
cn03	1	A	A	A	A	A	A	A	A	A	A	A
cn04	1	A	A	A	A	A	A	A	A	A	A	A
id01	2	A	A	A	A	A	A	B	B	B	B	B
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	B	B	B	A	A	A	A	A
ph01	4	A	A	A	B	B	B	C	C	C	C	D
ru01	3	A	A	A	B	B	B	C	C	C	C	A
ru02	4	A	B	A	C	B	A	D	D	D	D	C
th01	2	A	B	A	B	B	B	A	A	A	A	A
th02	2	A	A	A	B	B	B	B	B	B	B	B
vn01	2	A	A	B	B	B	B	B	B	B	B	B

"-": No information, "A", "B", "C", and "D" 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 related to the cases 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-}	$NO3^-$	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	$NH4^+$
cn01	12	12	12	12	12	12	12	12	12	12	12
cn02	5	5	13	13	13	13	4	4	4	4	4
cn03	5	5	5	5	5	5	5	5	5	5	5
cn04	8	8	8	8	8	8	8	8	8	8	8
id01	1	1	1	1	1	1	1	1	1	1	1
id02	2	2	12	2	2	2	12	12	12	12	12
jp01	1	1	1	1	1	1	1	1	1	1	1
jp02	1	1	1	1	8	1	1	1	1	1	8
mn01	6	6	6	6	6	6	6	6	6	6	6
ph01	4	4	4	2.5	2.5	2.5	4	4	4	4	1.8
ru01	25	25	25	17	17	17	17	17	17	17	25
ru02	44	24	44	10	24	44	13	13	13	13	10
th01	6	1	6	1	1	1	6	6	6	6	6
th02	6	6	6	7	7	7	7	7	7	7	7
vn01	1	1	18	18	18	18	18	18	18	18	18

Reverse mesh: Data were flagged by "E" or "X" in sample

1 year means experience of 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	2	13%
1	5	33%
2	5	33%
3	1	7%
4	0	0%
5	1	7%
6	0	0%
7	0	0%
8	1	7%

Number of laboratories with excellent results (without flagged data) was only 3, which was equivalent to 13% of the whole participating laboratories. These results are not so good compared with last year.

One laboratory had 8 flagged data. This cause seems that they don't have ion chromatography, and concerning Ca^{2+} and Mg^{2+}, they use titration (calculation) method.
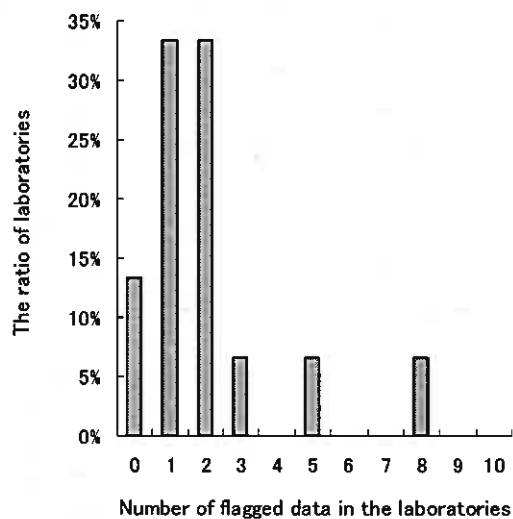

Fig. 16 The distribution of laboratories with the number of flagged data

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

The inter-laboratory comparison projects of EANET were carried out four times, in 2000, 2001, 2002 and 2003. The number of flagged data in these projects 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%, for the second project (2001), it was about 88.6%, for the third project (2002), it was about 84.4% and it was about 81.2%, for the fourth project (2003).

In the four attempts, this result of fourth one was the worst. As one of the reasons, total number of flags was dependent on accuracy of NH4$^+$ determination, because one third of all flags was attributed to NH4$^+$ determination. One of the possible causes was that the concentration of NH4$^+$ of the sample was prepared as the lowest among the four projects.

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.
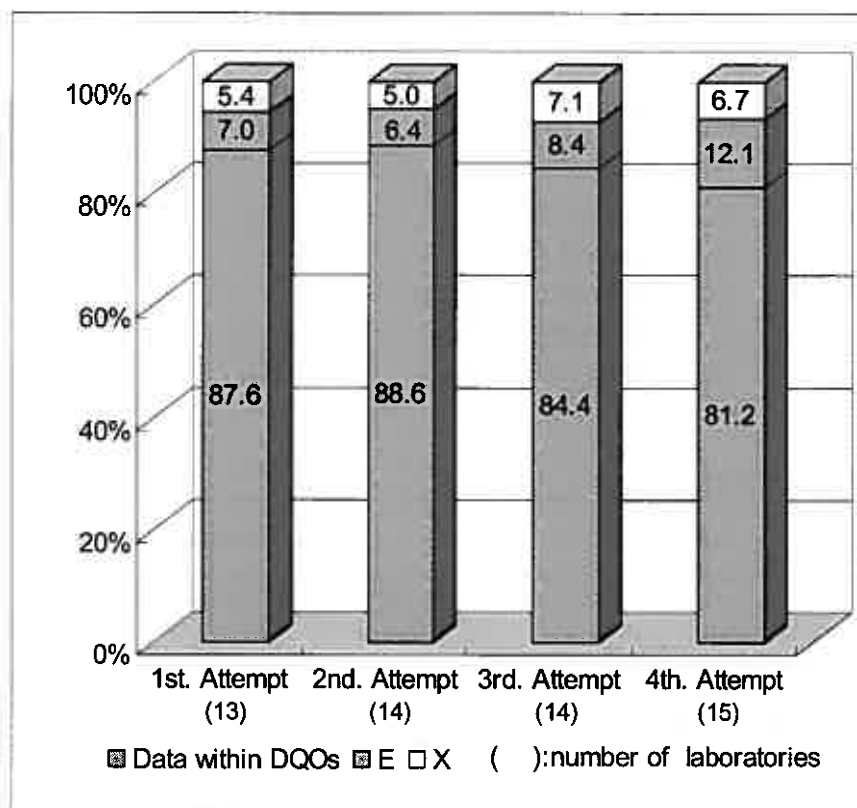

Fig. 17 Comparison of 1st,2nd , 3rd and 4th inter-laboratory comparison projects

5. REFERENCES

1) Technical Manual 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 ; 2nd attempt, November 2002 and 3rd attempt, November 2003.

6. CONTACT INFORMATION

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