Report of the Inter-laboratory Comparison Project 2004 on Soil (Draft)

6th Attempt

September 2005

Acid Deposition and Oxidant Research Center

Contents

1. INTRODUCTION

Since 1998, according to the QA/QC programs in EANET, the National Centers and the (Interim) Network Center ((I) NC) have carried out various QA/QC activities for the EANET monitoring. The Inter-laboratory comparison project on soil sample analysis started in 1999 as one of the activities within the QA/QC programs.

The purposes of this project are, through the evaluation of analytical results by statistical analyses, analytical equipments, operating condition of equipments and other practical problems,

(1) To recognize the analytical precision and accuracy with equipment analysis and titration methods of each participating laboratory, within-laboratory precision, inter-laboratory precision,

(2) To give an opportunity to improve the quality of the analysis on soil monitoring of EANET, and

(3) To improve reliability of analytical data through the assessment of suitable analytical methods and techniques.

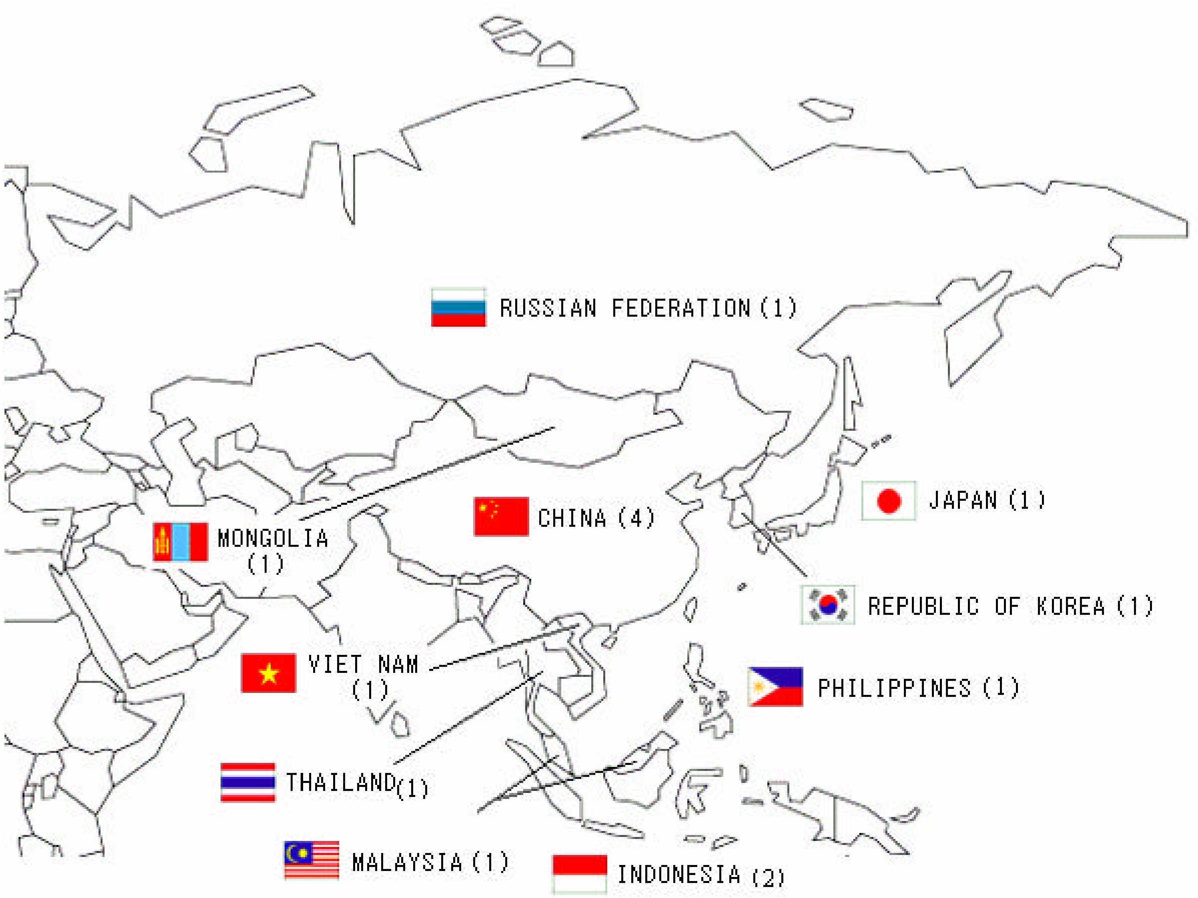

Figure 1. Laboratories participated in Inter-laboratory comparison project 2004 on soil

Number of parenthesis describes the number of laboratories of each EANET country.

1.1 Outlines of the previous projects

Steps in the procedures of soil analysis might be related to the variation among laboratories; e.g. extraction, instrumental analysis and/or titration. Results of the first three projects from 1999 to 2001 suggested that instrumental analysis have relatively large effect on the total precision of soil analysis, and the following analytical conditions could affect results:

- Addition of La or Sr solution for AAS analysis of Ex-Ca
- Preparation method of standard solution
- Instrument for Ex-K and Na

The participating laboratories shared the information on these possible factors to improve the precisions. However, clear improvement of the inter-laboratories precisions was not observed in the 4th project in 2002 unfortunately, and it was suggested that changes of analysts and/or analytical system in several laboratories might cause calculation/writing mistakes on the reporting process.

In the 5th project, NC provided two soil samples (No.031 and 032) to laboratories and a digital format for calculation/reporting of the data in order to avoid easy mistake. NC recommended the laboratories to follow the instructions, such as addition of Sr/La in order to improve the inter-laboratories precision. By using digital formats, no obvious calculation mistake was found in the data. The inter-laboratories precisions were still relatively large but clearly improved compared with the previous projects.

1.2 Objective of the 6th project

In the 6th project, NC provided two soil samples (No.041 and 042) to laboratories to improve the inter-laboratory precision further more by standardization of the methods. Fourteen laboratories of 10 countries participated in the 6th project. Countries and number of laboratories, which participated in the 6th project, are shown in the Figure 1. Names of the participating laboratories are listed in Appendix 1.

In this report, the data from participating laboratories were evaluated statistically according to the QA/QC program for soil monitoring, and the results may be utilized for estimation of inter-laboratory variability in soil monitoring, and provide useful information to improve precision of soil analysis on EANET.

2. PROCEDURE

2.1. Dispatched Soil Samples

The characteristics of the samples were as follows:

Sample No. 041: Andosols (black soil)
Sample No. 042: Cambisols (brown forest soil)

Soil was collected from from B horizon in a man-made forest of *Chamaecyparis obtusa* in Tottori prefecture, Japan.

The soils was air-dried, sieved to separate the fine earth fraction (< 2 mm), and mixed well by the following procedures: the bulk sample was divided into two parts, each part was mixed well, the parts were joined and mixed well, and then the sample was divided again. This procedure was repeated 15 times to ensure a completely homogeneous bulk sample. Finally, portions of ca. 500 g were weighed out, packed in 500 ml plastic bottles, and then, sterilized using radioisotope (20kGy) for distributing (exporting) to the participating countries.

2.2. Parameters

All the participating laboratories were expected to measure all the parameters (Table 1).

Table 1. Parameters to be measured

Parameters	Unit	No. 041 and 042
a) Moisture Content	wt %	M
b) pH (H_2O)		M
c) pH (KCl)		M
d) Exchangeable Ca	cmol(+) kg^{-1}	M
e) Exchangeable Mg	cmol(+) kg^{-1}	M
f) Exchangeable K	cmol(+) kg^{-1}	M
g) Exchangeable Na	cmol(+) kg^{-1}	M
h) Exchangeable Acidity	cmol(+) kg^{-1}	M
i) Exchangeable Al	cmol(+) kg^{-1}	M
j) Exchangeable H	cmol(+) kg^{-1}	M

M: Mandatory items

“Exchangeable” were abbreviated to “Ex-“ in this report; e.g. Ex-Ca, Ex-Mg, etc.

2.3. Procedures for chemical analysis

All the procedures for chemical analysis were carried out basically according to the “Technical Manual for Soil and Vegetation Monitoring in East Asia” (2^{nd} ISAG, 2000).

In the respective laboratories, all the parameters except moisture content were analyzed three

times under the same conditions (repeatability condition: analyst, time, and instrument are the same; three replicates). Then, under within-laboratory-reproducibility condition (part or all of analyst, time, and instrument are different), all the analytical procedures should be repeated twice.

Moisture content was analyzed with three replicates, and the average is used for calculation of all the parameters.

2.3.1. Standardization of methods

All the procedures for chemical analysis should be carried out basically according to the "Technical Documents for Soil and Vegetation Monitoring in East Asia (March 2000, Adopted at: The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia)".

In the 6th project,

1) **Atomic absorption spectrometry (AAS)** method should be used basically for analysis of Ex-Ca, Mg, K and Na. (If it is impossible to use AAS, Flame (emission) photometry method is allowable for Ex-K and Na).
2) **Titration method** should be used for analysis of EX-acidity, Al and H.
3) **Calibration curve method** should be used for determination of Ex-Ca, Mg, K and Na.
4) The Samples should be extracted and diluted with **1M CH_3COONH_4 (pH 7.0)** for analysis of Ex-Ca, Mg, K and Na. Then, 1M CH_3COONH_4 (pH 7.0) solution should be used to prepare each standard solution as the solvent.
5) **Sr** should be added to the samples and each standard solution to eliminate the interference of the sample for analysis of Ex-Ca and Mg. These are to be the same concentration Sr. (If Sr can not be obtained, La is allowable.)

2.3.2. Procedures for Ex-base cations

(1) Extract from air-dry sample with 1M CH_3COONH_4 (pH 7.0) solution. (According to the "Technical Documents for Soil and Vegetation Monitoring in East Asia")
(2) Pipette an appropriate aliquot of the soil extract into volumetric flask and add 100g-Sr/L solution to be 1000mg-Sr/L as final concentration Sr. ($SrCl_2$ solution eliminates the interference of the sample.) And then make to volume with 1M CH_3COONH_4 (pH 7.0). This solution is named " Prepared sample".
(3) Prepare three "prepared samples".
(4) Prepare each standard solution with diluting 1M CH_3COONH_4 (pH 7.0) solution.
(5) Add 100g-Sr/L solution to each standard solution to be the same concentration $SrCl_2$ as the sample.
(6) Analyze the standard solution and the prepared samples by AAS.
(7) Store the calibration curves certainly and report them together with reporting formats.
(8) **Repeat the procedure 1) - 7) twice.**
(9) Calculation of content in the soil

Content in the soil could be calculated by the following formulas:

Ex-Ca (cmol(+)/kg soil) = [A * B * V * mcf]/[10 * 20.04 * S]

Ex-Mg (cmol(+)/kg soil) = [A * B * V * mcf]/[10 * 12.15 * S]

Ex-K (cmol(+)/kg soil) = [A * B * V* mcf]/[10 * 39.10 * S]

Ex-Na (cmol(+)/kg soil) = [A * B * V* mcf]/[10 * 23.00 * S]

Where

A = Measurement values of prepared (diluted) samples (mg/L)

B = Dilution ratio (B = 2, if 25mL sample was diluted to 50 mL for making prepared sample.)

mcf = Moisture correction factor (Measured value)

S = Weight of air-dry sample (g)

V = Volume of extract (mL)

2.3.3. Procedures for Ex-acidity

(1) Extraction and titration would be carried out according to the "Technical Documents for Soil and Vegetation Monitoring in East Asia" basically.

(2) Prepare three samples. Analyze each sample and at least one blank.

(3) Repeat the procedure twice

(4) Calculation of content in the soil

Content in the soil could be calculated by the following formulas:

$$\text{Ex-Acidity (cmol (+)/kg)} = [(A_{NaOH} - bl_{NaOH}) * M_{NaOH} * c * 100 * mcf] / S$$

$$\text{Ex-Al (cmol (+)/kg)} = [(A_{HCl} - bl_{HCl}) * M_{HCl} * c * 100 * mcf] / S$$

$$\text{Ex-H (cmol (+)/kg)} = [(A_{NaOH} - bl_{NaOH}) * M_{NaOH} - (A_{HCl} - bl_{HCl}) * M_{HCl}] * c * 100 * mcf] / S$$

Where

A_{NaOH} = Titration volume of 0.025 M NaOH solution needed for percolate (mL)

A_{HCl} = Titration volume of 0.02 M HCl solution needed for percolate (mL)

bl_{NaOH} = Titration volume of 0.025M NaOH solution needed for blank (mL)

bl_{HCl} = Titration volume of 0.02M HCl solution needed for blank (mL)

M_{NaOH} = Molarity of NaOH solution (mol/L)

M_{HCl} = Molarity of HCl solution (mol/L)

S = Weight of air-dry sample (g)

c = Aliquot factor (c = 2, if 50mL percolate of 100mL is used.)

2.3.4. Reporting

(1) Preparation of the report

Digital formats (Microsoft Excel) for reporting were provided to the participating laboratories, and the laboratories were requested to fill in the formats. Contents in the soil sample would be calculated automatically by the formula above if the formats were filled in.

(2) Submission of the report

Data reporting formats together with all of the copy of calibration curve were submitted by using digital devices.

2.4. Statistical analysis

Data were statistically evaluated according to the following procedures described in the "Technical Manual for Soil and Vegetation Monitoring in East Asia" (2nd ISAG, 2000). Data of the soil content with two decimal places were used for the analysis.

1) Verification of data

Evenness of within-laboratory precision was verified by Cochran methods, then the laboratory averages was verified by Grubbs methods.

2) Analysis of variance and estimation of precision

Total variation among laboratories includes within-laboratory and inter-laboratories variation. As described in the following equation, Total sum of square (S_T) is consisted of Sum of square inter-laboratories (S_R), Sum of square within-laboratory (S_{RW}) and Sum of square repeatability (S_r).

$$S_T = S_R + S_{RW} + S_r$$

Based on the above equation, Inter-laboratories variance, Within-laboratory-reproducibility variance, and Repeatability variance were calculated, and then the precisions were estimated.

3) Calculation of permissible tolerance

Permissible tolerances were calculated based on the above precisions.

3. RESULTS

3.1. Outline of the results

Basic statistics calculated from the laboratory averages are presented in Table 2 for the respective parameters, and especially coefficients of variation (CVs) among laboratories were shown in Figure 2. For both entire (non-verified) data and verified data, the statistics were calculated. Outliers detected by Cochran-Grubbs methods were removed for the verified data.

As for the entire data, the variations (CVs) among the participating laboratories were different in parameter. CVs were very small, 2.5 – 3.8%, in pH(H_2O) and pH(KCl) probably due to their simple analytical procedure and logarithmic values as discussed in the previous reports (ADORC, 2001a; 2000b). However, remarkably large CVs (larger than 200%) were observed in Ex-Ca and Na because of significantly large value (more than ten times larger) by one laboratory. Variations in Ex-acidity and Al were different in sample also because of significantly large values in No.041.

As for the verified data, the variations (CVs) of pH(H_2O) and pH(KCl) were also smaller than 4%. CVs for other parameters were improved after removing outliers. However, CVs of Ex-base cations were relatively high, larger than 50%. CVs of Ex-acidity and Al were relatively small, around 15% probably due to their simple procedures by titration methods also as discussed in the previous reports (ADORC, 2001a; 2000b). Concentrations of exchangeable cations were relatively low, and difference of concentrations between samples was not clear.

The averages of triplicate analyses (three-time analysis in repeatability condition) and the average of repeat analyses (in within-laboratory-reproducibility condition) in each laboratory were shown in Figure 3.1, 3.2, 3.3 and 3.4. Error bar shows standard deviation of triplicate analyses but it cannot be found in most figures due to its small length. This indicates that triplicate analyses were carried out with high precision under the repeatability condition. Averages of triplicate samples for the respective laboratories were of similar values, and the repeat analyses might also be carried out with high precision under the within-laboratory-reproducibility condition.

Table 2. Basic statistics of the eintire data and the verified data

(Entire data)

Statistics	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol(+)/kg						
No. 041									
Number of Laboratories	14	14	13	13	13	13	14	14	14
Total average	5.0	4.1	0.64	0.27	0.36	0.35	5.83	5.09	0.69
Median	5.0	4.1	0.11	0.16	0.33	0.17	4.19	3.55	0.45
Maximum	5.2	4.4	6.14	1.02	1.47	2.65	26.76	22.76	4.00
Minimum	4.7	3.9	0.00	0.00	0.00	0.00	3.24	2.91	-0.33
Standard deviation	0.1	0.1	1.66	0.29	0.36	0.70	6.06	5.13	1.01
CV (%)*1	2.5	3.5	260.3	104.8	99	201	103.9	100.6	147
No. 042									
Number of Laboratories	14	14	13	13	13	13	14	14	14
Total average	4.9	4.1	0.29	0.23	0.17	0.25	3.02	2.69	0.37
Median	5.0	4.1	0.05	0.14	0.11	0.08	3.08	2.58	0.27
Maximum	5.1	4.4	2.85	1.00	0.99	2.26	3.58	3.65	0.94
Minimum	4.7	3.8	0.00	0.00	0.00	0.00	2.37	1.97	-0.14
Standard deviation	0.1	0.2	0.77	0.27	0.26	0.61	0.45	0.47	0.30
CV (%)*1	2.8	3.8	269.5	117.9	148	243	15.0	17.5	83

(Verified data)*2

Statistics	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol(+)/kg						
No. 041									
Number of Laboratories	13	12	9	12	11	12	10	12	13
Total average	5.0	4.1	0.10	0.21	0.25	0.16	4.07	3.63	0.43
Median	5.0	4.1	0.09	0.15	0.27	0.17	3.93	3.50	0.38
Maximum	5.2	4.4	0.22	0.59	0.42	0.33	5.12	4.87	0.99
Minimum	4.7	3.9	0.00	0.00	0.00	0.00	3.24	2.91	-0.33
Standard deviation	0.1	0.1	0.07	0.19	0.13	0.09	0.64	0.60	0.34
CV (%)*1	2.6	3.3	75.5	88.7	50.6	55.0	15.7	16.6	79.3
No. 042									
Number of Laboratories	14	14	9	10	10	12	10	13	14
Total average	4.9	4.1	0.04	0.13	0.08	0.08	2.94	2.66	0.37
Median	5.0	4.1	0.04	0.14	0.09	0.08	2.81	2.55	0.27
Maximum	5.1	4.4	0.09	0.23	0.13	0.18	3.58	3.65	0.94
Minimum	4.7	3.8	0.00	0.00	0.00	0.00	2.37	1.97	-0.14
Standard deviation	0.1	0.2	0.03	0.07	0.04	0.06	0.48	0.47	0.30
CV (%)*1	2.8	3.8	67.3	55.3	56.6	69.6	16.4	17.7	82.6

Note: *1. CV, Coefficient of variance (%) = (standard deviation/average)*100 *2.Outliers judged by Cochran-Grubbs methods and calculation mistakes were removed.

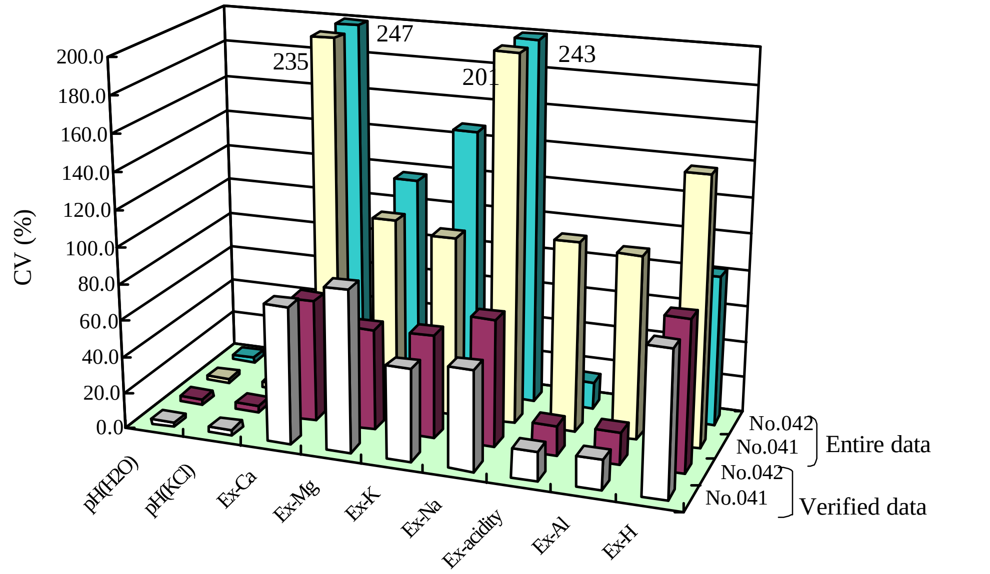

Figure 2. CV among laboratories

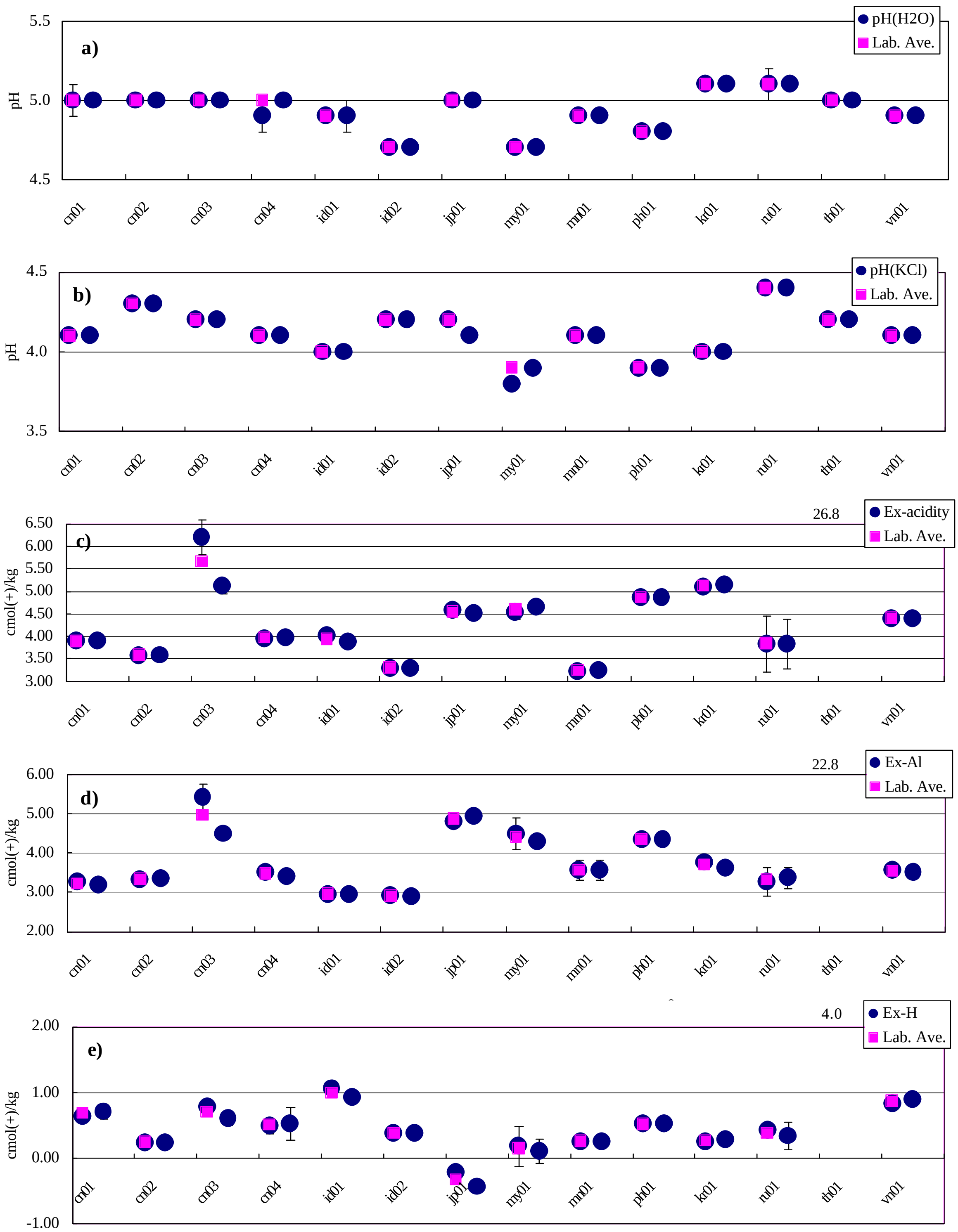

Figure 3.1. Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 041. Error bar shows standard deviation of triplicate analysis.

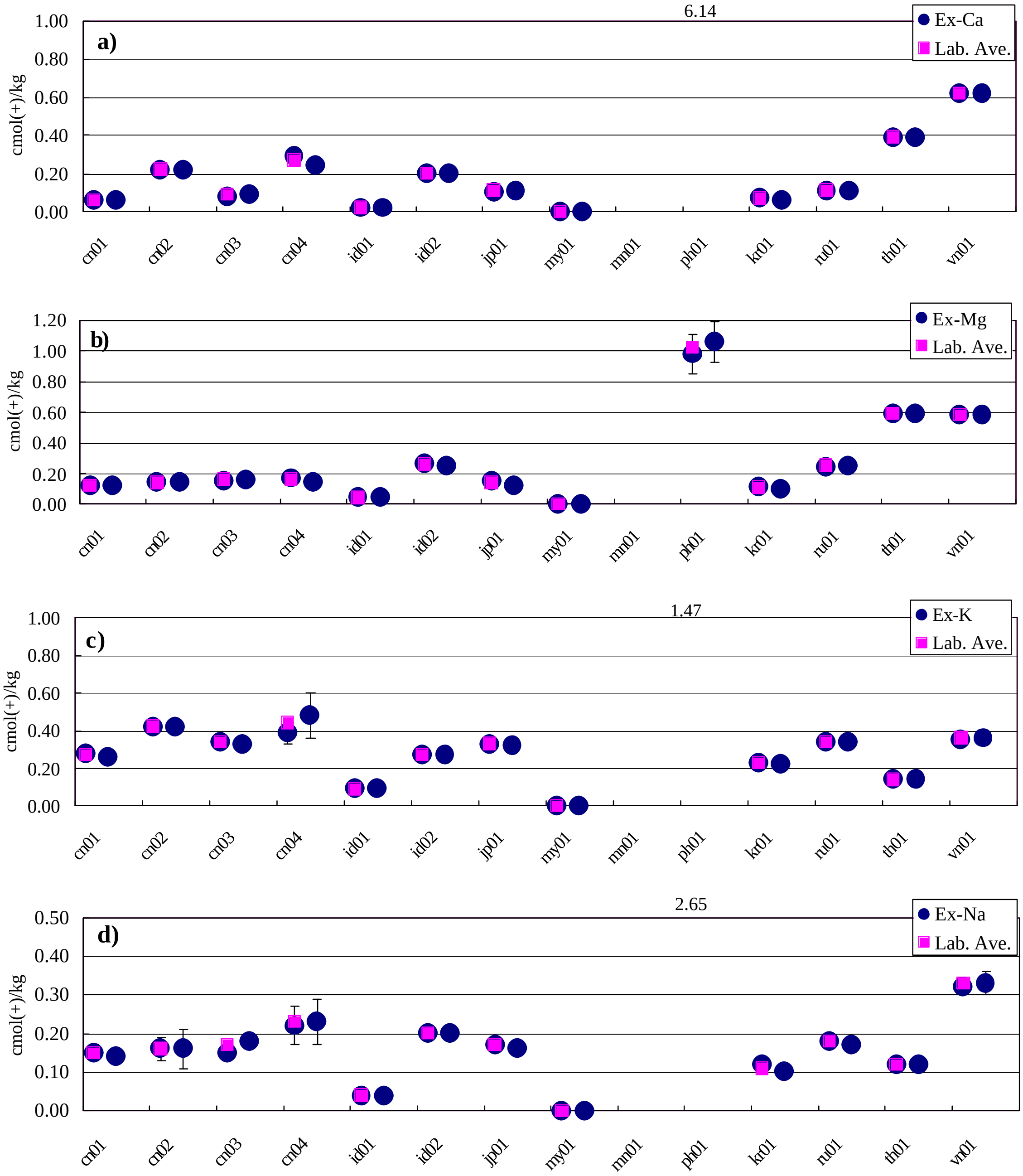

Figure 3.2. Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 041. Error bar shows standard deviation of triplicate analysis.

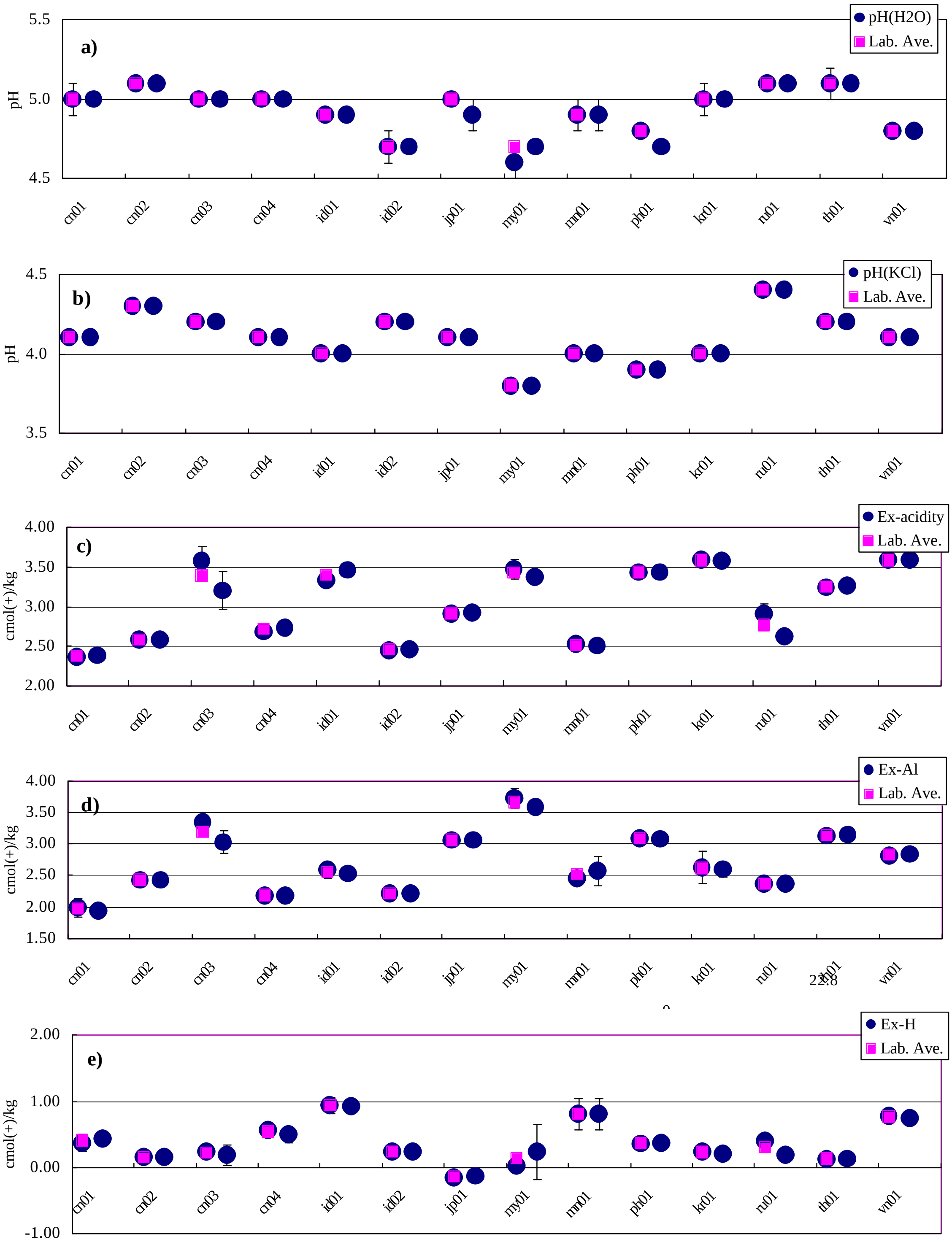

Figure 3.3. Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 042. Error bar shows standard deviation of triplicate analysis.

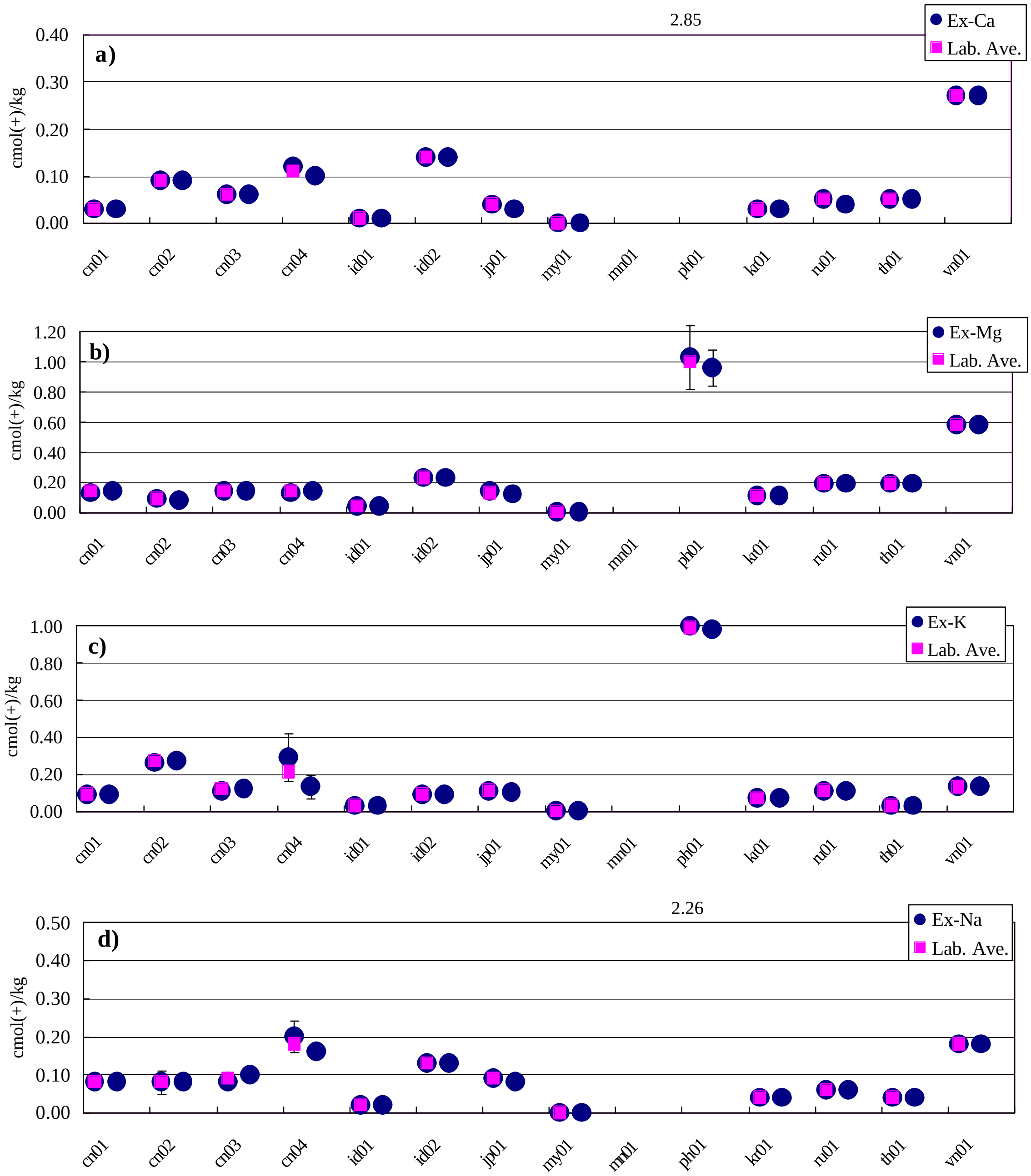

Figure 3.4. Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 042. Error bar shows standard deviation of triplicate analysis.

3.2. Verification of data

3.2.1. Detection of outliers

The results of verification by Cochran-Grubbs methods were presented in Table 3.1 and 3.2.

Laboratories, which have large difference in repeat analyses, were judged as outliers by Cochran method (examination of the evenness of within-laboratory precision): e.g. “cn03” in Ex-acidity and Al of No.041, “cn04” in Ex-K of No.041, “id01” and “my01” in Ex-acidity of No. 041, etc. Then, the rest of data were tested, and laboratories, which have remarkably large or small average, were judged as outliers by Grubbs method (examination of the average value of each laboratory): e.g. “ph01” in Ex-K and Na of No.041, “th01” in Ex-Ca, acidity, Al and H of No. 041, “vn01” in Ex-Ca of No.041, etc. No outlier was detected in pH(H_2O) and pH(KCl) of No. 042. Two to four outliers were detected in most parameters. More than four outliers were observed in two laboratories, namely “ph01” of both samples and “th01” of No.041.

3.2.2. Moisture content and moisture correction factor

Measured moisture contents of the samples and measurement conditions were shown in Table 4. Sample No. 041 had probably at least two times larger moisture content than No. 042. It seems that an original soil of No. 041, Andosols (black soil), had high water retentivity probably due to its high organic matter content.

Oven-drying period was recommended to be more than 12 hours based on the discussion in the Third Session of Scientific Advisory Committee (SAC3) in 2003. Almost all laboratories followed the recommendation, while one laboratory did not report the information on the drying period.

3.2.3. Analytical condition

1) Number of analysts and their experience

Number of analysts and years of their experience were shown in Table 5.1. As for the number of analyst, it seemed that different analysts carried out the repeat analyses in “cn04”, “id02”, and “my01”. Different analysts operated AAS (or titration in “vn01”) for Ca/Mg and FEP for K/Na respectively in “ph01”.

As for years of experience on soil analysis, analyst of “cn01” had just one-year experience. But no outlier was detected in “cn01” probably because the analyst had much experience (20 years) in chemical analysis. Clear relationship between the experience and the outliers was not suggested.

2) Analytical instruments and condition of instruments

Analytical instruments used for the measurement, procedures for extraction of Ex-base cations, and size of burette used for the titration method in Ex-acidity were shown in Table 5.2. All the laboratories except “vn01” used AAS for measurement of Ex-Ca and Mg, and two laboratories used FEP for Ex-K and Na. Years in use of instruments were varied from 4 to 22 in AAS. All the laboratories applied Sr or La for measurement of Ex-Ca and Mg by AAS. One laboratory, “mn01” did not analyze Ex-base cation due to lack of instruments.

As for procedures for extraction of Ex-base cations, five laboratories used percolation tube procedures, four laboratories used centrifuge procedures, three laboratories used Buchner funnel procedures, and one laboratory used automatic extractor procedures, respectively. No clear difference was observed among data by different procedures. As for size of burette for titration of Ex-acidity, capacities were varied from 5 to 50 ml, but minimum graduates were 0.05 or 0.1 ml in most laboratories.

3) Date of analysis

Date of analysis in the respective laboratories and days used for the analysis were shown in Table 5.3. Most laboratories carried out the analysis by March, while one laboratory finished in July. There were no significant implication between date of analysis and the data. Days used for the analysis were only one or two days in most laboratories. Interval between the first and second analyses of the repeat analyses was varied from 0 (in a same day) to 36 days. NC suggested that repeat analyses would be carried out with several-day interval (three days or more) in order to estimate actual within-laboratory reproducibility, as a supplementary instruction for the project, based on the discussion at SAC3. However, only half of the laboratories followed this instruction. Unfortunately, the information was not enough disseminated among laboratories.

Table 3.1. Data verified by Cochran-Grubbs methods: No. 041

Lab.	Repeat Analysis	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
				cmol(+)/kg						
cn01	1st	5.0	4.1	0.06	0.12	0.28	0.15	3.89	3.26	0.64
	2nd	5.0	4.1	0.06	0.12	0.26	0.14	3.89	3.18	0.71
cn02	1st	5.0	4.3	0.22	0.14	0.42	0.16	3.57	3.33	0.24
	2nd	5.0	4.3	0.22	0.14	0.42	0.16	3.58	3.34	0.24
cn03	1st	5.0	4.2	0.08	0.15	0.34	0.15	6.20*c	5.42*c	0.78
	2nd	5.0	4.2	0.09	0.16	0.33	0.18	5.11*c	4.49*c	0.61
cn04	1st	4.9*c	4.1	0.29*c	0.17	0.39*c	0.22	3.95	3.51	0.49
	2nd	5.0*c	4.1	0.24*c	0.14	0.48*c	0.23	3.98	3.40	0.53
id01	1st	4.9	4.0	0.02	0.04	0.09	0.04	4.01*c	2.95	1.06
	2nd	4.9	4.0	0.02	0.04	0.09	0.04	3.87*c	2.94	0.92
id02	1st	4.7	4.2	0.20	0.26	0.27	0.20	3.29	2.91	0.38
	2nd	4.7	4.2	0.20	0.25	0.27	0.20	3.28	2.90	0.38
jp01	1st	5.0	4.2*c	0.10	0.15	0.33	0.17	4.57	4.79	0.00
	2nd	5.0	4.1*c	0.11	0.12	0.32	0.16	4.51	4.95	0.00
my01	1st	4.7	3.8*c	0.00	0.00	0.00	0.00	4.54*c	4.49	0.18
	2nd	4.7	3.9*c	0.00	0.00	0.00	0.00	4.64*c	4.30	0.11
mn01	1st	4.9	4.1					3.22	3.56	0.26
	2nd	4.9	4.1					3.25	3.56	0.26
ph01	1st	4.8	3.9	6.09*c	0.98*c	1.46*g	2.67*g	4.86	4.34	0.52
	2nd	4.8	3.9	6.18*c	1.06*c	1.48*g	2.63*g	4.86	4.34	0.52
kr01	1st	5.1	4.0	0.07	0.11	0.23	0.12	5.09	3.76	0.26
	2nd	5.1	4.0	0.06	0.10	0.22	0.10	5.14	3.61	0.28
ru01	1st	5.1	4.4	0.11	0.24	0.34	0.18	3.83	3.27	0.42
	2nd	5.1	4.4	0.11	0.25	0.34	0.17	3.83	3.36	0.34
th01	1st	5.0	4.2	0.39*g	0.59	0.14	0.12	26.76*g	22.75*g	4.00*g
	2nd	5.0	4.2	0.39*g	0.59	0.14	0.12	26.75*g	22.76*g	3.99*g
vn01	1st	4.9	4.1	0.62*g	0.58	0.35	0.32	4.40	3.57	0.83
	2nd	4.9	4.1	0.62*g	0.58	0.36	0.33	4.40	3.50	0.90

Note: The outliers judged by Cochran and Grubbs methods were marked with asterisk c and g, respectively. Minus value (non detection) was treated as "0" for the analysis.

Table 3.2. Data verified by Cochran-Grubbs methods: No. 042

Lab.	Repeat Analysis	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
				cmol(+)/kg						
cn01	1st	5.0	4.1	0.03	0.13	0.09	0.08	2.36	1.99	0.37
	2nd	5.0	4.1	0.03	0.14	0.09	0.08	2.38	1.94	0.44
cn02	1st	5.1	4.3	0.09	0.09	0.26*g	0.08	2.58	2.42	0.16
	2nd	5.1	4.3	0.09	0.08	0.27*g	0.08	2.58	2.42	0.16
cn03	1st	5.0	4.2	0.06	0.14	0.11	0.08	3.57*c	3.33*c	0.24
	2nd	5.0	4.2	0.06	0.14	0.12	0.10	3.20*c	3.02*c	0.19
cn04	1st	5.0	4.1	0.12*c	0.13	0.29*c	0.20	2.68	2.18	0.57
	2nd	5.0	4.1	0.10*c	0.14	0.13*c	0.16	2.73	2.18	0.50
id01	1st	4.9	4.0	0.01	0.04	0.03	0.02	3.33*c	2.58	0.94
	2nd	4.9	4.0	0.01	0.04	0.03	0.02	3.46*c	2.52	0.93
id02	1st	4.7	4.2	0.14*g	0.23	0.09	0.13	2.44	2.20	0.24
	2nd	4.7	4.2	0.14*g	0.23	0.09	0.13	2.45	2.21	0.24
jp01	1st	5.0	4.1	0.04	0.14*c	0.11	0.09	2.90	3.05	0.00
	2nd	4.9	4.1	0.03	0.12*c	0.10	0.08	2.92	3.05	0.00
my01	1st	4.6	3.8	0.00	0.00	0.00	0.00	3.47*c	3.72	0.03
	2nd	4.7	3.8	0.00	0.00	0.00	0.00	3.37*c	3.57	0.24
mn01	1st	4.9	4.0					2.52	2.44	0.81
	2nd	4.9	4.0					2.50	2.57	0.81
ph01	1st	4.8	3.9	2.83*c	1.03*c	1.00*c	2.28*g	3.43	3.08	0.36
	2nd	4.7	3.9	2.87*c	0.96*c	0.98*c	2.24*g	3.43	3.07	0.37
kr01	1st	5.0	4.0	0.03	0.11	0.07	0.04	3.58	2.62	0.24
	2nd	5.0	4.0	0.03	0.11	0.07	0.04	3.57	2.59	0.21
ru01	1st	5.1	4.4	0.05	0.19	0.11	0.06	2.90*c	2.36	0.40
	2nd	5.1	4.4	0.04	0.19	0.11	0.06	2.62*c	2.36	0.19
th01	1st	5.1	4.2	0.05	0.19	0.03	0.04	3.24	3.12	0.12
	2nd	5.1	4.2	0.05	0.19	0.03	0.04	3.26	3.14	0.13
vn01	1st	4.8	4.1	0.27*g	0.58*g	0.13	0.18	3.58	2.80	0.78
	2nd	4.8	4.1	0.27*g	0.58*g	0.13	0.18	3.58	2.83	0.75

Note: The outliers judged by Cochran and Grubbs methods were marked with asterisk c and g, respectively. Minus value (non detection) was treated as "0" for the analysis.

Table 4. Measured moisture content, moisture correction factor, and measurement condition

Lab.	No. 041			No. 042			Oven temp.	Drying period
	wt%	mcf	Mean mcf	wt%	mcf	Mean mcf	°C	hours
cn01	7.7	1.08	1.08	2.2	1.02	1.02	105	17
	7.7	1.08		2.3	1.02			
	7.8	1.08		2.2	1.02			
cn02	7.6	1.08	1.08	2.2	1.02	1.02	105	14
	7.6	1.08		2.2	1.02			
	7.5	1.08		2.2	1.02			
cn03	7.2	1.07	1.07	2.0	1.02	1.02	105	24
	7.2	1.07		1.9	1.02			
	7.2	1.07		2.1	1.02			
cn04	8.3	1.08	1.08	2.4	1.02	1.02	105	15
	8.4	1.08		2.3	1.02			
	8.3	1.08		2.3	1.02			
id01	5.4	1.05	1.06	1.0	1.01	1.01	105	24
	5.9	1.06		1.5	1.01			
	5.7	1.06		1.3	1.01			
id02	5.9	1.06	1.06	1.6	1.02	1.02	105	16
	6.0	1.06		1.6	1.02			
	6.0	1.06		1.6	1.02			
jp01	7.4	1.07	1.07	2.2	1.02	1.02	105	25
	7.4	1.07		2.2	1.02			
	7.4	1.07		2.2	1.02			
my01	6.0	1.06	1.06	1.3	1.01	1.01	105	24
	5.8	1.06		1.2	1.01			
	5.9	1.06		1.3	1.01			
mn01	7.1	1.07	1.07	1.6	1.02	1.02	105	19
	6.7	1.07		1.5	1.01			
	6.9	1.07		1.7	1.02			
ph01	4.8	1.05	1.05	1.2	1.01	1.01	105	24
	4.8	1.05		1.2	1.01			
	4.8	1.05		1.2	1.01			
kr01	7.3	1.07	1.07	2.2	1.02	1.02	105	16
	7.4	1.07		2.2	1.02			
	7.4	1.07		2.2	1.02			
ru01	7.1	1.07	1.08	2.0	1.02	1.02	105	NI
	8.3	1.08		2.1	1.02			
	7.2	1.07		2.0	1.02			
th01	5.9	1.06	1.06	1.6	1.02	1.02	105	12
	5.9	1.06		1.6	1.02			
	5.9	1.06		1.6	1.02			
vn01	0.02	1.00	1.00	0.1	1.00	1.00	105	18
	0.03	1.00		0.1	1.00			
	0.03	1.00		0.1	1.00			

Note: NI, no information

Table 5.1. Number and experience of analyst

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience Chemical	Years of experience Soil	Number of analyst	Years of experience Chemical	Years of experience Soil	
cn01	1	20	1	1	20	1	s
cn02	1	9	6	1	9	6	d
cn03	1	7	4	1	14	6	d
cn04	3	4	4	2	4	4	d
id01	1	7	-	1	7	2	d
id02	2	25/23	25/23	1	9	9	d
jp01	1	6	6	1	6	6	s
my01	2	5/5	5/5	1	5	5	d
mn01	-	-	-	1	11	11	-
ph01	2[*1]	15/15	15/15	1	28	28	d
kr01	1	15	10	1	15	10	s
ru01	1	8	8	1	8	8	s
th01	1	3	2	1	3	2	s
vn01	1	11	6	1	11	6	s

Note: *1. Ca/Mg and K/Na were analyzed by different analysts; -, Not measured; s, Same analysts; d, Different analysts

Table 5.2. Analytical instruments and condition of the instruments for exchangeable cations

Lab.	Sample	Ex-Ca		Ex-Mg			Ex-K		Ex-Na			Procedures for extraction of Ex-base cations	Ex-Acidity, Al and H		
													method	Size of burette (ml)	
		Instrument	Years*1	Instrument	Years		Instrument	Years	Instrument	Years				Capacity	Minimum graduate
cn01	No.041	(AAS)	(6)	(AAS)	(6)	(La)	(AAS)	(6)	(AAS)	(6)	(La)	Centrifuge	Titration	50	0.1
	No.042	(AAS)	(6)	(AAS)	(6)	(La)	(AAS)	(6)	(AAS)	(6)	(La)				
cn02	No.041	AAS	15	AAS	15	(Sr)	AAS	15	AAS	15	(Sr)	Automatic extractor	Titration	5	0.00125
	No.042	AAS	15	AAS	15	(Sr)	AAS	15	AAS	15	(Sr)				
cn03	No.041	AAS	4	AAS	4	Sr	AAS	4	AAS	4	Sr	Centrifuge	Titration	25	0.1
	No.042	AAS	4	AAS	4	Sr	AAS	4	AAS	4	Sr				
cn04	No.041	AAS	7	AAS	7	Sr	AAS	7	AAS	7	na	Centrifuge	Titration	25	0.1
	No.042	AAS	7	AAS	7	Sr	AAS	7	AAS	7	na				
id01	No.041	AAS	12	AAS	12	Sr	AAS	12	AAS	12	Sr	Centrifuge	Titration	50	0.05
	No.042	AAS	12	AAS	12	Sr	AAS	12	AAS	12	Sr				
id02	No.041	AAS	18	AAS	18	(Sr)	FEP	36	FEP	36	(Sr)	Percolation tube	Titration	50	0.01
	No.042	AAS	18	AAS	18	(Sr)	FEP	36	FEP	36	(Sr)				
jp01	No.041	AAS	19	AAS	19	Sr	FEP	19	FEP	19	na	Percolation tube	Titration	25/10	0.1/0.05
	No.042	AAS	19	AAS	19	Sr	FEP	19	FEP	19	na			(NaOH/HCl)	(NaOH/HCl)
my01	No.041	AAS	2.5	AAS	2.5	Sr	FEP	2.5	FEP	2.5	Sr	Percolation tube	Titration	25	0.05
	No.042	AAS	2.5	AAS	2.5	Sr	FEP	2.5	FEP	2.5	Sr				
mn01	No.041	-	-	-	-	-	-	-	-	-	-	-	Titration	25	0.1
	No.042	-	-	-	-	-	-	-	-	-	-				
ph01	No.041	AAS	14	AAS	14	Sr	AAS	14	AAS	14	na	Buchner funnel	Titration	50	0.01
	No.042	AAS	14	AAS	14	Sr	AAS	14	AAS	14	na				
kr01	No.041	AAS	11	AAS	4	Sr	AAS	4	AAS	4	Sr	Buchner funnel	Titration	50	0.1
	No.042	AAS	11	AAS	4	Sr	AAS	4	AAS	4	Sr				
ru01	No.041	AAS	22	AAS	22	La	AAS	22	AAS	22	Cs	Percolation tube	Titration	50	0.1
	No.042	AAS	22	AAS	22	La	AAS	22	AAS	22	Cs				
th01	No.041	AAS	8	AAS	8	(Sr)	AAS	8	AAS	8	(Cs)	Percolation tube	Titration	50	0.05
	No.042	AAS	8	AAS	8	(Sr)	AAS	8	AAS	8	(Cs)				
vn01	No.041	Titration		Titration		na	FEP	7	FEP	7	na	Buchner funnel	Titration	10	0.05
	No.042	Titration		Titration		na	FEP	7	FEP	7	na				

Note: AAS, Atomic absorption spectrometry; FEP, Flame (emission) photometry; -, Not measured; +, No information. *1. Years in use of instrument.

Table 5.3. Date of analysis

Lab.	Repeat	pH			Ex-Ca and Mg			Ex-K and Na			Ex-acidity, Al and H		
		Date[*1]	Analysis[*2] Days	Interval[*3] Days	Date[*1]	Analysis[*2] Days	Interval[*3] Days	Date[*1]	Analysis[*2] Days	Interval[*3] Days	Date[*1]	Analysis[*2] Days	Interval[*3] Days
cn01	1st	28-Feb	1	1	3-Mar	13	0	3-Mar	13	0	27-Feb	1	2
	2nd	1-Mar	1		3-Mar	10		3-Mar	10		1-Mar	1	
cn02	1st	21-Jan	3	14	21-Jan	5	14	21-Jan	5	14	27-Jan	3	8
	2nd	4-Feb	4		4-Feb	4		4-Feb	4		4-Feb	4	
cn03	1st	17-Jan	1	36	25-Jan	2	30	25-Jan	2	30	17-Jan	4	33
	2nd	22-Feb	1		24-Feb	2		24-Feb	2		19-Feb	8	
cn04	1st	17-Feb	1	7	17-Feb	2	6	17-Feb	2	6	19-Feb	2	6
	2nd	24-Feb	1		23-Feb	2		23-Feb	2		25-Feb		
id01	1st	22-Dec	1	12	11-Jan	9	0	11-Jan	9	0	28-Dec	6	7
emc	2nd	3-Jan	1		11-Jan	9		11-Jan	9		4-Jan	2	
id02	1st	6-Jan	1	0	6-Jan	1	7	6-Jan	1	7	6-Jan	1	7
	2nd	6-Jan	1		13-Jan	1		13-Jan	1		13-Jan	1	
jp01	1st	10-Feb	1	7	15-Feb	6	3	15-Feb	6	3	15-Feb	6	3
	2nd	17-Feb	1		18-Feb	2		18-Feb	2		18-Feb	2	
my01	1st	22-Jun	1	20	18-Jul	2	2	18-Jul	2	2	1-Jul	1	12
	2nd	12-Jul	1		20-Jul	2		20-Jul	2		13-Jul	1	
mn01	1st	4-Feb	1	0	-	-	-	-	-	-	4-Feb	1	3
	2nd	16-Feb	1		-	-		-	-		7-Feb	1	
ph01	1st	22-Mar	1	7	24-Mar	1	7	24-Mar	1	7	22-Mar	1	7
	2nd	29-Mar	1		31-Mar	1		31-Mar	1		29-Mar	1	
kr01	1st	20-Jan	1	6	28-Jan	2	6	28-Jan	2	6	28-Jan	2	6
	2nd	26-Jan	1		3-Feb	2		3-Feb	2		3-Feb	2	
ru01	1st	5-Feb	2	2	11-Feb	2	2	11-Feb	2	2	16-Feb	2	1
	2nd	7-Feb	2		13-Feb	2		13-Feb	2		17-Feb	1	
th01	1st	27-Jan	1	1	4-Feb	1	1	4-Feb	1	1	6-Feb	1	1
	2nd	28-Jan	1		5-Feb	1		5-Feb	1		7-Feb	1	
vn01	1st	18-Jan	1	3	18-Jan	1	3	18-Jan	1	3	18-Jan	1	3
	2nd	21-Jan	1		21-Jan	1		21-Jan	1		21-Jan	1	

Note: *1. Finish date of 1st and 2nd analyses. *2. Days used for analysis. *3. Interval between the repeat analyses. +, not reported.

3.3. Analysis of variance and estimation of precision

Analysis of variance (ANOVA) for the entire data and verified data were shown in Table 6.1 and 6.2, respectively. “Repeatability-precision”, “within-laboratory-precision” and “inter-laboratories-precision” were estimated. In the following section, the results of verified data were mainly discussed (see Table 6.2).

1) Repeatability-precision

Repeatability standard deviations were relatively small for most of the parameters in the verified data, and CVs of most parameters were smaller than 10%. Especially CVs of pH(H_2O) and pH(KCl) in both samples were smaller than 1%, and that of Ex-acidity in No.042 was about 1.2%.

It seems that triplicate analyses were carried out under the same condition. Process on extraction, dilution of the sample, and stability of the instruments might affect the results. The small CVs suggested that the participating laboratories could analyze the parameters with their own standard procedures and stable instruments.

2) Within-laboratory-precision

Within-laboratory standard deviations were relatively small for most of the parameters in the verified data, and CVs of most parameters were smaller than 5%. Especially CVs of pH(H_2O), pH(KCl) and Ex-acidity in both samples were smaller than 1%, and CVs of Ex-base cations in No. 041 were smaller than 5%.

The values were almost same as repeatability-precision. For some parameters, the CVs were smaller than ones of repeatability precision. It was suggested that the average of triplicate analyses under the repeatability condition could be representative value for the analysis in a laboratory. It was also suggested that the participating laboratories could analyze the parameters with their own standard procedures.

3) Inter-laboratories precision

Inter-laboratories standard deviation was still large. CVs of Ex-base cations were larger than 50% probably because both samples were relatively acidic and concentrations of base cations were limited. CV of Ex-acidity was the smallest among exchangeable cations in both samples.

4) Calculation of permissible tolerance

As for the repeatability limit and within-laboratory reproducibility limit, values might be enough small, and it could be used as a reference value for the repeat analysis on the instrumental analysis in the respective laboratories.

As for the reproducibility limit, inter-laboratories precision should be improved for Ex-base cations, and then the discussion should be carried out.

Table 6.1. Analysis of variance for the entire data

Statistics	No. 041								
	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of lab	14	14	13	13	13	13	14	14	14
Total sum of square	171479	119439	2459	453	790	722	239924	182885	3552
ST/lmd	2041	1422	32	6	10	9	2856	2177	42
Number of Laboratories	14	14	13	13	13	13	14	14	14
Number of Data	84	84	78	78	78	78	84	84	84
Total sum	414.1	345.6	49.59	21.28	28.11	26.87	489.82	427.65	59.60
Total average	4.9	4.1	0.64	0.27	0.36	0.34	5.83	5.09	0.71
Sum of square inter-laboratories (S_R)	1.2	1.7	198.45	5.97	9.15	35.01	2866.09	2050.32	75.79
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.02	0.01	0.01	0.00	1.83	1.45	0.10
Sum of square repeatablility (S_r)	0.0	0.0	0.05	0.07	0.06	0.06	1.96	1.53	0.55
Total sum of square (S_T)	1.3	1.7	198.52	6.04	9.23	35.08	2869.87	2053.31	76.45
Inter-laboratories degree of freedom (ϕ_R)	13	13	12	12	12	12	13	13	13
Within-laboratory degree of freedom (ϕ_{RW})	14	14	13	13	13	13	14	14	14
Repeatability degree of freedom (ϕ_r)	56	56	52	52	52	52	56	56	56
Total degree of freedom (ϕ_T)	83	83	77	77	77	77	83	83	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.09	0.13	16.537	0.497	0.763	2.918	220.468	157.717	5.830
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.001	0.001	0.001	0.000	0.131	0.104	0.007
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.001	0.001	0.001	0.001	0.035	0.027	0.010
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.02	0.02	2.756	0.083	0.127	0.486	36.723	26.269	0.970
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	0.000	0.000	0.000	0.000	0.032	0.025	-0.001
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.001	0.001	0.001	0.001	0.035	0.027	0.010
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.1	0.1	1.66	0.29	0.36	0.70	6.06	5.13	0.99
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.02	0.02	0.02	0.01	0.21	0.19	0.05
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.03	0.04	0.03	0.03	0.19	0.17	0.10
Inter-laboratories precision CV (%)	2.5	3.6	261.13	105.52	98.94	202.42	103.95	100.71	138.93
Within-laboratory precision CV (%)	0.3	0.6	3.25	5.91	5.30	3.10	3.58	3.65	7.02
Repeatability precision CV (%)	0.4	0.0	5.01	13.28	9.40	9.99	3.21	3.25	13.99
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.35	0.41	4.649	0.806	0.998	1.953	16.973	14.356	2.760
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.05	0.07	0.058	0.045	0.053	0.030	0.584	0.521	0.139
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.07	0.00	0.105	0.120	0.112	0.114	0.617	0.546	0.327

Statistics	No. 042								
	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of lab	14	14	13	13	13	13	14	14	14
Total sum of square	171313	118611	498	313	180	381	64496	51121	979
ST/lmd	2039	1412	6	4	2	5	768	609	12
Number of Laboratories	14	14	13	13	13	13	14	14	14
Number of Data	84	84	78	78	78	78	84	84	84
Total sum	413.9	344.4	22.31	17.68	13.41	19.53	253.96	226.10	31.29
Total average	4.9	4.1	0.29	0.23	0.17	0.25	3.02	2.69	0.37
Sum of square inter-laboratories (S_R)	1.7	1.9	42.98	5.22	4.72	26.51	16.07	17.34	6.40
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.01	0.04	0.00	0.36	0.22	0.15
Sum of square repeatablility (S_r)	0.1	0.0	0.04	0.12	0.05	0.06	0.33	0.60	0.71
Total sum of square (S_T)	1.8	1.9	43.03	5.35	4.81	26.58	16.77	18.16	7.26
Inter-laboratories degree of freedom (ϕ_R)	13	13	12	12	12	12	13	13	13
Within-laboratory degree of freedom (ϕ_{RW})	14	14	13	13	13	13	14	14	14
Repeatability degree of freedom (ϕ_r)	56	56	52	52	52	52	56	56	56
Total degree of freedom (ϕ_T)	83	83	77	77	77	77	83	83	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.13	0.15	3.582	0.435	0.394	2.209	1.237	1.334	0.492
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.000	0.001	0.003	0.000	0.026	0.016	0.011
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.001	0.002	0.001	0.001	0.006	0.011	0.013
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.02	0.02	0.597	0.072	0.065	0.368	0.202	0.220	0.080
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	0.000	-0.001	0.001	0.000	0.007	0.002	-0.001
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.001	0.002	0.001	0.001	0.006	0.011	0.013
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.1	0.2	0.77	0.27	0.26	0.61	0.45	0.47	0.29
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.01	0.01	0.03	0.01	0.09	0.07	0.06
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.03	0.05	0.03	0.03	0.08	0.10	0.11
Inter-laboratories precision CV (%)	3.0	3.8	270.13	118.82	148.99	242.34	15.02	17.52	76.90
Within-laboratory precision CV (%)	0.6	0.0	3.16	6.36	18.12	4.36	3.08	2.68	16.04
Repeatability precision CV (%)	0.6	0.0	10.09	20.93	17.37	13.93	2.54	3.86	30.17
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.41	0.44	2.163	0.754	0.717	1.699	1.271	1.320	0.802
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.08	0.00	0.025	0.040	0.087	0.031	0.261	0.202	0.167
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.10	0.00	0.095	0.157	0.099	0.115	0.254	0.343	0.371

Table 6.2. Analysis of variance for the verified data

Statistics	No. 041								
	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of lab	13	12	9	12	11	12	10	12	13
Total sum of square	147686	88566	27	230	278	120	59634	68314	1269
ST/lmd	1893	1230	0	3	4	2	994	949	16
Number of Laboratories	13	12	9	12	11	12	10	12	13
Number of Data	78	72	54	72	66	72	60	72	78
Total sum	384.3	297.6	5.16	15.16	16.67	10.97	244.20	261.37	35.63
Total average	4.9	4.1	0.10	0.21	0.25	0.15	4.07	3.63	0.46
Sum of square inter-laboratories (S_R)	1.2	1.2	0.26	2.34	0.98	0.46	22.22	24.10	6.05
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.01	0.17	0.10
Sum of square repeatablility (S_r)	0.0	0.0	0.00	0.00	0.00	0.02	1.51	1.28	0.55
Total sum of square (S_T)	1.2	1.2	0.27	2.34	0.99	0.49	23.74	25.55	6.70
Inter-laboratories degree of freedom (ϕ_R)	12	11	8	11	10	11	9	11	12
Within-laboratory degree of freedom (ϕ_{RW})	13	12	9	12	11	12	10	12	13
Repeatability degree of freedom (ϕ_r)	52	48	36	48	44	48	40	48	52
Total degree of freedom (ϕ_T)	77	71	53	71	65	71	59	71	77
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.10	0.11	0.033	0.213	0.098	0.042	2.468	2.191	0.504
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.000	0.000	0.000	0.000	0.001	0.014	0.008
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.038	0.027	0.011
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.02	0.02	0.005	0.035	0.016	0.007	0.411	0.363	0.083
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	0.000	0.000	0.000	0.000	-0.012	-0.004	-0.001
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.038	0.027	0.011
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.1	0.1	0.07	0.19	0.13	0.08	0.64	0.60	0.29
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.00	0.01	0.01	0.01	0.02	0.07	0.05
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.01	0.01	0.01	0.02	0.19	0.16	0.10
Inter-laboratories precision CV (%)	2.6	3.3	77.63	89.38	50.71	54.86	15.76	16.65	63.44
Within-laboratory precision CV (%)	0.2	0.0	3.29	3.60	2.44	4.95	0.51	1.87	11.29
Repeatability precision CV (%)	0.4	0.0	6.83	4.19	3.55	14.43	4.78	4.50	22.54
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.36	0.38	0.208	0.527	0.359	0.234	1.796	1.692	0.811
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.03	0.00	0.009	0.021	0.017	0.021	0.059	0.190	0.144
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.06	0.00	0.022	0.029	0.030	0.073	0.642	0.539	0.340

Statistics	No. 042								
	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of lab	14	14	9	10	10	12	10	13	14
Total sum of square	171313	118611	4	56	21	36	31025	42866	979
ST/lmd	2039	1412	0	1	0	0	517	550	12
Number of Laboratories	14	14	9	10	10	12	10	13	14
Number of Data	84	84	54	60	60	72	60	78	84
Total sum	413.9	344.4	2.11	7.45	4.60	5.96	176.14	207.04	31.29
Total average	4.9	4.1	0.04	0.12	0.08	0.08	2.94	2.65	0.37
Sum of square inter-laboratories (S_R)	1.7	1.9	0.03	0.26	0.10	0.22	12.61	15.82	6.40
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.01	0.07	0.15
Sum of square repeatablility (S_r)	0.1	0.0	0.00	0.00	0.00	0.01	0.05	0.48	0.71
Total sum of square (S_T)	1.8	1.9	0.03	0.27	0.10	0.23	12.66	16.37	7.26
Inter-laboratories degree of freedom (ϕ_R)	13	13	8	9	9	11	9	12	13
Within-laboratory degree of freedom (ϕ_{RW})	14	14	9	10	10	12	10	13	14
Repeatability degree of freedom (ϕ_r)	56	56	36	40	40	48	40	52	56
Total degree of freedom (ϕ_T)	83	83	53	59	59	71	59	77	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.13	0.15	0.004	0.029	0.011	0.020	1.401	1.318	0.492
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.000	0.000	0.000	0.000	0.001	0.005	0.011
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.001	0.009	0.013
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.02	0.02	0.001	0.005	0.002	0.003	0.233	0.219	0.080
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	0.000	0.000	0.000	0.000	0.000	-0.001	-0.001
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.001	0.009	0.013
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.1	0.2	0.03	0.07	0.04	0.06	0.48	0.47	0.29
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.00	0.00	0.00	0.01	0.02	0.04	0.06
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.00	0.01	0.00	0.01	0.04	0.10	0.11
Inter-laboratories precision CV (%)	3.0	3.8	67.75	56.18	56.27	69.11	16.46	17.66	76.90
Within-laboratory precision CV (%)	0.6	0.0	9.21	3.65	3.07	10.33	0.54	1.60	16.04
Repeatability precision CV (%)	0.6	0.0	9.21	7.50	6.07	14.38	1.19	3.61	30.17
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.41	0.44	0.074	0.195	0.121	0.160	1.353	1.312	0.802
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.08	0.00	0.010	0.013	0.007	0.024	0.045	0.119	0.167
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.10	0.00	0.012	0.031	0.015	0.039	0.116	0.316	0.371

4. DISCUSSION

By using digital formats, no obvious calculation mistake was found in the data. However, some outliers have ten times larger than averages and some have low within-laboratory reproducibility. It was suggested that quality control within the laboratories and standard operating procedures and reporting system should be elaborated in such laboratories.

Repeatability precisions and within-laboratory-reproducibility precisions were relatively larger in Ex-base cations, especially in Ex-Ca and Mg. Level of the concentrations might affect the precisions as discussed above. Further investigation should be considered taking concentrations of the samples into account.

5. ACKNOWLEDGMENT

ADORC wishes to thank Tottori Prefecture for their cooperation on collecting soil samples.

6. REFERENCES

1) Environment Agency, Government of Japan (1997): Monitoring Guidelines and Technical Manuals for Soil and Vegetation Monitoring.

2) The second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia (2000): Technical Manuals for Soil and Vegetation Monitoring in East Asia.

3) Japanese Standard Association (1991): General rules for permissible tolerance of chemical analyses and physical tests (JIS Z-8402-$_{1991}$), Japanese Industrial Standard.

4) Acid Deposition and Oxidant Research Center (2001a): Report of the inter-laboratory comparison project 1999 on soil.

5) Acid Deposition and Oxidant Research Center (2001b): Report of the inter-laboratory comparison project 2000 on soil.

6) Acid Deposition and Oxidant Research Center (2002): Report of the inter-laboratory comparison project 2001 on soil.

7. CONTACT INFORMATION

Please address all inquiries, comments and suggestions about this report to:

Acid Deposition and Oxidant Research Center (ADORC)
1182 Sowa, Niigata city 950-2144 Japan
Tel: +81-25-263-0550
Fax: +81-25-263-0566
E-mail: eanetdata@adorc.gr.jp
URL: http://www.adorc.gr.jp

Contact persons:

Name	Department & E-mail address
Dr. Hiroyuki SASE	Ecological Impact Research Department/ Data Management Department E-mail: sase@adorc.gr.jp
Mr. Masato KAMISAKO	Ecological Impact Research Department/ Data Management Department E-mail: kamisako@adorc.gr.jp
Mr. Shinji NAKAYAMA (EANET QA/QC Manager)	Dept. Head, Data Management Department E-mail: nakayama@adorc.gr.jp

APPENDIX 1: Participating laboratories

1. CHINA

1) Chongqing Key Lab of Agricultural Resources and Environment	**cn01**
2) Xi'an Environmental Monitoring Station	**cn02**
3) Xiamen Environmental Monitoring Central Station	**cn03**
4) Zhuhai Environmental Monitoring Station	**cn04**

2. INDONESIA

Environmental Management Center	**id01**
Soil Research Institute	**id02**

3. JAPAN

Shimane Agricultural Experimental Station	**jp01**

4. MALAYSIA

Department of Environmental Sciences, Universiti Putra Malaysia	**my01**

5. MONGOLIA

Central Laboratory of Environmental Monitoring	**mn01**

6. PHILIPPINES

Environmental Management Bureau	**ph01**

7. Republic of KOREA

Soil Environmental Division, National Institute of Environmental Research	**kr01**

8. RUSSIA

Limnological Institute Russian Academy of Science/Siberian Branch	**ru01**

9. THAILAND

King Mongkut's University of Technology Thonburi	**th01**

10. VIET NAM

Institute of Meteorology and Hydrology, MoNRE	**vn01**

Appendix 3.1. Entire data of pH in Sample No. 042

Lab.	pH(H_2O) Lab. Ave.	pH(H_2O) Average	pH(H_2O) repeat	pH(KCl) Lab. Ave.	pH(KCl) Average	pH(KCl) repeat
cn01	5.0	5.0 (0.1)	5.0	4.1	4.1 (0.0)	4.1
chongqing			5.0			4.1
			4.9			4.1
		5.0 (0.0)	5.0		4.1 (0.0)	4.1
			5.0			4.1
			5.0			4.1
cn02	5.1	5.1 (0.0)	5.1	4.3	4.3 (0.0)	4.3
xian			5.1			4.3
			5.1			4.3
		5.1 (0.0)	5.1		4.3 (0.0)	4.3
			5.1			4.3
			5.1			4.3
cn03	5.0	5.0 (0.0)	5.0	4.2	4.2 (0.0)	4.2
xiamen			5.0			4.2
			5.0			4.2
		5.0 (0.0)	5.0		4.2 (0.0)	4.2
			5.0			4.2
			5.0			4.2
cn04	5.0	5.0 (0.0)	5.0	4.1	4.1 (0.0)	4.1
zhuhai			5.0			4.1
			5.0			4.1
		5.0 (0.0)	5.0		4.1 (0.0)	4.1
			5.0			4.1
			5.0			4.1
id01	4.9	4.9 (0.0)	4.9	4.0	4.0 (0.0)	4.0
emc			4.9			4.0
			4.9			4.0
		4.9 (0.0)	4.9		4.0 (0.0)	4.0
			4.9			4.0
			4.9			4.0
id02	4.7	4.7 (0.1)	4.7	4.2	4.2 (0.0)	4.2
csar			4.6			4.2
			4.7			4.2
		4.7 (0.0)	4.7		4.2 (0.0)	4.2
			4.7			4.2
			4.7			4.2
jp01	5.0	5.0 (0.0)	5.0	4.1	4.1 (0.0)	4.1
			5.0			4.1
			5.0			4.1
		4.9 (0.1)	4.9		4.1 (0.0)	4.1
			4.9			4.1
			5.0			4.1
my01	4.7	4.6 (0.1)	4.7	3.8	3.8 (0.0)	3.8
			4.6			3.8
			4.6			3.8
		4.7 (0.0)	4.7		3.8 (0.0)	3.8
			4.7			3.8
			4.7			3.8
mn01	4.9	4.9 (0.1)	4.9	4.0	4.0 (0.0)	4.0
			5.0			4.0
			4.9			4.0
		4.9 (0.1)	4.9		4.0 (0.0)	4.0
			4.9			4.0
			5.0			4.0
ph01	4.8	4.8 (0.0)	4.8	3.9	3.9 (0.0)	3.9
			4.8			3.9
			4.8			3.9
		4.7 (0.0)	4.7		3.9 (0.0)	3.9
			4.7			3.9
			4.7			3.9
kr01	5.0	5.0 (0.1)	5.1	4.0	4.0 (0.0)	4.0
			5.0			4.0
			5.0			4.0
		5.0 (0.0)	5.0		4.0 (0.0)	4.0
			5.0			4.0
			5.0			4.0
ru01	5.1	5.1 (0.0)	5.1	4.4	4.4 (0.0)	4.4
			5.1			4.4
			5.1			4.4
		5.1 (0.0)	5.1		4.4 (0.0)	4.4
			5.1			4.4
			5.1			4.4
th01	5.1	5.1 (0.1)	5.1	4.2	4.2 (0.0)	4.2
			5.0			4.2
			5.1			4.2
		5.1 (0.0)	5.1		4.2 (0.0)	4.2
			5.1			4.2
			5.1			4.2
vn01	4.8	4.8 (0.0)	4.8	4.1	4.1 (0.0)	4.1
			4.8			4.1
			4.8			4.1
		4.8 (0.0)	4.8		4.1 (0.0)	4.1
			4.8			4.1
			4.8			4.1

Appendix 3.2. Entire data of exchangeable base cations in Sample No. 042

Lab.	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
	cmol(+)/kg											
	Lab. Ave	Average	repeat	Lab. Ave	Average	repeat	Lab. Ave	Average	repeat	Lab. Ave	Average	repeat
cn01	0.03	0.03 (0.00)	0.03	0.14	0.13 (0.01)	0.12	0.09	0.09 (0.00)	0.09	0.08	0.08 (0.00)	0.08
			0.03			0.13			0.09			0.08
			0.03			0.13			0.09			0.08
		0.03 (0.01)	0.03		0.14 (0.01)	0.13		0.09 (0.00)	0.09		0.08 (0.00)	0.08
			0.04			0.14			0.09			0.08
			0.03			0.14			0.09			0.08
cn02	0.09	0.09 (0.01)	0.08	0.09	0.09 (0.01)	0.08	0.27	0.26 (0.01)	0.25	0.08	0.08 (0.03)	0.10
			0.09			0.09			0.27			0.05
			0.09			0.09			0.26			0.10
		0.09 (0.00)	0.09		0.08 (0.01)	0.07		0.27 (0.01)	0.26		0.08 (0.02)	0.10
			0.09			0.08			0.28			0.07
			0.09			0.08			0.28			0.07
cn03	0.06	0.06 (0.00)	0.06	0.14	0.14 (0.00)	0.14	0.12	0.11 (0.01)	0.12	0.09	0.08 (0.00)	0.08
			0.06			0.14			0.11			0.08
			0.06			0.14			0.11			0.08
		0.06 (0.00)	0.06		0.14 (0.01)	0.14		0.12 (0.01)	0.12		0.10 (0.01)	0.09
			0.06			0.14			0.13			0.10
			0.06			0.13			0.11			0.11
cn04	0.11	0.12 (0.01)	0.12	0.14	0.13 (0.00)	0.13	0.21	0.29 (0.13)	0.37	0.18	0.20 (0.04)	0.24
			0.13			0.13			0.36			0.19
			0.11			0.13			0.14			0.16
		0.10 (0.01)	0.10		0.14 (0.01)	0.13		0.13 (0.06)	0.18		0.16 (0.01)	0.16
			0.10			0.15			0.15			0.17
			0.11			0.15			0.07			0.16
id01	0.01	0.01 (0.00)	0.01	0.04	0.04 (0.00)	0.04	0.03	0.03 (0.00)	0.03	0.02	0.02 (0.00)	0.02
			0.01			0.04			0.03			0.02
			0.01			0.04			0.03			0.02
		0.01 (0.00)	0.01		0.04 (0.00)	0.04		0.03 (0.00)	0.03		0.02 (0.00)	0.02
			0.01			0.04			0.03			0.02
			0.01			0.04			0.03			0.02
id02	0.14	0.14 (0.01)	0.14	0.23	0.23 (0.00)	0.23	0.09	0.09 (0.01)	0.09	0.13	0.13 (0.00)	0.13
			0.14			0.23			0.08			0.13
			0.13			0.23			0.09			0.13
		0.14 (0.00)	0.14		0.23 (0.01)	0.22		0.09 (0.00)	0.09		0.13 (0.01)	0.13
			0.14			0.23			0.09			0.13
			0.14			0.23			0.09			0.12
jp01	0.04	0.04 (0.01)	0.04	0.13	0.14 (0.01)	0.14	0.11	0.11 (0.01)	0.11	0.09	0.09 (0.01)	0.09
			0.03			0.15			0.10			0.10
			0.04			0.14			0.11			0.09
		0.03 (0.01)	0.03		0.12 (0.00)	0.12		0.10 (0.00)	0.10		0.08 (0.00)	0.08
			0.03			0.12			0.10			0.08
			0.02			0.12			0.10			0.08
my01	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00
			0.00			0.00			0.00			0.00
			0.00			0.00			0.00			0.00
		0.00 (0.00)	0.00		0.00 (0.00)	0.00		0.00 (0.00)	0.00		0.00 (0.00)	0.00
			0.00			0.00			0.00			0.00
			0.00			0.00			0.00			0.00
mn01												
ph01	2.85	2.83 (0.08)	2.74	1.00	1.03 (0.21)	1.23	0.99	1.00 (0.03)	0.96	2.26	2.28 (0.11)	2.17
			2.87			1.03			1.02			2.39
			2.87			0.82			1.02			2.28
		2.87 (0.13)	2.99		0.96 (0.12)	1.03		0.98 (0.03)	0.96		2.24 (0.13)	2.17
			2.74			0.82			1.02			2.39
			2.87			1.03			0.96			2.17
kr01	0.03	0.03 (0.01)	0.04	0.11	0.11 (0.00)	0.11	0.07	0.07 (0.00)	0.07	0.04	0.04 (0.01)	0.05
			0.03			0.11			0.07			0.04
			0.03			0.11			0.07			0.03
		0.03 (0.00)	0.03		0.11 (0.00)	0.11		0.07 (0.01)	0.08		0.04 (0.01)	0.04
			0.03			0.11			0.06			0.05
			0.03			0.11			0.07			0.04
ru01	0.05	0.05 (0.01)	0.05	0.19	0.19 (0.04)	0.19	0.11	0.11 (0.01)	0.11	0.06	0.06 (0.01)	0.07
			0.05			0.15			0.10			0.05
			0.06			0.22			0.11			0.07
		0.04 (0.01)	0.05		0.19 (0.01)	0.19		0.11 (0.01)	0.10		0.06 (0.01)	0.05
			0.04			0.18			0.11			0.06
			0.04			0.20			0.12			0.07
th01	0.05	0.05 (0.00)	0.05	0.19	0.19 (0.01)	0.19	0.03	0.03 (0.00)	0.03	0.04	0.04 (0.00)	0.04
			0.05			0.18			0.03			0.04
			0.05			0.19			0.03			0.04
		0.05 (0.00)	0.05		0.19 (0.01)	0.19		0.03 (0.00)	0.03		0.04 (0.01)	0.04
			0.05			0.18			0.03			0.04
			0.05			0.19			0.03			0.05
vn01	0.27	0.27 (0.00)	0.27	0.58	0.58 (0.00)	0.58	0.13	0.13 (0.00)	0.13	0.18	0.18 (0.00)	0.18
			0.27			0.58			0.13			0.18
			0.27			0.58			0.13			0.18
		0.27 (0.00)	0.27		0.58 (0.00)	0.58		0.13 (0.00)	0.13		0.18 (0.01)	0.18
			0.27			0.58			0.13			0.19
			0.27			0.58			0.13			0.18

Appendix 3.3. Entire data of exchangeable acidity and acid cations in Sample No. 042

Lab.	Ex-acidity			Ex-Al			Ex-H		
	cmol(+)/kg								
	Lab. Ave	Average	repeat	Lab. Ave	Average	repeat	Lab. Ave	Average	repeat
cn01	2.37	2.36 (0.01)	2.37	1.97	1.99 (0.14)	2.15	0.41	0.37 (0.13)	0.22
			2.35			1.91			0.44
			2.35			1.91			0.44
		2.38 (0.02)	2.37		1.94 (0.03)	1.96		0.44 (0.04)	0.41
			2.36			1.94			0.42
			2.40			1.91			0.49
cn02	2.58	2.58 (0.07)	2.52	2.42	2.42 (0.07)	2.36	0.16	0.16 (0.00)	0.16
			2.65			2.49			0.16
			2.58			2.42			0.16
		2.58 (0.07)	2.58		2.42 (0.07)	2.42		0.16 (0.00)	0.16
			2.64			2.48			0.16
			2.51			2.35			0.16
cn03	3.39	3.57 (0.18)	3.68	3.18	3.33 (0.17)	3.47	0.22	0.24 (0.04)	0.21
			3.67			3.39			0.28
			3.36			3.14			0.22
		3.20 (0.24)	3.47		3.02 (0.18)	3.22		0.19 (0.15)	0.25
			3.14			2.86			0.29
			3.00			2.98			0.02
cn04	2.71	2.68 (0.05)	2.73	2.18	2.18 (0.12)	2.05	0.54	0.57 (0.00)	0.57
			2.65			2.25			0.57
			2.65			2.25			0.57
		2.73 (0.02)	2.72		2.18 (0.12)	2.25		0.50 (0.12)	0.57
			2.72			2.25			0.57
			2.75			2.05			0.37
id01	3.40	3.33 (0.08)	3.29	2.55	2.58 (0.13)	2.60	0.94	0.94 (0.12)	0.85
			3.29			2.70			0.90
			3.42			2.44			1.08
		3.46 (0.06)	3.43		2.52 (0.03)	2.54		0.93 (0.05)	0.88
			3.43			2.49			0.94
			3.53			2.54			0.98
id02	2.45	2.44 (0.01)	2.45	2.21	2.20 (0.01)	2.21	0.24	0.24 (0.00)	0.24
			2.45			2.21			0.24
			2.43			2.19			0.24
		2.45 (0.00)	2.45		2.21 (0.00)	2.21		0.24 (0.00)	0.24
			2.45			2.21			0.24
			2.45			2.21			0.24
jp01	2.91	2.90 (0.05)	2.95	3.05	3.05 (0.03)	3.07	-0.14	-0.15 (0.03)	-0.12
			2.87			3.06			-0.18
			2.87			3.01			-0.15
		2.92 (0.05)	2.97		3.05 (0.01)	3.04		-0.13 (0.05)	-0.07
			2.89			3.05			-0.16
			2.89			3.05			-0.16
my01	3.42	3.47 (0.12)	3.54	3.65	3.72 (0.15)	3.85	0.14	0.03 (0.06)	0.10
			3.34			3.75			0.00
			3.54			3.55			0.00
		3.37 (0.08)	3.39		3.57 (0.06)	3.64		0.24 (0.41)	0.71
			3.44			3.54			0.00
			3.29			3.54			0.00
mn01	2.51	2.52 (0.05)	2.47	2.51	2.44 (0.00)	2.44	0.81	0.81 (0.23)	0.68
			2.55			2.44			0.68
			2.55			2.44			1.07
		2.50 (0.05)	2.55		2.57 (0.23)	2.84		0.81 (0.23)	0.68
			2.47			2.44			1.07
			2.47			2.44			0.68
ph01	3.43	3.43 (0.02)	3.42	3.08	3.08 (0.01)	3.07	0.37	0.36 (0.01)	0.36
			3.46			3.09			0.37
			3.42			3.07			0.36
		3.43 (0.01)	3.42		3.07 (0.00)	3.07		0.37 (0.01)	0.36
			3.44			3.07			0.37
			3.44			3.07			0.37
kr01	3.58	3.58 (0.03)	3.55	2.61	2.62 (0.26)	2.66	0.23	0.24 (0.06)	0.28
			3.58			2.86			0.27
			3.61			2.35			0.18
		3.57 (0.03)	3.61		2.59 (0.12)	2.66		0.21 (0.06)	0.28
			3.55			2.45			0.18
			3.55			2.66			0.18
ru01	2.76	2.90 (0.14)	2.82	2.36	2.36 (0.00)	2.36	0.30	0.40 (0.00)	0.40
			2.82			2.36			0.40
			3.06			2.36			0.40
		2.62 (0.05)	2.57		2.36 (0.00)	2.36		0.19 (0.00)	0.19
			2.65			2.36			0.19
			2.65			2.36			0.19
th01	3.25	3.24 (0.00)	3.24	3.13	3.12 (0.01)	3.12	0.13	0.12 (0.00)	0.12
			3.24			3.11			0.12
			3.24			3.12			0.12
		3.26 (0.01)	3.26		3.14 (0.01)	3.13		0.13 (0.00)	0.13
			3.27			3.14			0.13
			3.26			3.14			0.13
vn01	3.58	3.58 (0.03)	3.60	2.82	2.80 (0.00)	2.80	0.77	0.78 (0.03)	0.80
			3.60			2.80			0.80
			3.55			2.80			0.75
		3.58 (0.03)	3.60		2.83 (0.06)	2.80		0.75 (0.05)	0.80
			3.60			2.90			0.70
			3.55			2.80			0.75