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

## Report of the Inter-laboratory Comparison Project 2005 on Inland Aquatic Environment

6<sup>th</sup> Attempt

November 2006

Acid Deposition and Oxidant Research Center

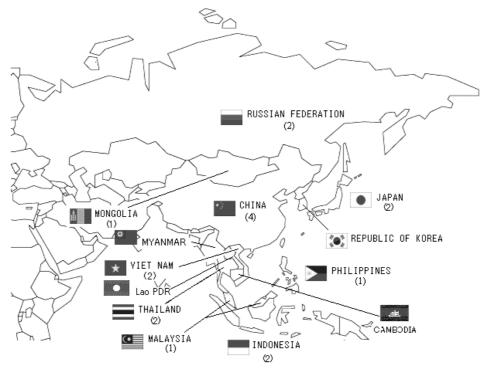
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#### 1. INTRODUCTION

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 practical information, (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  $SO_4^{2-}$ ,  $NO_3^-$ ,  $CI^-$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  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 (17 laboratories from 9 countries)

Fig.1 Laboratories participated in the inter-laboratory comparison project 2005 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. From 2005 the laboratory of Vietnam (Lab.ID vn.02) participated in this inter-laboratory comparison project on inland aquatic environment. The Network Center (NC) shipped artificial inland aquatic environment samples to all of these 17 laboratories, and all laboratories submitted their analytical data to NC.

#### 2.2 Artificial Inland Aquatic Environment Samples

Artificial inland aquatic environment samples were distributed to the participating laboratories by NC in November 2005 with expected submission of results by February 28, 2006.

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

#### Table1 Outline of the artificial inland aquatic environment sample

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 the range described in Table 3.

#### Table2 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 <sub>3</sub> <sup>-</sup>	milli gram/liter	mg/L
Cl	milli gram/liter	mg/L
$Na^+$	milli gram/liter	mg/L
$\mathbf{K}^+$	milli gram/liter	mg/L
Ca <sup>2+</sup>	milli gram/liter	mg/L
$Mg^{2+}$	milli gram/liter	mg/L
$\mathrm{NH_4}^+$	milli gram/liter	mg/L

Parameter	Range	Parameter	Range
pH EC Alkalinity SO <sub>4</sub> <sup>2-</sup> NO <sub>3</sub> <sup>-</sup> Cl <sup>-</sup>	5.0 - 8.0 1.5 - 15  mS/m 0.05 - 0.5  meq/L 2 - 20  mg/L 1 - 10  mg/L 1 - 10  mg/L	Na <sup>+</sup> K <sup>+</sup> Ca <sup>2+</sup> Mg <sup>2+</sup> NH <sub>4</sub> <sup>+</sup>	2 – 20 mg/L 0.2 – 2.0 mg/L 1 – 10 mg/L 0.2 – 2.0 mg/L 0.05 – 0.5 mg/L

Table3 Concentration range of artificial inland aquatic environment sample

#### **2.3 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.

Parameter	Analytical method
pH	Glass electrode
EC	Conductivity cell
Alkalinity	Titration by Burette or Digital Burette with pH Meter (end-point pH4.8)
SO4 <sup>2-</sup> NO3 <sup>-</sup>	Ion Chromatography or Spectrophotometry
Cl	Ion Chromatography or Titration
$Na^+$ $K^+$ $Ca^{2+}$ $Mg^{2+}$	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
$\mathrm{NH_4}^+$	Ion Chromatography or Spectrophotometry (Indophenol blue)

Table4 Analytical methods specified in the manual

#### 2.4 Data Checking Procedures

#### a) Calculation of ion balance (R<sub>1</sub>)

 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<sub>3</sub><sup>-</sup>).

A ( $\mu$ eq/L) =  $\Sigma$ n C<sub>Ai</sub> ( $\mu$ mol/L) = 2C (SO<sub>4</sub><sup>2-</sup>) + C (NO<sub>3</sub><sup>-</sup>) + C (Cl<sup>-</sup>) + (ALK) C<sub>Ai</sub>: electric charge of ion and concentration ( $\mu$ mol/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).

 $C (\mu eq/L) = \Sigma n C_{Ci} (\mu mol/L) = 10^{(6-pH)} + C (NH_4^+) + C (Na^+) + C (K^+)$  $+ 2C (Ca^{2+}) + 2C (Mg^{2+})$  $C_{Ci}: electric charge of ion and concentration (\mu mol/L) of cation "i".$ 

- (3) Calculation of ion balance ( $R_1$ )  $R_1 = 100 \text{ x (C-A) / (C+A) [\%]}$
- (4) R<sub>1</sub>, 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<sub>1</sub> is not within the range.

Tables Allowable ranges I	or $\mathbf{K}_1$ in different concentration ranges
(C+A) [µeq/L]	R <sub>1</sub> [%]
< 50	+30 ~ -30
$50 \sim 100$	+15 ~ -15
<100	+8 ~ -8

Table5 Allowable ranges for R<sub>1</sub> in different concentration ranges

(Reference) "Technical Manual for Monitoring on Inland Aquatic Environment in East Asia (2000)"

#### b) Comparison between calculated and measured electrical conductivity (R<sub>2</sub>)

(1) Total electric conductivity (Acalc)should be calculated as follows;

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

C: Molar concentrations ( $\mu$ 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 (HCO<sub>3</sub><sup>-</sup>).

 Ratio (R<sub>2</sub>) of calculations (Λcalc) to measurements(Λcalc) in electric conductivity should be calculated as follows;

 $R_2 = 100 \text{ x}$  (Acalc-Ameas)/(Acalc +Ameas) [%]

(3) R<sub>2</sub>, 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<sub>2</sub> is not within the range.

Table6 Allowable ranges to	r R <sub>2</sub> in different concentration ranges
Ameas[mS/m]	R <sub>2</sub> [%]
< 0.5	+ 2020
0.5 - 3	+1313
> 3	+99

Table6 Allowable ranges for  $R_2$  in different concentration ranges

(Reference) "Technical Manual for Monitoring on Inland Aquatic Environment in East Asia (2000)"

#### 3. RESULTS

#### 3.1 Outline of Results

Received 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  $\pm 10\%$ .

Constituents	3	Prepared	Average	S.D	Ν	Min.	Max.
pН		7.18	7.13	0.18	17	6.56	7.38
EC	(mS/m)	6.06	5.79	0.14	17	5.44	6.00
Alkalinity	(meq/L)	0.179	0.179	0.022	17	0.121	0.213
$SO_4^{2-}$	(mg/L)	8.00	7.87	0.52	17	6.34	8.73
NO <sub>3</sub> <sup>-</sup>	(mg/L)	3.33	3.20	0.58	17	1.01	3.58
Cl	(mg/L)	3.67	3.70	0.40	17	3.34	5.17
$Na^+$	(mg/L)	6.48	6.24	0.52	17	4.52	6.73
$K^+$	(mg/L)	0.71	0.67	0.09	17	0.38	0.80
Ca <sup>2+</sup>	(mg/L)	3.01	3.21	0.39	17	2.57	4.04
$Mg^{2+}$	(mg/L)	0.43	0.43	0.03	17	0.37	0.47
$\mathrm{NH_4}^+$	(mg/L)	0.29	0.30	0.08	17	0.22	0.54

Table7 Summary of analytical results of the artificial inland aquatic environment sample

(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 criteria: 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 2.4 of this report. The flag "I" was put for poor ion balance data sets, and the flag "C" was put for poor conductivity agreement data sets.

The results were evaluated following the two aspects: i) comparison of individual parameters, and ii) comparison of circumstance of analysis in each participating laboratory. Evaluation of data for each constituent is 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, 9 analytical data out of 187 exceeded the DQOs by a factor of 2 and flagged by "E". 9 analytical data out of 187 exceeded the DQOs more than a factor of 2 and flagged by "X. Data flagged by "E" and "X" were 9 out of 187 and shared about 9.6% of all reported data of samples.

#### Table8 Number of flagged data

Flag <sup>*</sup>	pН	EC	Alkalinity	SO4 <sup>2-</sup>	NO <sub>3</sub> -	Cl	Na <sup>+</sup>	$K^+$	Ca <sup>2+</sup>	$Mg^{2+}$	$\mathrm{NH_4}^+$	Total	Ratio
Е	0	0	1	1	0	0	0	2	1	0	4	9	4.8%
Х	0	0	1	0	1	1	1	1	2	0	2	9	4.8%
Data within DQOs	17	17	15	16	16	16	16	14	14	17	11	169	90.4%
Flagged(%)	0.0	0.0	11.8	5.9	5.9	5.9	5.9	17.6	17.6	0.0	35.3	9.6	

\*E : Value exceeded the DQO by a factor of 2 of the DQO ( $\pm 15\% - \pm 30\%$ )

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

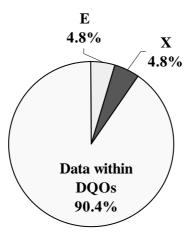


Fig.2 Percentage of flagged data

	ЪН	EC	Alkalinity	$SO_4^2$	NO3 <sup>-</sup>	CI.	$Na^+$	$\mathbf{K}^{\dagger}$	$Ca^{2+}$	$Mg^{2+}$	NH4 <sup>+</sup>	RI	R2
		(mS/m)	(meq/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
cn01	7.23	5.73	0.193	7.92	3.58	3.68	6.38	0.69	3.27	0.44	0.28	60-	3.8
cn02	7.15	6.00	0.185	7.90	3.30	3.61	6.41	0.69	3.23	0.47	E 0.22	0.4	0.7
cn03	7.15	5.77	0.196	7.85	3.53	3.82	6.53	0.72	3.43	0.46	0.26	0.2	4,4
cn04	7.2	5.80	0.190	7.91	335	3.63	6.40	0.69	3.27	0.46	0.29	0.2	3.0
id01	7.23	5.68	X 0.121	7.75	3.32	3.80	X 4.52	0.62	X 4.00	0.42	X 0.46	32	02
id02	6.90	6.00	0.159	8.73	X 1.01	X 5.17	6.13	0.80	X 4.04	0.45	0.28	3.7	32
10di	7.07	5.93	0.162	8.04	3.33	3.57	6.33	0.73	2.93	0.44	0.31	1.0	0.0
jp02	7.28	5.71	0.176	8.05	3.31	3.51	6.61	0.66	2.76	0.45	0.31	0.0	2.3
mn01	6.98	5.75	0.200	8.20	3.47	3.62	6.73	0.76	2.90	0.46	X 0.54	-0.4	4.8
ph01	6.56	5.84	0.159	8.28	3.28	3.75	6.31	E 0.59	3.33	0.42	E 0.24	1.4	1.7
ru01	7.19	5.88	0.166	8.26	3.36	3.52	6.40	0.73	2.76	0.40	0.30	-0.7	0.3
ru02	7.20	5.84	0.171	8.10	3.45	3.68	6.36	0.70	3.20	0.41	0.31	0.6	2.0
th01	7.15	5.62	E 0.213	7.95	3.29	3.63	6.57	0.69	3.12	0.46	0.27	-2.1	-3.0
th02	7.13	5.96	0.200	E 6.34	3.16	3.34	6.48	0.68	3.08	0.44	0.25	2.6	-1.5
vn01	7.07	5.72	0.182	7.80	3.22	3.48	5.78	0.72	E 3.50	0.43	0.25	-0.1	2.0
vn02	7.38	5.81	0.191	7.20	3.19	3.61	5.66	X 0.38	2.57	0.37	E 0.22	-73	-2.6
my01	7.26	5.44	0.173	7.40	3.23	3.50	6.45	E 0.60	3.12	0.37	E 0.24	1.8	3.5
Expected value	7.18	90'9	0.179	8.00	333	3.67	6.48	0.71	3.01	0.43	0.29		•
Number of data	17	17	17	17	17	17	17	17	17	17	17		•
Average	7.13	5.79	0.179	7.86	3.20	3.70	6.24	0.67	3.21	0.43	0.30		
Minimum	6.56	5.44	0.121	6.34	1.01	3.34	4.52	0.38	2.57	0.37	0.22	-7.3	-3.0
Maximum	7.38	6.00	0.213	8.73	3.58	5.17	6.73	0.80	4.04	0.47	0.54	3.7	4.8
Standard deviation	0.18	0.14	0.022	0.52	85.0	0.40	0.52	0.09	0°39	0.03	0.08		
E: Value exceeded the DQO(±15) by a factor of 2	0QO(±15)	by a fact	or of 2		I:Poorion	I:Poor ion balance (R1	(I)						

#### 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 shown in table for each analytical parameter.

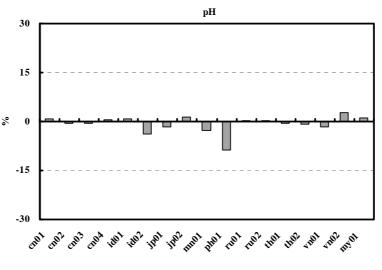


Fig.3 Distribution of pH data normalized by prepared value

All participating laboratories used pH meter with glass electrode for measurement of pH. Obtained data were almost agreed with the prepared value. All of obtained data were agreed with prepared value. One laboratory was flagged in 2003 and 2004, but in this year the result was good .

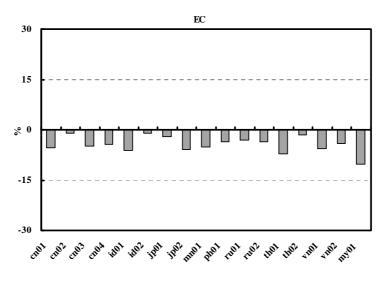


Fig.4 Distribution of EC data normalized by prepared value

All participating laboratories used conductivity cell for the measurement of EC. As well as the result of last year (2004), all of obtained data were agreed with prepared value.

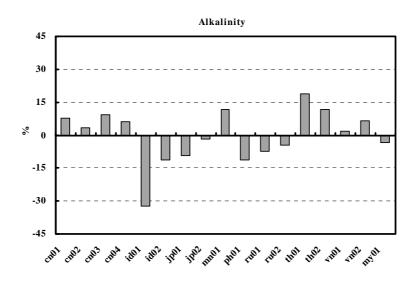


Fig.5 Distribution of Alkalinity data normalized by prepared concentration

All participating laboratories used titration for the determination of alkalinity. Data from 2 laboratories data were flagged. Especially result of Lab.id02 was significantly deviated from prepared value.

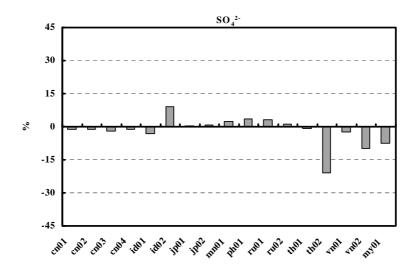


Fig.6 Distribution of SO<sub>4</sub><sup>2-</sup> data normalized by prepared concentration

Most of participating laboratories used ion chromatography for the determination of  $SO_4^{2^\circ}$ , while 2 laboratories used spectrophotometry.

Result of 1 laboratory that used ion chromatography was flagged.

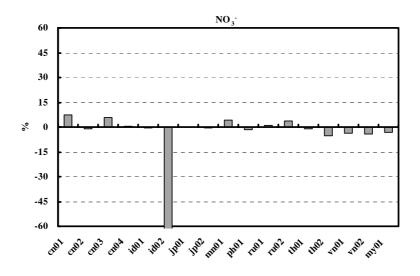


Fig.7 Distribution of NO<sub>3</sub><sup>-</sup> data normalized by prepared concentration

As well as  $SO_4^{2-}$ , the most of participating laboratories used ion chromatography for the determination of  $NO_3^{-}$ . 2 laboratories used spectrophotometry. And 1 laboratory used other method (ion-selected electrode).

Most of obtained data were agreed with prepared value with very low deviation. But only Data from Lab.id02 which was obtained by spectrophotometry was significantly deviated from prepared value. It was much lower value than prepared value as well as the result of last year (2004). So This laboratory needs to clarify the cause of this result.



Fig.8 Distribution of CI data normalized by prepared concentration

Most of participating laboratories used ion chromatography for the determination of Cl<sup>-</sup> ,and 2 laboratories used titration method.

Data from Lab.id02 which was obtained by titration method was significantly deviated from prepared value. This laboratory need to clarify the cause of this result.

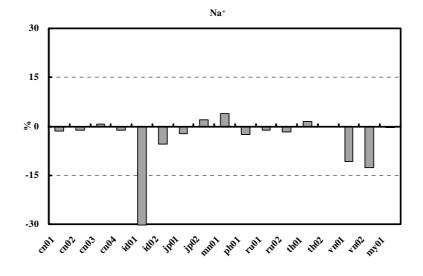


Fig.9 Distribution of Na<sup>+</sup> data normalized by prepared concentration

Among 17 participating laboratories, 13 laboratories used ion chromatography, while 4 laboratories used atomic absorption/flame (emission) photometry for the determination of  $Na^+$ .

Data from Lab.id01 which was obtained by atomic absorption was flagged by "x".

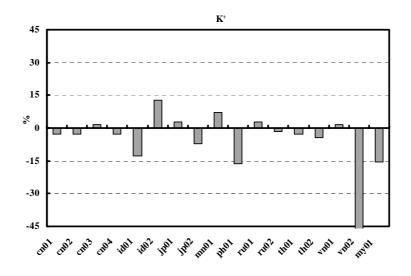


Fig.10 Distribution of K<sup>+</sup> data normalized by prepared concentration

As well as  $Na^+$ , 13 laboratories used ion chromatography, and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of  $K^+$ .

Data from 3 laboratories were flagged. Especially data from Lab.vn02 was significantly deviated from prepared value.

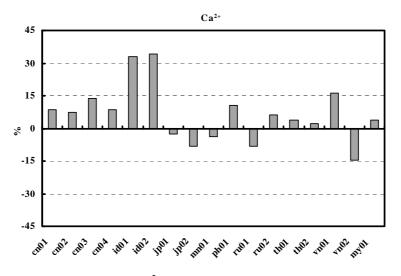


Fig.11 Distribution of Ca<sup>2+</sup> data normalized by prepared concentration

Among 17 participating laboratories, 13 laboratories used ion chromatography and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of  $Ca^{2+}$ .

Data from 3 laboratories were flagged. Especially data from Lab.id01 and id02 which were obtained by atomic absorption were significantly deviated from prepared value.

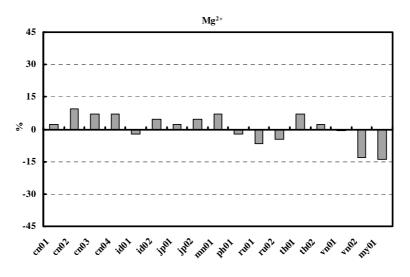


Fig.12 Distribution of Mg<sup>2+</sup> data normalized by prepared concentration

Among 17 participating laboratories, 13 laboratories used ion chromatography and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of  $Mg^{2+}$ .

All of obtained data were agreed with prepared value.

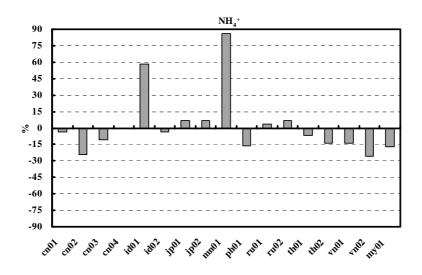


Fig.13 Distribution of NH<sub>4</sub><sup>+</sup> data normalized by prepared concentration

Among 17 participating laboratories, 11 laboratories used ion chromatography, 3 laboratories used spectrophotometry (Indophenol) and 3 laboratories used spectrophotometry (other method) for the determination of  $\rm NH_4^+$ .

Data from 6 laboratories were flagged. Especially data from Lab.mn01 which was obtained by ion chromatography and id01 which was obtained by indophenol method were significantly deviated from prepared value with flag "x".

The percentage of flagged values was 35.3% and this results were worst among the all ion constituents.

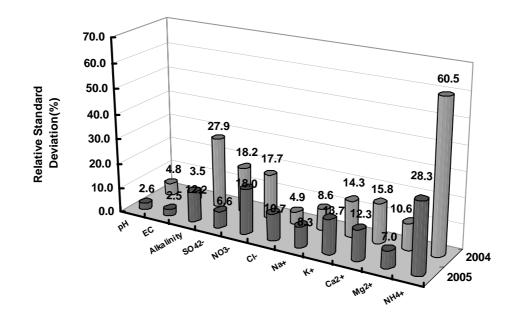
Degree of deviation of flagged data from prepared value is very large, and there is large difference in accuracy between laboratories. This situation is same to the result of last attempt. Each laboratories need to clarify the cause of this result.

#### **Overall Evaluation**

The relative standard deviation of  $NH_4^+$  and  $NO_3^-$  results from laboratories was larger than other ions.

Concerning NO<sub>3</sub><sup>-</sup> only one data was significantly lower than deviated from prepared value and the other data were agreed with prepared value with very low deviation. So the relative standard deviation became large.

Variation among laboratories was the largest in the results of  $NH_4^+$ . The situation is similar to those of last attempt (2004). So it is necessary to clarify the cause of this difference, and it is important to improve measurement procedure.



(Relative standard deviation (%) = Standard deviation / Average x 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, the participating laboratories used recommended methods of EANET except measurement of  $NO_3^-$  and  $NH_4^+$  by some of them. The codes for the various analytical methods used and their using in this project are shown in Table 21 and 22. As well as in last year (2004), 1 laboratory used ion-selected electrode for  $NO_3^-$  analysis, and for  $NH_4^+$  analysis, 2 laboratories used spectrophotometry instead of indophenol blue. No clear relationship between analytical methods and flagged data was observed.

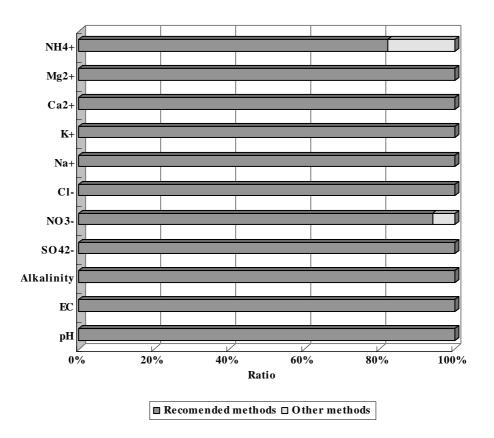


Fig.15 Ratio of recommended methods used in the project

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

#### **Table21 List of methods**

## Table22 Analytical Method

Code	pН	EC	Alkalinity	SO4 <sup>2-</sup>	NO <sub>3</sub>	Cľ	Na <sup>+</sup>	$K^+$	Ca <sup>2+</sup>	Mg <sup>2+</sup>	$\mathrm{NH_4}^+$
0	17										
1		17									
2			17(1)			2(1)					
3							4(1)	4	4(2)	4	
4				15(1)	14	15	13	13(3)	13(1)	13	11(4)
5											
6											
7				2	2(1)						3
8											3(2)
9											
10											
11					1						
Flagged E	0	0	0	1	0	0	0	2	1	0	4
Flagged X	0	0	1	0	1	1	1	1	2	0	2

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 6 laboratories. In other laboratories, 2 - 6 persons carried out them.

Lab.ID	Total	pН	EC	Alkalinity	SO4 <sup>2-</sup>	NO3	Cl	Na <sup>+</sup>	$K^+$	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH4 <sup>+</sup>
cn01	1	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α
cn02	3	Α	Α	В	С	С	С	С	С	С	С	С
cn03	1	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α
cn04	1	Α	Α	А	А	Α	Α	Α	Α	А	Α	Α
id01	4	Α	Α	В	С	С	С	D	D	D	D	D
id02	6	Α	В	С	С	D	Е	В	В	А	В	F
jp01	1	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α	Α
jp02	3	Α	Α	Α	В	С	Α	Α	Α	Α	Α	В
mn01	3	Α	В	С	В	В	В	Α	Α	А	Α	Α
ph01	4	Α	Α	А	В	В	В	С	С	С	С	D
ru01	4	Α	Α	А	В	В	В	С	С	С	С	D
ru02	4	Α	В	Α	С	В	Α	D	D	D	D	С
th01	2	Α	В	Α	В	В	В	Α	Α	Α	Α	Α
th02	2	Α	Α	Α	В	В	В	В	В	В	В	В
vn01	2	Α	Α	Α	В	В	В	Α	Α	Α	Α	Α
vn02	1	Α	Α	Α	Α	Α	А	Α	А	Α	Α	А
my01	1	Α	Α	Α	Α	Α	Α	Α	А	Α	Α	А

#### Table23 Staff in charge of measurement

"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

As well as the result of last year (2004), there are not so many flagged data exactly related to the cases of less experience. It seems that data quality is not related to years of experience.

Tuster Teurs of experience												
Lab.ID	pН	EC	Alkalinity	SO4 <sup>2-</sup>	NO <sub>3</sub>	Cl	Na <sup>+</sup>	$K^+$	Ca <sup>2+</sup>	${\rm Mg}^{2+}$	$\mathrm{NH_4}^+$	
cn01	14	14	14	14	14	14	14	14	14	14	14	
cn02	7	7	20	4	4	4	4	4	4	4	4	
cn03	7	7	7	7	7	7	7	7	7	7	7	
cn04	10	10	10	10	10	10	10	10	10	10	10	
id01	3	3	2	3	3	3	2	2	2	2	2	
id02	5	15	2.5	2.5	13	27	15	15	5	15	1.2	
jp01	1	1	1	1	1	1	1	1	1	1	1	
jp02	3	3	3	7	1	7	7	7	7	7	1	
mn01	8	8	7	8	8	8	8	8	8	8	8	
ph01	5	5	5	4.5	4.5	4.5	6	6	6	6	1	
ru01	3	3	3	2	2	2	18	18	18	18	12	
ru02	45	25	45	11	25	45	14	14	14	14	11	
th01	8	3	8	3	3	3	8	8	8	8	8	
th02	2	2	2	8	8	8	8	8	8	8	8	
vn01	11	11	11	20	20	20	11	11	11	11	11	
vn02	2	2	2	2	2	2	2	2	2	2	2	
my01	1	1	1	1	1	1	1	1	1	1	1	

#### Table24 Years of experience

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

#### Number of Flagged Data in Laboratories

The attribution of flagged data in each laboratory is as shown in Table 25.

#### Table25 Number of flagged data in each laboratory

Number of flagged data	Number of laboratories	Share
0	7	41%
1	5	29%
2	3	18%
3	1	6%
4	1	6%
5	0	0%
Total	17	100%

There were a lot of laboratories without the flag data in this year. In last year (2004), number of laboratories without flagged data was only 1, which was equivalent to 6% of the whole participating laboratories. Fig.16 shows the distribution of laboratories with the number of flagged data in the case of 2004 and 2005.

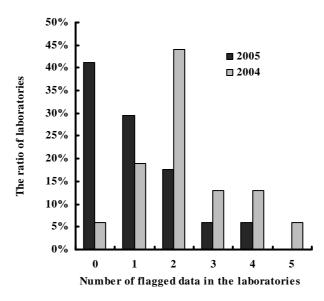


Fig.16 The distribution of laboratories with the number of flagged data

# 4. COMPARISON OF 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup> 5<sup>th</sup> AND 6<sup>th</sup> INTER-LABORATORY SURVEYS

The inter-laboratory comparison projects of EANET were carried out six times, in 2000, 2001, 2002, 2003, 2004 and 2005. The number of good results and flagged data of these projects are shown in Fig.17. And the comparison for each parameter from  $1^{st}$  to  $6^{th}$  attempt with each prepared value is showed in Fig.18. There is difference about the accuracy for each year.

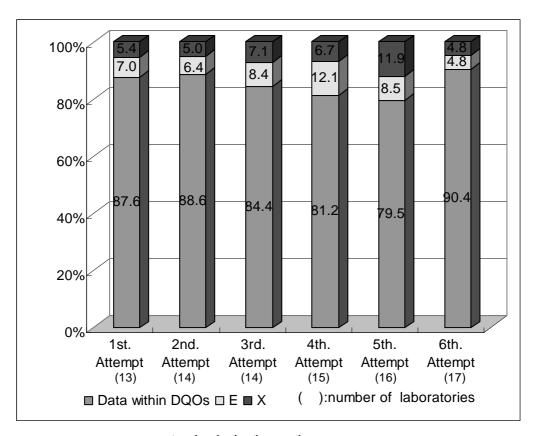
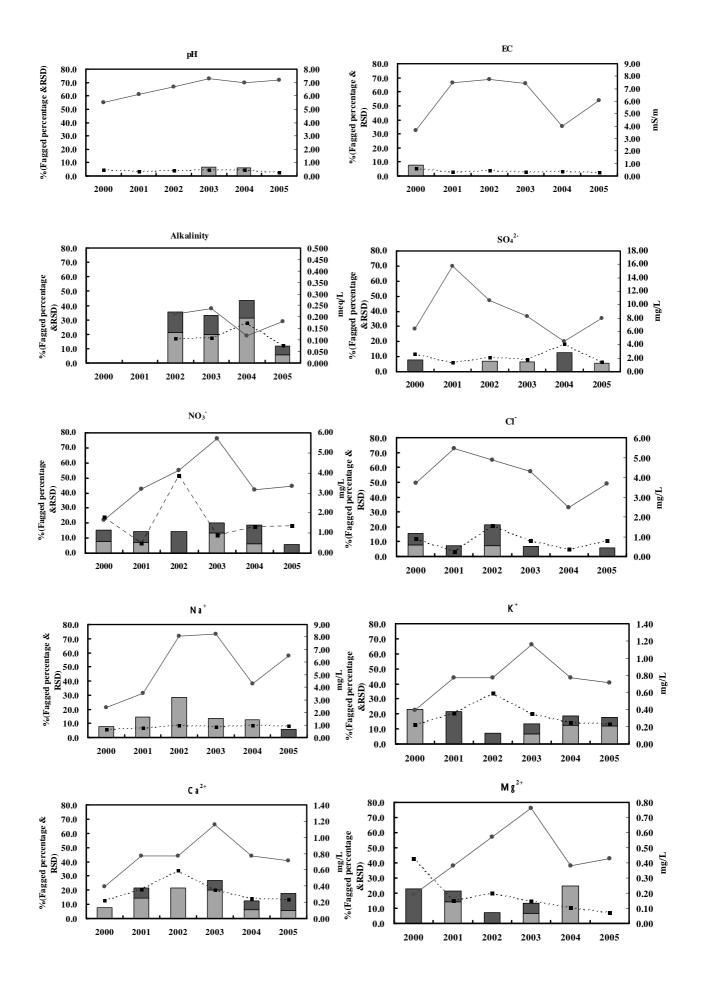


Fig. 17 Comparison of 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup> and 6<sup>th</sup> inter-laboratory comparison projects



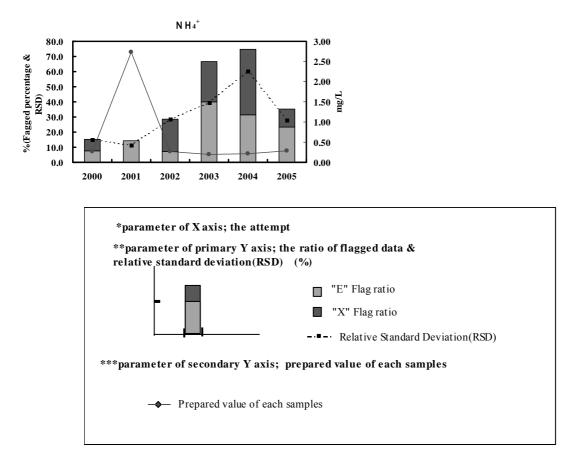


Fig.18 Comparison for each parameter in inter-laboratory comparison project

#### **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.
- 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.
- Report on the Inter-laboratory Comparison Project 2000 on Inland Aquatic Environment, 1<sup>St</sup> attempt, November 2001, 2<sup>nd</sup> attempt, November 2002, 3<sup>rd</sup> attempt, November 2003, 4<sup>th</sup> attempt, November 2004, and 5<sup>th</sup> attempt, November 2004.

## 6. CONTACT INFORMATION

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## **APPENDIX 1** Participating laboratories

## 1. CHINA

1) Zhuhai Environmental Monitoring Station	(cn01)
2) Environmental Monitoring Station of Xiamen	(cn02)
3) Xi'an Environmental Monitoring Station	(cn03)
4) Chongqing Institute of Environmental Science	(cn04)
2 INDONESIA	
5)Environmental Management Center (EMC) Serpong Indonesia	(id01)
6)Research Institute for Water Resources(RIWR), Agency for Research and Development,	(id02)
Ministry of Settlement and Regional Infrastructures	
3.JAPAN	
7)Gifu Prefectural Institute of Health and Environmental Science	(jp01)
8)Shimane Prefectural Institute of Public Health and Environmental Science	(jp02)
4.MALAYSIA	
9)Faculty of Applied Science University Technology Mara	(my01)
5.MONGOLIA	( 01)
10)Central Laboratory of Environmental Monitoring,	(mn01)
<u>6. PHILIPPINES</u>	
11)Environmental Management Bureau (EMB),	(ph01)
7. RUSSIA	
12)Limnologcal Institute of Russian Academy of Science/Siberian Branch(RAS/SB)	(ru01)
13) Laboratory for Monitoring of Atmosphere and Soil Pollution	(n:02)
8.THAILAND	
14)Environmental Research and Training Center (ERTC)	(th01)
15) Air Quality and Noise Management Division, Pollution Control Department(PCD)	(th02)
Ministry of Science Technology and Environment(MSTE)	(1102)
9.VIET NAM	
16) Institute of Meteorology and Hydrology (IMH) Hydrometeorological Service of Viet Nam	(vn01)
(HMS)	
17) Middle of Central regional Hydro-Meteorological Observatory	(vn 02)
National Hydro -Meteorological Center (NHMS)	

#### **APPENDIX 2**

## Original Data

	pН	EC	Alkalinity	SO4 <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl	Na <sup>+</sup>	$\mathbf{K}^+$	Ca <sup>2+</sup>	Mg <sup>2+</sup>	$NH_4^+$
Lab. ID	-	(mS/m)	(meq/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
cn01	7.23	5.73	0.193	7.92	3.58	3.68	6.38	0.69	3.27	0.44	0.28
cn02	7.15	6.00	0.185	7.90	3.30	3.61	6.41	0.69	3.23	0.47	0.22
cn03	7.15	5.77	0.196	7.85	3.53	3.82	6.53	0.72	3.43	0.46	0.26
cn04	7.22	5.80	0.190	7.91	3.35	3.63	6.40	0.69	3.27	0.46	0.29
id01	7.23	5.68	0.121	7.75	3.32	3.80	4.52	0.62	4.00	0.42	0.46
id02	6.90	6.00	0.159	8.73	1.01	5.17	6.13	0.80	4.04	0.45	0.28
jp01	7.07	5.93	0.162	8.04	3.33	3.57	6.33	0.73	2.93	0.44	0.31
jp02	7.28	5.71	0.176	8.05	3.31	3.51	6.61	0.66	2.76	0.45	0.31
mn01	6.98	5.75	0.200	8.20	3.47	3.62	6.73	0.76	2.90	0.46	0.54
ph01	6.56	5.84	0.159	8.28	3.28	3.75	6.31	0.59	3.33	0.42	0.24
ru01	7.19	5.88	0.166	8.26	3.36	3.52	6.40	0.73	2.76	0.40	0.30
ru02	7.20	5.84	0.171	8.10	3.45	3.68	6.36	0.70	3.20	0.41	0.31
th01	7.15	5.62	0.213	7.95	3.29	3.63	6.57	0.69	3.12	0.46	0.27
th02	7.13	5.96	0.200	6.34	3.16	3.34	6.48	0.68	3.08	0.44	0.25
vn01	7.07	5.72	0.182	7.80	3.22	3.48	5.78	0.72	3.50	0.43	0.25
vn02	7.38	5.81	0.191	7.20	3.19	3.61	5.66	0.38	2.57	0.37	0.22
my01	7.26	5.44	0.173	7.40	3.23	3.50	6.45	0.60	3.12	0.37	0.24
Expected value	7.18	6.06	0.179	8.00	3.33	3.67	6.48	0.71	3.01	0.43	0.29
Number of data	17	17	17	17	17	17	17	17	17	17	17
Average	7.13	5.79	0.179	7.86	3.20	3.70	6.24	0.67	3.21	0.43	0.30
Minimum	6.56	5.44	0.121	6.34	1.01	3.34	4.52	0.38	2.57	0.37	0.22
Maximum	7.38	6.00	0.213	8.73	3.58	5.17	6.73	0.80	4.04	0.47	0.54
Standard deviation	0.18	0.14	0.022	0.52	0.58	0.40	0.52	0.09	0.39	0.03	0.08

	pН	EC	Alkalinity	SO4 <sup>2-</sup>	NO <sub>3</sub>	Cl	$Na^+$	$\mathbf{K}^{+}$	Ca <sup>2+</sup>	Mg <sup>2+</sup>	$NH_4^+$
Lab. ID	-	(mS/m)	(meq/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)
0	-	(mS/m)	(meq/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)
cn01	7.23	5.73	0.193	82.45	57.73	103.81	277.51	17.65	81.59	18.10	15.52
cn02	7.15	6.00	0.185	82.24	53.22	101.83	278.82	17.65	80.59	19.33	12.20
cn03	7.15	5.77	0.196	81.72	56.93	107.76	284.04	18.41	85.58	18.92	14.41
cn04	7.22	5.80	0.190	82.34	54.02	102.40	278.38	17.65	81.59	18.92	16.08
id01	7.23	5.68	0.121	80.68	53.54	107.19	196.61	15.86	99.80	17.28	25.50
id02	6.90	6.00	0.159	90.88	16.26	145.84	266.64	20.46	100.80	18.51	15.52
jp01	7.07	5.93	0.162	83.70	53.70	100.71	275.34	18.67	73.10	18.10	17.18
jp02	7.28	5.71	0.176	83.80	53.38	99.01	287.52	16.88	68.86	18.51	17.18
mn01	6.98	5.75	0.200	85.36	55.96	102.12	292.74	19.44	72.36	18.92	29.93
ph01	6.56	5.84	0.159	86.20	52.89	105.78	274.47	15.17	83.08	17.32	13.53
ru01	7.19	5.88	0.166	85.99	54.18	99.29	278.38	18.67	68.86	16.50	16.63
ru02	7.20	5.84	0.171	84.32	55.64	103.81	276.64	17.90	79.84	16.87	17.18
th01	7.15	5.62	0.213	82.76	53.06	102.40	285.78	17.65	77.84	18.92	14.97
th02	7.13	5.96	0.200	66.00	50.96	94.22	281.86	17.39	76.85	18.10	13.86
vn01	7.07	5.72	0.182	81.16	51.86	98.11	251.33	18.44	87.33	17.61	13.80
vn02	7.38	5.81	0.191	74.95	51.38	101.69	246.28	9.80	64.12	15.34	11.97
my01	7.26	5.44	0.17	77.04	52.09	98.73	280.56	15.35	77.84	15.22	13.30
Expected value	7.18	6.06	0.179	83.28	53.70	103.53	281.86	18.16	75.10	17.69	16.08
Number of data	17	17	17	17	17	17	17	17	17	17	17
Average	7.13	5.79	0.179	81.86	51.58	104.39	271.35	17.24	80.00	17.79	16.40
Minimum	6.56	5.44	0.121	66.00	16.26	94.22	196.61	9.80	64.12	15.22	11.97
Maximum	7.38	6.00	0.213	90.88	57.73	145.84	292.74	20.46	100.80	19.33	29.93
Standard deviation	0.18	0.14	0.022	5.41	9.29	11.21	22.59	2.35	9.84	1.24	4.64

\*These were caliculated by NC.

### APPENDIX3

## Data normalized by prepared value

Lab. ID	pН	EC	Alkalinity	SO4 <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl	$Na^+$	$\mathbf{K}^+$	Ca <sup>2+</sup>	$Mg^{2+}$	$\mathrm{NH_4}^+$
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
cn01	0.7	-5.4	7.8	-1.0	7.5	0.3	-1.5	-2.8	8.6	2.3	-3.4
cn02	-0.4	-1.0	3.4	-1.3	-0.9	-1.6	-1.1	-2.8	7.3	9.3	-24.1
cn03	-0.4	-4.8	9.5	-1.9	6.0	4.1	0.8	1.4	14.0	7.0	-10.3
cn04	0.6	-4.3	6.1	-1.1	0.6	-1.1	-1.2	-2.8	8.6	7.0	0.0
id01	0.7	-6.3	-32.4	-3.1	-0.3	3.5	-30.2	-12.7	32.9	-2.3	58.6
id02	-3.9	-1.0	-11.2	9.1	-69.7	40.9	-5.4	12.7	34.2	4.7	-3.4
jp01	-1.5	-2.1	-9.5	0.5	0.0	-2.7	-2.3	2.8	-2.7	2.3	6.9
jp02	1.4	-5.8	-1.7	0.6	-0.6	-4.4	2.0	-7.0	-8.3	4.7	6.9
mn01	-2.8	-5.1	11.7	2.5	4.2	-1.4	3.9	7.0	-3.7	7.0	86.2
ph01	-8.6	-3.6	-11.2	3.5	-1.5	2.2	-2.6	-16.5	10.6	-2.1	-15.9
ru01	0.1	-3.0	-7.3	3.3	0.9	-4.1	-1.2	2.8	-8.3	-6.7	3.4
ru02	0.3	-3.6	-4.5	1.3	3.6	0.3	-1.9	-1.4	6.3	-4.7	6.9
th01	-0.4	-7.3	19.0	-0.6	-1.2	-1.1	1.4	-2.8	3.7	7.0	-6.9
th02	-0.7	-1.7	11.7	-20.8	-5.1	-9.0	0.0	-4.2	2.3	2.3	-13.8
vn01	-1.5	-5.6	1.7	-2.6	-3.4	-5.2	-10.8	1.5	16.3	-0.5	-14.1
vn02	2.8	-4.1	6.7	-10.0	-4.3	-1.8	-12.6	-46.1	-14.6	-13.3	-25.5
my01	1.1	-10.2	-3.4	-7.5	-3.0	-4.6	-0.5	-15.5	3.7	-14.0	-17.2
Minimum	-8.6	-10.2	-32.4	-20.8	-69.7	-9.0	-30.2	-46.1	-14.6	-14.0	-25.5
Maximum	2.8	-1.0	19.0	9.1	7.5	40.9	3.9	12.7	34.2	9.3	86.2
Average	-0.7	-4.4	-0.2	-1.7	-4.0	0.8	-3.7	-5.1	6.5	0.6	2.0

(Original data / Expected Value - 1) \* 100 ( % )