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

Report of the Inter-laboratory Comparison Project 2003 on Soil

5th Attempt

November 2004
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 samples 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.

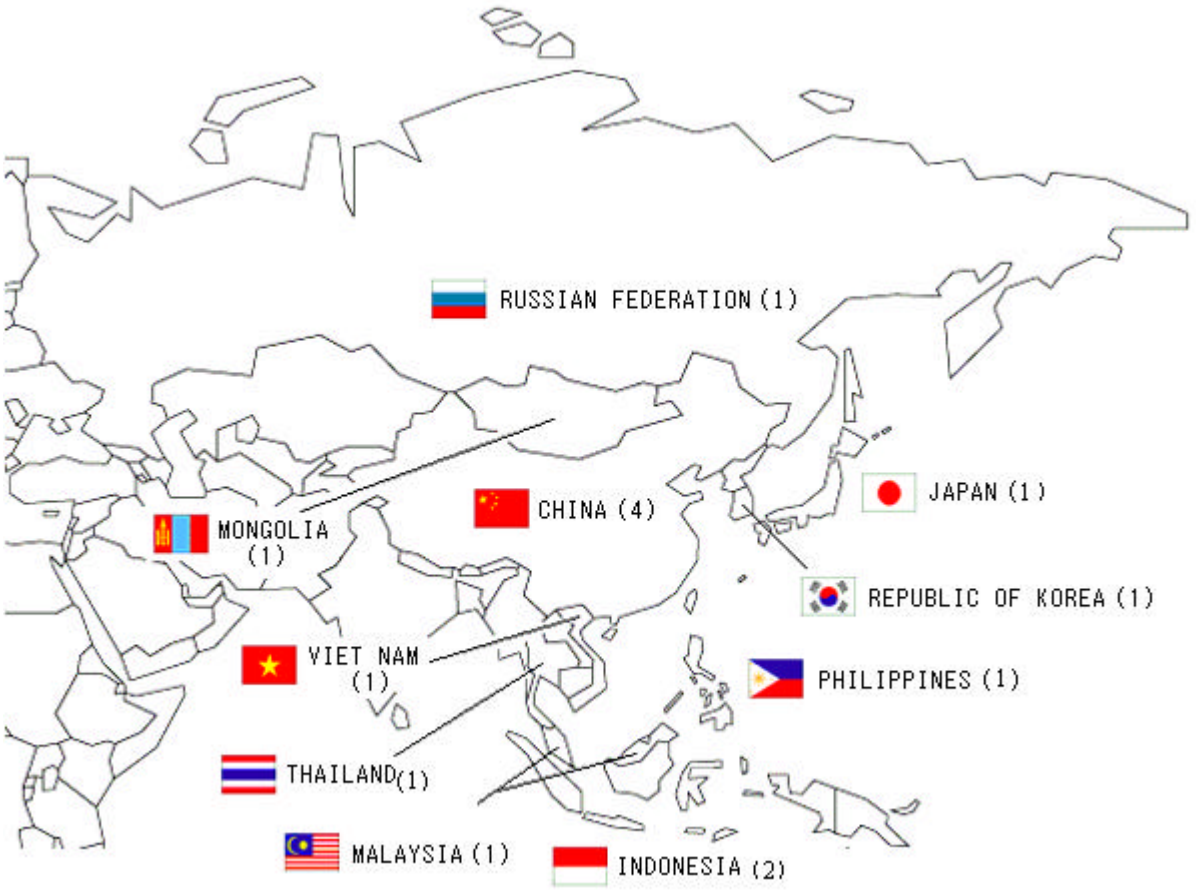

Figure 1. Laboratories participating in the Inter-laboratory comparison project 2003 on soil
Number of parenthesis shows the number of laboratories of each EANET country.

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.

1.2 Objective of the 5th project

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 again to follow the instructions, such as addition of Sr/La in order to improve the inter-laboratories precision. Countries and number of laboratories, which participated in the 5th project, are shown in the Figure 1. Fourteen laboratories of ten countries participated in the 5th project. Names of the participating laboratories are shown 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. 031: Cambisols (brown forest soil)

Soil was collected from deeper horizon after removing surface organic layer in a man-made forest of *Cryptomeria japonica* in the compound of Niigata Prefectural Institute for Forest Science in Asahi village, Niigata prefecture, Japan.

Sample No. 032: Arenosols (red soil)

Soil was collected from B horizon in a secondary forest, which consists of mainly deciduous tree species, in Murakami city, Niigata 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. 031 and 032
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 (2nd 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 5th 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:

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

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

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 shown 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, 5 - 7%, for pH(H_2O) and pH(KCl) probably due to its simple analytical procedure as discussed in the previous reports (ADORC, 2001a; 2000b). However, remarkably large CVs (larger than 300%) were observed for Ex-K and Na because of significantly large value (larger than ten times than others) by one laboratory. CVs were relatively small for Ex-acidity and Al, ca. 40% and larger than 100% for Ex-H. Variations for Ex-Ca were different in sample. CV in No. 031 with relatively high content of Ex-Ca was significantly smaller than that in No. 032.

As for the verified data, the variations (CVs) of pH(H_2O) and pH(KCl) were smaller than 5%. CVs for other parameters were improved after removing outliers. CV of Ex-Ca was the smallest among parameters in No. 031 but one in No. 032 was still over 50%. CV of Ex-acidity was smaller than 20% in both samples, especially ca. 10% in No. 031 with high content. It was suggested again that content level affected precisions of these analyses as discussed in the previous report. CVs of Ex-H were relatively large since the parameter was calculated values based on the data of Ex-acidity and Al.

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 show 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. 031								
Number of Laboratories	14	14	13	13	13	13	14	14	14
Total average	4.7	3.8	2.73	0.70	2.32	9.51	4.12	2.54	1.19
Median	4.8	3.8	3.06	0.79	0.20	0.09	3.67	2.50	0.82
Maximum	5.2	4.4	3.66	1.03	27.53	122.46	9.20	3.78	5.20
Minimum	4.0	3.5	0.65	0.25	0.11	0.05	2.42	0.11	0.26
Standard deviation	0.3	0.2	0.82	0.24	7.58	33.94	1.82	0.97	1.29
CV (%)[*1]	5.6	5.3	30.1	34.0	327	357	44.2	38.0	108
	No. 032								
Number of Laboratories	14	14	13	13	13	13	14	14	14
Total average	4.6	3.8	0.83	0.74	2.78	9.30	29.83	20.84	6.36
Median	4.7	3.8	0.50	0.73	0.43	0.13	25.52	22.27	3.43
Maximum	5.1	4.1	3.41	1.89	30.98	118.77	63.17	28.52	25.89
Minimum	3.7	3.5	0.12	0.04	0.23	0.08	20.15	10.66	0.18
Standard deviation	0.3	0.2	1.05	0.47	8.48	32.89	11.63	5.41	7.02
CV (%)[*1]	7.0	4.9	125.9	63.3	305	354	39.0	26.0	110
(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. 031								
Number of Laboratories	12	12	9	12	10	9	11	11	12
Total average	4.8	3.8	3.05	0.69	0.20	0.08	3.40	2.59	0.76
Median	4.8	3.8	3.21	0.75	0.20	0.06	3.43	2.34	0.64
Maximum	5.0	4.0	3.66	1.03	0.27	0.12	4.65	3.78	1.56
Minimum	4.5	3.5	2.34	0.25	0.11	0.05	2.42	1.66	0.26
Standard deviation	0.1	0.1	0.38	0.25	0.05	0.02	0.67	0.66	0.43
CV (%)[*1]	2.5	3.3	12.5	35.6	24.2	30.4	19.7	25.6	55.9
	No. 032								
Number of Laboratories	12	14	11	9	10	11	12	13	10
Total average	4.7	3.8	0.41	0.68	0.40	0.14	25.51	21.00	5.26
Median	4.7	3.8	0.48	0.73	0.42	0.12	25.26	23.06	3.43
Maximum	5.1	4.1	0.78	0.90	0.48	0.26	30.25	28.52	12.13
Minimum	4.4	3.5	0.12	0.39	0.29	0.08	20.15	10.66	0.29
Standard deviation	0.2	0.2	0.22	0.15	0.07	0.06	2.75	5.59	4.19
CV (%)[*1]	4.1	4.9	53.9	21.9	16.7	43.0	10.8	26.6	79.6

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

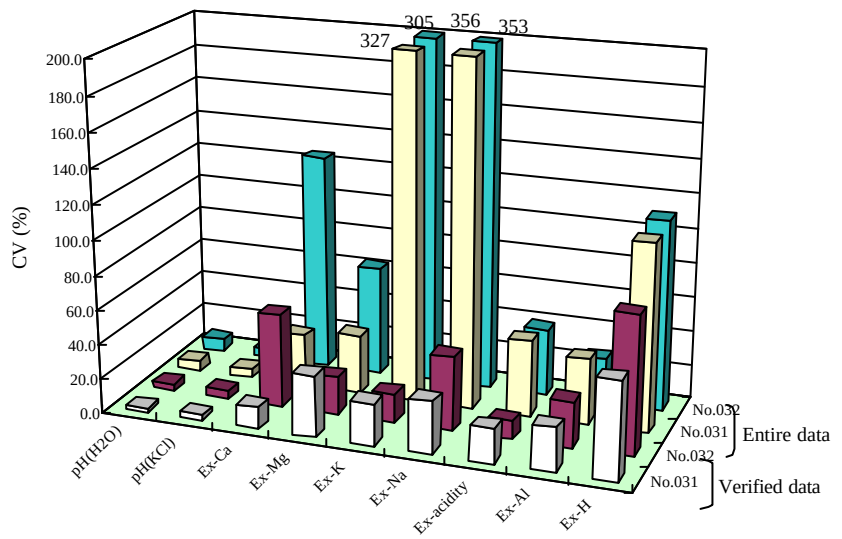

Figure 2. CV among laboratories

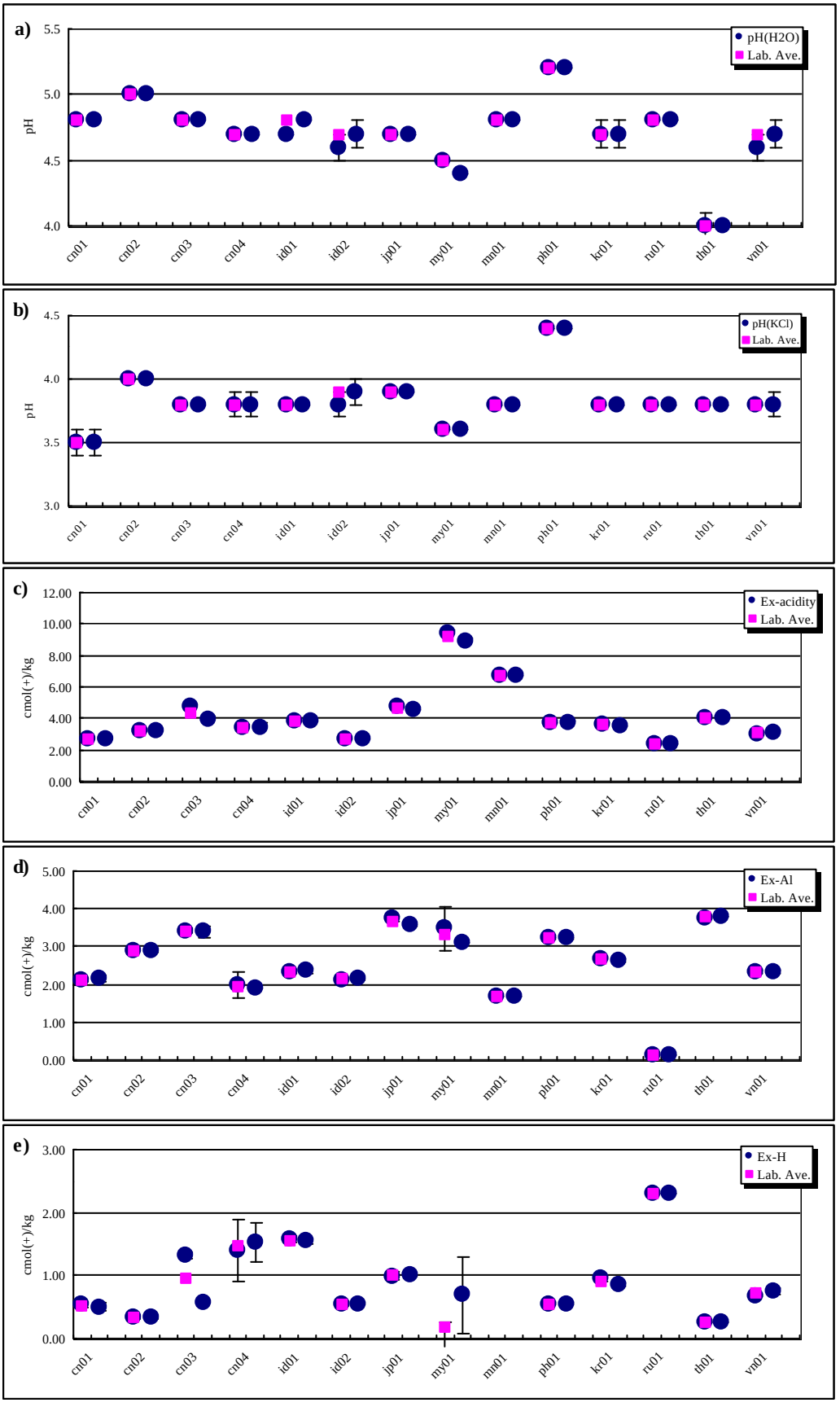

Figure 3.1. Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 031. Error bar shows standard deviation of triplicate analysis.

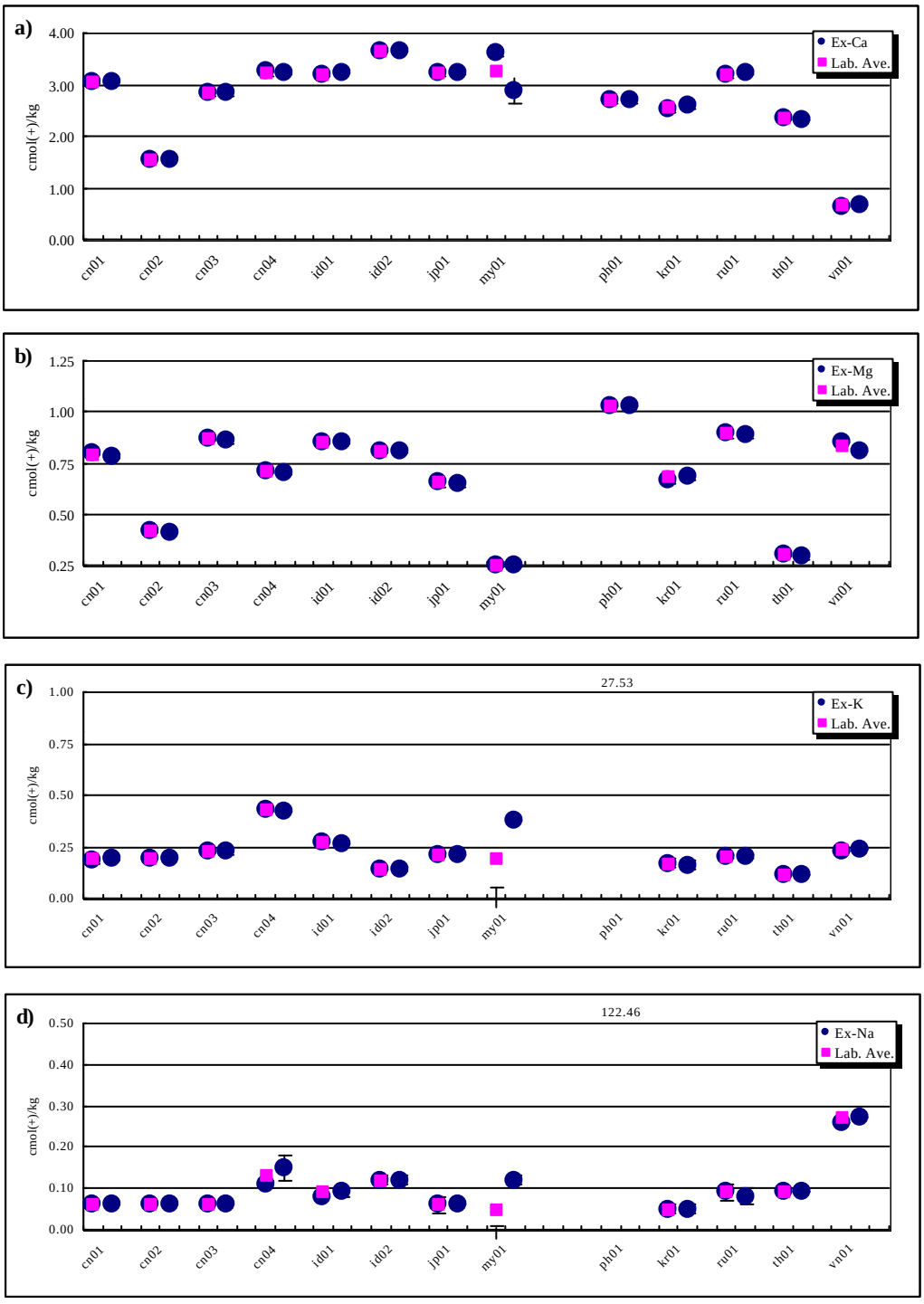

Figure 3.2. Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 031. Error bar shows standard deviation of triplicate analysis.

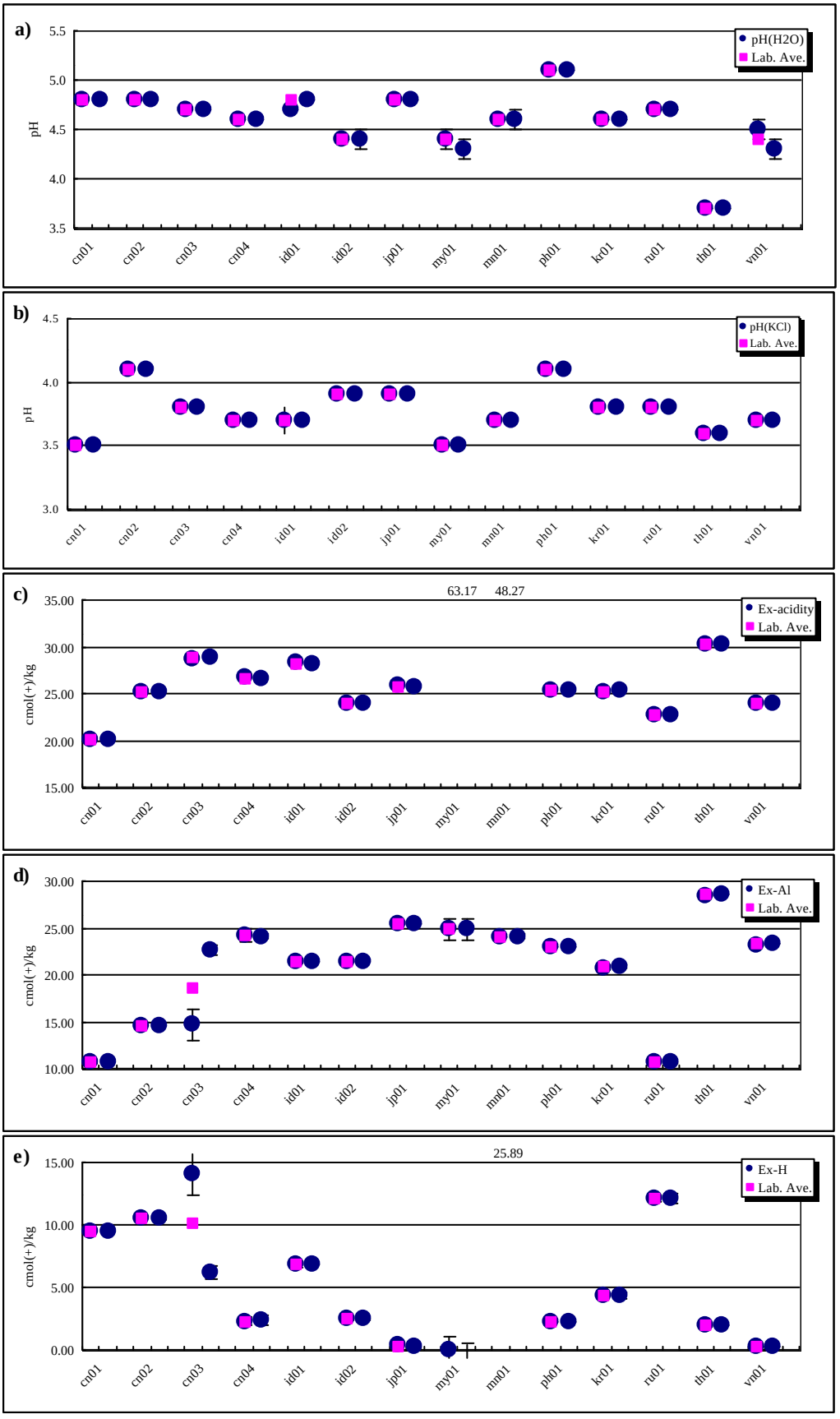

Figure 3.3. Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 032. Error bar shows standard deviation of triplicate analysis.

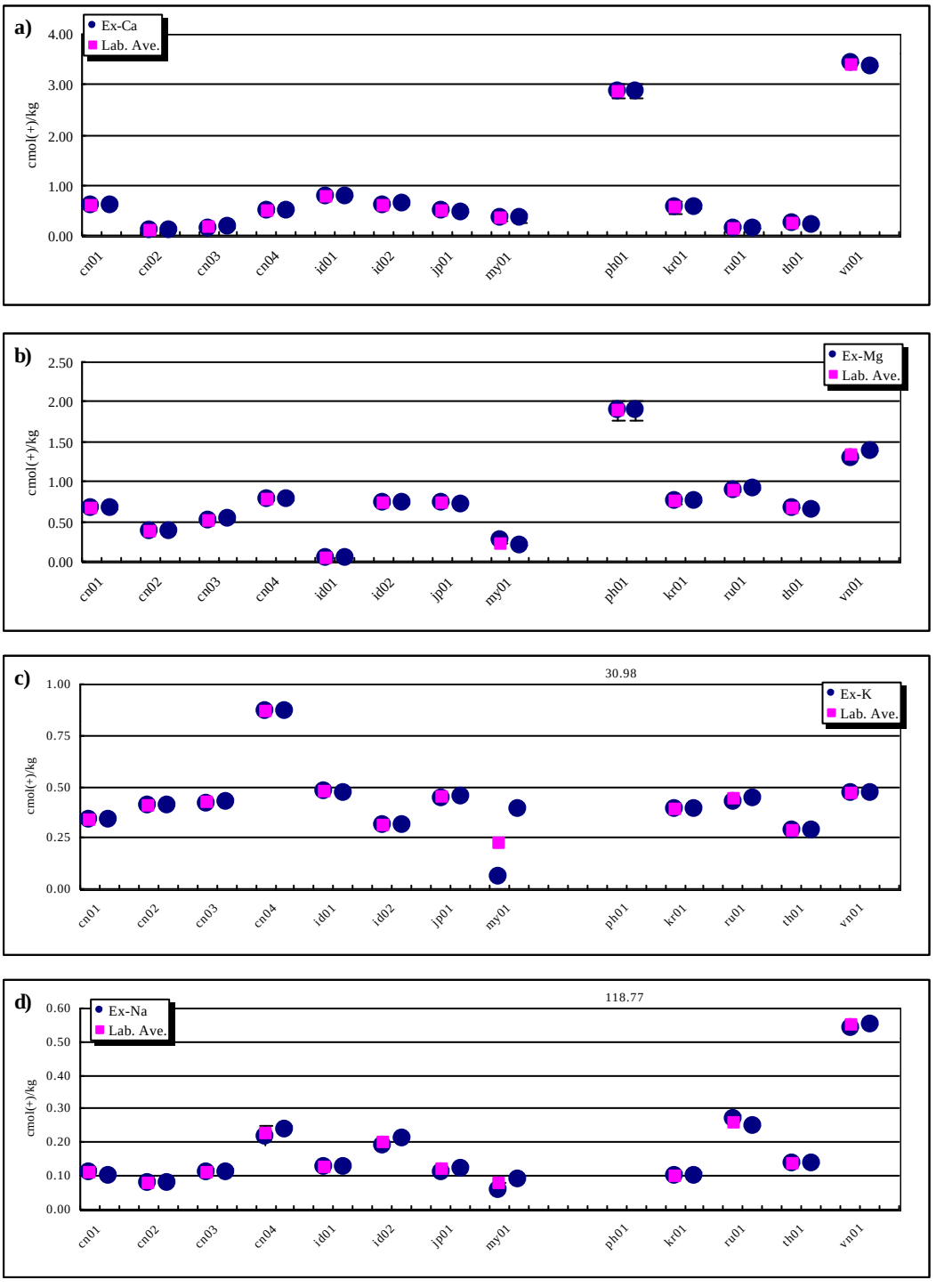

Figure 3.4. Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 032. Error bar shows standard deviation of triplicate analysis.

3.2. Verification of data

3.2.1. Detection of outliers

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" for Ex-acidity of No.031, "my01" for Ex-Ca and Ex-K of No.031, "jp01" for Ex-Al of No. 031, etc. Then, for the rest of data, 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" and "th01" for pH(H_2O) of No.031, "vn01" for Ex-Ca, Mg and K of No.031, etc.

The results of verification by Cochran-Grubbs methods were shown in Table 3.1 and 3.2.
No outlier was detected for pH(KCl) of No. 032. Two to four outliers were detected for other parameters. More than three outliers were observed in three laboratories, namely "my01", "ph01" and "vn01".

3.2.2. Moisture content and moisture correction factor

Exchangeable cations should be expressed on basis of oven-dry soil. In this connection, moisture content was measured, and moisture correction factor (mcf) was calculated based on the average moisture content of triplicate measurements. The mcfs were used for all calculation of Ex-cations. Therefore moisture content and mcf were basis of the final results; the final results would be changed if moisture content and calculation of mcf were mistaken. However some calculation mistakes were found for mcf in the 4th project. Therefore, digital formats were provided to the laboratories to avoid possible mistakes in the 5th project in 2003. In addition, drying period was recommended to be more than 12 hours based on the discussion in the Third Session of Scientific Advisory Committee (SAC3).

Measured moisture contents of sample No.021 and measurement conditions were shown in Table 4. Sample No. 032 had probably at least two times larger moisture content than No. 031. It seems that an original soil of No. 032, Acrisols (red soil), had high water retentivity due to its high clay content. As for mcf, no calculation mistake can be observed by using the digital reporting format. As for drying period, two hours of "id01" seemed to be too short but clear difference from other laboratories cannot be observed in mcf. Therefore, the data of Ex-cations might be calculated based on appropriate values of mcfs.

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 number of analyst, it seemed that different analysts carried out the repeat analyses in two laboratories, namely "cn04" and "my01". Some data of "my01" were judged as outliers by Cochran method. It was suggested that repeat analyses by different analysts affected the within-laboratory reproducibility for the results of "my01". Different analysts operated AAS (or titration in "vn01") for Ca/Mg and FEP for K/Na respectively in three laboratories, namely "id02", "ph01" and "vn01".

As for years of experience on soil analysis, analysts of "id01", "tho1" and "vn01" had just one-year

experience. A few outliers were detected in the laboratories "id01" and "tho1" but three and four outliers were detected for No. 031 and No. 032 respectively in "vn01". As for "vn01", change of analysts might be one of the possible causes for the outliers since few outliers were detected until the 4th project in the laboratory.

Analysts for Ex-base cations were different from ones for Ex-acidity in five laboratories, namely "cn01", "cn02", "cn03", "cn04", "id02", and "ph01".

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 titration of Ex-acidity were shown in Table 5.2. All the laboratories except "vn01" used AAS for measurement of Ex-Ca and Mg, and five laboratories used FEP for Ex-K and Na. Years in use of instruments were varied from 4 to 18 years old for AAS. All the laboratories except "ru01" applied Sr or La for measurement of Ex-Ca and Mg by AAS.

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. 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 14 days. NC suggested that repeat analyses should 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. Probably the information was not enough disseminated among laboratories.

Table 3.1. Data verified by Cochran-Grubbs methods: No. 031

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	4.8	3.5	3.05	0.80	0.18	0.06	2.65	2.12	0.54
	2nd	4.8	3.5	3.07	0.78	0.19	0.06	2.64	2.14	0.50
cn02	1st	5.0	4.0	1.56*g	0.42	0.19	0.06	3.20	2.87	0.33
	2nd	5.0	4.0	1.56*g	0.41	0.19	0.06	3.20	2.87	0.33
cn03	1st	4.8	3.8	2.83	0.87	0.23	0.06	4.73*c	3.42	1.31
	2nd	4.8	3.8	2.83	0.86	0.23	0.06	3.97*c	3.39	0.58
cn04	1st	4.7	3.8	3.25	0.71	0.43*g	0.11*c	3.40	1.98	1.40
	2nd	4.7	3.8	3.22	0.70	0.42*g	0.15*c	3.46	1.91	1.53
id01 emc	1st	4.7	3.8	3.18	0.85	0.27	0.08	3.87	2.32	1.57
	2nd	4.8	3.8	3.23	0.85	0.26	0.09	3.87	2.35	1.54
id02 csar	1st	4.6	3.8*c	3.65	0.81	0.14	0.12	2.70	2.13	0.55
	2nd	4.7	3.9*c	3.66	0.81	0.14	0.12	2.70	2.15	0.55
jp01	1st	4.7	3.9	3.23	0.66	0.21	0.06	4.74	3.74*c	0.99
	2nd	4.7	3.9	3.24	0.65	0.21	0.06	4.56	3.56*c	1.00
my01	1st	4.5	3.6	3.63*c	0.25	0.02*c	0.00*c	9.46*c	3.47*c	0.00
	2nd	4.4	3.6	2.89*c	0.25	0.38*c	0.12*c	8.93*c	3.12*c	0.69
mn01	1st	4.8	3.8	-	-	-	-	6.76*g	1.66	5.07*g
	2nd	4.8	3.8	-	-	-	-	6.76*g	1.66	5.33*g
ph01	1st	5.2*g	4.4*g	2.70	1.03	27.53*g	122.46*g	3.75	3.22	0.55
	2nd	5.2*g	4.4*g	2.70	1.03	27.53*g	122.46*g	3.77	3.22	0.55
kr01	1st	4.7	3.8	2.51*c	0.67	0.17	0.05	3.65	2.69	0.96
	2nd	4.7	3.8	2.59*c	0.68	0.16	0.05	3.48	2.62	0.85
ru01	1st	4.8	3.8	3.20	0.90	0.20	0.09	2.42	0.11*g	2.31*g
	2nd	4.8	3.8	3.22	0.89	0.20	0.08	2.42	0.11*g	2.31*g
th01	1st	4.0*g	3.8	2.35	0.30	0.11	0.09	4.05	3.77	0.25
	2nd	4.0*g	3.8	2.32	0.29	0.11	0.09	4.03	3.79	0.26
vn01	1st	4.6	3.8	0.64*g	0.85*c	0.23	0.26*g	3.02	2.32	0.68
	2nd	4.7	3.8	0.65*g	0.81*c	0.24	0.27*g	3.15	2.33	0.76

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. 032

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	4.8	3.5	0.61	0.68	0.34	0.11	20.14	10.64	9.50
	2nd	4.8	3.5	0.60	0.67	0.34	0.10	20.16	10.69	9.47
cn02	1st	4.8	4.1	0.12	0.39	0.41	0.08	25.13	14.58	10.55
	2nd	4.8	4.1	0.12	0.39	0.41	0.08	25.10	14.60	10.50
cn03	1st	4.7	3.8	0.15	0.51	0.42	0.11	28.75	14.70*c	14.05*c
	2nd	4.7	3.8	0.16	0.53	0.43	0.11	28.80	22.61*c	6.19*c
cn04	1st	4.6	3.7	0.49	0.78	0.87*g	0.22	26.71	24.24	2.28
	2nd	4.6	3.7	0.50	0.78	0.87*g	0.24	26.59	24.09	2.32
id01 emc	1st	4.7	3.7	0.79	0.04*g	0.48	0.13	28.28	21.45	6.84
	2nd	4.8	3.7	0.77	0.04*g	0.47	0.13	28.17	21.45	6.84
id02 csar	1st	4.4	3.9	0.60	0.73	0.31	0.19	23.98	21.44	2.48
	2nd	4.4	3.9	0.62	0.73	0.31	0.21	23.95	21.49	2.46
jp01	1st	4.8	3.9	0.49	0.73	0.44	0.11	25.87	25.46	0.41*c
	2nd	4.8	3.9	0.46	0.72	0.45	0.12	25.63	25.41	0.22*c
my01	1st	4.4	3.5	0.35	0.26*c	0.06*c	0.06	66.19*c	24.84	0.36*c
	2nd	4.3	3.5	0.34	0.20*c	0.39*c	0.09	60.15*c	24.84	0.00*c
mn01	1st	4.6	3.7	-	-	-	-	48.25*g	23.96	25.96*c
	2nd	4.6	3.7	-	-	-	-	48.29*g	24.11	25.81*c
ph01	1st	5.1	4.1	2.88*g	1.89*g	31.00*c	118.77*g	25.29	23.06	2.23
	2nd	5.1	4.1	2.88*g	1.89*g	30.95*c	118.77*g	25.29	23.06	2.23
kr01	1st	4.6	3.8	0.55	0.75	0.39	0.10	25.14	20.77	4.37
	2nd	4.6	3.8	0.57	0.75	0.39	0.10	25.29	20.90	4.39
ru01	1st	4.7	3.8	0.15	0.89	0.43	0.27	22.79	10.66	12.13
	2nd	4.7	3.8	0.14	0.91	0.44	0.25	22.79	10.66	12.13
th01	1st	3.7*g	3.6	0.24	0.66	0.29	0.14	30.24	28.50	1.91
	2nd	3.7*g	3.6	0.23	0.65	0.29	0.14	30.26	28.54	1.92
vn01	1st	4.5*c	3.7	3.45*c	1.29*c	0.47	0.54*g	23.87	23.24	0.31
	2nd	4.3*c	3.7	3.36*c	1.38*c	0.47	0.55*g	23.99	23.35	0.27

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 of Sample No. 031 and measurement condition

Lab.	No.031		No.032		mcf of No. 031	mcf of No. 032	Oven temp.	Drying period
		wt%		wt%			℃	hours
cn01	4.7	4.8	13.4	13.4	1.05	1.13	103±2	24
	4.8		13.4					
	4.8		13.4					
cn02	5.1	5.2	13.9	13.9	1.05	1.14	105	12
	5.2		13.9					
	5.2		13.9					
cn03	4.6	5.3	14.5	14.3	1.05	1.14	105	+
	5.7		14.3					
	5.5		14.3					
cn04	5.9	5.9	14.7	14.7	1.06	1.15	105	15
	5.9		14.7					
	6.0		14.7					
id01	3.7	3.7	11.5	11.4	1.04	1.11	105	2
	3.7		11.4					
	3.7		11.3					
id02	5.0	5.0	13.1	13.1	1.05	1.13	105	18
	5.0		13.1					
	5.0		13.0					
jp01	4.8	4.8	13.5	13.5	1.05	1.13	105	23
	4.7		13.5					
	4.7		13.5					
my01	3.3	3.7	8.8	7.8	1.04	1.08	105	24
	3.2		6.4					
	4.7		8.1					
mn01	4.7	4.7	13.9	13.8	1.05	1.14	105	5
	4.7		13.8					
	4.7		13.6					
ph01	4.7	4.8	13.5	13.5	1.05	1.13	105	24
	4.8		13.4					
	4.8		13.4					
kr01	5.1	5.0	13.8	13.8	1.05	1.14	105	24
	5.1		13.8					
	5.0		13.8					
ru01	4.7	4.7	13.4	13.4	1.05	1.13	105	5
	4.6		13.3					
	4.7		13.4					
th01	4.2	4.4	10.6	10.4	1.04	1.10	105	12
	4.4		10.3					
	4.7		10.3					
vn01	4.4	4.5	12.6	12.6	1.04	1.13	105	24
	4.5		12.8					
	4.5		12.5					
Average		4.8		12.8	1.05	1.13		

Note: mcf, moisture correction factor; +, not reported.

Table 5.1. Number and experience of analyst

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience		Number of analyst	Years of experience		
		Chemical	Soil		Chemical	Soil	
cn01	1	19	18	1	18	17	d
cn02	1	8	5	1	8	5	d
cn03	1	7	4	1	12	5	d
cn04	2	10/10	10/10	1	15	15	d
id01	1	6	1	1	6	1	s
id02	2[*1]	34/24	34/24	1	7	6	d
jp01	1	5	5	1	5	5	s
my01	2	3/3	2/2	2	3/3	2/2	s
mn01	-	-	-	1	10	10	-
ph01	2[*1]	14/14	14/14	1	27	27	d
kr01	1	8	6	1	8	6	s
ru01	1	6	6	1	6	6	s
th01	1	2	1	1	2	1	s
vn01	2[*1]	1/5	1/5	1	5	5	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		
		Instrument	Years*1	Instrument	Years		Instrument	Years	Instrument	Years			method	Size of burette (ml)	
														Capacity	Minimum graduate
cn01	No.031	AAS	5	AAS	5	La	AAS	5	AAS	5	La	Centrifuge	Titration	10	0.05
	No.032	AAS	5	AAS	5	La	AAS	5	AAS	5	La				
cn02	No.031	AAS	14	AAS	14	(Sr)	AAS	14	AAS	14	(Sr)	extractor	Titration	5	0.00125
	No.032	AAS	14	AAS	14	(Sr)	AAS	14	AAS	14	(Sr)	procedure			
cn03	No.031	AAS	3	AAS	3	La	AAS	3	AAS	3	La	Centrifuge	Titration	25	0.1
	No.032	AAS	3	AAS	3	La	AAS	3	AAS	3	La				
cn04	No.031	AAS	6	AAS	6	Sr	AAS	6	AAS	6	na	Centrifuge	Titration	25	0.1
	No.032	AAS	6	AAS	6	Sr	AAS	6	AAS	6	na				
id01	No.031	AAS	11	AAS	11	La	AAS	11	AAS	11	La	Centrifuge	Titration	50	0.05
	No.032	AAS	11	AAS	11	La	AAS	11	AAS	11	La				
id02	No.031	AAS	7	AAS	7	La	FEP	34	FEP	34	La	Percolation tube	Titration	50	0.01
	No.032	AAS	7	AAS	7	La	FEP	34	FEP	34	La				
jp01	No.031	AAS	18	AAS	18	Sr	FEP	17	FEP	17	na	Percolation tube	Titration	25/10	0.1/0.05
	No.032	AAS	18	AAS	18	Sr	FEP	17	FEP	17	na			(NaOH/HCl)	(NaOH/HCl)
my01	No.031	AAS	13	AAS	13	Sr	FEP	13	FEP	13	Sr	Percolation tube	Titration	50	0.1
	No.032	AAS	13	AAS	13	Sr	FEP	13	FEP	13	Sr				
mn01	No.031	-	-	-	-	-	-	-	-	-	-	-	Titration	25	0.1
	No.032	-	-	-	-	-	-	-	-	-	-				
ph01	No.031	AAS	13	AAS	13	Sr	AAS	13	AAS	13	Sr	Buchner funnel	Titration	50	0.01
	No.032	AAS	13	AAS	13	Sr	AAS	13	AAS	13	Sr				
kr01	No.031	AAS	4	AAS	4	Sr	AAS	4	AAS	4	La	Buchner funnel	Titration	25	0.05
	No.032	AAS	4	AAS	4	Sr	AAS	4	AAS	4	La				
ru01	No.031	AAS	20	AAS	20	na	FEP	20	FEP	20	na	Percolation tube	Titration	50/25	0.1/0.05
	No.032	AAS	20	AAS	20	na	FEP	20	FEP	20	na				
th01	No.031	AAS	7	AAS	7	(Sr)	AAS	7	AAS	7	(Cs)	Percolation tube	Titration	50	0.05
	No.032	AAS	7	AAS	7	(Sr)	AAS	7	AAS	7	(Cs)				
vn01	No.031	Titration		Titration		na	FEP	7	FEP	6	na	Buchner funnel	Titration	10	0.1
	No.032	Titration		Titration		na	FEP	7	FEP	6	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	Interval*3	Date*1	Analysis*2	Interval*3	Date*1	Analysis*2	Interval*3	Date*1	Analysis*2	Interval*3
			Days			Days			Days			Days	
cn01	1st	27-Feb	1	7	28-Feb	2	7	28-Feb	2	7	1-Mar	1	8
	2nd	5-Mar	1		6-Mar	2		6-Mar	2		9-Mar	1	
cn02	1st	18-Feb	3	2	18-Feb	3	2	18-Feb	3	2	18-Feb	3	2
	2nd	20-Feb	3		20-Feb	3		20-Feb	3		20-Feb	3	
cn03	1st	24-Feb	1	0	24-Feb	1	0	24-Feb	1	0	16-Mar	2	0
	2nd	24-Feb	1		24-Feb	1		24-Feb	1		16-Mar	2	
cn04	1st	10-Feb	1	7	18-Feb	2	9	13-Feb	2	7	17-Feb	2	7
	2nd	17-Feb	1		27-Feb	2		20-Feb	2		24-Feb	2	
id01	1st	19-Jan	1	1	23-Jan	3	0	23-Jan	3	0	19-Jan	1	2
emc	2nd	20-Jan	1		23-Jan	3		23-Jan	3		21-Jan	2	
id02	1st	+			19-Feb	15	0	19-Feb	15	0	19-Feb	15	0
	2nd	+			19-Feb	15		19-Feb	15		19-Feb	15	
jp01	1st	4-Mar	1	12	9-Mar	2	10	9-Mar	2	10	16-Mar	2	4
	2nd	16-Mar	1		19-Mar	3		19-Mar	3		20-Mar	2	
my01	1st	29-Mar	1	1	6-Apr	2	11	6-Apr	2	11	1-Apr	2	18
	2nd	30-Mar	1		17-Apr	2		17-Apr	2		19-Apr	1	
mn01	1st	4-Mar	1	0	-	-	-	-	-	-	10-Mar	1	1
	2nd	4-Mar	1		-	-		-	-		11-Mar	1	
ph01	1st	15-Mar	1	3	12-Mar	4	7	12-Mar	4	7	8-Mar	1	4
	2nd	18-Mar	1		19-Mar	4		19-Mar	4		12-Mar	1	
kr01	1st	18-Feb	1	3	25-Feb	2	10	25-Feb	2	10	3-Mar	1	5
	2nd	21-Feb	1		6-Mar	2		6-Mar	2		8-Mar	1	
ru01	1st	3-Mar	1	1	6-Mar	2	2	6-Mar	2	2	6-Mar	2	2
	2nd	4-Mar	1		8-Mar	2		8-Mar	2		8-Mar	2	
th01	1st	19-Jan	1	12	25-Jan	2	14	25-Jan	2	14	20-Jan	1	14
	2nd	31-Jan	1		8-Feb	2		8-Feb	2		3-Feb	1	
vn01	1st	12-Apr	1	0	16-Apr	5	0	16-Apr	5	0	22-Apr	7	0
	2nd	12-Apr	1		16-Apr	5		16-Apr	5		22-Apr	7	

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

Table of 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.

1) Repeatability-precision

Repeatability standard deviations were relatively small for most of the parameters in the verified data, and CVs of the most parameters were smaller than 5%. Especially CVs of pH(H_2O) and pH(KCl) in both samples and CV of Ex-Acidity in No. 032 were smaller than 1%. CVs of Ex-Ca in No. 031 and Ex-Mg in No. 032 were lower than 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) and pH(KCl) in both samples, CVs of Ex-Ca, Mg and Al in No. 031, and CV of Ex-acidity and Al in No. 032 were lower than 1%.

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 relatively large but smaller than before; CVs were 11 - 55% for Ex-base cations, acidity and Al. CVs of Ex-Ca was the smallest in No. 031 and Ex-acidity was the smallest in No. 032. The sample No. 031 was relatively Ca-rich soil and No. 032 was strong acidic soil. It seems that level of content might affect the precisions. However, “inter-laboratories precision” was probably improved even if the content level was taken into account.

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. 031									No. 032								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H	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	14	14	13	13	13	13	14	14	14
Total sum of square	156737	103684	45331	2955	32598	549822	119709	45403	9968	148842	100299	4202	3326	46820	525741	6276177	3062500	285509
ST/lmd	1866	1234	581	38	418	7049	1425	541	119	1772	1194	54	43	600	6740	74716	36458	3399
Number of Laboratories	14	14	13	13	13	13	14	14	14	14	14	13	13	13	13	14	14	14
Number of Data	84	84	78	78	78	78	84	84	84	84	84	78	78	78	78	84	84	84
Total sum	395.9	322.0	212.91	54.36	180.55	741.50	345.99	213.08	99.84	385.8	316.7	64.82	57.67	216.38	725.08	2505.23	1750.00	534.33
Total average	4.7	3.8	2.73	0.70	2.31	9.51	4.12	2.54	1.19	4.6	3.8	0.83	0.74	2.77	9.30	29.82	20.83	6.36
Sum of square inter-laboratories (S_R)	5.5	3.1	48.77	4.09	4134.26	82935.47	258.06	72.75	129.24	8.3	2.7	79.63	15.78	5170.47	77900.90	10552.77	2280.31	3840.40
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.82	0.00	0.20	0.02	1.41	0.25	1.68	0.1	0.0	0.02	0.02	0.16	0.00	55.04	94.06	92.96
Sum of square repeatablility (S_r)	0.0	0.0	0.23	0.01	0.03	6.28	0.44	1.04	1.66	0.0	0.0	0.13	0.08	0.10	7.68	3.72	12.32	8.72
Total sum of square (S_T)	5.6	3.1	49.81	4.10	4134.48	82941.77	259.91	74.04	132.58	8.4	2.7	79.78	15.87	5170.73	77908.59	10611.53	2386.68	3942.09
Inter-laboratories degree of freedom (ϕ_R)	13	13	12	12	12	12	13	13	13	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	14	14	13	13	13	13	14	14	14
Repeatability degree of freedom (ϕ_r)	56	56	52	52	52	52	56	56	56	56	56	52	52	52	52	56	56	56
Total degree of freedom (ϕ_T)	83	83	77	77	77	77	83	83	83	83	83	77	77	77	77	83	83	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.42	0.24	4.064	0.341	344.522	6911.289	19.850	5.597	9.942	0.64	0.21	6.636	1.315	430.873	6491.742	811.752	175.408	295.416
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.063	0.000	0.015	0.002	0.101	0.018	0.120	0.00	0.00	0.001	0.001	0.013	0.000	3.931	6.718	6.640
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.004	0.000	0.000	0.121	0.008	0.019	0.030	0.00	0.00	0.003	0.001	0.002	0.148	0.066	0.220	0.156
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.07	0.04	0.667	0.057	57.418	1151.881	3.292	0.930	1.637	0.11	0.03	1.106	0.219	71.810	1081.957	134.637	28.115	48.129
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	0.020	0.000	0.005	-0.040	0.031	0.000	0.030	0.00	0.00	0.000	0.000	0.004	-0.049	1.288	2.166	2.161
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.004	0.000	0.000	0.121	0.008	0.019	0.030	0.00	0.00	0.003	0.001	0.002	0.148	0.066	0.220	0.156
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.3	0.2	0.82	0.24	7.58	33.94	1.82	0.97	1.29	0.3	0.2	1.05	0.47	8.47	32.89	11.63	5.41	7.02
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.15	0.01	0.07	0.02	0.18	0.08	0.20	0.0	0.0	0.02	0.02	0.06	0.01	1.14	1.50	1.49
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.07	0.01	0.02	0.35	0.09	0.14	0.17	0.0	0.0	0.05	0.04	0.04	0.38	0.26	0.47	0.39
Inter-laboratories precision CV (%)	5.6	5.2	30.15	34.20	327.36	357.02	44.16	38.07	108.30	7.1	4.9	126.55	63.31	305.48	353.85	39.00	25.95	110.31
Within-laboratory precision CV (%)	0.6	0.2	5.32	1.40	3.06	0.25	4.45	3.02	16.83	0.8	0.2	2.48	2.92	2.34	0.09	3.84	7.18	23.39
Repeatability precision CV (%)	0.6	0.8	2.42	1.69	0.95	3.66	2.16	5.38	14.47	0.6	0.3	6.06	5.21	1.56	4.14	0.86	2.25	6.20
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.74	0.55	2.304	0.667	21.217	95.030	5.093	2.704	3.604	0.91	0.52	2.945	1.311	23.728	92.101	32.568	15.139	19.647
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.08	0.02	0.407	0.027	0.198	0.067	0.514	0.214	0.560	0.11	0.02	0.058	0.060	0.182	0.024	3.205	4.190	4.166
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.10	0.10	0.218	0.039	0.073	1.147	0.293	0.450	0.568	0.09	0.04	0.166	0.127	0.142	1.269	0.851	1.548	1.302

Table 6.2. Analysis of variance for the verified data

Statistics	No. 031									No. 032								
	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of lab	12	12	9	12	10	9	11	11	12	12	14	11	9	10	11	12	13	10
Total sum of square	116008	74256	27159	2438	135	16	50257	29162	3001	113704	100299	735	1348	574	84	3373100	2683306	99414
ST/lmd	1611	1031	503	34	2	0	761	442	42	1579	1194	11	25	10	1	46849	34401	1657
Number of Laboratories	12	12	9	12	10	9	11	11	12	12	14	11	9	10	11	12	13	10
Number of Data	72	72	54	72	60	54	66	66	72	72	84	66	54	60	66	72	78	60
Total sum	340.6	272.5	164.80	49.38	11.60	4.00	224.18	170.77	54.78	337.2	316.7	27.11	36.72	23.96	9.19	1836.60	1638.08	315.30
Total average	4.7	3.8	3.05	0.69	0.19	0.07	3.40	2.59	0.76	4.7	3.8	0.41	0.68	0.40	0.14	25.51	21.00	5.26
Sum of square inter-laboratories (S_R)	1.1	1.0	7.02	3.98	0.11	0.02	27.06	26.40	11.98	2.7	2.7	3.03	1.07	0.23	0.23	498.88	2249.60	946.02
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.01	0.00	0.00	0.00	0.13	0.02	1.57	0.0	0.0	0.00	0.00	0.00	0.00	0.19	0.13	0.01
Sum of square repeatablility (S_r)	0.0	0.0	0.08	0.01	0.00	0.00	0.27	0.31	1.44	0.0	0.0	0.05	0.00	0.00	0.00	1.67	6.10	1.25
Total sum of square (S_T)	1.2	1.0	7.11	3.98	0.11	0.03	27.46	26.73	14.99	2.7	2.7	3.09	1.08	0.23	0.24	500.74	2255.82	947.27
Inter-laboratories degree of freedom (ϕ_R)	11	11	8	11	9	8	10	10	11	11	13	10	8	9	10	11	12	9
Within-laboratory degree of freedom (ϕ_{RW})	12	12	9	12	10	9	11	11	12	12	14	11	9	10	11	12	13	10
Repeatability degree of freedom (ϕ_r)	48	48	36	48	40	36	44	44	48	48	56	44	36	40	44	48	52	40
Total degree of freedom (ϕ_T)	71	71	53	71	59	53	65	65	71	71	83	65	53	59	65	71	77	59
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.10	0.09	0.878	0.361	0.012	0.003	2.706	2.640	1.089	0.24	0.21	0.303	0.134	0.026	0.023	45.353	187.467	105.113
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.001	0.000	0.000	0.000	0.011	0.002	0.131	0.00	0.00	0.000	0.000	0.000	0.000	0.016	0.010	0.001
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.002	0.000	0.000	0.000	0.006	0.007	0.030	0.00	0.00	0.001	0.000	0.000	0.000	0.035	0.117	0.031
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.02	0.01	0.146	0.060	0.002	0.001	0.449	0.440	0.160	0.04	0.03	0.050	0.022	0.004	0.004	7.556	31.243	17.519
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	0.002	-0.002	0.034	0.00	0.00	0.000	0.000	0.000	0.000	-0.006	-0.036	-0.010
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.002	0.000	0.000	0.000	0.006	0.007	0.030	0.00	0.00	0.001	0.000	0.000	0.000	0.035	0.117	0.031
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.1	0.1	0.38	0.25	0.05	0.02	0.67	0.66	0.43	0.2	0.2	0.22	0.15	0.07	0.06	2.75	5.59	4.19
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.02	0.01	0.00	0.00	0.06	0.02	0.21	0.0	0.0	0.01	0.01	0.01	0.01	0.07	0.06	0.02
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.05	0.01	0.01	0.01	0.08	0.08	0.17	0.0	0.0	0.03	0.01	0.01	0.01	0.19	0.34	0.18
Inter-laboratories precision CV (%)	2.8	3.2	12.53	35.78	23.57	30.44	19.77	25.64	55.99	4.3	4.9	54.71	21.95	16.34	44.54	10.78	26.62	79.65
Within-laboratory precision CV (%)	0.6	0.2	0.54	0.89	2.25	3.35	1.82	0.93	27.48	0.6	0.2	2.82	1.17	1.45	6.60	0.29	0.27	0.38
Repeatability precision CV (%)	0.6	0.7	1.53	1.79	3.72	10.39	2.32	3.26	22.79	0.5	0.3	8.48	1.66	2.55	6.73	0.73	1.63	3.36
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.37	0.34	1.071	0.687	0.128	0.063	1.880	1.857	1.193	0.56	0.52	0.629	0.418	0.183	0.174	7.698	15.651	11.720
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.09	0.02	0.046	0.017	0.012	0.007	0.173	0.067	0.585	0.09	0.02	0.032	0.022	0.016	0.026	0.204	0.159	0.056
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.10	0.09	0.154	0.040	0.024	0.025	0.260	0.278	0.572	0.08	0.04	0.115	0.037	0.034	0.031	0.615	1.130	0.583

4. DISCUSSION

In the 5th project, the following two objectives were raised:

i) To avoid possible mistakes on reporting process by using digital formats

ii) To improve inter-laboratories-precision by following standard methods such as addition of Sr/La

By using digital formats, no obvious calculation mistake was found in the data. However, some outliers have 100 times larger than averages and some have low within-laboratory reproducibility. It was suggested that quality control within the respective laboratories does not work as appropriate since some values could be judged as outliers by general knowledge of soil science. Standard operating procedures and reporting system should be elaborated.

Repeatability precisions and within-laboratory-reproducibility precisions were significantly small in some Ex-cations; e.g. lower than 2%. These precisions were quite better than ones of the previous projects. The precisions within the respective laboratories were improved probably by standard procedures suggested in this project. This high within-laboratory-precision might affect inter-laboratories precisions. The inter-laboratories precisions were still relatively large but clearly improved compared with the previous projects.

5. ACKNOWLEDGMENT

ADORC wishes to thank Niigata 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 (2001): Report of the inter-laboratory comparison project 1999 on soil.

5) Acid Deposition and Oxidant Research Center (2001): 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. Akiomi TAKAHASHI	Ecological Impact Research Department/ Data Management Department E-mail: takahashi@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 2.1. Entire data of pH in Sample No. 031

	pH(H_2O)			pH(KCl)		
Lab.	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat
cn01	4.8	4.8 (0.0)	4.8	3.5	3.5 (0.1)	3.5
			4.8			3.5
			4.8			3.6
		4.8 (0.0)	4.8		3.5 (0.1)	3.5
			4.8			3.5
			4.8			3.6
cn02	5.0	5.0 (0.0)	5.0	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
cn03	4.8	4.8 (0.0)	4.8	3.8	3.8 (0.0)	3.8
			4.8			3.8
			4.8			3.8
		4.8 (0.0)	4.8		3.8 (0.0)	3.8
			4.8			3.8
			4.8			3.8
cn04	4.7	4.7 (0.0)	4.7	3.8	3.8 (0.1)	3.8
			4.7			3.8
			4.7			3.7
		4.7 (0.0)	4.7		3.8 (0.1)	3.7
			4.7			3.8
			4.7			3.8
id01	4.8	4.7 (0.0)	4.7	3.8	3.8 (0.0)	3.8
emc			4.7			3.8
			4.7			3.8
		4.8 (0.0)	4.8		3.8 (0.0)	3.8
			4.8			3.8
			4.8			3.8
id02	4.7	4.6 (0.1)	4.7	3.9	3.8 (0.1)	3.9
csar			4.6			3.8
			4.6			3.8
		4.7 (0.1)	4.7		3.9 (0.1)	3.9
			4.6			3.8
			4.7			3.9
jp01	4.7	4.7 (0.0)	4.7	3.9	3.9 (0.0)	3.9
			4.7			3.9
			4.7			3.9
		4.7 (0.0)	4.7		3.9 (0.0)	3.9
			4.7			3.9
			4.7			3.9
my01	4.5	4.5 (0.0)	4.5	3.6	3.6 (0.0)	3.6
			4.5			3.6
			4.5			3.6
		4.4 (0.0)	4.4		3.6 (0.0)	3.6
			4.4			3.6
			4.4			3.6
mn01	4.8	4.8 (0.0)	4.8	3.8	3.8 (0.0)	3.8
			4.8			3.8
			4.8			3.8
		4.8 (0.0)	4.8		3.8 (0.0)	3.8
			4.8			3.8
			4.8			3.8
ph01	5.2	5.2 (0.0)	5.2	4.4	4.4 (0.0)	4.4
			5.2			4.4
			5.2			4.4
		5.2 (0.0)	5.2		4.4 (0.0)	4.4
			5.2			4.4
			5.2			4.4
kr01	4.7	4.7 (0.1)	4.7	3.8	3.8 (0.0)	3.8
			4.6			3.8
			4.7			3.8
		4.7 (0.1)	4.6		3.8 (0.0)	3.8
			4.7			3.8
			4.7			3.8
ru01	4.8	4.8 (0.0)	4.8	3.8	3.8 (0.0)	3.8
			4.8			3.8
			4.8			3.8
		4.8 (0.0)	4.8		3.8 (0.0)	3.8
			4.8			3.8
			4.8			3.8
th01	4.0	4.0 (0.1)	4.1	3.8	3.8 (0.0)	3.8
			4.0			3.8
			4.0			3.8
		4.0 (0.0)	4.0		3.8 (0.0)	3.8
			4.0			3.8
			4.0			3.8
vn01	4.7	4.6 (0.1)	4.6	3.8	3.8 (0.0)	3.8
			4.6			3.8
			4.7			3.8
		4.7 (0.1)	4.7		3.8 (0.1)	3.8
			4.7			3.9
			4.6			3.8

Appendix 2.2. Entire data of exchangeable base cations in Sample No. 031

	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
Lab.	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat
cn01	3.06	3.05 (0.04)	3.09	0.79	0.80 (0.01)	0.80	0.19	0.18 (0.01)	0.18	0.06	0.06 (0.00)	0.06
			3.04			0.79			0.19			0.06
			3.02			0.80			0.18			0.06
		3.07 (0.03)	3.07		0.78 (0.01)	0.78		0.19 (0.01)	0.18		0.06 (0.00)	0.06
			3.09			0.79			0.19			0.06
			3.04			0.78			0.19			0.06
cn02	1.56	1.56 (0.01)	1.56	0.42	0.42 (0.01)	0.41	0.19	0.19 (0.00)	0.19	0.06	0.06 (0.00)	0.06
			1.56			0.42			0.19			0.06
			1.57			0.42			0.19			0.06
		1.56 (0.00)	1.56		0.41 (0.00)	0.41		0.19 (0.00)	0.19		0.06 (0.00)	0.06
			1.56			0.41			0.19			0.06
			1.56			0.41			0.19			0.06
cn03	2.83	2.83 (0.06)	2.77	0.87	0.87 (0.01)	0.86	0.23	0.23 (0.01)	0.22	0.06	0.06 (0.00)	0.06
			2.83			0.88			0.24			0.06
			2.88			0.88			0.22			0.06
		2.83 (0.07)	2.90		0.86 (0.02)	0.88		0.23 (0.02)	0.24		0.06 (0.00)	0.06
			2.82			0.85			0.23			0.06
			2.77			0.84			0.21			0.06
cn04	3.24	3.25 (0.09)	3.35	0.71	0.71 (0.01)	0.72	0.43	0.43 (0.01)	0.44	0.13	0.11 (0.01)	0.12
			3.23			0.70			0.43			0.10
			3.17			0.70			0.42			0.10
		3.22 (0.02)	3.25		0.70 (0.01)	0.71		0.42 (0.00)	0.42		0.15 (0.03)	0.15
			3.21			0.70			0.42			0.12
			3.21			0.70			0.42			0.18
id01	3.21	3.18 (0.01)	3.17	0.85	0.85 (0.01)	0.85	0.27	0.27 (0.00)	0.27	0.09	0.08 (0.00)	0.08
			3.18			0.85			0.27			0.08
			3.19			0.86			0.27			0.08
		3.23 (0.01)	3.24		0.85 (0.01)	0.86		0.26 (0.00)	0.26		0.09 (0.01)	0.09
			3.22			0.84			0.26			0.08
			3.22			0.85			0.26			0.09
id02	3.66	3.65 (0.01)	3.65	0.81	0.81 (0.01)	0.81	0.14	0.14 (0.00)	0.14	0.12	0.12 (0.01)	0.12
			3.65			0.80			0.14			0.11
			3.66			0.81			0.14			0.12
		3.66 (0.01)	3.67		0.81 (0.01)	0.81		0.14 (0.01)	0.14		0.12 (0.01)	0.13
			3.65			0.81			0.15			0.12
			3.66			0.80			0.14			0.12
jp01	3.24	3.23 (0.06)	3.27	0.66	0.66 (0.03)	0.64	0.21	0.21 (0.01)	0.21	0.06	0.06 (0.02)	0.05
			3.17			0.69			0.22			0.08
			3.26			0.65			0.21			0.06
		3.24 (0.05)	3.30		0.65 (0.02)	0.65		0.21 (0.00)	0.21		0.06 (0.00)	0.06
			3.20			0.66			0.21			0.06
			3.23			0.63			0.21			0.06
my01	3.26	3.63 (0.07)	3.56	0.25	0.25 (0.01)	0.26	0.19	-0.01 (0.06)	-0.08	0.05	-0.02 (0.03)	0.01
			3.70			0.25			0.03			-0.03
			3.62			0.24			0.03			-0.04
		2.89 (0.25)	3.18		0.25 (0.01)	0.26		0.38 (0.00)	0.38		0.12 (0.01)	0.11
			2.70			0.25			0.38			0.12
			2.80			0.24			0.38			0.12
mn01												
ph01	2.70	2.70 (0.07)	2.74	1.03	1.03 (0.00)	1.03	27.53	27.53 (0.08)	27.49	122.46	122.46 (1.25)	123.91
			2.74			1.03			27.62			121.74
			2.62			1.03			27.49			121.74
		2.70 (0.07)	2.74		1.03 (0.00)	1.03		27.53 (0.08)	27.62		122.46 (1.25)	123.91
			2.74			1.03			27.49			121.74
			2.62			1.03			27.49			121.74
kr01	2.55	2.51 (0.04)	2.53	0.68	0.67 (0.02)	0.65	0.17	0.17 (0.02)	0.16	0.05	0.05 (0.01)	0.05
			2.54			0.69			0.17			0.04
			2.47			0.67			0.19			0.05
		2.59 (0.06)	2.53		0.68 (0.01)	0.68		0.16 (0.02)	0.15		0.05 (0.01)	0.05
			2.64			0.68			0.16			0.04
			2.60			0.67			0.18			0.05
ru01	3.21	3.20 (0.07)	3.21	0.90	0.90 (0.03)	0.90	0.20	0.20 (0.01)	0.20	0.09	0.09 (0.02)	0.10
			3.27			0.87			0.20			0.09
			3.13			0.92			0.21			0.07
		3.22 (0.01)	3.21		0.89 (0.02)	0.88		0.20 (0.01)	0.20		0.08 (0.02)	0.10
			3.21			0.91			0.20			0.09
			3.23			0.88			0.19			0.06
th01	2.34	2.35 (0.02)	2.37	0.30	0.30 (0.01)	0.30	0.11	0.11 (0.00)	0.11	0.09	0.09 (0.00)	0.09
			2.34			0.30			0.11			0.09
			2.35			0.31			0.11			0.09
		2.32 (0.02)	2.32		0.29 (0.01)	0.29		0.11 (0.00)	0.11		0.09 (0.00)	0.09
			2.30			0.29			0.11			0.09
			2.33			0.30			0.11			0.09
vn01	0.65	0.64 (0.00)	0.64	0.83	0.85 (0.00)	0.85	0.24	0.23 (0.00)	0.23	0.27	0.26 (0.00)	0.26
			0.64			0.85			0.23			0.26
			0.64			0.85			0.23			0.26
		0.65 (0.00)	0.65		0.81 (0.00)	0.81		0.24 (0.00)	0.24		0.27 (0.00)	0.27
			0.65			0.81			0.24			0.27
			0.65			0.81			0.24			0.27

Appendix 2.3. Entire data of exchangeable acidity and acid cations in Sample No. 031

	Ex-acidity			Ex-Al			Ex-H		
Lab.	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat
cn01	2.65	2.65 (0.03)	2.67	2.13	2.12 (0.05)	2.17	0.52	0.54 (0.04)	0.51
			2.62			2.09			0.53
			2.67			2.09			0.59
		2.64 (0.03)	2.67		2.14 (0.09)	2.24		0.50 (0.06)	0.43
			2.62			2.09			0.53
			2.62			2.09			0.53
cn02	3.20	3.20 (0.01)	3.20	2.87	2.87 (0.00)	2.87	0.33	0.33 (0.01)	0.33
			3.20			2.87			0.33
			3.19			2.87			0.32
		3.20 (0.00)	3.20		2.87 (0.01)	2.87		0.33 (0.01)	0.33
			3.20			2.87			0.33
			3.20			2.86			0.34
cn03	4.35	4.73 (0.11)	4.84	3.41	3.42 (0.06)	3.49	0.95	1.31 (0.05)	1.35
			4.72			3.41			1.31
			4.63			3.37			1.26
		3.97 (0.16)	3.79		3.39 (0.16)	3.20		0.58 (0.02)	0.59
			4.08			3.49			0.59
			4.04			3.48			0.56
cn04	3.43	3.40 (0.17)	3.22	1.95	1.98 (0.33)	2.33	1.47	1.40 (0.49)	0.86
			3.45			1.91			1.52
			3.54			1.69			1.82
		3.46 (0.31)	3.26		1.91 (0.00)	1.91		1.53 (0.31)	1.33
			3.31			1.91			1.38
			3.82			1.91			1.89
id01	3.87	3.87 (0.00)	3.87	2.34	2.32 (0.05)	2.35	1.56	1.57 (0.05)	1.54
			3.87			2.26			1.62
			3.87			2.35			1.54
		3.87 (0.00)	3.87		2.35 (0.05)	2.39		1.54 (0.05)	1.49
			3.87			2.35			1.54
			3.87			2.30			1.58
id02	2.70	2.70 (0.02)	2.72	2.14	2.13 (0.02)	2.14	0.55	0.55 (0.04)	0.58
			2.68			2.10			0.50
			2.70			2.14			0.56
		2.70 (0.02)	2.70		2.15 (0.02)	2.14		0.55 (0.01)	0.56
			2.72			2.18			0.54
			2.68			2.14			0.54
jp01	4.65	4.74 (0.01)	4.73	3.65	3.74 (0.07)	3.66	1.00	0.99 (0.06)	1.06
			4.74			3.76			0.97
			4.74			3.79			0.95
		4.56 (0.03)	4.54		3.56 (0.02)	3.55		1.00 (0.01)	0.99
			4.55			3.55			1.00
			4.59			3.58			1.01
my01	9.20	9.46 (0.16)	9.55	3.30	3.47 (0.60)	4.16	0.17	-0.35 (0.60)	-1.04
			9.27			3.12			0.00
			9.55			3.12			0.00
		8.93 (0.15)	9.10		3.12 (0.00)	3.12		0.69 (0.60)	1.04
			8.84			3.12			1.04
			8.84			3.12			0.00
mn01	6.76	6.76 (0.00)	6.76	1.66	1.66 (0.00)	1.66	5.20	5.07 (0.23)	5.20
			6.76			1.66			4.80
			6.76			1.66			5.20
		6.76 (0.00)	6.76		1.66 (0.00)	1.66		5.33 (0.23)	5.60
			6.76			1.66			5.20
			6.76			1.66			5.20
ph01	3.76	3.75 (0.01)	3.76	3.22	3.22 (0.01)	3.23	0.55	0.55 (0.01)	0.56
			3.76			3.21			0.56
			3.74			3.21			0.54
		3.77 (0.01)	3.78		3.22 (0.01)	3.23		0.55 (0.01)	0.54
			3.76			3.21			0.54
			3.76			3.21			0.56
kr01	3.57	3.65 (0.07)	3.57	2.66	2.69 (0.02)	2.67	0.91	0.96 (0.06)	0.90
			3.70			2.69			1.01
			3.68			2.71			0.97
		3.48 (0.01)	3.47		2.62 (0.04)	2.60		0.85 (0.02)	0.86
			3.47			2.60			0.86
			3.49			2.67			0.82
ru01	2.42	2.42 (0.00)	2.42	0.11	0.11 (0.00)	0.11	2.31	2.31 (0.00)	2.31
			2.42			0.11			2.31
			2.42			0.11			2.31
		2.42 (0.00)	2.42		0.11 (0.00)	0.11		2.31 (0.00)	2.31
			2.42			0.11			2.31
			2.42			0.11			2.31
th01	4.04	4.05 (0.01)	4.06	3.78	3.77 (0.01)	3.78	0.26	0.25 (0.00)	0.25
			4.04			3.76			0.25
			4.06			3.78			0.25
		4.03 (0.01)	4.03		3.79 (0.01)	3.80		0.26 (0.00)	0.26
			4.02			3.78			0.26
			4.04			3.80			0.26
vn01	3.09	3.02 (0.05)	2.97	2.33	2.32 (0.03)	2.30	0.72	0.68 (0.02)	0.67
			3.06			2.30			0.70
			3.02			2.35			0.67
		3.15 (0.05)	3.11		2.33 (0.03)	2.35		0.76 (0.05)	0.70
			3.14			2.30			0.79
			3.20			2.35			0.79

Appendix 3.1. Entire data of pH in Sample No. 032

	pH(H_2O)			pH(KCl)		
Lab.	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat
cn01	4.8	4.8 (0.0)	4.8	3.5	3.5 (0.0)	3.5
			4.8			3.5
			4.8			3.5
		4.8 (0.0)	4.8		3.5 (0.0)	3.5
			4.8			3.5
			4.8			3.5
cn02	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
cn03	4.7	4.7 (0.0)	4.7	3.8	3.8 (0.0)	3.8
			4.7			3.8
			4.7			3.8
		4.7 (0.0)	4.7		3.8 (0.0)	3.8
			4.7			3.8
			4.7			3.8
cn04	4.6	4.6 (0.0)	4.6	3.7	3.7 (0.0)	3.7
			4.6			3.7
			4.6			3.7
		4.6 (0.0)	4.6		3.7 (0.0)	3.7
			4.6			3.7
			4.6			3.7
id01	4.8	4.7 (0.0)	4.7	3.7	3.7 (0.1)	3.6
emc			4.7			3.7
			4.7			3.7
		4.8 (0.0)	4.8		3.7 (0.0)	3.7
			4.8			3.7
			4.8			3.7
id02	4.4	4.4 (0.0)	4.4	3.9	3.9 (0.0)	3.9
csar			4.4			3.9
			4.4			3.9
		4.4 (0.1)	4.5		3.9 (0.0)	3.9
			4.4			3.9
			4.4			3.9
jp01	4.8	4.8 (0.0)	4.8	3.9	3.9 (0.0)	3.9
			4.8			3.9
			4.8			3.9
		4.8 (0.0)	4.8		3.9 (0.0)	3.9
			4.8			3.9
			4.8			3.9
my01	4.4	4.4 (0.1)	4.3	3.5	3.5 (0.0)	3.5
			4.4			3.5
			4.4			3.5
		4.3 (0.1)	4.3		3.5 (0.0)	3.5
			4.3			3.5
			4.2			3.5
mn01	4.6	4.6 (0.0)	4.6	3.7	3.7 (0.0)	3.7
			4.6			3.7
			4.6			3.7
		4.6 (0.1)	4.7		3.7 (0.0)	3.7
			4.6			3.7
			4.6			3.7
ph01	5.1	5.1 (0.0)	5.1	4.1	4.1 (0.0)	4.1
			5.1			4.1
			5.1			4.1
		5.1 (0.0)	5.1		4.1 (0.0)	4.1
			5.1			4.1
			5.1			4.1
kr01	4.6	4.6 (0.0)	4.6	3.8	3.8 (0.0)	3.8
			4.6			3.8
			4.6			3.8
		4.6 (0.0)	4.6		3.8 (0.0)	3.8
			4.6			3.8
			4.6			3.8
ru01	4.7	4.7 (0.0)	4.7	3.8	3.8 (0.0)	3.8
			4.7			3.8
			4.7			3.8
		4.7 (0.0)	4.7		3.8 (0.0)	3.8
			4.7			3.8
			4.7			3.8
th01	3.7	3.7 (0.0)	3.7	3.6	3.6 (0.0)	3.6
			3.7			3.6
			3.7			3.6
		3.7 (0.0)	3.7		3.6 (0.0)	3.6
			3.7			3.6
			3.7			3.6
vn01	4.4	4.5 (0.1)	4.4	3.7	3.7 (0.0)	3.7
			4.5			3.7
			4.5			3.7
		4.3 (0.1)	4.3		3.7 (0.0)	3.7
			4.4			3.7
			4.3			3.7

Appendix 3.2. Entire data of exchangeable base cations in Sample No. 032

	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
Lab.	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat
cn01	0.61	0.61 (0.01)	0.60	0.68	0.68 (0.02)	0.70	0.34	0.34 (0.02)	0.36	0.11	0.11 (0.01)	0.11
			0.62			0.67			0.33			0.10
			0.61			0.66			0.34			0.11
		0.60 (0.01)	0.60		0.67 (0.02)	0.67		0.34 (0.01)	0.34		0.10 (0.00)	0.10
			0.61			0.69			0.35			0.10
			0.59			0.66			0.33			0.10
cn02	0.12	0.12 (0.00)	0.12	0.39	0.39 (0.00)	0.39	0.41	0.41 (0.01)	0.41	0.08	0.08 (0.00)	0.08
			0.12			0.39			0.42			0.08
			0.12			0.39			0.41			0.08
		0.12 (0.00)	0.12		0.39 (0.01)	0.39		0.41 (0.00)	0.41		0.08 (0.00)	0.08
			0.12			0.39			0.41			0.08
			0.12			0.38			0.41			0.08
cn03	0.16	0.15 (0.01)	0.14	0.52	0.51 (0.01)	0.50	0.43	0.42 (0.01)	0.41	0.11	0.11 (0.01)	0.11
			0.15			0.51			0.43			0.11
			0.15			0.51			0.41			0.10
		0.16 (0.01)	0.15		0.53 (0.02)	0.51		0.43 (0.02)	0.41		0.11 (0.01)	0.11
			0.16			0.54			0.44			0.11
			0.16			0.55			0.45			0.12
cn04	0.50	0.49 (0.03)	0.47	0.78	0.78 (0.01)	0.78	0.87	0.87 (0.00)	0.87	0.23	0.22 (0.03)	0.19
			0.53			0.78			0.87			0.23
			0.48			0.77			0.87			0.24
		0.50 (0.01)	0.49		0.78 (0.01)	0.78		0.87 (0.01)	0.87		0.24 (0.01)	0.23
			0.50			0.78			0.88			0.24
			0.50			0.77			0.86			0.24
id01	0.78	0.79 (0.01)	0.80	0.04	0.04 (0.00)	0.04	0.48	0.48 (0.02)	0.47	0.13	0.13 (0.00)	0.13
			0.79			0.04			0.48			0.13
			0.79			0.04			0.50			0.13
		0.77 (0.00)	0.77		0.04 (0.00)	0.04		0.47 (0.01)	0.46		0.13 (0.00)	0.13
			0.77			0.04			0.46			0.13
			0.77			0.04			0.48			0.13
id02	0.61	0.60 (0.01)	0.59	0.73	0.73 (0.01)	0.73	0.31	0.31 (0.01)	0.32	0.20	0.19 (0.01)	0.20
			0.60			0.73			0.31			0.19
			0.61			0.74			0.31			0.18
		0.62 (0.01)	0.62		0.73 (0.01)	0.74		0.31 (0.00)	0.31		0.21 (0.01)	0.21
			0.61			0.73			0.31			0.20
			0.62			0.73			0.31			0.22
jp01	0.48	0.49 (0.01)	0.50	0.73	0.73 (0.00)	0.73	0.45	0.44 (0.01)	0.44	0.12	0.11 (0.01)	0.11
			0.49			0.73			0.45			0.11
			0.49			0.73			0.44			0.10
		0.46 (0.01)	0.46		0.72 (0.01)	0.72		0.45 (0.01)	0.45		0.12 (0.01)	0.12
			0.45			0.71			0.44			0.12
			0.46			0.72			0.45			0.11
my01	0.35	0.35 (0.07)	0.27	0.23	0.26 (0.03)	0.23	0.23	0.06 (0.02)	0.05	0.08	0.06 (0.02)	0.06
			0.39			0.25			0.05			0.04
			0.39			0.29			0.09			0.08
		0.34 (0.08)	0.27		0.20 (0.01)	0.21		0.39 (0.00)	0.39		0.09 (0.01)	0.10
			0.31			0.21			0.39			0.08
			0.43			0.19			0.39			0.08
mn01												
ph01	2.88	2.88 (0.14)	2.88	1.89	1.89 (0.13)	2.04	30.98	31.00 (0.16)	31.09	118.77	118.77 (1.39)	119.57
			2.74			1.81			30.81			119.57
			3.02			1.81			31.09			117.17
		2.88 (0.14)	2.88		1.89 (0.13)	2.04		30.95 (0.14)	30.81		118.77 (1.39)	119.57
			3.02			1.81			31.09			117.17
			2.74			1.81			30.95			119.57
kr01	0.56	0.55 (0.11)	0.44	0.75	0.75 (0.03)	0.75	0.39	0.39 (0.02)	0.41	0.10	0.10 (0.01)	0.11
			0.66			0.72			0.39			0.09
			0.55			0.77			0.38			0.09
		0.57 (0.03)	0.60		0.75 (0.02)	0.76		0.39 (0.01)	0.40		0.10 (0.01)	0.09
			0.55			0.73			0.38			0.11
			0.55			0.75			0.38			0.09
ru01	0.15	0.15 (0.01)	0.14	0.90	0.89 (0.01)	0.90	0.44	0.43 (0.01)	0.43	0.26	0.27 (0.01)	0.27
			0.15			0.89			0.44			0.27
			0.15			0.89			0.43			0.26
		0.14 (0.01)	0.14		0.91 (0.01)	0.90		0.44 (0.02)	0.44		0.25 (0.00)	0.25
			0.14			0.91			0.45			0.25
			0.15			0.91			0.42			0.25
th01	0.24	0.24 (0.02)	0.26	0.66	0.66 (0.00)	0.66	0.29	0.29 (0.01)	0.29	0.14	0.14 (0.00)	0.14
			0.23			0.66			0.29			0.14
			0.23			0.66			0.28			0.14
		0.23 (0.01)	0.22		0.65 (0.01)	0.65		0.29 (0.00)	0.29		0.14 (0.00)	0.14
			0.23			0.66			0.29			0.14
			0.24			0.65			0.29			0.14
vn01	3.41	3.45 (0.00)	3.45	1.34	1.29 (0.00)	1.29	0.47	0.47 (0.00)	0.47	0.55	0.54 (0.00)	0.54
			3.45			1.29			0.47			0.54
			3.45			1.29			0.47			0.54
		3.36 (0.00)	3.36		1.38 (0.00)	1.38		0.47 (0.00)	0.47		0.55 (0.00)	0.55
			3.36			1.38			0.47			0.55
			3.36			1.38			0.47			0.55

Appendix 3.3. Entire data of exchangeable acidity and acid cations in Sample No. 032

	Ex-acidity			Ex-Al			Ex-H		
Lab.	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat
cn01	20.15	20.14 (0.06)	20.14	10.67	10.64 (0.09)	10.64	9.49	9.50 (0.03)	9.50
			20.20			10.72			9.48
			20.08			10.55			9.53
		20.16 (0.03)	20.14		10.69 (0.05)	10.64		9.47 (0.04)	9.50
			20.20			10.72			9.48
			20.14			10.72			9.42
cn02	25.12	25.13 (0.08)	25.08	14.59	14.58 (0.00)	14.58	10.53	10.55 (0.08)	10.50
			25.22			14.58			10.64
			25.08			14.58			10.50
		25.10 (0.09)	25.00		14.60 (0.04)	14.58		10.50 (0.08)	10.42
			25.15			14.65			10.50
			25.15			14.58			10.57
cn03	28.78	28.75 (0.05)	28.81	18.66	14.70 (1.69)	13.17	10.12	14.05 (1.73)	15.64
			28.72			16.51			12.21
			28.72			14.41			14.31
		28.80 (0.11)	28.90		22.61 (0.51)	22.23		6.19 (0.53)	6.68
			28.81			23.19			5.63
			28.68			22.41			6.27
cn04	26.65	26.71 (0.48)	26.69	24.17	24.24 (0.66)	23.86	2.30	2.28 (0.33)	2.65
			26.24			23.86			2.19
			27.20			25.00			2.00
		26.59 (0.31)	26.95		24.09 (0.23)	24.09		2.32 (0.40)	2.67
			26.39			24.32			1.89
			26.44			23.86			2.40
id01	28.23	28.28 (0.00)	28.28	21.45	21.45 (0.24)	21.45	6.84	6.84 (0.24)	6.84
			28.28			21.21			7.07
			28.28			21.68			6.60
		28.17 (0.00)	28.17		21.45 (0.00)	21.45		6.84 (0.00)	6.84
			28.17			21.45			6.84
			28.17			21.45			6.84
id02	23.97	23.98 (0.03)	24.01	21.47	21.44 (0.03)	21.42	2.47	2.48 (0.07)	2.40
			23.96			21.47			2.49
			23.96			21.42			2.54
		23.95 (0.02)	23.96		21.49 (0.03)	21.47		2.46 (0.05)	2.49
			23.92			21.52			2.40
			23.96			21.47			2.49
jp01	25.75	25.87 (0.11)	25.74	25.44	25.46 (0.07)	25.40	0.32	0.41 (0.07)	0.34
			25.95			25.54			0.41
			25.92			25.43			0.48
		25.63 (0.08)	25.57		25.41 (0.02)	25.39		0.22 (0.09)	0.18
			25.72			25.40			0.32
			25.60			25.43			0.16
my01	63.17	66.19 (0.77)	65.32	24.84	24.84 (1.08)	24.84	-0.36	0.00 (1.08)	0.00
			66.48			25.92			-1.08
			66.78			23.76			1.08
		60.15 (0.65)	59.54		24.84 (1.08)	23.76		-0.72 (1.25)	0.00
			60.84			24.84			0.00
			60.06			25.92			-2.16
mn01	48.27	48.25 (0.00)	48.25	24.04	23.96 (0.00)	23.96	25.89	25.96 (0.00)	25.96
			48.25			23.96			25.96
			48.25			23.96			25.96
		48.29 (0.06)	48.25		24.11 (0.26)	24.41		25.81 (0.25)	25.52
			48.25			23.96			25.96
			48.36			23.96			25.96
ph01	25.29	25.29 (0.02)	25.31	23.06	23.06 (0.01)	23.07	2.23	2.23 (0.01)	2.24
			25.29			23.07			2.22
			25.27			23.05			2.22
		25.29 (0.02)	25.31		23.06 (0.01)	23.07		2.23 (0.01)	2.24
			25.29			23.07			2.22
			25.27			23.05			2.22
kr01	25.22	25.14 (0.21)	25.06	20.84	20.77 (0.22)	20.62	4.38	4.37 (0.07)	4.44
			24.98			20.67			4.31
			25.38			21.03			4.35
		25.29 (0.41)	24.84		20.90 (0.14)	20.76		4.39 (0.27)	4.08
			25.63			21.03			4.60
			25.41			20.92			4.49
ru01	22.79	22.79 (0.33)	22.60	10.66	10.66 (0.07)	10.62	12.13	12.13 (0.26)	11.98
			23.17			10.74			12.43
			22.60			10.62			11.98
		22.79 (0.33)	22.60		10.66 (0.07)	10.74		12.13 (0.36)	11.87
			22.60			10.62			11.98
			23.17			10.62			12.54
th01	30.25	30.24 (0.03)	30.21	28.52	28.50 (0.03)	28.48	1.92	1.91 (0.01)	1.90
			30.24			28.50			1.91
			30.27			28.53			1.91
		30.26 (0.02)	30.24		28.54 (0.02)	28.52		1.92 (0.01)	1.92
			30.27			28.55			1.92
			30.26			28.55			1.91
vn01	23.93	23.87 (0.11)	23.93	23.30	23.24 (0.06)	23.20	0.29	0.31 (0.00)	0.31
			23.93			23.31			0.31
			23.74			23.20			0.31
		23.99 (0.11)	24.12		23.35 (0.06)	23.42		0.27 (0.03)	0.25
			23.93			23.31			0.25
			23.93			23.31			0.31

Appendix 4. Variation on chemical properties among bottles

			%			cmol(+)/kg						
Sample No.	Serial No.	Repeat	Moist	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-Acidity	Ex-Al	Ex-H
031	20	1st	4.8	4.8	3.8	2.63	0.63	0.19	0.04	3.04	2.08	0.96
		2nd		4.7	3.8	2.82	0.67	0.22	0.05	2.98	2.19	0.79
	21	1st	4.8	4.8	3.8	2.98	0.70	0.22	0.05	3.15	2.12	0.96
		2nd		4.7	3.8	2.92	0.70	0.22	0.06	3.02	2.32	0.70
	22	1st	4.6	4.8	3.8	3.05	0.70	0.21	0.05	3.15	2.16	0.98
		2nd		4.7	3.8	2.85	0.68	0.21	0.06	3.06	2.37	0.68
	41	1st	4.9	4.8	3.8	2.89	0.66	0.22	0.06	3.02	2.02	1.00
		2nd		4.7	3.8	2.83	0.69	0.21	0.06	2.83	2.24	0.59
	42	1st	5.0	4.8	3.8	2.85	0.68	0.21	0.06	3.20	2.17	1.03
		2nd		4.7	3.8	2.87	0.72	0.23	0.06	2.93	2.23	0.71
032	20	1st	13.6	4.7	3.7	0.42	0.75	0.42	0.10	23.87	23.48	0.40
		2nd		4.6	3.8	0.39	0.75	0.42	0.11	24.15	23.24	0.91
	21	1st	13.7	4.7	3.7	0.42	0.74	0.41	0.10	23.79	23.45	0.34
		2nd		4.6	3.8	0.39	0.74	0.42	0.12	24.16	23.39	0.77
	22	1st	13.7	4.7	3.8	0.43	0.74	0.41	0.09	23.78	23.39	0.39
		2nd		4.6	3.8	0.38	0.74	0.42	0.12	24.18	23.26	0.92
	41	1st	13.6	4.7	3.7	0.42	0.73	0.41	0.09	23.80	23.60	0.20
		2nd		4.6	3.8	0.40	0.75	0.42	0.11	24.14	23.54	0.60
	42	1st	13.7	4.7	3.8	0.42	0.75	0.41	0.09	23.81	23.61	0.20
		2nd		4.6	3.8	0.38	0.75	0.43	0.11	24.37	23.56	0.81

Averages of 3 prepared samples

<Exchangeable base cations (Ca,Mg,K,Na)> *Analyzed by ADORC*

Procedure of extraction			Date of AAS analysis
No.031	1st	Centrifuge Procedure	22-23 Jan. 2004
	2nd	Centrifuge Procedure	13 Feb. 2004
No.032	1st	Centrifuge Procedure	29 Jun. 2004
	2nd	Buchner funnel Procedure	3-4 Nov. 2004