

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

Report of the Inter-laboratory Comparison Project 2002
on Soil

4th Attempt

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Acid Deposition and Oxidant Research Center

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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.

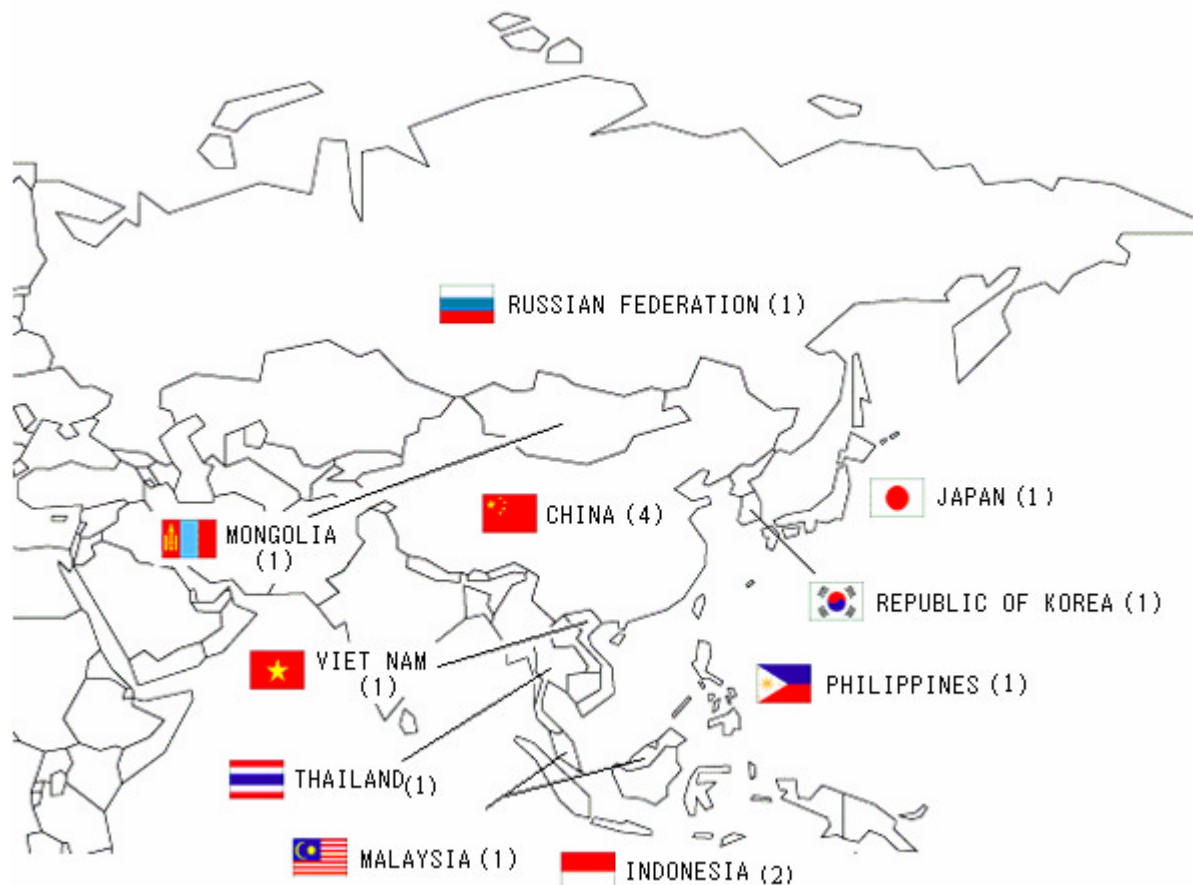


Figure 1. Laboratories participating in Inter-laboratory comparison project 2002 on soil

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

1.1 Outlines of the previous projects

For the 1st (in 1999) and 2nd (in 2000) projects, (I) NC dispatched sets of two soil samples (No.991 and 992 in 1999, and No.001 and 002 in 2000) to the laboratories, which were in charge of soil monitoring in the

participating countries. The samples were extracted and analyzed in the respective participating laboratories, and the results were submitted to (I) NC and evaluated statistically. The results suggested that steps in the procedures of soil analysis might be related to the variation among laboratories; e.g. extraction, instrumental analysis and/or titration. Therefore, it should be clarified which steps were most effective for precisions in order to improve the analytical quality, at the first. In this connection, NC dispatched two soil extract samples (No.011 and 012) for the 3rd project in 2001 in order to evaluate precision of instrumental analysis in the procedures on soil analyses.

Based on the results in the three projects, it was 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

NC has provided the information on these possible factors on variations of soil analysis data for improvement of the precisions.

1.2 Objective of the 4th project

In the 4th project, NC provides soil sample (No.021) and soil extract sample (No.022) to laboratories in order to improve inter-laboratories precision and evaluate variation on the extraction process. Countries and number of laboratories, which participated in the 4th project, are shown in the Figure 1. Fourteen laboratories of ten countries participated in the 4th 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. 021: Soil sample

Black soil (Andosol) was air-dried, sieved, mixed well, packed in 500 ml plastic bottles, and then, sterilized using radioisotope (20kGy).

Sample No. 022: Soil extract by Ammonium acetate solution for Exchangeable base cations

Air-dried soil (Andosol) was shaken with 1N-Ammonium acetate ($\text{CH}_3\text{COONH}_4$) solution for one hour, and laid for one day; the ratio of soil to 1N-Ammonium acetate was 1:10. Soil extract was filtered by No.6 filter paper and membrane filter (pore size 0.45 μm), and then packed in 500 ml plastic bottles.

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.021	No.022
a) Moisture Content	wt %	M	
b) pH (H_2O)		M	
c) pH (KCl)		M	
d) Exchangeable Ca	$\text{cmol}(+) \text{kg}^{-1}$	M	M
e) Exchangeable Mg	$\text{cmol}(+) \text{kg}^{-1}$	M	M
f) Exchangeable K	$\text{cmol}(+) \text{kg}^{-1}$	M	M
g) Exchangeable Na	$\text{cmol}(+) \text{kg}^{-1}$	M	M
h) Exchangeable Acidity	$\text{cmol}(+) \text{kg}^{-1}$	M	
i) Exchangeable Al	$\text{cmol}(+) \text{kg}^{-1}$	M	
j) Exchangeable H	$\text{cmol}(+) \text{kg}^{-1}$	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 4th project, the following procedures were also standardized based on results of the previous projects.

- 1) **Atomic absorption spectrometry (AAS) method should be used basically for analysis of Ex-Ca, Mg, K and Na.** (If there is difficulty of using AAS, Flame (emission) photometry method was 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 Sample No.021 should be extracted and diluted with 1M CH₃COONH₄ (pH 7.0) for analysis of Ex-Ca, Mg, K and Na. Then, **1M CH₃COONH₄ (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, Mg, K and Na. These are to be the same concentration Sr.

2.3.2. Procedures

< No.021 >

- 1) Extract from Sample No.021 with 1M CH₃COONH₄ (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 100 g-Sr/L solution (180.9g/L SrCl₂ Solution) to be 1000 mg-Sr/L as final Sr concentration. And then make to volume with 1M CH₃COONH₄ (pH 7.0). This solution was named “ Prepared sample”.
- 3) Prepare three “prepared samples”.
- 4) Prepare each standard solution with diluting 1M CH₃COONH₄ (pH 7.0) solution.
- 5) Add 100 g-Sr/L solution to each standard solution to be the same Sr concentration 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.

< No.022 >

- 1) Pipette an appropriate aliquot of the soil extract into volumetric flask and add 100 g-Sr/L solution (180.9g/L SrCl₂ Solution) to be 1000 mg-Sr/L as final concentration Sr. And then make to volume with 1M CH₃COONH₄ (pH 7.0). This solution was named “ Prepared sample”.
- 2) Prepare three “prepared samples”.
- 3) Prepare each standard solution with diluting 1M CH₃COONH₄ (pH 7.0) solution.
- 4) Add 100 g-Sr/L solution to each standard solution to be the same Sr concentration as the sample.
- 5) Analyze the standard solution and the prepared samples by AAS.

- 6) Store the calibration curves certainly and report them together with reporting formats.
- 7) Repeat the procedure 1) - 6) twice.

Note:

As for the factors, such as preparation method of standard solution, addition of Sr solution, and instrument (AAS or FEP), which could affect the reproducibility, optional experiments with alternative factors were also proposed in order to clarify which factors are the most effective (see Appendix 4). However, only one laboratory of Japan carried out the optional experiments, and the results were not included in the report. Information of the results would be shown in some opportunity in the near future.

2.3.3. Calculation of content in the soil

“Content in the soil” was calculated by the following formulas:

$$\text{Ex-Ca (cmol(+) / kg soil)} = [A * B * V * C] / [10 * 20.04 * S]$$

$$\text{Ex-Mg (cmol(+) / kg soil)} = [A * B * V * C] / [10 * 12.15 * S]$$

$$\text{Ex-K (cmol(+) / kg soil)} = [A * B * V * C] / [10 * 39.10 * S]$$

$$\text{Ex-Na (cmol(+) / kg soil)} = [A * B * V * C] / [10 * 23.00 * S]$$

Where

A = “ Measurement values of prepared samples (concentrations of prepared sample) ” in mg/L.

B = “Dilution ratio”

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

C = “Moisture correction factor”

Sample No.021: measured value

Sample No.022: C=1

S = “weight of air-dry sample” in gram

Sample No.021: Used weight (g)

Sample No.022: S = 10

V = “Volume of extract” in mL

Sample No.021: Volume (mL)

Sample No.022: V = 100

Note:

As for the Sample No.022, soil was extracted with ten times volume of 1M CH₃COONH₄ (pH 7.0) solution. Therefore, S and V were 10 and 100, respectively for the above formula.

Concentration of extract (prepared sample), content in soil, and information on the analytical conditions were included in the report from the participating laboratories,

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 of the soil contents are shown in Table 2, 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 and data with calculation mistakes were removed for the verified data. As described later, obvious calculation mistakes were found in results of some laboratories.

As for the entire data, the variations (CVs) among the participating laboratories were remarkably high, higher than 100 % for exchangeable base cations, such as Ex-Ca, Mg, K and Na, although ones for pH(H₂O) and pH(KCl) were less than 5%. No clear difference between CVs of No.021 and 022 was observed for exchangeable base cations. CVs of Ex-acidity and Al were relatively low probably due to simple method of titration. CV of Ex-H was relatively high because it was calculated as a value based on data of Ex-acidity and Al.

As for the verified data, the variations (CVs) of pH(H₂O) and pH(KCl) were also less than 5%. CVs for other parameters were improved after removing outliers although they were still 14-106%. CV of Ex-K was the lowest in No.021, however, one of Ex-Mg was the lowest in No.022. No clear difference between CVs of No.021 and 022 was observed for exchangeable base cations.

It was expected that effect of extraction process would be evaluated by comparing results of soil sample (No.021) and soil extract sample (No.022) in the 4th project. Effect of instrumental analysis seems to be relatively larger than one of extraction process for inter-laboratories variation since no clear trend in CVs was observed for No.021 and 022.

The averages of triplicate analyses (three times analysis in repeatability condition) and the average of repeat analysis (in within-laboratory-reproducibility condition) in each laboratory were shown in Figure 3.1, 3.2, and 3.3. Error bar shows standard deviation of triplicate analyses.

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

(Entire data)													
Statistics	No. 021: soil sample									No. 022: soil extract sample			
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H	Ex-Ca	Ex-Mg	Ex-K	Ex-Na
			cmol(+)/kg									cmol(+)/kg	
Number of Laboratories	14	14	13	13	13	13	14	14	14	12	12	13	13
Total average	4.9	4.3	1.46	0.60	0.26	0.42	2.41	1.95	0.62	1.00	0.25	0.17	0.25
Median	4.9	4.3	1.08	0.23	0.12	0.13	2.55	1.94	0.51	0.51	0.11	0.08	0.05
Maximum	5.1	4.6	7.59	3.85	1.70	2.81	4.00	3.44	2.68	6.46	0.98	1.07	2.04
Minimum	4.4	4.0	0.01	0.09	0.00	0.03	0.25	0.58	0.11	0.08	0.05	0.00	0.01
Standard deviation	0.2	0.2	1.89	1.02	0.45	0.76	0.84	0.68	0.62	1.75	0.30	0.28	0.55
CV (%) ^{*1}	4.3	3.8	129.25	170.47	174.32	183.45	34.62	35.01	99.64	174.89	122.94	164.98	222.29
(Verified data ^{*2})													
Statistics	No. 021: soil sample									No. 022: soil extract sample			
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H	Ex-Ca	Ex-Mg	Ex-K	Ex-Na
			cmol(+)/kg									cmol(+)/kg	
Number of Laboratories	13	13	7	7	6	6	6	8	6	10	9	11	10
Total average	4.8	4.3	0.85	0.25	0.12	0.12	2.43	2.06	0.39	0.42	0.10	0.07	0.09
Median	4.9	4.3	1.05	0.16	0.12	0.11	2.72	2.26	0.37	0.42	0.11	0.07	0.05
Maximum	5.1	4.6	1.48	0.76	0.15	0.23	2.91	3.44	0.70	0.72	0.14	0.15	0.28
Minimum	4.4	4.0	0.01	0.09	0.10	0.03	1.66	0.58	0.11	0.08	0.05	0.00	0.01
Standard deviation	0.2	0.2	0.52	0.23	0.02	0.07	0.57	0.87	0.24	0.21	0.03	0.04	0.10
CV (%)	4.2	3.8	61.25	92.95	13.83	54.63	23.56	41.97	61.27	50.12	24.64	48.51	105.99

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

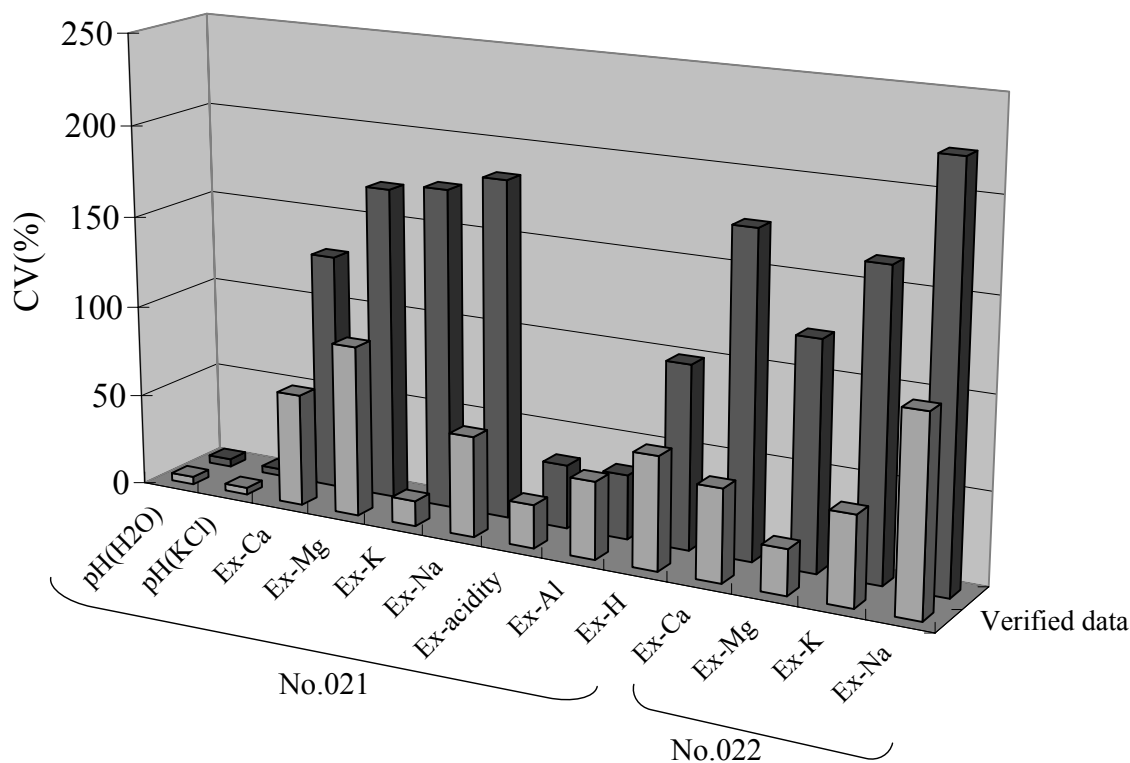


Figure 2. CV among laboratories

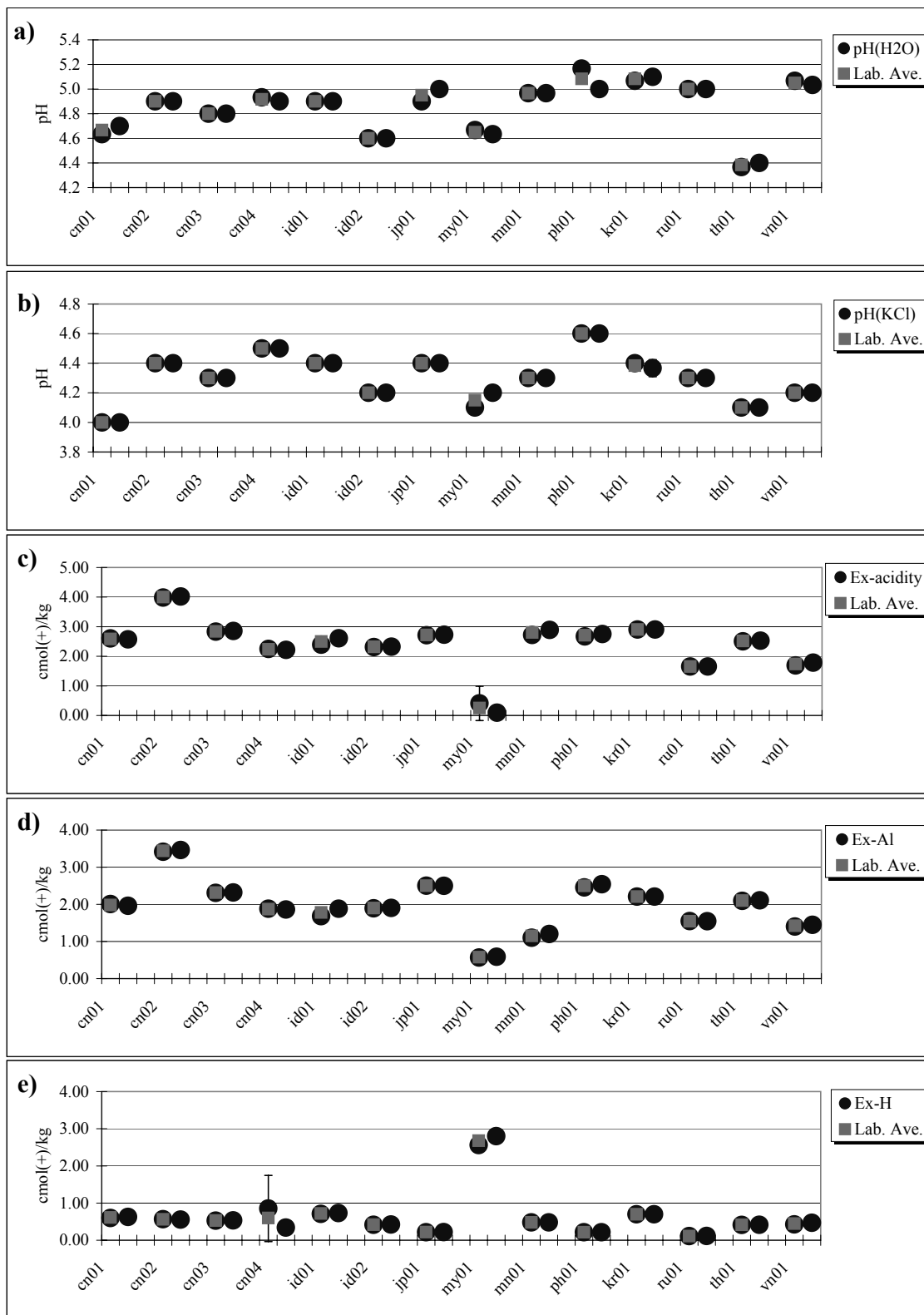


Figure 3.1. Averages of triplicate analysis and the laboratory average for a) pH(H₂O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 021. Error bar shows standard deviation of triplicate analysis.

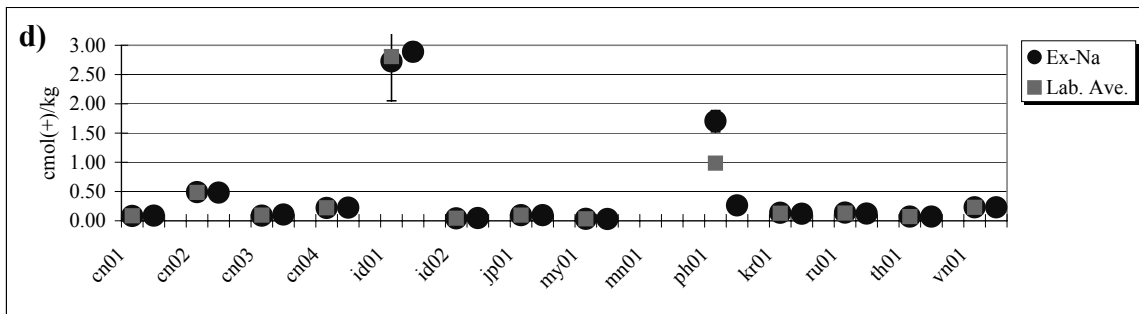
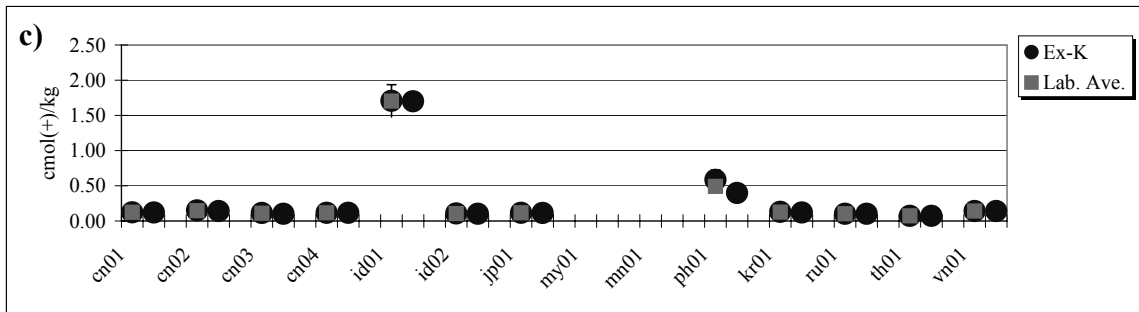
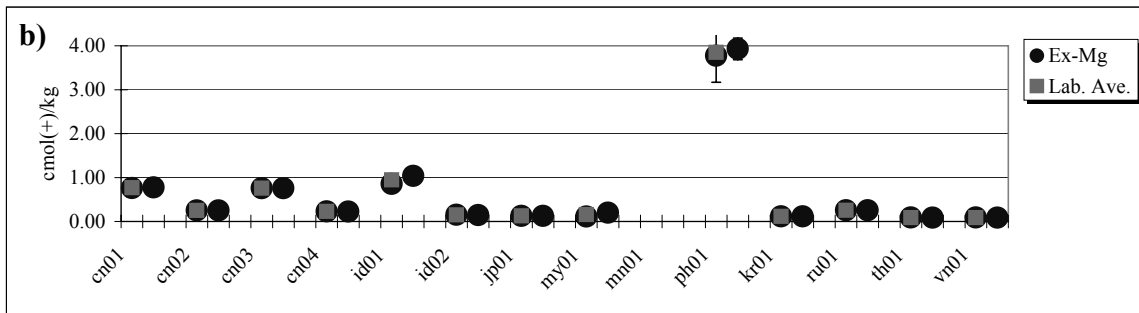
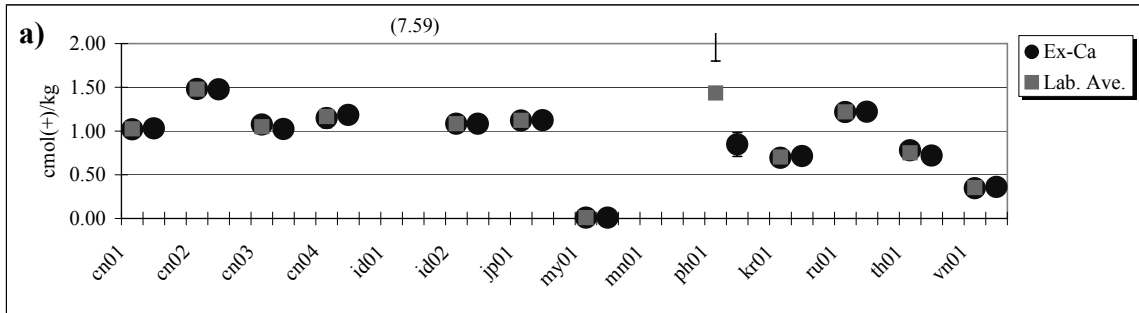


Figure 3.2. Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 021. Error bar shows standard deviation of triplicate analysis.

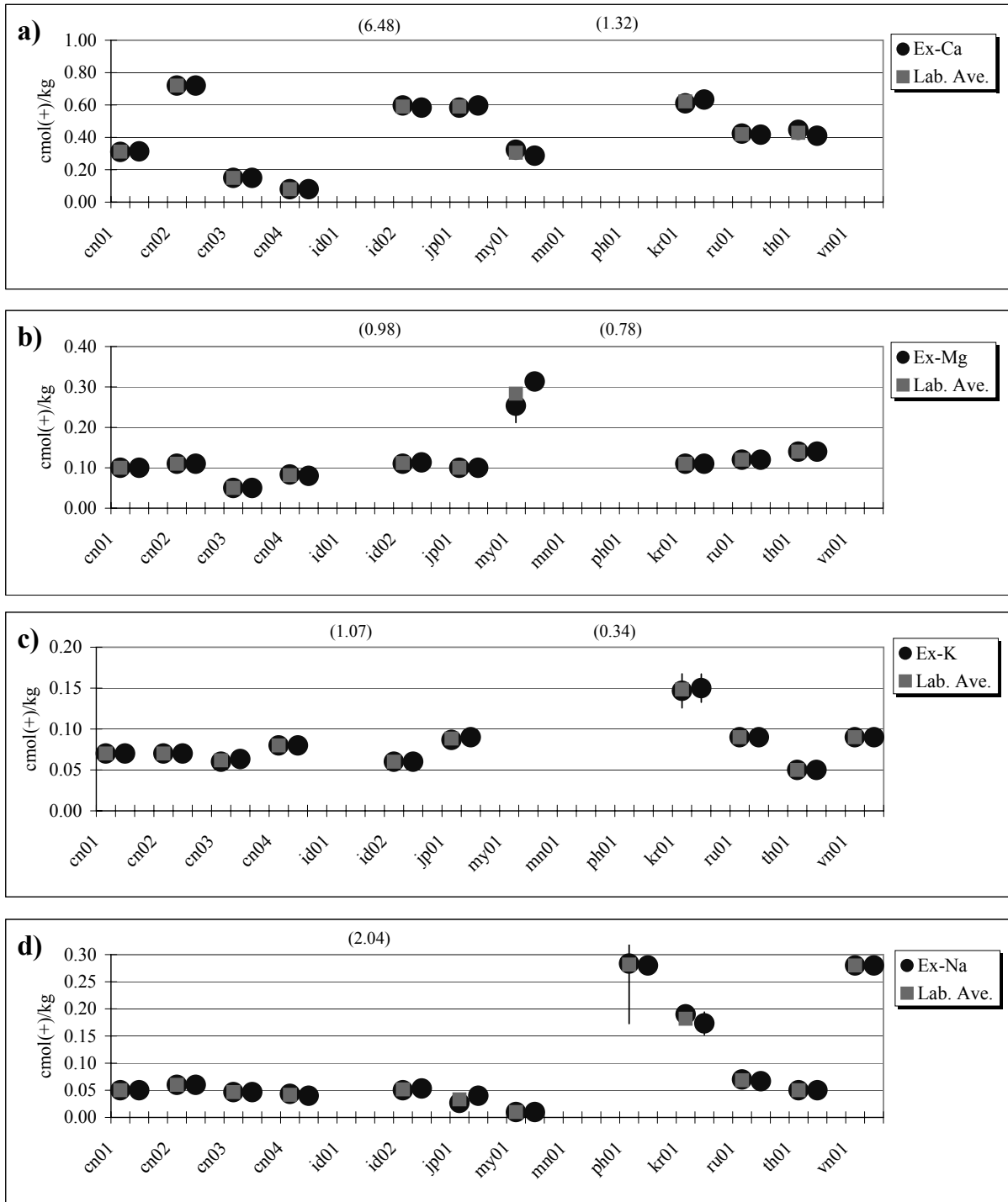


Figure 3.3. Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 022. Error bar shows standard deviation of triplicate analysis.

3.2. Verification of data

3.2.1. Detection of outliers

Laboratories, which have remarkably large difference between repeat analyses, were judged as outliers by Cochran method (examination of the evenness of within-laboratory precision): e.g. “my01” for pH(KCl) of No.021, “id01” and “ph01” for Ex-Ca of No.021, etc. Then, laboratories, which have remarkably large or low average, were judged as outliers by Grubbs method (examination of the average value of each laboratory): e.g. “ph01” for Ex-Mg of No.021, “id01” and “my01” for Ex-K of No.021.

The results of verification by Cochran-Grubbs methods were shown in Table 3.

One outlier was detected for pH(H₂O) and pH(KCl), respectively. Two or three outliers were detected for other parameters. Most of the outliers were observed in three laboratories, namely “id01”, “my01” and “ph01”.

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 mcf was used for all calculation of Ex-cations of sample No.021. 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.

Measured moisture contents of sample No.021 and measurement conditions were shown in Table 4. In five laboratories, namely “cn01”, “cn04”, “id01”, “id02”, and “mn01”, reported mcf were obviously different from recalculated values that were calculated by NC based on the reported moisture contents, and calculation or writing mistakes were suggested in these laboratories. Thus, it was also suggested that the final results of Ex-cations in the laboratories were miscalculated for No. 021 with their mistaken mcf. Ex-cations data of No.021 in the above five laboratories were removed with other outliers for statistical analysis of verified data as described later.

The laboratory “id01” was one of the laboratories where some outliers were detected by Cochran or Grubbs methods as described above. Calculation mistake related to mcf might be one of causes for these outliers. However, the mistaken mcf could not explain all the outliers since most outliers of “id01” were approximately ten times larger than data of other laboratories and outliers were detected also for No.022 (soil extract sample: mcf was decided as “1”). After communications with an analyst of “id01”, it was clarified that some calculation mistakes other than mcf had been made, and that the recalculated data were comparable to other laboratories.

The moisture content of “th01” was significantly lower than others although mcf could be calculated as appropriate. This significantly lower moisture content could be detected by Grubbs method, and the data of “th01” for Ex-cations of No.021 were treated as outliers for further statistical analyses.

Table 3. Data verified by Cochran-Grubbs methods

Lab.	Analysis	No. 021: soil sample									No. 022: soil extract sample			
		pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H	Ex-Ca	Ex-Mg	Ex-K	Ex-Na
		cmol(+)/kg									cmol(+)/kg			
cn01	1st	4.6	4.0	1.02	0.76	0.12	0.08	2.60	2.01	0.60*c	0.31	0.10	0.07	0.05
	2nd	4.7	4.0	1.03	0.78	0.12	0.09	2.57	1.96	0.63*c	0.31	0.10	0.07	0.05
cn02	1st	4.9	4.4	1.48	0.25	0.15	0.49*g	3.98*g	3.42	0.57	0.72	0.11	0.07	0.06
	2nd	4.9	4.4	1.48	0.25	0.14	0.48*g	4.02*g	3.46	0.56	0.72	0.11	0.07	0.06
cn03	1st	4.8	4.3	1.07	0.76	0.11	0.09	2.83	2.31	0.53	0.15	0.05	0.06	0.05
	2nd	4.8	4.3	1.02	0.76	0.10	0.11	2.85	2.32	0.53	0.15	0.05	0.06	0.05
cn04	1st	4.9	4.5	1.15	0.23	0.12	0.22	2.25	1.88	0.85*c	0.08	0.08	0.08	0.04
	2nd	4.9	4.5	1.18	0.23	0.12	0.22	2.22	1.86	0.34*c	0.08	0.08	0.08	0.04
id01	1st	4.9	4.4	7.29*c	0.86	1.71*g	2.72*c	2.39	1.68*c	0.71*c	6.46*g	0.97*c	1.08*c	2.07*c
	2nd	4.9	4.4	7.89*c	1.04	1.70*g	2.89*c	2.61	1.88*c	0.73*c	6.45*g	0.99*c	1.05*c	2.00*c
id02	1st	4.6	4.2	1.08	0.15	0.11	0.04	2.31	1.89	0.42	0.60	0.11	0.06	0.05
	2nd	4.6	4.2	1.08	0.15	0.10	0.05	2.33	1.90	0.42	0.58	0.11	0.06	0.05
jp01	1st	4.9	4.4	1.12	0.13	0.12	0.10	2.71	2.50	0.21	0.58	0.10	0.09	0.03*c
	2nd	5.0	4.4	1.12	0.13	0.11	0.10	2.73	2.50	0.22	0.60	0.10	0.09	0.04*c
my01	1st	4.7	4.1*c	0.01	0.11	0.00*g	0.03	0.41*c	0.57	2.56*c	0.32	0.25*c	0.00	0.01
	2nd	4.6	4.2*c	0.01	0.20	0.00*g	0.03	0.09*c	0.59	2.80*c	0.29	0.31*c	0.00	0.01
mn01	1st	5.0	4.3	-	-	-	-	2.72	1.10	0.48	-	-	-	-
	2nd	5.0	4.3	-	-	-	-	2.89	1.20	0.48	-	-	-	-
ph01	1st	5.2*c	4.6	2.02*c	3.77*g	0.58*c	1.70*c	2.67	2.46	0.21	1.37*c	0.71*c	0.36*c	0.28
	2nd	5.0*c	4.6	0.85*c	3.93*g	0.40*c	0.26*c	2.75	2.54	0.21	1.27*c	0.85*c	0.31*c	0.28
kr01	1st	5.1	4.4	0.69	0.12	0.13	0.14	2.91	2.21	0.70	0.61	0.11	0.15	0.19*c
	2nd	5.1	4.4	0.71	0.12	0.12	0.12	2.91	2.21	0.70	0.63	0.11	0.15	0.17*c
ru01	1st	5.0	4.3	1.22	0.26	0.10	0.14	1.66	1.55	0.11	0.42	0.12	0.09	0.07
	2nd	5.0	4.3	1.22	0.26	0.10	0.12	1.66	1.54	0.11	0.42	0.12	0.09	0.07
th01	1st	4.4	4.1	0.78	0.09	0.07	0.07	2.51	2.09	0.41	0.45	0.14	0.05	0.05
	2nd	4.4	4.1	0.72	0.09	0.07	0.07	2.53	2.11	0.42	0.41	0.14	0.05	0.05
vn01	1st	5.1	4.2	0.35	0.09	0.14	0.23	1.69	1.40	0.43*c	-	-	0.09	0.28
	2nd	5.0	4.2	0.36	0.09	0.14	0.23	1.79	1.45	0.47*c	-	-	0.09	0.28

Note: The outliers judged by Cochran and Grubbs methods were marked with asterisk c and g, respectively. ND for Ex-K in my01 was used as "o" for the analysis.

Table 4. Measured moisture content of Sample No. 021 and measurement condition

Lab.	Average	Measured value	Oven temp.	Drying period	Reported mcf (recalculated value)
		wt%	°C	hours	
cn01	25.7	25.7	103±2	6	0.80
		25.7			(1.26)
		25.7			
cn02	27.0	26.9	105	12	1.27
		27.1			(1.27)
		27.1			
cn03	25.5	25.9	105	48	1.26
		25.1			(1.26)
		25.6			
cn04	18.2	18.4	108	5	1
		18.0			(1.18)
		18.2			
id01	24.5	24.9	105	24	1.00
		24.6			(1.25)
		24.1			
id02	19.5	19.5	105	3	1.24
		19.6			(1.20)
		19.5			
jp01	26.7	26.6	105	21	1.27
		26.8			(1.27)
		26.6			
my01	20.1	22.7	105	24	1.20
		19.2			(1.20)
		20.1			
mn01	26.9	27.1	105	5	1.2
		26.7			(1.27)
		26.9			
ph01	26.8	26.3	105	24	1.3
		26.9			(1.27)
		27.2			
kr01	27.2	27.0	105	24	1.27
		27.3			(1.27)
		27.2			
ru01	26.6	26.9	105	5	1.27
		26.2			(1.27)
		26.6			
th01	9.0	9.0	105	24	1.090
		9.0			(1.09)
		9.0			
vn01	23.5	23.5	105	4	1.24
		23.4			(1.24)
		23.6			

Note: mcf, moisture correction factor; Highlighted values show calculation/writing mistakes for moisture correction factor. In parenthesis, recalculated values, which were calculated by Network Center based on reported moisture contents, were shown.

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. For measurement of Ex-base cations, it seemed that different analysts carried out the repeat analyses in three laboratories, namely “id02”, “my01” and “ru01”. 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”.

As for years of experience, analysts of four laboratories, namely “id01”, “ph01”, “th01” and “vn01”, have just 1 years or less of experience for soil analysis.

Analysts for Ex-base cations were different from ones for Ex-acidity in five laboratories, namely “cn01”, “cn03”, “id02”, “ph01” and “th01”.

Analysts of five laboratories, namely “cn04”, “id01”, “my01”, “ph01” and “th01”, were changed from analysts of the year 2001 although history of analysts in the respective laboratories was not shown here. In addition, analytical system of “ph01” was changed; “extraction procedures” and “instrumental analysis” were carried out in different laboratories respectively. These changes in analyst and analytical system may also affect inter-laboratories variations.

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 four laboratories used FEP for Ex-K and Na. Years in use of instruments were varied from 4 to 18 years old for AAS. Implication between the years in use of instruments and the outliers were not observed.

As for procedures for extraction of Ex-base cations, five laboratories used percolation tube procedures, and four laboratories used centrifuge procedures and Buchner funnel procedures, respectively. No clear difference was observed among data by three kinds of procedures. As for size of burette for titration of Ex-acidity, capacities were varied from 10 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 35 days. The intervals for Ex-base cations in “id01” and “ph01” were 31 and 11 days, respectively. Probably the outliers by Cochran method in “id01” and “ph01” were related to the intervals.

Table 5.1. Number and experience of analysts

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	18	17	1	17	16	d
cn02	1	7	4	1	7	4	
cn03	1	5	3	1	15	5	d
cn04	1	10	10	1	10	10	
id01	1	5	1	1	5	1	
id02	2	30/21	30/21	1	5	5	d
jp01	1	4	4	1	4	4	
my01	2	3/+	2/+	2	3/+	2/+	
mn01	-	-	-	1	9	9	
ph01	1	6	0	1	26	26	d
kr01	1	7	5	1	7	5	
ru01	2	5/14	5/5	1	5	5	
th01	1	1	0.5	1	0.5	0.5	d
vn01	1	+	1	1	+	1	

Note: -, Not measured; +, No information; d, Different analysts analyzed Ex-base cations and Ex-acidity, respectively.

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.021	AAS	4	AAS	4	AAS	4	AAS	4	Centrifuge	Titration	20	0.05
	No.022	AAS	4	AAS	4	AAS	4	AAS	4				
cn02	No.021	AAS	13	AAS	13	AAS	13	AAS	13	Centrifuge	Titration	12.5	0.001
	No.022	AAS	13	AAS	13	AAS	13	AAS	13				
cn03	No.021	AAS	17	AAS	17	AAS	17	AAS	17	Percolation tube	Titration	25	0.1
	No.022	AAS	17	AAS	17	AAS	17	AAS	17				
cn04	No.021	AAS	4	AAS	4	AAS	4	AAS	4	Centrifuge	Titration	10	0.05
	No.022	AAS	4	AAS	4	AAS	4	AAS	4				
id01	No.021	AAS	10	AAS	10	AAS	10	AAS	10	Centrifuge	Titration	50	0.05
	No.022	AAS	10	AAS	10	AAS	10	AAS	10				
id02	No.021	AAS	16	AAS	16	FEP	34	FEP	34	Percolation tube	Titration	+	+
	No.022	AAS	16	AAS	16	FEP	34	FEP	34				
jp01	No.021	AAS	17	AAS	17	FEP	17	FEP	17	Percolation tube	Titration	25/10 (NaOH/HCl)	0.1/0.05 (NaOH/HCl)
	No.022	AAS	17	AAS	17	FEP	17	FEP	17				
my01	No.021	AAS	13	AAS	13	AAS	13	AAS	13	Buchner funnel	Titration	25	+
	No.022	AAS	13	AAS	13	AAS	13	AAS	13				
mn01	No.021	-	-	-	-	-	-	-	-	-	Titration	25	0.1
	No.022	-	-	-	-	-	-	-	-				
ph01	No.021	AAS	10	AAS	10	AAS	10	AAS	10	Buchner funnel	Titration	50	0.1
	No.022	AAS	10	AAS	10	AAS	10	AAS	10				
kr01	No.021	AAS	10	AAS	10	AAS	10	AAS	10	Buchner funnel	Titration	25	0.05
	No.022	AAS	10	AAS	10	AAS	10	AAS	10				
ru01	No.021	AAS	18	AAS	18	FEP	18	FEP	18	Percolation tube	Titration	25	0.05
	No.022	AAS	18	AAS	18	FEP	18	FEP	18				
th01	No.021	AAS	6	AAS	6	AAS	6	AAS	6	Percolation tube	Titration	25	0.05
	No.022	AAS	6	AAS	6	AAS	6	AAS	6				
vn01	No.021	Titration	-	Titration	-	FEP	7	FEP	6	Buchner funnel	Titration	10	0.02
	No.022	-	-	-	-	FEP	7	FEP	6				

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-base cations			Ex-acidity, Al and H		
		Date *1	Analysis *2	Interval *3	Date *1	Analysis *2	Interval *3	Date *1	Analysis *2	Interval *3
			Days			Days			Days	
cn01	1st	21-Mar	2	5	26-Mar	2	3	22-Mar	1	5
	2nd	26-Mar	2		29-Mar	2		27-Mar	1	
cn02	1st	17-Mar	1	1	18-Mar	2	2	24-Mar	1	1
	2nd	18-Mar	1		20-Mar	2		25-Mar	1	
cn03	1st	20-Feb	1	0	5-Mar	2	13	27-Mar	4	6
	2nd	20-Feb	1		18-Mar	2		2-Apr	7	
cn04	1st	12-Mar	1	2	12-Mar	1	2	12-Mar	1	0
	2nd	14-Mar	1		14-Mar	1		12-Mar	1	
id01	1st	29-Jan	1	29	31-Jan	3	31	24-Jan	2	35
	2nd	27-Feb	1		3-Mar	5		28-Feb	1	
id02	1st	7-Mar	1	14	7-Mar	1	14	7-Mar	1	1
	2nd	21-Mar	1		21-Mar	1		8-Mar	1	
jp01	1st	4-Mar	1	7	7-Mar	5	7	7-Mar	4	5
	2nd	11-Mar	1		14-Mar	4		12-Mar	2	
my01	1st	17-Jun	1	1	25-Jun	1	1	25-Jun	1	1
	2nd	18-Jun	1		26-Jun	1		26-Jun	1	
mn01	1st	19-Feb	1	0				5-Mar	1	1
	2nd	19-Feb	1					5-Mar	1	
ph01	1st	2-Apr	1	0	17-May	59	(11) ^{*4}	29-Mar	2	0
	2nd	4-Apr	1		17-May	48		29-Mar	2	
kr01	1st	25-Feb	1	1	6-Mar	2	5	3-Mar	1	1
	2nd	26-Feb	1		11-Mar	2		4-Mar	1	
ru01	1st	13-Feb	1	1	9-Feb	1	1	5-Feb	1	1
	2nd	14-Feb	1		10-Feb	1		6-Feb	1	
th01	1st	16-Aug	1	1	7-Sep ^{*5}	3	(1) ^{*4}	25-Aug	1	1
	2nd	17-Aug	1		7-Sep	2		26-Aug	1	
vn01	1st	8-Mar	1	0	8-Mar	1	0	8-Mar	1	0
	2nd	8-Mar	1		8-Mar	1		8-Mar	1	

Note: *1. Finish date of 1st and 2nd analyses. *2. Days used for analysis. *3. Interval between the repeat analyses. *4. Start dates were different though finish dates were same. *5. Finish date of Ex-Ca analysis was 31 August (start dates were 29 and 30 August).

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, and “repeatability-precision”, “within-laboratory-precision” and “inter-laboratories-precision” were estimated. In ANOVA for the verified data, the data with calculation mistakes of mcf were removed in addition to the outliers judged by Cochran and Grubbs methods. 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 less than 10%. Especially for Ex-Acidity and Al, the CVs were ca. 2%. The CV of Ex-H was relatively small (11%) in the verified data although Ex-H was the calculation value from Ex-Acidity and Al. There is no clear difference between repeatability-precisions of No. 021 and No. 022.

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 all the parameters were less than 10%. Especially the CVs of Ex-Acidity, Al and H were less than 2%. There is no clear difference between repeatability-precisions of No. 021 and No. 022.

The values were almost same as repeatability-precision. For some parameters, the CVs were less 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 relatively large for Ex-base cations and Ex-acidity even in the verified data; CVs were 14 - 106%.

There is also no clear difference between repeatability-precisions of No. 021 and No. 022, and it was suggested that process on instrumental analysis had relatively large effect on the inter-laboratories-precision.

To improve the inter-laboratories precision, standard operating procedures should be elaborated based on discussions on analytical conditions/procedures in the respective laboratories.

4) Calculation of permissible tolerance

Concerning 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.

Concerning 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. 021									No. 022			
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H	Ex-Ca	Ex-Mg	Ex-K	Ex-Na
Number of Laboratories	14	14	13	13	13	13	14	14	14	12	12	13	13
Total sum of square	166219	130610	12971	2182	403	1053	41108	26811	2728	5178	317	176	366
ST/lmd	1979	1555	166	28	5	14	489	319	32	72	4	2	5
Number of Laboratories	14	14	13	13	13	13	14	14	14	12	12	13	13
Number of Data	84	84	78	78	78	78	84	84	84	72	72	78	78
Total sum	407.7	361.4	113.89	46.71	20.08	32.45	202.75	163.74	52.23	71.96	17.80	13.26	19.14
Total average	4.9	4.3	1.46	0.60	0.26	0.42	2.41	1.95	0.62	1.00	0.25	0.17	0.25
Sum of square inter-laboratories (S _R)	3.4	2.0	256.45	75.03	14.50	41.94	54.48	36.32	29.94	201.64	6.10	5.66	21.42
Sum of square within-laboratory (S _{RW})	0.1	0.0	2.62	0.10	0.05	3.15	0.30	0.10	0.49	0.02	0.04	0.00	0.01
Sum of square repeatability (S _r)	0.1	0.0	0.26	0.88	0.18	1.03	0.79	0.14	1.72	0.04	0.01	0.03	0.10
Total sum of square (S _T)	3.5	2.1	259.33	76.00	14.74	46.12	55.57	36.55	32.15	201.70	6.14	5.70	21.53
Inter-laboratories degree of freedom (φ _R)	13	13	12	12	12	12	13	13	13	11	11	12	12
Within-laboratory degree of freedom (φ _{RW})	14	14	13	13	13	13	14	14	14	12	12	13	13
Repeatability degree of freedom (φ _r)	56	56	52	52	52	52	56	56	56	48	48	52	52
Total degree of freedom (φ _T)	83	83	77	77	77	77	83	83	83	71	71	77	77
Inter-laboratories variance (V _R = S _R /φ _R)	0.26	0.16	21.371	6.253	1.208	3.495	4.191	2.794	2.303	18.331	0.554	0.472	1.785
Within-laboratory variance (V _{RW} = S _{RW} /φ _{RW})	0.01	0.00	0.201	0.007	0.004	0.242	0.021	0.007	0.035	0.002	0.003	0.000	0.001
Repeatability variance (V _r = S _r /φ _r)	0.00	0.00	0.005	0.017	0.004	0.020	0.014	0.002	0.031	0.001	0.000	0.001	0.002
Laboratory component of variance (s _b ² = (V _R -V _{RW})/(2*3))	0.04	0.03	3.528	1.041	0.201	0.542	0.695	0.464	0.378	3.055	0.092	0.079	0.297
Within-laboratory component of variance (s _c ² = (V _{RW} -V _r)/3)	0.00	0.00	0.065	-0.003	0.000	0.074	0.002	0.001	0.001	0.000	0.001	0.000	0.000
Repeatability component of variance (s _r ² = V _r)	0.00	0.00	0.005	0.017	0.004	0.020	0.014	0.002	0.031	0.001	0.000	0.001	0.002
Inter-laboratories standard deviation (s _R = SQRT(s _r ² /(2*3) + s _c ² /2 + s _b ²))	0.2	0.2	1.89	1.02	0.45	0.76	0.84	0.68	0.62	1.75	0.30	0.28	0.545
Within-laboratory standard deviation (s _{RW} = SQRT(s _r ² /3 + s _c ²))	0.0	0.0	0.26	0.05	0.04	0.28	0.08	0.05	0.11	0.02	0.03	0.01	0.014
Repeatability standard deviation (s _r = SQRT(s _r ²))	0.0	0.0	0.07	0.13	0.06	0.14	0.12	0.05	0.18	0.03	0.01	0.03	0.043
Inter-laboratories precision CV (%)	4.3	3.8	129.25	170.47	174.32	183.45	34.62	35.01	99.64	174.89	122.94	164.98	222.29
Within-laboratory precision CV (%)	0.9	0.5	17.74	8.34	14.30	68.34	3.50	2.47	17.31	2.35	12.98	6.43	5.87
Repeatability precision CV (%)	0.7	0.3	4.80	21.67	23.05	33.79	4.93	2.54	28.19	2.88	5.66	14.88	17.52
Reproducibility limit (R = D(2, 0.95)*s _R)	0.58	0.45	5.284	2.858	1.257	2.137	2.340	1.911	1.735	4.894	0.851	0.785	1.53
Within-laboratory-reproducibility limit (R _W = D(2, 0.95)*s _{RW})	0.12	0.06	0.725	0.140	0.103	0.796	0.237	0.135	0.301	0.066	0.090	0.031	0.04
Repeatability limit (r = D(3, 0.95)*s _r)	0.12	0.04	0.231	0.428	0.196	0.464	0.392	0.163	0.578	0.095	0.046	0.083	0.14

Table 6.2. Analysis of variance for the verified data

Statistics	No. 021									No. 022			
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H	Ex-Ca	Ex-Mg	Ex-K	Ex-Na
Number of Laboratories	13	13	7	7	6	6	6	8	6	10	9	11	10
Total sum of square	142280	113232	1267	110	20	18	7649	9809	196	640	31	24	32
ST/lmd	1824	1452	30	3	1	1	212	204	5	11	1	0	1
Number of Laboratories	13	13	7	7	6	6	6	8	6	10	9	11	10
Number of Data	78	78	42	42	36	36	36	48	36	60	54	66	60
Total sum	377.2	336.5	35.60	10.51	4.42	4.29	87.46	99.04	14.00	25.30	5.54	4.85	5.64
Total average	4.8	4.3	0.85	0.25	0.12	0.12	2.43	2.06	0.39	0.42	0.10	0.07	0.09
Sum of square inter-laboratories (S _R)	3.0	1.9	9.70	1.95	0.01	0.13	9.83	31.49	1.70	2.41	0.03	0.08	0.54
Sum of square within-laboratory (S _{RW})	0.0	0.0	0.00	0.01	0.00	0.00	0.03	0.02	0.00	0.01	0.00	0.00	0.00
Sum of square repeatability (S _r)	0.1	0.0	0.02	0.01	0.00	0.00	0.07	0.06	0.05	0.00	0.00	0.00	0.03
Total sum of square (S _T)	3.1	1.9	9.72	1.96	0.01	0.13	9.93	31.57	1.76	2.42	0.03	0.08	0.56
Inter-laboratories degree of freedom (φ _R)	12	12	6	6	5	5	5	7	5	9	8	10	9
Within-laboratory degree of freedom (φ _{RW})	13	13	7	7	6	6	6	8	6	10	9	11	10
Repeatability degree of freedom (φ _r)	52	52	28	28	24	24	24	32	24	40	36	44	40
Total degree of freedom (φ _T)	77	77	41	41	35	35	35	47	35	59	53	65	59
Inter-laboratories variance (V _R = S _R /φ _R)	0.25	0.16	1.617	0.325	0.002	0.025	1.966	4.499	0.341	0.268	0.004	0.008	0.060
Within-laboratory variance (V _{RW} = S _{RW} /φ _{RW})	0.00	0.00	0.001	0.002	0.000	0.000	0.004	0.002	0.000	0.001	0.000	0.000	0.000
Repeatability variance (V _r = S _r /φ _r)	0.00	0.00	0.001	0.000	0.000	0.000	0.003	0.002	0.002	0.000	0.000	0.000	0.001
Laboratory component of variance (s _b ² = (V _R -V _{RW})/(2*3))	0.04	0.03	0.269	0.054	0.000	0.004	0.327	0.749	0.057	0.045	0.001	0.001	0.010
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	0.000	-0.001	0.000	0.000	0.000	0.000
Repeatability component of variance (s _r ² = V _r)	0.00	0.00	0.001	0.000	0.000	0.000	0.003	0.002	0.002	0.000	0.000	0.000	0.001
Inter-laboratories standard deviation (s _R = SQRT(s _r ² /(2*3) + s _c ² /2 + s _b ²))	0.2	0.2	0.52	0.23	0.02	0.07	0.57	0.87	0.24	0.21	0.03	0.04	0.100
Within-laboratory standard deviation (s _{RW} = SQRT(s _r ² /3 + s _c ²))	0.0	0.0	0.01	0.02	0.01	0.01	0.04	0.03	0.00	0.01	0.00	0.00	0.001
Repeatability standard deviation (s _r = SQRT(s _r ²))	0.0	0.0	0.02	0.01	0.01	0.01	0.05	0.04	0.05	0.01	0.00	0.01	0.025
Inter-laboratories precision CV (%)	4.2	3.8	61.25	92.95	13.83	54.63	23.56	41.97	61.27	50.12	24.64	48.51	105.99
Within-laboratory precision CV (%)	0.6	0.2	1.76	9.26	4.15	7.53	1.55	1.32	1.05	3.20	1.08	1.68	1.59
Repeatability precision CV (%)	0.7	0.3	2.78	5.48	8.48	9.17	2.26	2.08	12.30	2.29	3.75	8.21	26.70
Reproducibility limit (R = D(2, 0.95)*s _R)	0.57	0.45	1.454	0.651	0.048	0.182	1.603	2.425	0.667	0.592	0.071	0.100	0.28
Within-laboratory-reproducibility limit (R _W = D(2, 0.95)*s _{RW})	0.08	0.02	0.042	0.065	0.014	0.025	0.106	0.076	0.011	0.038	0.003	0.003	0.00
Repeatability limit (r = D(3, 0.95)*s _r)	0.12	0.04	0.078	0.045	0.034	0.036	0.181	0.141	0.158	0.032	0.013	0.020	0.08

4. DISCUSSION

In the 4th project, the following two objectives were raised:

- i) To improve inter-laboratories-precision
- ii) To evaluate variation on the extraction process

As for inter-laboratories-precision, there was no clear improvement in the results although some possible factors related to the precisions were standardized based on the results of the previous projects. However, in the year 2002, analysts of five laboratories have been just changed, and certain laboratory changed their analytical system as described above. These changes in analyst and analytical system may also affect inter-laboratories variations, and it may be difficult to compare results of the 4th project and the previous projects directly. Especially in the 4th project, obvious calculation or writing mistakes were found out. Quality control in the respective laboratories should be promoted a little more and modification of reporting format by NC should also be considered in order to avoid easy mistakes. Thus, further effort should be made for improvement of precisions with promoting standardization of the procedures.

As for variation on the extraction process, there is no clear difference between precisions of No. 021 and No. 022, and it was suggested that process on instrumental analysis had relatively larger effect on precisions than the extraction process although further studies might be necessary.

5. ACKNOWLEDGMENT

ADORC wishes to thank Dr. Tomoyuki Hakamata for useful advice on planning the project.

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APPENDIX 1: Participating laboratories

1. CHINA

- | | |
|--|-------------|
| 1) Chong qing Institute of Environmental Science | 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 |
| Center for Soil and Agroclimate Research and Development | id02 |

3. JAPAN

- | | |
|---|-------------|
| Agricultural Experimental Station, Shimane Prefecture | jp01 |
|---|-------------|

4. MALAYSIA

- | | |
|---|-------------|
| Department of Environmental Sciences, Universiti Putra Malaysia | my01 |
|---|-------------|

5. MONGOLIA

- | | |
|--|-------------|
| Central Laboratory of Environmental Monitoring | mn01 |
|--|-------------|

6. PHILIPPINES

- | | |
|---|-------------|
| Department of Soil Science, University of the Philippines, Los Banos
(Instrumental analysis was done in Environmental Management Bureau) | ph01 |
|---|-------------|

7. Republic of KOREA

- | | |
|---|-------------|
| Soil Environmental Laboratory, 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, Hydro-Meteorological Service | vn01 |
|--|-------------|

Appendix 2.1. Entire data of pH in Sample No. 021

Lab.	pH(H ₂ O)			pH(KCl)			
	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	
cn01	4.7	4.6 (0.1)	4.7	4.0	4.0 (0.0)	4.0	
			4.6			4.0	
			4.6			4.0	
			4.7 (0.0)			4.0 (0.0)	4.0
			4.7			4.0	
4.7	4.0						
cn02	4.9	4.9 (0.0)	4.9	4.4	4.4 (0.0)	4.4	
			4.9			4.4	
			4.9			4.4	
			4.9 (0.0)			4.4 (0.0)	4.4
			4.9			4.4	
4.9	4.4						
cn03	4.8	4.8 (0.0)	4.8	4.3	4.3 (0.0)	4.3	
			4.8			4.3	
			4.8			4.3	
			4.8 (0.0)			4.3 (0.0)	4.3
			4.8			4.3	
4.8	4.3						
cn04	4.9	4.9 (0.1)	5.0	4.5	4.5 (0.0)	4.5	
			4.9			4.5	
			4.9			4.5	
			4.9 (0.0)			4.5 (0.0)	4.5
			4.9			4.5	
4.9	4.5						
id01	4.9	4.9 (0.0)	4.9	4.4	4.4 (0.0)	4.4	
			4.9			4.4	
			4.9			4.4	
			4.9 (0.0)			4.4 (0.0)	4.4
			4.9			4.4	
4.9	4.4						
id02	4.6	4.6 (0.0)	4.6	4.2	4.2 (0.0)	4.2	
			4.6			4.2	
			4.6			4.2	
			4.6 (0.0)			4.2 (0.0)	4.2
			4.6			4.2	
4.6	4.2						
jp01	5.0	4.9 (0.0)	4.9	4.4	4.4 (0.0)	4.4	
			4.9			4.4	
			4.9			4.4	
			5.0 (0.0)			4.4 (0.1)	4.4
			5.0			4.5	
5.0	4.4						
my01	4.7	4.7 (0.1)	4.7	4.2	4.1 (0.0)	4.1	
			4.7			4.1	
			4.6			4.1	
			4.6 (0.1)			4.2 (0.0)	4.2
			4.7			4.2	
4.6	4.2						
mn01	5.0	5.0 (0.1)	5.0	4.3	4.3 (0.0)	4.3	
			5.0			4.3	
			4.9			4.3	
			5.0 (0.1)			4.3 (0.0)	4.3
			5.0			4.3	
5.0	4.3						
ph01	5.1	5.2 (0.1)	5.1	4.6	4.6 (0.0)	4.6	
			5.2			4.6	
			5.2			4.6	
			5.0 (0.0)			4.6 (0.0)	4.6
			5.0			4.6	
5.0	4.6						
kr01	5.1	5.1 (0.1)	5.1	4.4	4.4 (0.0)	4.4	
			5.1			4.4	
			5.0			4.4	
			5.1 (0.0)			4.4 (0.1)	4.4
			5.1			4.3	
5.1	4.4						
ru01	5.0	5.0 (0.0)	5.0	4.3	4.3 (0.0)	4.3	
			5.0			4.3	
			5.0			4.3	
			5.0 (0.0)			4.3 (0.0)	4.3
			5.0			4.3	
5.0	4.3						
th01	4.4	4.4 (0.1)	4.3	4.1	4.1 (0.0)	4.1	
			4.4			4.1	
			4.4			4.1	
			4.4 (0.0)			4.1 (0.0)	4.1
			4.4			4.1	
4.4	4.1						
vn01	5.1	5.1 (0.1)	5.0	4.2	4.2 (0.0)	4.2	
			5.1			4.2	
			5.1			4.2	
			5.0 (0.1)			4.2 (0.0)	4.2
			5.0			4.2	
5.1	4.2						

Appendix 2.2. Entire data of exchangeable base cations in Sample No. 021

Lab.	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat
cn01	1.03	1.02 (0.01)	1.03	0.77	0.76 (0.01)	0.75	0.12	0.12 (0.01)	0.13	0.09	0.08 (0.01)	0.08
			1.01			0.77			0.12			0.09
			1.02			0.76			0.12			0.08
		1.03 (0.01)	1.04		0.78 (0.02)	0.77		0.12 (0.00)	0.12		0.09 (0.01)	0.09
			1.02			0.80			0.12			0.09
		1.03		0.76		0.12		0.08				
cn02	1.48	1.48 (0.00)	1.48	0.25	0.25 (0.00)	0.25	0.15	0.15 (0.00)	0.15	0.49	0.49 (0.00)	0.49
			1.48			0.25			0.15			0.49
			1.48			0.25			0.15			0.49
		1.48 (0.01)	1.48		0.25 (0.00)	0.25		0.14 (0.02)	0.15		0.48 (0.00)	0.48
			1.48			0.25			0.12			0.48
		1.47		0.25		0.15		0.48				
cn03	1.05	1.07 (0.07)	1.15	0.76	0.76 (0.04)	0.73	0.11	0.11 (0.01)	0.11	0.10	0.09 (0.01)	0.08
			1.01			0.74			0.11			0.08
			1.06			0.80			0.12			0.10
		1.02 (0.03)	0.99		0.76 (0.02)	0.75		0.10 (0.01)	0.10		0.11 (0.03)	0.14
			1.03			0.74			0.11			0.09
		1.05		0.78		0.10		0.09				
cn04	1.17	1.15 (0.11)	1.21	0.23	0.23 (0.00)	0.23	0.12	0.12 (0.02)	0.10	0.22	0.22 (0.01)	0.23
			1.21			0.23			0.14			0.22
			1.02			0.23			0.11			0.21
		1.18 (0.01)	1.18		0.23 (0.01)	0.23		0.12 (0.01)	0.11		0.22 (0.01)	0.22
			1.19			0.22			0.12			0.23
		1.18		0.23		0.12		0.22				
id01	7.59	7.29 (0.19)	7.51	0.95	0.86 (0.02)	0.87	1.70	1.71 (0.23)	1.96	2.81	2.72 (0.67)	2.65
			7.22			0.84			1.65			2.09
			7.15			0.86			1.51			3.43
		7.89 (0.05)	7.84		1.04 (0.10)	1.11		1.70 (0.09)	1.72		2.89 (0.16)	2.82
			7.94			1.08			1.60			2.77
		7.88		0.92		1.78		3.07				
id02	1.08	1.08 (0.01)	1.08	0.15	0.15 (0.01)	0.15	0.11	0.11 (0.01)	0.11	0.04	0.04 (0.00)	0.04
			1.08			0.16			0.10			0.04
			1.09			0.15			0.11			0.04
		1.08 (0.01)	1.09		0.15 (0.01)	0.14		0.10 (0.01)	0.10		0.05 (0.01)	0.05
			1.08			0.15			0.11			0.04
		1.08		0.15		0.10		0.05				
jp01	1.12	1.12 (0.02)	1.13	0.13	0.13 (0.01)	0.13	0.12	0.12 (0.01)	0.12	0.10	0.10 (0.01)	0.10
			1.10			0.12			0.11			0.09
			1.13			0.13			0.12			0.10
		1.12 (0.03)	1.12		0.13 (0.01)	0.13		0.11 (0.01)	0.12		0.10 (0.01)	0.10
			1.10			0.13			0.11			0.10
		1.15		0.12		0.11		0.09				
my01	0.01	0.01 (0.00)	0.01	0.16	0.11 (0.02)	0.10			ND	0.03	0.03 (0.01)	0.03
			0.01			0.14			ND			0.04
			0.01			0.10			ND			0.03
		0.01 (0.00)	0.01		0.20 (0.00)	0.20			ND		0.03 (0.00)	0.03
			0.01			0.20			ND			0.03
		0.01		0.20		ND		0.03				
mn01		-	-		-	-		-	-		-	-
		-	-			-			-			-
		-	-			-			-			-
		-	-			-			-			-
		-	-			-			-			-
ph01	1.44	2.02 (0.22)	1.84	3.85	3.77 (0.60)	4.07	0.49	0.58 (0.14)	0.61	0.98	1.70 (0.18)	1.87
			2.27			3.08			0.43			1.51
			1.96			4.17			0.71			1.73
		0.85 (0.14)	0.87		3.93 (0.25)	3.70		0.40 (0.09)	0.34		0.26 (0.02)	0.27
			0.70			3.90			0.50			0.28
	0.97		4.19		0.35		0.24					
kr01	0.70	0.69 (0.01)	0.70	0.12	0.12 (0.01)	0.12	0.13	0.13 (0.02)	0.14	0.13	0.14 (0.01)	0.13
			0.70			0.12			0.11			0.14
			0.68			0.11			0.14			0.14
		0.71 (0.01)	0.72		0.12 (0.01)	0.12		0.12 (0.02)	0.13		0.12 (0.00)	0.12
			0.72			0.12			0.13			0.12
		0.70		0.11		0.10		0.12				
ru01	1.22	1.22 (0.01)	1.22	0.26	0.26 (0.01)	0.25	0.10	0.10 (0.01)	0.11	0.13	0.14 (0.01)	0.15
			1.21			0.26			0.11			0.14
			1.22			0.26			0.09			0.13
		1.22 (0.00)	1.22		0.26 (0.01)	0.25		0.10 (0.01)	0.11		0.12 (0.02)	0.14
			1.22			0.26			0.11			0.12
		1.22		0.26		0.09		0.11				
th01	0.75	0.78 (0.01)	0.79	0.09	0.09 (0.00)	0.09	0.07	0.07 (0.01)	0.08	0.07	0.07 (0.00)	0.07
			0.77			0.09			0.07			0.07
			0.78			0.09			0.07			0.07
		0.72 (0.03)	0.75		0.09 (0.00)	0.09		0.07 (0.01)	0.08		0.07 (0.00)	0.07
			0.71			0.09			0.07			0.07
		0.70		0.09		0.07		0.07				
vn01	0.35	0.35 (0.01)	0.36	0.09	0.09 (0.00)	0.09	0.14	0.14 (0.00)	0.14	0.23	0.23 (0.00)	0.23
			0.34			0.09			0.14			0.23
			0.34			0.09			0.14			0.23
		0.36 (0.02)	0.38		0.09 (0.01)	0.08		0.14 (0.00)	0.14		0.23 (0.00)	0.23
			0.34			0.09			0.14			0.23
		0.36		0.09		0.14		0.23				

Note: ND, Not detected; -, not measured.

Appendix 2.3. Entire data of exchangeable acidity and acid cations in Sample No. 021

Lab.	Ex-acidity			Ex-Al			Ex-H		
	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat
cn01	2.59	2.60 (0.03)	2.62	1.98	2.01 (0.04)	2.03	0.61	0.60 (0.01)	0.59
			2.57			1.96			0.61
			2.62			2.03			0.59
			2.57 (0.00)			2.57			1.96 (0.00)
cn02	4.00	3.98 (0.01)	3.98	3.44	3.42 (0.01)	3.42	0.56	0.57 (0.01)	0.56
			3.99			3.42			0.57
			3.98			3.41			0.57
			4.02 (0.01)			4.01			3.46 (0.01)
cn03	2.84	2.83 (0.10)	2.81	2.32	2.31 (0.10)	2.31	0.53	0.53 (0.03)	0.50
			2.94			2.41			0.53
			2.75			2.21			0.55
			2.85 (0.07)			2.91			2.32 (0.07)
cn04	2.23	2.25 (0.10)	2.25	1.87	1.88 (0.01)	1.88	0.60	0.85 (0.89)	1.88
			2.15			1.89			0.34
			2.35			1.88			0.34
			2.22 (0.03)			2.20			1.86 (0.01)
id01	2.50	2.39 (0.00)	2.39	1.78	1.68 (0.00)	1.68	0.72	0.71 (0.00)	0.71
			2.39			1.68			0.71
			2.39			1.68			0.71
			2.61 (0.00)			2.61			1.88 (0.00)
id02	2.32	2.31 (0.03)	2.28	1.90	1.89 (0.03)	1.87	0.42	0.42 (0.01)	0.41
			2.32			1.89			0.43
			2.33			1.92			0.41
			2.33 (0.01)			2.32			1.90 (0.02)
jp01	2.72	2.71 (0.00)	2.71	2.50	2.50 (0.03)	2.48	0.22	0.21 (0.02)	0.23
			2.71			2.53			0.19
			2.71			2.50			0.22
			2.73 (0.01)			2.74			2.50 (0.03)
my01	0.25	0.41 (0.58)	0.05	0.58	0.57 (0.08)	0.62	2.68	2.56 (0.18)	2.76
			0.10			0.48			2.52
			1.08			0.60			2.40
			0.09 (0.01)			0.08			0.59 (0.04)
mn01	2.81	2.72 (0.00)	2.72	1.15	1.10 (0.17)	1.20	0.48	0.48 (0.00)	0.48
			2.72			0.90			0.48
			2.72			1.20			0.48
			2.89 (0.08)			2.98			1.20 (0.00)
ph01	2.71	2.67 (0.01)	2.67	2.50	2.46 (0.01)	2.46	0.21	0.21 (0.01)	0.22
			2.68			2.46			0.21
			2.66			2.45			0.21
			2.75 (0.01)			2.76			2.54 (0.01)
kr01	2.91	2.91 (0.10)	2.99	2.21	2.21 (0.03)	2.24	0.70	0.70 (0.08)	0.75
			2.93			2.19			0.74
			2.80			2.19			0.61
			2.91 (0.10)			2.80			2.21 (0.03)
ru01	1.66	1.66 (0.04)	1.65	1.55	1.55 (0.04)	1.54	0.11	0.11 (0.00)	0.11
			1.70			1.59			0.11
			1.62			1.51			0.11
			1.66 (0.02)			1.65			1.54 (0.03)
th01	2.52	2.51 (0.06)	2.56	2.10	2.09 (0.05)	2.14	0.42	0.41 (0.02)	0.43
			2.51			2.09			0.41
			2.45			2.05			0.40
			2.53 (0.03)			2.51			2.11 (0.07)
vn01	1.74	1.69 (0.02)	1.68	1.42	1.40 (0.04)	1.36	0.45	0.43 (0.03)	0.46
			1.68			1.41			0.41
			1.71			1.43			0.41
			1.79 (0.03)			1.77			1.45 (0.03)
			1.77			1.43			0.47
			1.82			1.48			0.47

Appendix 3. Entire data of exchangeable base cations in Sample No. 022

Lab.	Ex-Ca (cmol(+)/kg)			Ex-Mg (cmol(+)/kg)			Ex-K (cmol(+)/kg)			Ex-Na (cmol(+)/kg)		
	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat	Lab. Ave.	Average	Repeat
cn01	0.31	0.31 (0.00)	0.31 0.31 0.31	0.10	0.10 (0.00)	0.10 0.10 0.10	0.07	0.07 (0.00)	0.07 0.07 0.07	0.05	0.05 (0.00)	0.05 0.05 0.05
cn02	0.72	0.72 (0.00)	0.72 0.72 0.72	0.11	0.11 (0.00)	0.11 0.11 0.11	0.07	0.07 (0.00)	0.07 0.07 0.07	0.06	0.06 (0.00)	0.06 0.06 0.06
cn03	0.15	0.15 (0.00)	0.15 0.15 0.15	0.05	0.05 (0.00)	0.05 0.05 0.05	0.06	0.06 (0.00)	0.06 0.06 0.06	0.05	0.05 (0.01)	0.05 0.05 0.04
cn04	0.08	0.08 (0.00)	0.08 0.08 0.08	0.08	0.08 (0.01)	0.08 0.09 0.08	0.08	0.08 (0.00)	0.08 0.08 0.08	0.04	0.04 (0.01)	0.04 0.05 0.04
id01	6.46	6.46 (0.03)	6.50 6.44 6.45	0.98	0.97 (0.01)	0.96 0.97 0.98	1.07	1.08 (0.07)	1.14 1.10 1.00	2.04	2.07 (0.17)	2.26 2.01 1.94
id02	0.59	0.60 (0.01)	0.59 0.59 0.61	0.11	0.11 (0.00)	0.11 0.11 0.11	0.06	0.06 (0.00)	0.06 0.06 0.06	0.05	0.05 (0.00)	0.05 0.05 0.05
jp01	0.59	0.58 (0.01)	0.59 0.58 0.58	0.10	0.10 (0.00)	0.10 0.10 0.10	0.09	0.09 (0.01)	0.09 0.09 0.08	0.03	0.03 (0.01)	0.02 0.04 0.02
my01	0.31	0.32 (0.01)	0.32 0.33 0.32	0.28	0.25 (0.04)	0.30 0.22 0.24	ND	ND	ND ND ND	0.01	0.01 (0.00)	0.01 0.01 0.01
mn01	-	-	- - -	-	-	- - -	-	-	- - -	-	-	- - -
ph01	1.32	1.37 (0.10)	1.43 1.26 1.42	0.78	0.71 (0.04)	0.75 0.68 0.69	0.34	0.36 (0.06)	0.33 0.43 0.32	0.28	0.28 (0.11)	0.18 0.40 0.27
kr01	0.62	0.61 (0.00)	0.61 0.61 0.61	0.11	0.11 (0.00)	0.11 0.11 0.11	0.15	0.15 (0.02)	0.17 0.14 0.13	0.18	0.19 (0.02)	0.20 0.17 0.20
ru01	0.42	0.42 (0.02)	0.41 0.41 0.45	0.12	0.12 (0.01)	0.11 0.12 0.13	0.09	0.09 (0.00)	0.09 0.09 0.09	0.07	0.07 (0.01)	0.08 0.07 0.06
th01	0.43	0.45 (0.01)	0.45 0.44 0.45	0.14	0.14 (0.00)	0.14 0.14 0.14	0.05	0.05 (0.00)	0.05 0.05 0.05	0.05	0.05 (0.00)	0.05 0.05 0.05
vn01	-	-	- - -	-	-	- - -	0.09	0.09 (0.00)	0.09 0.09 0.09	0.28	0.28 (0.00)	0.28 0.28 0.28

Note: ND, Not detected; -, not measured.

Appendix 4. Optional experiments with the alternative factors

1. Introduction

The QA/QC program on soil monitoring proposed the methodologies to improve the reproducibility. In annex II of the Technical Manual for Soil and Vegetation Monitoring in East Asia, the detailed procedures were described (see Page 123 of the Technical Manual). According to the procedures, all stages on analysis should be checked, and potential factors capable to affect the precision should be listed. For the respective factors, alternative levels should be examined as the measurement condition. The results should be analyzed statistically, and then, the best combination of the respective factors should be clarified.

2. Objectives

The results in the previous (1st, 2nd, and 3rd) projects suggested that the reproducibility of soil analysis has been affected by various factors in the stages of the analytical procedures. Especially in the 3rd project, soil extract sample was sent to the participating laboratories, and precision on instrumental analysis was estimated. Based on the result on the 3rd project, the following factors were suggested to be potential factors capable to affect the reproducibility:

- 1) Preparation of standard solution (dilution by deionized water or extractant (1M CH₃COONH₄))**
- 2) Addition of Sr (or La/Cs) solution**
- 3) Instrument (AAS or FEP)**

For the analysis in the 4th project, the factors above would basically be unified to improve the reproducibility. In addition to the mandatory analysis, in order to clarify which factors are the most effective, the analyses with alternative factors will preferably be carried out in the participating laboratories.

3. Procedures

This optional analysis would be adopted for the following parameters:

Exchangeable Ca, Mg, K and Na

For the 4th project, the following alternative levels for the respective factors would be tested (Table 1). Characteristics of samples (soil or soil extract) and repeat analyses were also included in the factors. For five factors and two levels, sixteen experiments could be assigned as shown in Table 2 (Detailed assignment using the orthogonal array is shown in appendix).

The experiments No. 1 and No. 11 have already been carried out in the mandatory analyses as a standard condition. To get information on effect of the respective factors, it is suggested that the

participating laboratories will make an effort to carry out all the assigned experiments. Even if only little experiments could be carried out, it will be informative data.

Table 1. Factors and levels

Factors		Level 1	Level 2	Note
A	Repeat analysis	1 st analysis	2 nd analysis	Analysis would be repeated in different days
B	Instrument	AAS	FEP	For K and Na
C	Sample	Soil (No. 021)	Soil extract (No. 022)	
D	Solvent for preparation of samples and standard solution	1M CH ₃ COONH ₄	Deionized water	
E	Addition of Sr solution	Added	Not added	

AAS, Atomic Absorption Spectrometry; FEP, Flame (Emission) Photometry

Table 2. Assignment of the experiments

Exp. No.	A	B	C	D	E
1	1	1	1	1	1
2	1	1	1	2	2
3	1	1	2	1	2
4	1	1	2	2	1
5	1	2	1	1	2
6	1	2	1	2	1
7	1	2	2	1	1
8	1	2	2	2	2
9	2	1	1	1	2
10	2	1	1	2	1
11	2	1	2	1	1
12	2	1	2	2	2
13	2	2	1	1	1
14	2	2	1	2	2
15	2	2	2	1	2
16	2	2	2	2	1

Note: Value shows the levels of each factor.

4. Reporting

The Optional Reporting Format should be used for the report. Check boxes with bold frame should be checked to identify the experiment condition.

Appendix. The orthogonal array for assignment of the experiments (L16)

Experiment No.	1 A	2 B	3 AB	4 C	5 AC	6 BC	7 DE	8 D	9 AD	10 BD	11 CE	12 CD	13 BE	14 AE	15 E
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2
3	1	1	1	2	2	2	2	1	1	1	1	2	2	2	2
4	1	1	1	2	2	2	2	2	2	2	2	1	1	1	1
5	1	2	2	1	1	2	2	1	1	2	2	1	1	2	2
6	1	2	2	1	1	2	2	2	2	1	1	2	2	1	1
7	1	2	2	2	2	1	1	1	1	2	2	2	2	1	1
8	1	2	2	2	2	1	1	2	2	1	1	1	1	2	2
9	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
10	2	1	2	1	2	1	2	2	1	2	1	2	1	2	1
11	2	1	2	2	1	2	1	1	2	1	2	2	1	2	1
12	2	1	2	2	1	2	1	2	1	2	1	1	2	1	2
13	2	2	1	1	2	2	1	1	2	2	1	1	2	2	1
14	2	2	1	1	2	2	1	2	1	1	2	2	1	1	2
15	2	2	1	2	1	1	2	1	2	2	1	2	1	1	2
16	2	2	1	2	1	1	2	2	1	1	2	1	2	2	1

Corrigenda for the Report 2001

Mistakes of statistical analyses were found in the Table 5 of the Report of the Inter-laboratory Comparison Project 2001 on Soil. Different coefficient, $D(2, 0.95) (= 2.8)$, was used for calculation of permissible tolerances on the repeatability condition in the report instead of the coefficient, $D(3, 0.95) (= 3.3)$, because number of repetition was misunderstood (Values in the parenthesis of D , 2 and 3, shows number of repetition). Recalculated parts are shown in the extract of the Table 5 as follows.

Table 5. Analysis of variance in the entire data and the verified data (extract)

(Entire data)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Repeatability limit ($r = D(3, 0.95) * s_p$)	0.15	0.22	0.01	0.02	0.12	0.13	0.15
(Verified data)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Repeatability limit ($r = D(3, 0.95) * s_p$)	0.17	0.02	0.01	0.02	0.12	0.08	0.15

The recalculation does not influence on the final conclusions in the Report 2001