

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

**Report of the Inter-laboratory
Comparison Project 2004 on Inland Aquatic
Environment**

5th Attempt

November 2005

Acid Deposition and Oxidant Research Center

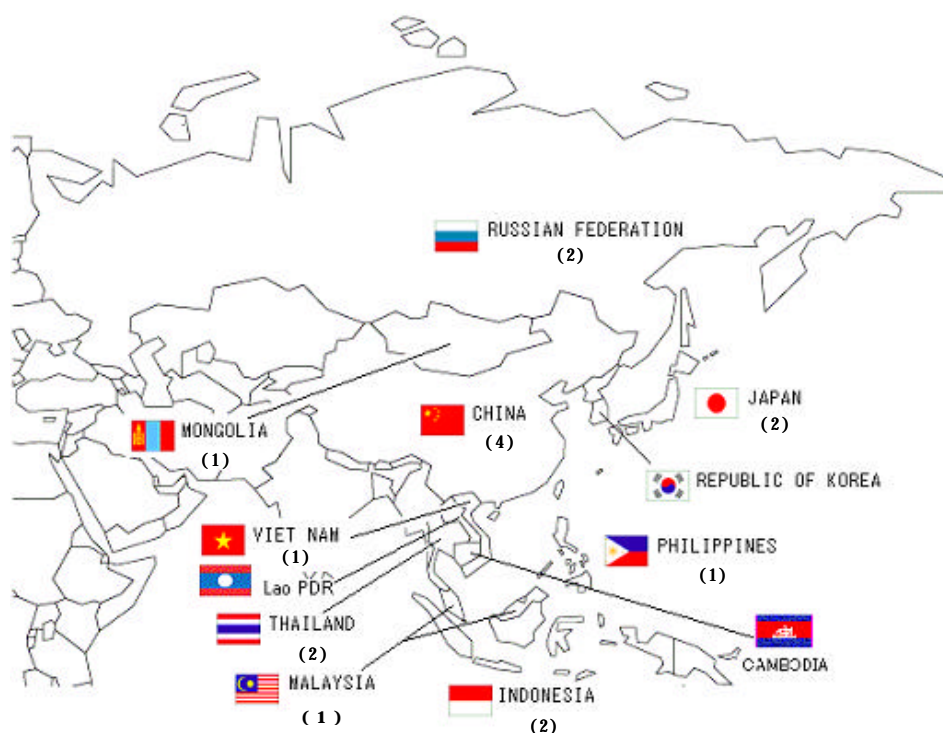
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1. INTRODUCTION

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 practices, (i) to recognize the analytical precision and accuracy of the data in each participating laboratory, and provide 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 (16 laboratories from 9 countries)

Fig.1 Laboratories participated in the inter-laboratory comparison project 2004 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. In 2004 the laboratory of Malaysia started participation in this inter-laboratory comparison project on inland aquatic environment. The Network Center (NC) sent artificial inland aquatic environment samples to all of these 16 laboratories, and all laboratories submitted their analytical data to NC.

2.2 Dispatched Artificial Inland Aquatic Environment Samples

Artificial inland aquatic environment samples were distributed to the participating laboratories by NC in December 2004 with expected submission of results by February 28, 2005.

Table 1 Outline of the 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 SO_4^{2-} , NO_3^- , Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and NH_4^+ . The participating laboratories were informed 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-}	milli gram/liter	mg/L
NO_3^-	milli gram/liter	mg/L
Cl^-	milli gram/liter	mg/L
Na^+	milli gram/liter	mg/L
K^+	milli gram/liter	mg/L
Ca^{2+}	milli gram/liter	mg/L
Mg^{2+}	milli gram/liter	mg/L
NH_4^+	milli gram/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 ($\mu\text{eq/L}$) is calculated by sum up the concentration of anions (C: $\mu\text{mol/L}$) and Alkalinity (ALK: $\mu\text{eq/L}^*$). Alkalinity considered to be corresponded to bicarbonate ions (HCO_3^-).

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

C_{A_i} : electric charge of ion and concentration ($\mu\text{mol/L}$) of anion "i".

$$* : \mu\text{eq/L} = \text{meq/L} \times 1000$$

(2) Total cation (C) equivalent concentration ($\mu\text{eq/L}$) is calculated by sum up the concentration of all cations (C: $\mu\text{mol/L}$).

$$C (\mu\text{eq/L}) = \sum n C_{C_i} (\mu\text{mol/L}) = 10^{(6-\text{pH})} + C (\text{NH}_4^+) + C (\text{Na}^+) + C (\text{K}^+) \\ + 2C (\text{Ca}^{2+}) + 2C (\text{Mg}^{2+})$$

C_{C_i} : electric charge of ion and concentration ($\mu\text{mol/L}$) 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) [$\mu\text{eq/L}$]	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 (R₂)

(1) Total electric conductivity (Λ_{calc}) should be calculated as follows;

$$\Lambda_{\text{calc}} \text{ (mS/m)} = \{349.7 \times 10^{(6-\text{pH})} + 80.0 \times 2C (\text{SO}_4^{2-}) + 71.5 \times C (\text{NO}_3^-) \\ + 76.3 \times C (\text{Cl}^-) + 73.5 \times C (\text{NH}_4^+) + 50.1 \times C (\text{Na}^+) + 73.5 \times C (\text{K}^+) \\ + 59.8 \times 2C (\text{Ca}^{2+}) + 53.3 \times 2C (\text{Mg}^{2+}) + 44.5 \times (\text{ALK})\} / 10000$$

C: Molar concentrations (μ mol/L) of ions in the parenthesis; each constant value is ionic equivalent conductance at 25°C. Alkalinity considered to be corresponded to bicarbonate ions (HCO₃⁻).

(2) Ratio (R₂) of calculations (Λ_{calc}) to measurements (Λ_{meas}) 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) R₂, 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 R₂ is not within the range.

Table 6 Allowable ranges for R₂ in different concentration ranges

Λ _{meas} [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

Obtained data on analytical results from all laboratories 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.). As shown in Table 7, average of submitted data were fairly well agreed with the prepared value/concentration within a range of $\pm 10\%$.

Table 7 Summary of analytical results of the artificial inland aquatic environment sample

Constituents		Prepared	Average	S.D	N	Min.	Max.
pH		7.00	6.82	0.33	16	5.69	7.10
EC	(mS/m)	4.00	3.86	0.14	16	3.62	4.15
Alkalinity	(meq/L)	0.119	0.125	0.035	16	0.056	0.225
SO ₄ ²⁻	(mg/L)	4.48	4.50	0.82	16	2.90	7.20
NO ₃ ⁻	(mg/L)	3.16	3.12	0.55	16	2.19	4.90
Cl ⁻	(mg/L)	2.46	2.37	0.12	16	2.26	2.72
Na ⁺	(mg/L)	4.31	4.09	0.35	16	3.11	4.39
K ⁺	(mg/L)	0.77	0.72	0.10	16	0.42	0.88
Ca ²⁺	(mg/L)	1.63	1.60	0.25	16	0.83	1.85
Mg ²⁺	(mg/L)	0.38	0.38	0.04	16	0.30	0.44
NH ₄ ⁺	(mg/L)	0.22	0.26	0.15	16	0.10	0.75

(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 $\pm 15\%$ 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 ($\pm 15\% \sim \pm 30\%$) 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 presented in "3.2 Analytical Parameters", and evaluation of data by circumstances of analysis such as analytical method used, experience of personnel, and other analytical conditions is described in "3.3 Circumstance of Sample Analysis".

As shown in Table 8, 9 and Fig. 2, there were 21 analytical data out of 176 exceeded the DQOs by a factor of 2 and flagged by "E". 15 values out of 176 exceeded the DQOs more than a factor of 2 and flagged by "X". Results flagged by "E" and "X" were 36 out of 176 and shared about 20.5% 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	5	0	1	0	2	2	1	4	5	21
X	0	0	2	2	2	0	0	1	1	0	7	15
Data within DQOs	15	16	9	14	13	16	14	13	14	12	4	140
Flagged(%)	6.3	0.0	43.8	12.5	18.8	0.0	12.5	18.8	12.5	25.0	75.0	20.5

*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 $> 30\%$)

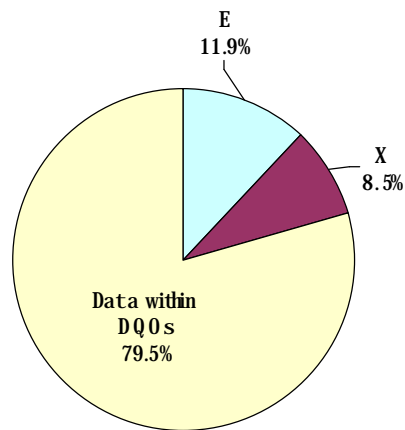


Fig.2 Percentage of flagged data

Table 9 Analytical Results of Sample No.041 (artificial inland aquatic environment sample : EANET in 2004)

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)	R1	R2
cn01	6.99	3.85	E 0.140	4.46	3.04	2.34	4.21	0.75	1.80	0.42	E 0.16	-1.8	-
cn02	6.82	3.75	0.133	4.41	3.05	2.31	4.33	0.70	1.81	E 0.44	X 0.12	0.1	3.6
cn03	6.96	4.01	0.130	4.40	3.11	2.31	4.31	0.73	1.73	0.40	X 0.13	-0.6	-0.2
cn04	6.98	3.75	0.128	4.39	3.10	2.29	4.24	0.77	1.73	0.39	E 0.26	0.4	3.4
id01	6.85	3.76	E 0.090	4.16	3.08	2.52	E 3.62	E 0.64	1.80	0.37	X 0.10	0.4	-1.6
id02	6.67	3.99	0.122	X 2.90	X 2.19	2.38	E 3.11	0.88	1.64	0.40	X 0.34	1.2	-7.3
jp01	6.90	3.96	0.118	4.46	3.13	2.30	4.30	E 0.62	1.54	0.39	0.24	-0.1	-0.6
jp02	7.10	3.76	0.114	4.44	3.15	2.39	4.31	0.77	X 0.83	0.31	0.20	-6.5	-1.2
mn01	6.98	3.83	X 0.225	4.32	3.12	2.72	4.31	0.75	1.66	0.41	E 0.26	-13.4	8.4
ph01	6.77	3.85	0.105	4.64	3.21	2.41	3.71	0.78	1.54	E 0.31	E 0.16	-4.7	-1.3
ru01	6.92	3.99	0.104	4.40	3.15	2.43	4.39	0.66	E 1.30	0.40	X 0.75	4.9	0.6
ru02	6.92	4.15	E 0.140	4.58	E 2.41	2.26	3.92	0.81	1.44	0.38	E 0.27	-4.4	-3.5
th01	6.96	3.62	0.115	4.40	3.03	2.31	4.27	0.74	1.85	0.39	0.20	3.0	-2.3
th02	6.60	3.71	E 0.141	4.47	3.01	2.27	3.91	0.69	1.65	0.41	X 0.31	-3.8	3.7
vn01	E 5.69	3.92	E 0.146	4.43	3.28	2.29	4.26	X 0.42	1.62	E 0.30	X 0.37	-4.7	2.3
my01	6.93	3.87	X 0.056	X 7.20	X 4.90	2.38	4.21	0.77	1.62	0.39	0.22	-3.5	5.7
Expected value	7.00	4.00	0.119	4.48	3.16	2.46	4.31	0.77	1.63	0.38	0.22	-	-
Number of data	16	16	16	16	16	16	16	16	16	16	16	-	-
Average	6.82	3.86	0.125	4.50	3.12	2.37	4.09	0.72	1.60	0.38	0.26	-	-
Minimum	5.69	3.62	0.056	2.90	2.19	2.26	3.11	0.42	0.83	0.30	0.10	-13.4	-7.3
Maximum	7.10	4.15	0.225	7.20	4.90	2.72	4.39	0.88	1.85	0.44	0.75	4.9	8.4
Standard deviation	0.33	0.14	0.035	0.82	0.55	0.12	0.35	0.10	0.25	0.04	0.15	0.00	0.00

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

!: Poor ion balance (R1)

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

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 presented in table for each analytical parameter.

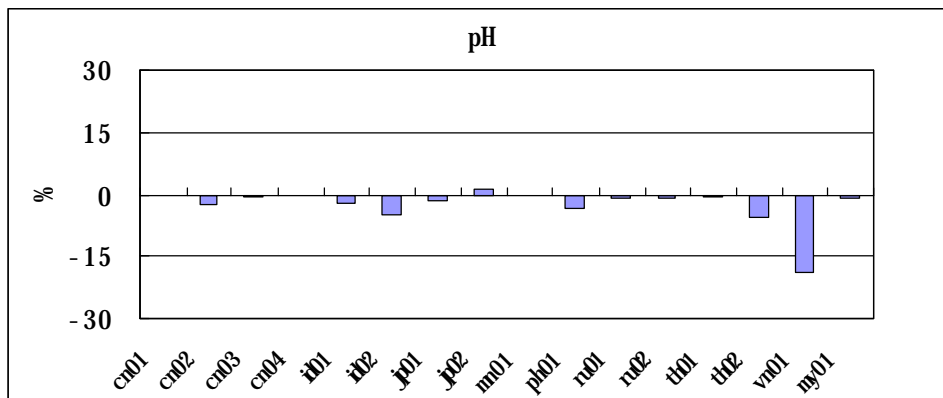


Fig.3 Distribution of pH data normalized by prepared value

Table 10 Analytical method and flagged data of pH

Analytical Method			
pH meter and electrode			16/16
Flagged data			
	E	X	Flagged (%)
Sample	1	0	6.3

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” as well as the result of the last year (2003). Lab.vn01 needs to check the conditions of the instruments or procedure of measurement.

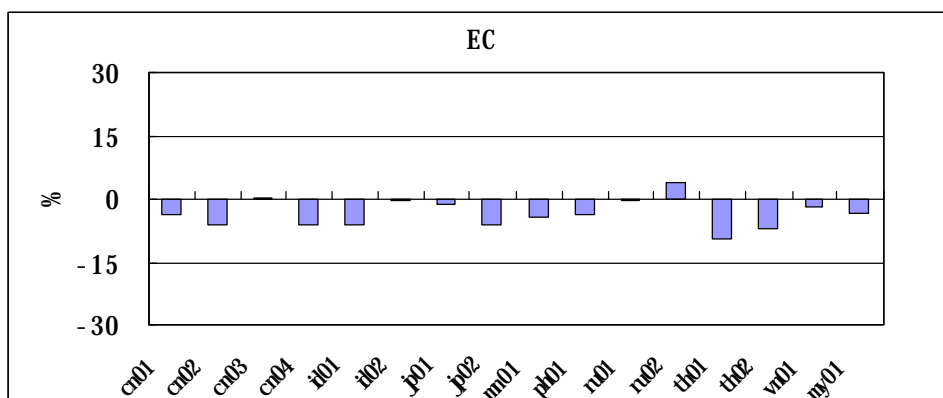


Fig.4 Distribution of EC data normalized by prepared value

Table 11 Analytical method and flagged data of EC

Analytical Method			
Conductivity meter and cell			16/16
Flagged data			
	E	X	Flagged (%)
Sample	0	0	0.0

All participating laboratories used conductivity cell for the measurement of EC. All of obtained data were agreed with prepared value.

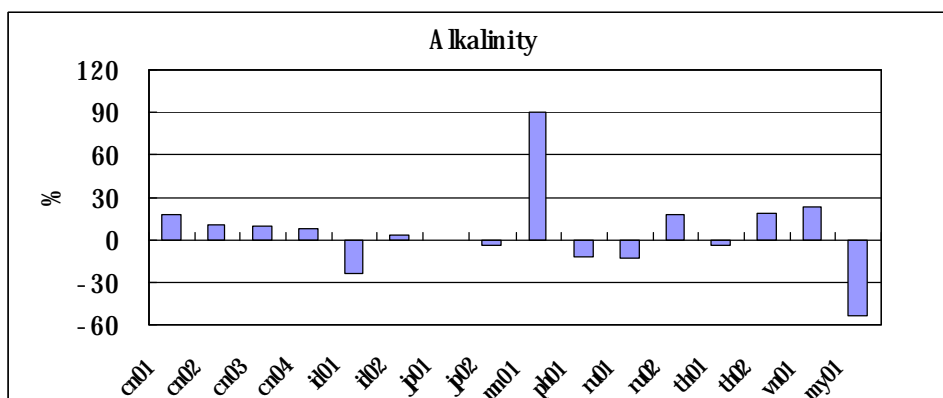


Fig.5 Distribution of Alkalinity data normalized by prepared concentration

Table 12 Analytical method and flagged data of Alkalinity

Analytical Method			
Titration			16/16
Flagged data			
	E	X	Flagged (%)
Sample	5	2	43.8

All participating laboratories used titration for the determination of Alkalinity.

Data from 7 laboratories were flagged. Especially results of Lab.mn01 and my01 were significantly deviated from prepared value.

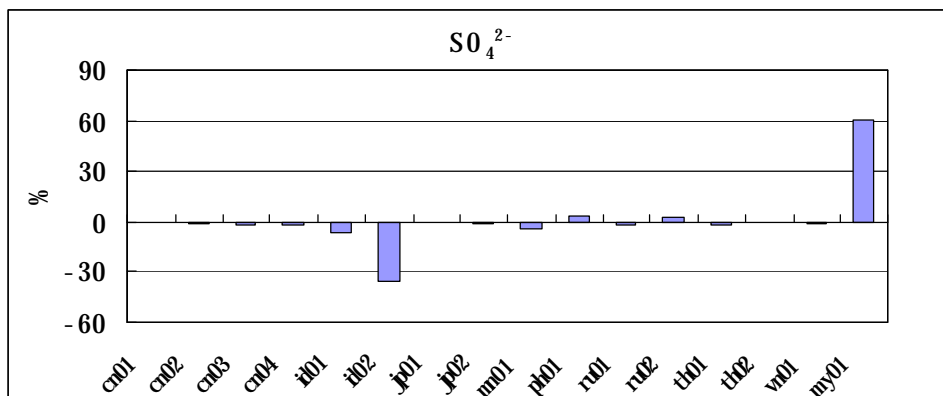


Fig.6 Distribution of SO₄²⁻ data normalized by prepared concentration

Table 13 Analytical method and flagged data of SO₄²⁻

Analytical Method			
Ion chromatography			14/16
spectrophotometry			2/16
Flagged data			
	E	X	Flagged (%)
Sample	0	2	12.5

Most of participating laboratories used ion chromatography for the determination of SO₄²⁻. The data from Lab.id02 and my01 were significantly deviated from prepared value. Lab.id02 used the spectrophotometry and Lab.my01 used ion chromatography. These laboratories need to clarify the cause of flagged results.

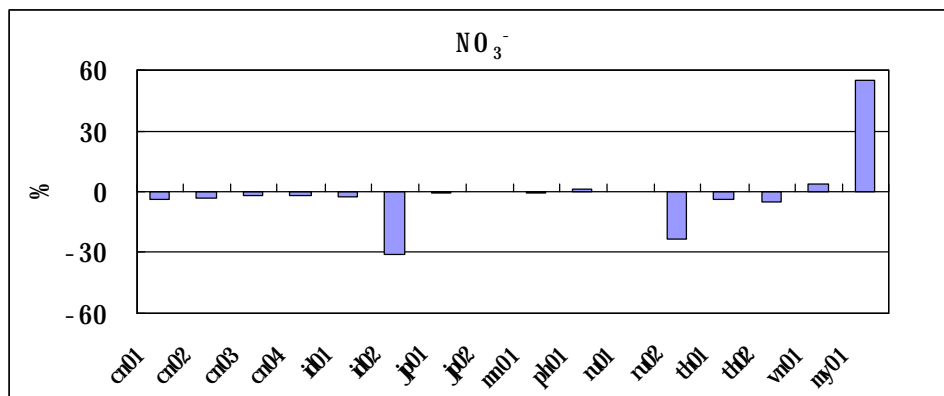


Fig.7 Distribution of NO₃⁻ data normalized by prepared concentration

Table 14 Analytical method and flagged data of NO₃⁻

Analytical Method			
Ion chromatography			13/16
spectrophotometry			2/16
Other method			1/16
Flagged data			
	E	X	Flagged (%)
Sample	1	2	18.8

As well as SO₄²⁻, most of participating laboratories used ion chromatography for the determination of NO₃⁻. 2 laboratories used spectrophotometry. And one laboratory used other method (ion-selected electrode). Data from Lab.id02 which were obtained by spectrophotometry and data from Lab.ru02, which were obtained by ion-selected electrode were flagged as well as their results of last year (2003). These laboratories should improve the analysis. Concerning my01, it is necessary to check the condition of instrument or measurement procedure of ion chromatography, because the results of both SO₄²⁻ and NO₃⁻ were flagged.

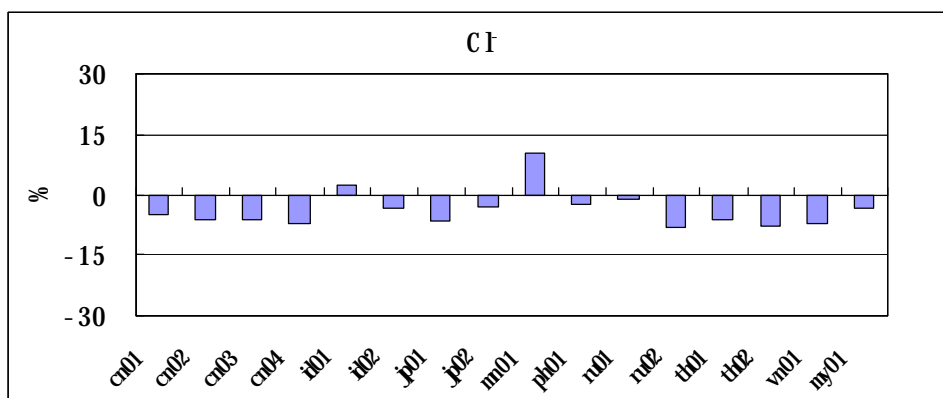


Fig.8 Distribution of Cl⁻ data normalized by prepared concentration

Table 15 Analytical method and flagged data of Cl⁻

Analytical Method			
Ion chromatography			14/16
Titration method			2/16
Flagged data			
	E	X	Flagged (%)
Sample	0	0	0.0

Most of participating laboratories used ion chromatography for the determination of Cl⁻. 2 laboratories used titration method. All data were agreed with prepared value.

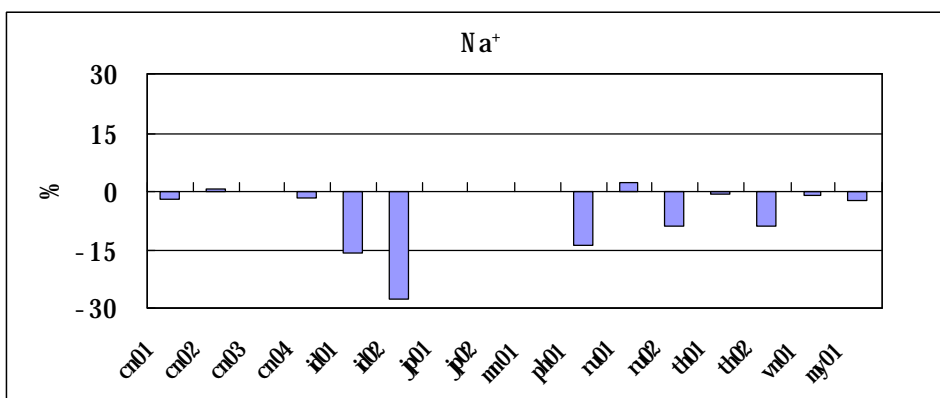


Fig.9 Distribution of Na⁺ data normalized by prepared concentration

Table 16 Analytical method and flagged data of Na⁺

Analytical Method			
Ion chromatography			12/16
A tomic absorption / Flame (em ission) photometry			4/16
Flagged data			
	E	X	Flagged (%)
Sample	2	0	12.5

Among 15 participating laboratories, 12 laboratories used ion chromatography, while 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Na⁺. Data from Lab.id01 and id02 were flagged.

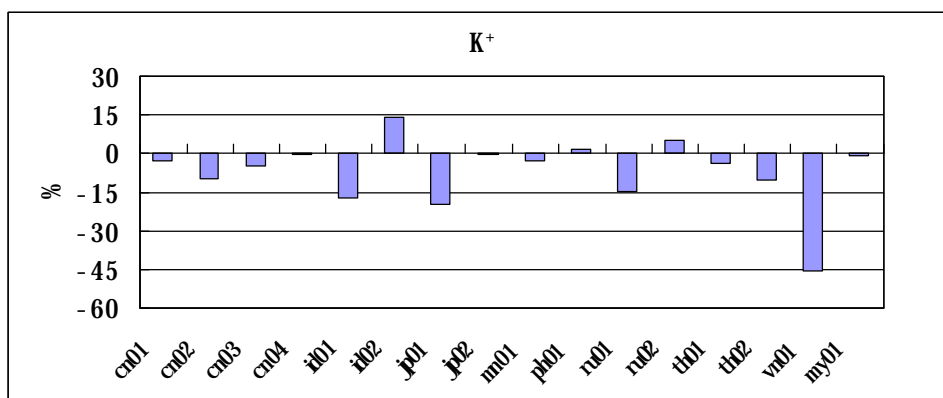


Fig.10 Distribution of K⁺ data normalized by prepared concentration

Table 17 Analytical method and flagged data of K⁺

Analytical Method			
Ion chromatography			12/16
Atomic absorption / Flame (emission) photometry			4/16
Flagged data			
	E	X	Flagged (%)
Sample	2	1	18.8

As well as for Na⁺, 12 laboratories used ion chromatography, and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of K⁺. Results of 3 laboratories were flagged. Especially value from Lab.vn01 was significantly deviated from prepared value as well as the result of last year (2003). Lab.vn01 need to clarify the cause of flagged results

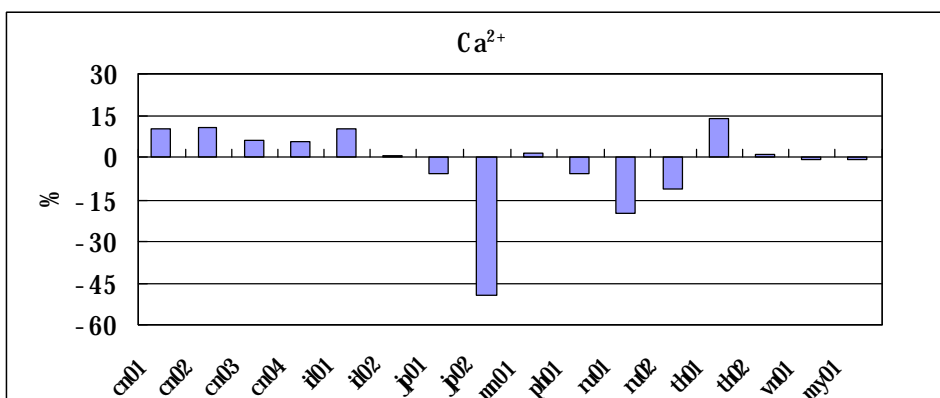


Fig.11 Distribution of Ca²⁺ data normalized by prepared concentration

Table 18 Analytical method and flagged data of Ca²⁺

Analytical Method			
Ion chromatography			12/16
Atomic absorption / Flame (emission) photometry			4/16
Flagged data			
	E	X	Flagged (%)
Sample	1	1	12.5

Among 16 participating laboratories, 12 laboratories used ion chromatography and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Ca²⁺. Data from 2 laboratories were flagged. Especially result from Lab.jp02 was significantly deviated from prepared value. Lab.jp02 needs to check the condition of instrument or measurement procedure of ion chromatography.

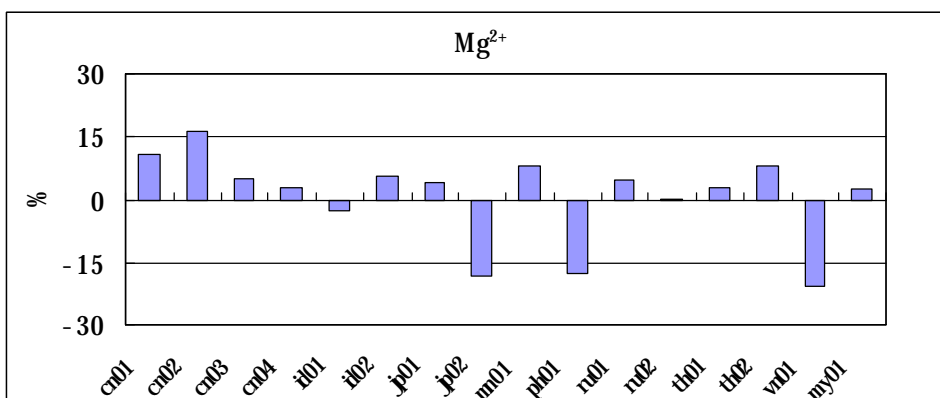


Fig.12 Distribution of Mg²⁺ data normalized by prepared concentration

Table 19 Analytical method and flagged data of Mg²⁺

Analytical Method			
Ion chromatography	12/16		
Atomic absorption / Flame (emission) photometry	4/16		
Flagged data			
	E	X	Flagged (%)
Sample	4	0	25.0

Among 16 participating laboratories, 12 laboratories used ion chromatography and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Mg²⁺. Data from 4 laboratories were flagged.

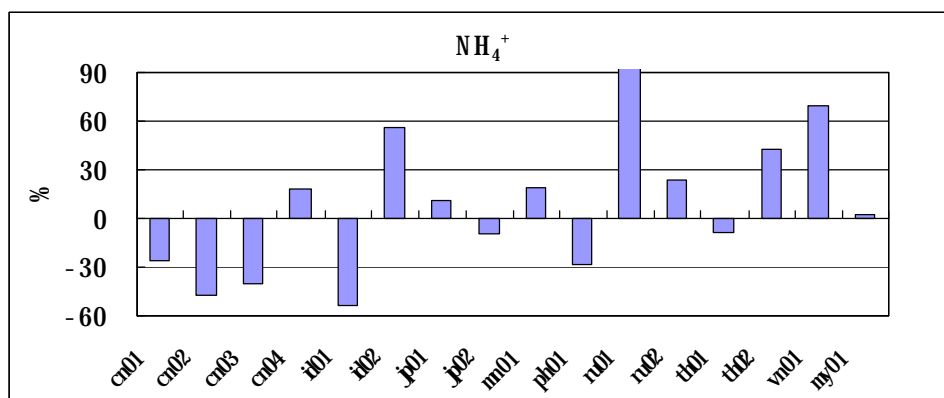


Fig.13 Distribution of NH₄⁺ data normalized by prepared concentration

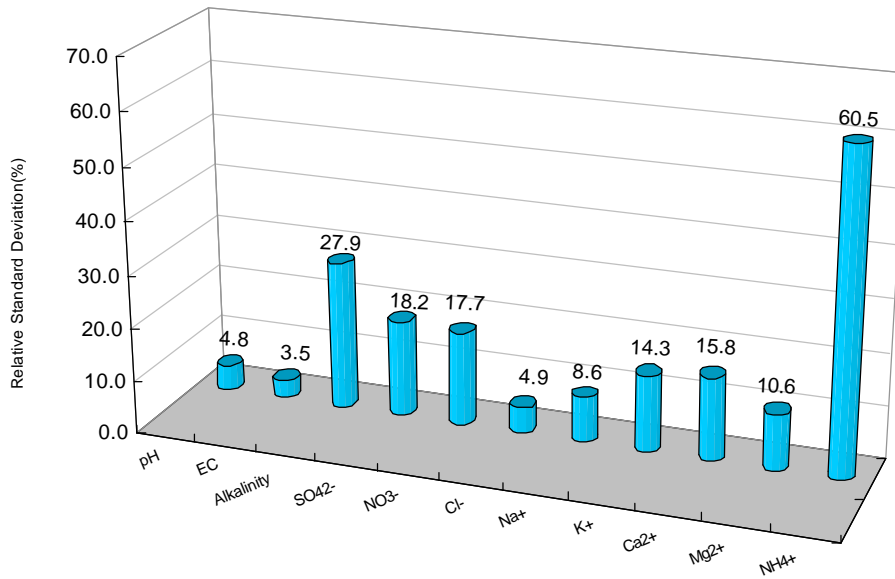
Table 20 Analytical method and flagged data of NH₄⁺

Analytical Method			
Ion chromatography			11/16
Spectrophotometry (Indophenol)			3/16
Spectrophotometry (Other method)			2/16
Flagged data			
	E	X	Flagged (%)
Sample	5	7	75.0

Among 16 participating laboratories, 11 laboratories used ion chromatography, 3 laboratories used spectrophotometry (Indophenol) and 2 laboratories used spectrophotometry (other method) for the determination of NH₄⁺. The percentage of flagged was 75.0% and these results were the worst among the all ions as well as in the last year (2003). These laboratories need to check the calibration curve, chromatogram of ion chromatography, standard solutions for calibration curve and so on.

Overall Evaluation

The relative standard deviation of Alkalinity, SO_4^{2-} , NO_3^- and NH_4^+ were larger than other ion constituents as demonstrated in Fig.14. Concerning SO_4^{2-} and NO_3^- the large deviation of analytical data seems to be caused by a result from one laboratory significantly far from prepared value. As one of the reason, it seemed that the condition of measurement for anion was not good in this laboratory. 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 laboratory.



(Relative standard deviation (%) = Standard deviation / Average \times 100)

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 except measurement of NH_4^+ and NO_3^- by some laboratories. The codes for the various analytical methods used in this project are presented in Table 21 and their application for analysis is summarized in Table 22. Until last year (2003) one laboratory used titration (calculation) method for analysis of Ca^{2+} and Mg^{2+} , however this laboratory applied atomic absorption method on this year. As the result, values of Ca^{2+} and Mg^{2+} from this laboratory were not flagged. An ion-selected electrode is used for NO_3^- analysis by one laboratory. 2 laboratories used spectrophotometry instead of indophenol blue for NH_4^+ analysis. There are some flagged data in results related using the non- recommended methods. These laboratories should change analytical procedures to the recommended methods of EANET.

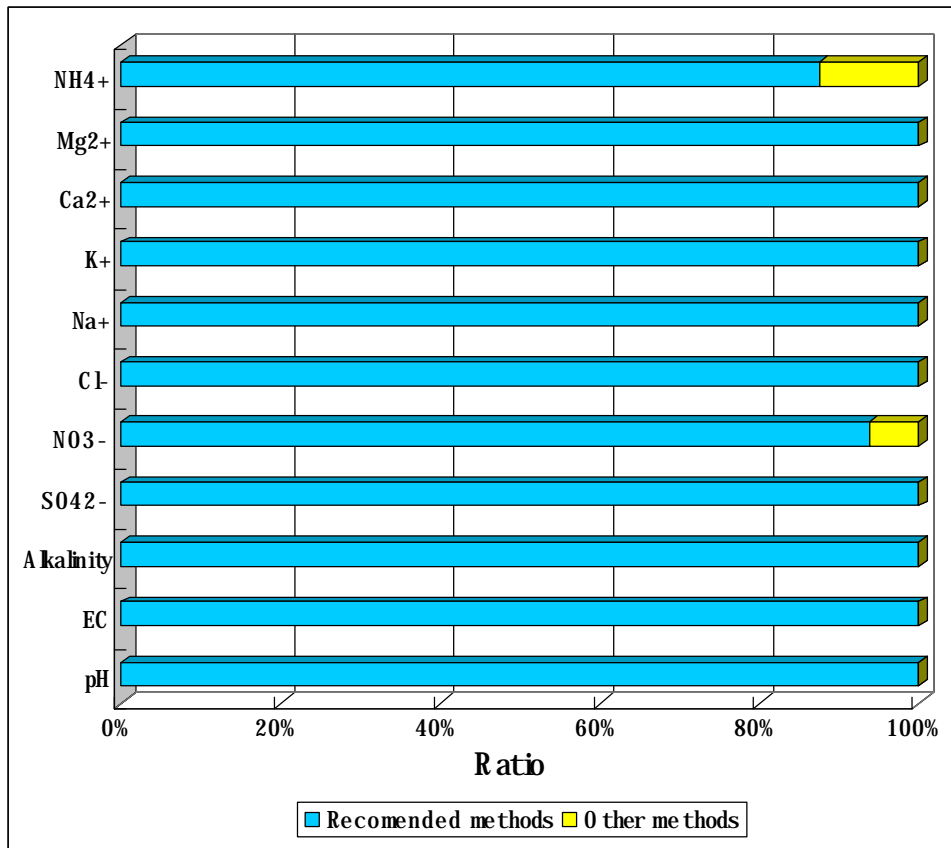


Fig.15 Ratio of recommended methods used in the project

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	Spectrophotometry (Indophenol)
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	Graphite Furnace Atomic Absorption spectrometry (GFAA)
11	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	16(1)										
1		16									
2			16(7)			2					
3							4(1)	4	4(1)	4(1)	
4				14(1)	13(1)	14	12(1)	12(3)	12(1)	12(3)	11(8)
5											
6											
7				2(1)	2(1)						2(2)
8											3(2)
9											
10											
11					1(1)						
?											
Flagged E	1	0	5	0	1	0	2	2	1	4	5
Flagged X	0	0	2	2	2	0	0	1	1	0	7

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 7 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 ions analysis.

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	1	A	A	A	A	A	A	A	A	A	A	A
id02	3	A	A	B	A	A	A	C	C	C	C	B
jp01	1	A	A	A	A	A	A	A	A	A	A	A
jp02	2	A	A	A	A	A	A	A	A	A	A	B
mn01	3	A	B	C	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	C	A	D	D	D	D	C
th01	2	A	B	A	B	B	B	A	A	A	A	A
th02	1	A	A	A	A	A	A	A	A	A	A	A
vn01	2	A	A	A	B	B	B	A	A	A	A	A
my01	1	A	A	A	A	A	A	A	A	A	A	A

“A”, “B”, “C”, and “D” represent individuals of staff in each laboratory who are in charge of measurement. Reverse mesh: “E” or “X” flagged Data.

Years of Experience

According to information obtained through this project, there are not so many flagged data evidently 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⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
cn01	13	13	13	13	13	13	13	13	13	13	13
cn02	6	6	19	13	13	13	3	3	3	3	3
cn03	6	6	6	6	6	6	6	6	6	6	6
cn04	9	9	9	9	9	9	9	9	9	9	9
id01	2	2	2	2	2	2	2	2	2	2	2
id02	3	3	1.5	3	3	3	13	13	13	13	1.5
jp01	2	2	2	2	2	2	2	2	2	2	2
jp02	2	2	2	2	9	9	2	2	2	2	9
mn01	7	7	6	7	7	7	7	7	7	7	7
ph01	4	4	4	2.5	2.5	2.5	5	5	5	5	2.5
ru01	26	26	26	26	26	26	17	17	17	17	26
ru02	45	25	45	11	11	45	14	14	14	14	11
th01	7	2	7	2	2	2	7	7	7	7	7
th02	8	8	8	8	8	8	8	8	8	8	8
vn01	10	10	10	19	19	19	10	10	10	10	10
my01	0	0	0	0	0	0	0	0	0	0	0

Reverse mesh: Data were flagged by “E” or “X”

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	1	6%
1	3	19%
2	7	44%
3	2	13%
4	2	13%
5	1	6%
6	0	0%
7	0	0%
8	0	0%
9	0	0%
10	0	0%
Total	16	100%

There is only one laboratory with excellent overall results (without flagged data) in 2004 project, which was equivalent to 6% of the number of participating laboratories. These results seemed to be not so good comparing with last year (2003) as presented Fig.16. Last year (2003) one laboratory had 8 flagged data, however the number of errors in this laboratory was decreased twice due to use the atomic absorption method for measurement of cations.

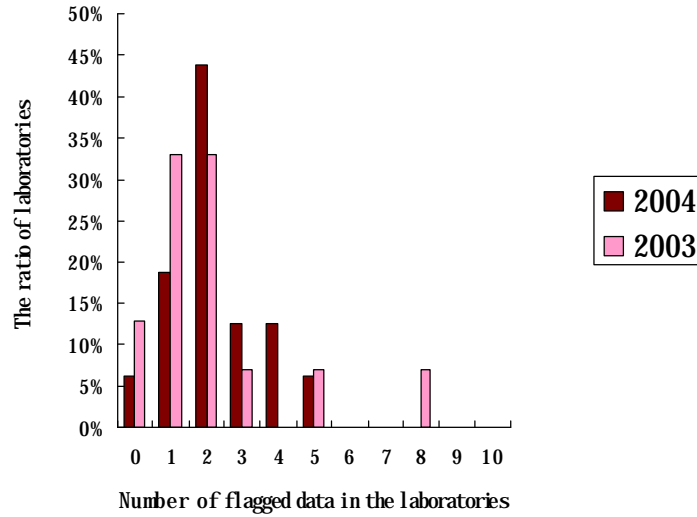


Fig.16 The distribution of laboratories with the number of flagged data

4. COMPARISON OF 1st, 2nd, 3rd, 4th AND 5th INTER-LABORATORY SURVEYS

The inter-laboratory comparison projects of EANET were carried out five times annually, in 2000, 2001, 2002, 2003 and 2004. The numbers of flagged data in these projects are presented in Fig.17.

The rate of data that satisfied the required data quality objectives (DQOs) was slightly decreased from 88.6% in 2001 to 79.5% in 2004. As one of the reason, the total number of the flags was seriously dependent on accuracy of NH_4^+ determination. The results were similar to ones of last year's project. The expected value of NH_4^+ on this project was almost same concentration of last years. The laboratories which NH_4^+ concentration were flagged are needed an improvement of correspondent analysis.

And then as other reason it was considered that total EC was lower than last year (2003). For the low concentration of constituents, a contamination from used instrument, measurement apparatus and so on should be checked and prevented. It is also important to secure the reduction of background noise and to keep the linearity of calibration curve in analytical process.

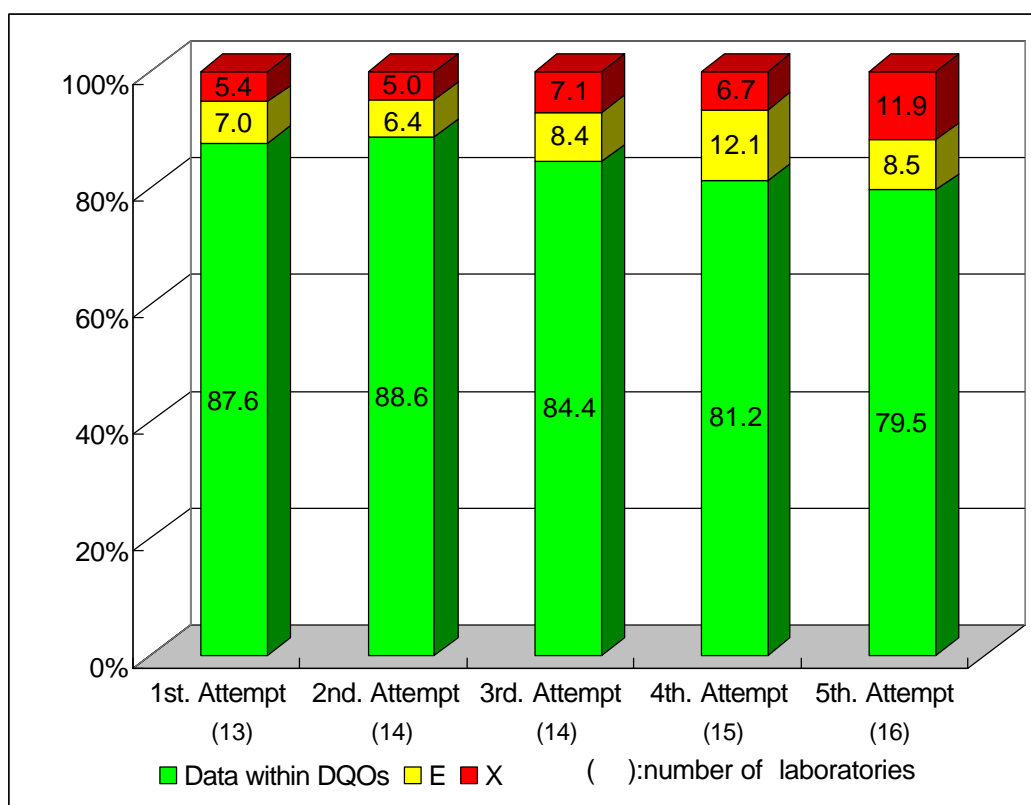


Fig. 17 Comparison of 1st, 2nd, 3rd, 4th and 5th inter-laboratory comparison projects

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.
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- 3) Report on the Inter-laboratory Comparison Project 2000 on Inland Aquatic Environment, 1st attempt, November 2001, 2nd attempt, November 2002, 3rd attempt, November 2003 and 4th attempt, November 2004.

6. CONTACT INFORMATION

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