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

Report of the Inter-laboratory Comparison Project 2001

on Soil

3rd Attempt

November 2002
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 (INC) 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, which could be achieved through the evaluation of analytical results by statistical analysis, analytical instrument and its operating condition and other practical problems, are:

(i) To recognize the analytical precision and accuracy with instrumental analysis and titration methods of each participating laboratory, within-laboratory–precision, and inter-laboratories–precision for receiving an opportunity to improve the quality of the soil chemical analysis on EANET, and

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

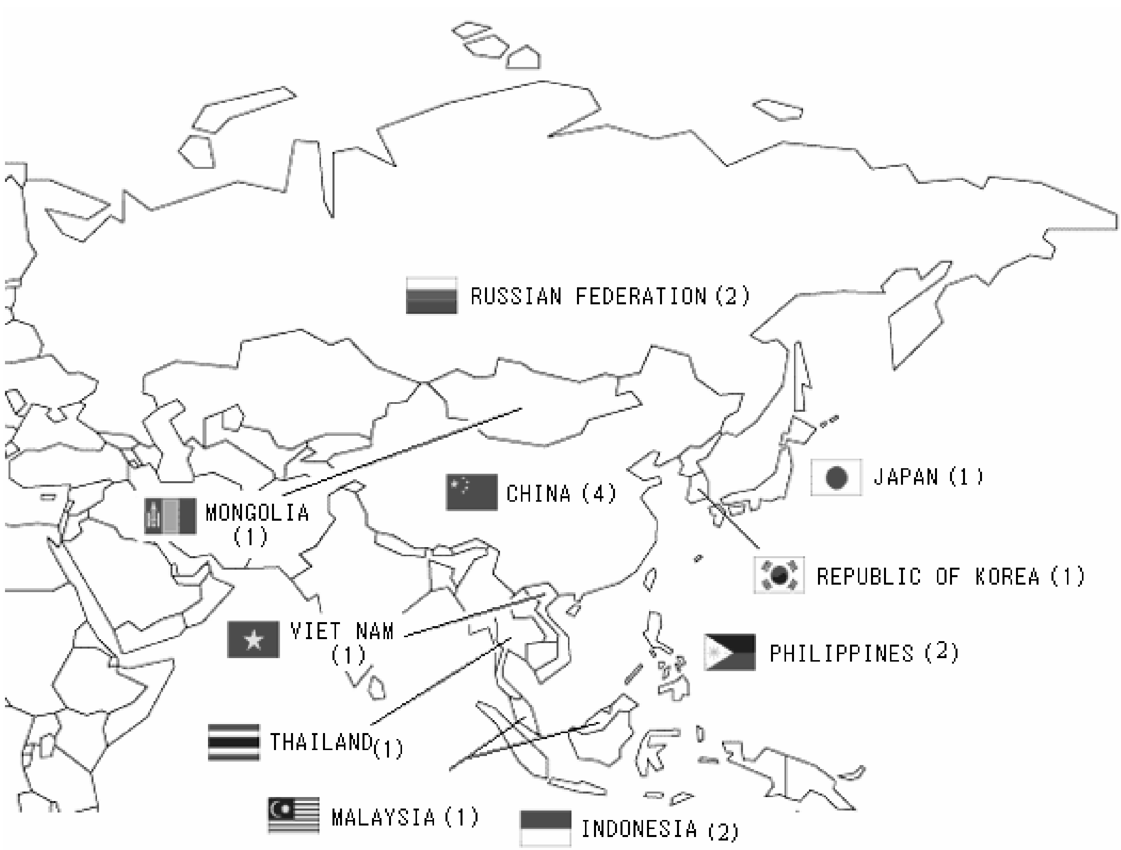

Figure 1. Laboratories participating in Inter-laboratory comparison project 2001 on soil
Number of parenthesis shows the number of laboratories of each EANET country.

1.1 Outlines of the 1st and 2nd Project

During the 1st (in 1999) and 2nd (in 2000) project, the Network Center (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 NC and evaluated statistically.

Based on the results of these projects, it was suggested that complicated procedures on soil analysis might be related to the variation among laboratories. Soil analyses have some steps in the procedures; e.g. extraction, instrumental analysis and/or titration. Therefore, in order to improve the analytical quality, at the first, it should be clarified which steps were most effective.

1.2 Objective of the 3rd project

Based on the discussion before, the objective of the 3rd project was to evaluate precision of instrumental analysis in the procedures on soil analyses. NC dispatched two soil extract samples, Sample No. 011 and 012, to laboratories for soil monitoring in the participating countries in January 2002. Fifteen laboratories of 10 countries analyzed chemical properties of the soil samples, and the results were submitted to NC by the end of June 2002.

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 Extract Samples

The characteristics of the samples were as follows:

Sample No. 011: Soil extract by Ammonium acetate solution for Exchangeable base cations

Air-dried soil (Andosol) was shaken with 1N-Ammonium acetate (CH_3COONH_4) solution for one hour, and laid for one day; the ratio of soil to 1N-Ammonium acetate was 1:25. 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.

Sample No. 012: Soil extract by Potassium chloride solution for Exchangeable Acidity, Al and H

Air-dried soil (Andosol) was shaken with 1N-Potassium chloride (KCl) for one hour; the ratio of soil to 1M KCl was 1:10. The extract was filtered by No.3 filter paper and membrane filter (pore size 0.2 μm), and then packed in 500 ml plastic bottles.

As the Network Center, Acid Deposition and Oxidant Research Center (ADORC) analyzed the above sample by some different methods and the results were shown in the Annex 3.1 and 3.2 as a reference.

2.2. Parameters

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

Table 1. Parameters to be measured

Soil Extract Sample No.	Parameters to be measured	Recommended analytical methods
011	a) Exchangeable Base Cations (Ca, Mg, K and Na)	AAS, FEP, ICP-AES, or ICP-MS
012	b) Exchangeable Acidity c) Exchangeable H d) Exchangeable Al	Titration Titration Titration, AAS, ICP-AES, or ICP-MS

Note: AAS, Atomic Absorption Spectrometry; FEP, Flame Emission Photometry; ICP-AES, Inductively Coupled Plasma Atomic Emission Spectroscopy; ICP-MS, Inductively Coupled Plasma Mass Spectrometry

"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)".

<u>In the respective laboratories, all the parameters were analyzed three times under the same conditions (repeatability condition; analyst, time, and instrument are the same). Then, under</u>

within-laboratory-reproducibility condition (part or all of analyst, time, and instrument are different), all the analytical procedures should be repeated twice.

2.3.1. Procedures for sample No.011

Ex-base cations in the sample No.011 were analyzed according to the following procedures.

1) Pipette an appropriate aliquot of the Sample No.011 into volumetric flask, add La, Sr or Cs solution to eliminate the interference of the sample if necessary, and then fill up to volume with pure water. This solution is named " Prepared sample". When La, Sr or Cs solution is added to the sample, add one to each standard solution to be a same concentration of La, Sr or Cs.
2) Prepare three sets of the above "prepared sample".
3) Analyze the prepared samples with AAS, ICP-AES, ICP-MS.
4) Store the calibration curves certainly and report them together with report formats.

Soil contents (cmol(+)/kg) of the sample were calculated by the following equations:

Ex-Ca (cmol(+)/kg soil) = [A ∗ B ∗ 250 ∗ 1]/[10 ∗ 20.04 ∗ 10]

Ex-Mg (cmol(+)/kg soil) = [A ∗ B ∗ 250 ∗ 1]/[10 ∗ 12.15 ∗ 10]

Ex-K (cmol(+)/kg soil) = [A ∗ B ∗ 250 ∗ 1]/[10 ∗ 39.10 ∗ 10]

Ex-Na (cmol(+)/kg soil) = [A ∗ B ∗ 250 ∗ 1]/[10 ∗ 23.00 ∗ 10]

Where

A = "Measurement values of prepared samples□concentrations of prepared sample□" in mg/l.

B = "Dilution volume"(B=2, in case of 25 ml sample is used in 50 ml volumetric flask)

2.3.2. Procedures for sample No.012

Ex-Acidity, Al and H in the sample No.012 were analyzed according to the following procedures. The procedures were carried out three times under the same condition.

1) Pipette 40 ml of the sample No.012 into a 250-mL beaker, and add 5 drops of phenolphthalein indicator.
2) Titrate the solution with 0.025 M NaOH to a permanent pink end point with alternate stirring and standing. If needed, add a few more drops of indicator to replace that adsorbed by the precipitate of $Al(OH)_3$. The amount of base used is equivalent to the total amount of acidity in the aliquot taken.
3) Add a few drop of 0.1 N HCl to bring the solution back to the colorless condition, and add 10 ml of NaF solution.
4) Titrate the solution with 0.02 N HCl until the color just disappears while stirring the solution constantly. Add 1 or 2 drops of indicator. If the color appears, continue addition of acid until the color just disappears and does not return within 2 minutes.

Soil contents (cmol(+)/kg) of the sample were calculated by the following equations:

Ex- Acidity (cmol (+) / kg soil) = $[A * M_{NaOH} * 2.5 * 100 * 1] / 10$

Ex- Al (cmol (+) / kg soil) = $[B * M_{HCl} * 2.5 * 100 * 1] / 10$

Ex- H (cmol (+) / kg soil) = $[(A * M_{NaOH} – B * M_{HCl}) * 2.5 * 100 * 1] / 10$

Where

A = "Titration volume of 0.025 M NaOH solution" in mL

B = “Titration volume of 0.02 M HCl solution” in mL
M_{HCl} = molarity of HCl solution
M_{NaOH} = molarity of NaOH solution

Extract concentration, (calculated) soil content, 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) can be divided into 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 by Cochran and Grubbs methods, the statistics were calculated.

The variations (CVs) among the participating laboratories were relatively high, within 32 – 72 % in the entire data. CVs of Ex-Ca, Na, and H were still 39 – 72 % even in the verified data. CV of Ex-K was the lowest although the values were almost same as Ex-Mg. It seems that variation among the laboratories depends on the parameters even if the same instruments (e.g. AAS) were used. Analytical condition for each parameter should be discussed. CV of Ex-Acidity was relatively low probably due to simple method of titration.

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

Statistics	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-Acidity	Ex-Al	Ex-H
	cmol(+)/kg						
	(Entire data)						
Number of Laboratories	15	15	15	15	16	15	15
Total average	0.72	0.12	0.10	0.07	2.06	1.79	0.30
Median	0.75	0.10	0.08	0.07	2.23	1.93	0.31
Maximum	1.17	0.28	0.22	0.14	2.88	2.88	0.78
Minimum	0.25	0.05	0.07	0.00	0.13	0.13	0.00
Standard deviation	0.23	0.06	0.04	0.03	0.65	0.60	0.21
CV(%)	31.4	49.2	44.6	42.8	31.7	33.3	71.7
	(Verified data)						
Number of Laboratories	10	12	12	13	15	12	15
Total average	0.72	0.09	0.08	0.07	2.19	1.92	0.30
Median	0.77	0.10	0.08	0.07	2.24	1.95	0.31
Maximum	1.17	0.13	0.09	0.14	2.88	2.88	0.78
Minimum	0.25	0.05	0.07	0.00	1.26	1.17	0.00
Standard deviation	0.28	0.02	0.01	0.03	0.41	0.42	0.21
CV(%)	38.7	24.6	7.3	46.3	18.9	22.0	71.7

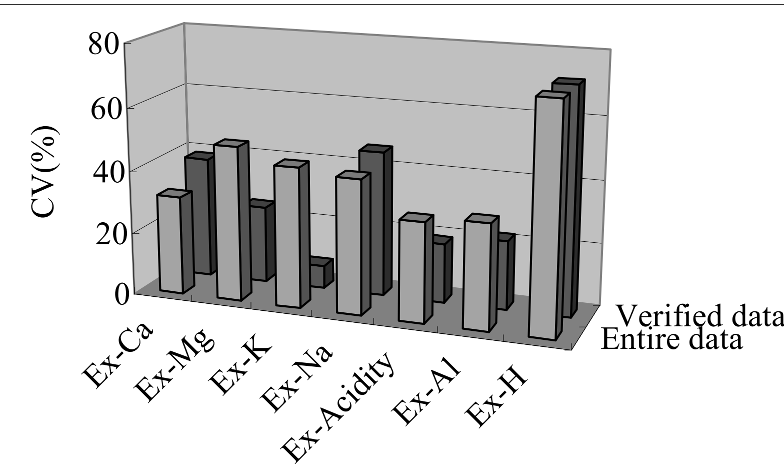

Figure 2. CV among laboratories

Note: CV, Coefficient of variation (%) = (standard deviation/average)*100

In the previous results on the second project (Acid Deposition and Oxidant Research Center, 2001) variations (CV) on the same soil type, Andosol, were a little higher, 46 - 53 % in Ex-base cations (Ca, Mg, K and Na). In the second project, air-dried samples were distributed to the laboratories, and samples were extracted at first in each laboratory and then analyzed. Therefore, the variations in the second project might include effect of the processes on extraction and instrumental analysis. In this project, extract sample was distributed and process on the instrumental analysis was only evaluated. Comparing the results of the second and third project, it seems that instrumental analysis has relatively large effect on variation among the laboratories.

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 and 3.2. Error bar shows 95% confidence interval.

The results in ADORC were relatively large value compared with the results of the participating laboratories (see Appendix 3.1 and 3.2). In Ex-Acidity, Al and H, reproducibility was obtained in these analyses. In Ex-base cations, the results were varied a little depending on the method as described below.

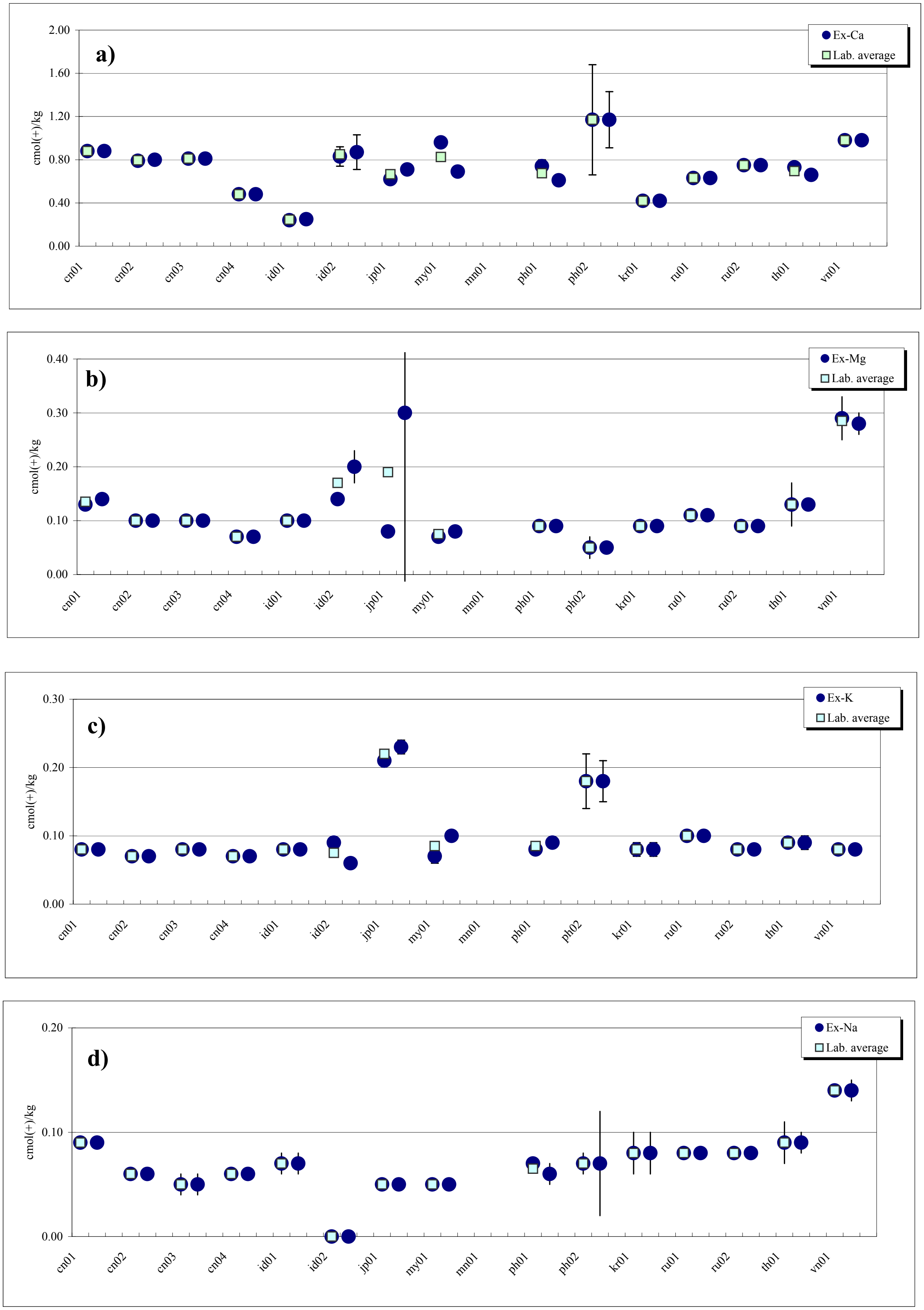

Figure 3.1. The averages of triplicate analysis and the laboratory average in a) Ex-Ca, b) Ex-Mg, c) Ex-K, and d) Ex-Na. Error bar shows 95% confidence interval calculated from the triplicate analysis.

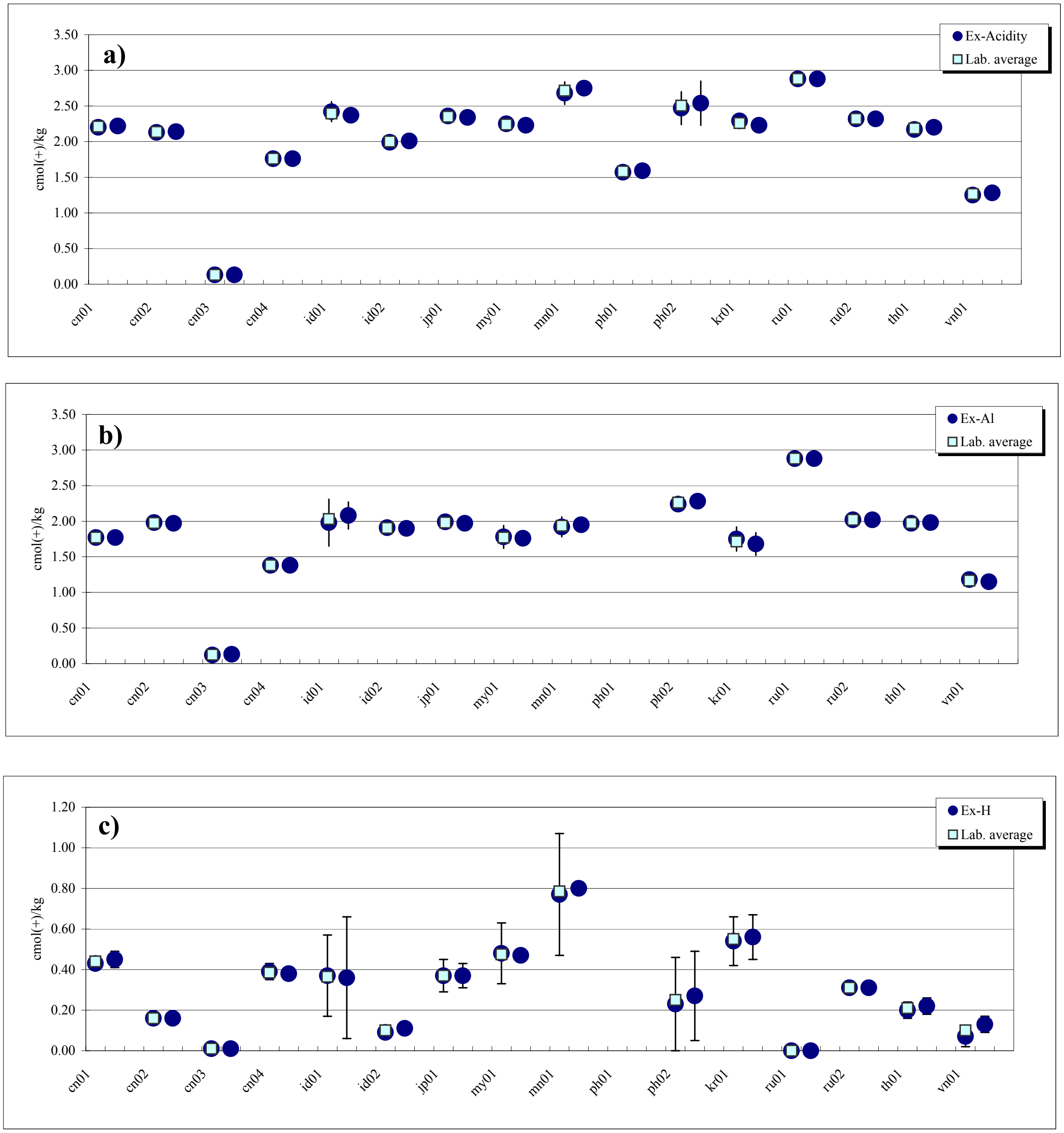

Figure 3.2. The averages of triplicate analysis and the laboratory average in a) Ex-Acidity, b) Ex-Al, and c) Ex-H. Error bar shows 95% confidence interval calculated from the triplicate analysis.

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. “id02”, “jp01”, “my01”, “ph01” and “th01” for Ex-Ca, “id02” and “jp01” for Ex-Mg. Then, laboratories, which have remarkably large average, were judged as outliers by Grubbs method (examination of the average value of each laboratory): e.g. “vn01” for Ex-Mg, “jp01”, “ph02”, and “ru01” for Ex-K.

The results of verification were shown in Table 3.

Result of Ex-Ca was relatively varied in the within-laboratory condition and inter-laboratories condition, however outliers were not detected by Grubbs method probably due to normal distribution of the data. In Ex-H also, outliers were not detected although the results were significantly varied.

For the data of Ex-Mg in “jp01”, the second triplicate analyses were varied (see Appendix 2.1) and detected as outliers. The Network Center received the comment from the laboratory that it was an error in writing.

3.2.2. Analytical condition

1) Number of analyst and their experience

Number of analyst and their years of experience were shown in Table 4.1. For measurement of Ex-base cations, different analysts might carry out the repeat analysis in three laboratories, namely “cn02”, “ph01”, and “ru01”. A few results of “ph01” were detected as outliers by Cochran method, and for these results the repeat analysis by different analysts may affect the within-laboratory reproducibility. In “id02”, different analysts operated AAS and FEP, and the same analysts carried out the repeat analysis. For Ex-Acidity, Al, and H, one analyst carried out all the procedures in each laboratory. Years of experience of analysts were varied, and the implication between experience and data was not observed.

2) Analytical instrument

Analytical instruments used for the measurement were shown in Table 4.2.

For Ex-Ca and Mg, all the laboratories except “vn01” used AAS. Laboratory “my01” used also ICP-AES for the repeat analysis, and it might be main factor for the outliers of Ex-Ca detected by Cochran method. In “ph01”, the 1^{st} and 2^{nd} analysis were carried out by different makers of AAS, therefore, it might also be one of the factors for the outliers. Data of Ex-Mg in “vn01” calculated from Ex-Ca (by titration) and hardness were relatively large and detected by Grubbs methods.

Seven laboratories and six laboratories used FEP for Ex-K and Ex-Na, respectively. The data on Ex-K by FEP were significantly larger than ones by AAS ($P < 0.05$), and more variable; averages and 95% confidence intervals (in parenthesis) of the data by AAS and FEP were 0.08 (0.00) and 0.12 (0.03) cmol(+)/kg, respectively. In Ex-Na, there were no significant difference between AAS and FEP; averages were 0.07 (0.01) and 0.07 (0.02) cmol(+)/kg, respectively.

For Ex-Acidity, all the laboratories used titration method, and some laboratories used AAS, ICP-AES, and photometry for Ex-Al. Any implication between these instruments and trend on the data were not observed.

Years in use of instruments were shown in Table 4.3. Seven laboratories used instruments older than ten years, 12 – 33 years. Even 33 years old instrument of "id02" could make comparable values for Ex- Ca, Mg, and K, although results of the repeat analysis were a little varied. However, the old instrument (FEP) could not detect Ex-Na. On the other hand, "cn04" used brand-new instrument (AAS) for Ex-Ca and Mg. The results were relatively small (Ex-Ca, 0.48 cmol(+)/kg) compared with the total average (0.72 cmol(+)/kg), although outliers were not detected.

3) Analytical condition for AAS and FEP

As analytical conditions for AAS and FEP, background (BG) correction method and added solution were shown in Table 4.4 a). Concerning BG correction, D2 and Zeeman were used in three laboratories, respectively. Specific implication between BG correction and the results were not observed. Nine laboratories and seven laboratories added La or Sr solution for Ex-Ca and Ex-Mg, respectively, in the sample solution for AAS analysis. Five laboratories and four laboratories added Cs or Sr solution for Ex-K and Ex-Na, respectively, in the sample solution for AAS or FEP analysis.

In general, La and Cs solution were frequently used for AAS analysis of Ca and K in order to suppress effect of other constituent ions in the solution. For soil extract sample, Sr solution was also used for the same purpose. The sensitivity of instruments for Ca and K would be improved by adding these solutions. An effect of La, Sr, and Cs solution was shown in Table 4.4 b). Average of the data on Ex-Ca was slightly larger when these solutions were added than that of the data without the solutions although the difference was not significant. The average of "Added" group excluding specific small value (0.48 cmol(+)/kg in "id01") would be 0.79 (0.10) cmol(+)/kg. It was suggested that addition of La or Sr solution could improve sensitivity of AAS, and provide larger value for measurement of Ex-Ca. Significant difference between "Added" and "Not added" group was not observed for Ex-Mg. As for Ex-K and Na, "Not added" group made rather larger values than "Added" group. Most laboratories of "Not added" group used FEP for the analysis of Ex-K, and as described above, the instrument might affect the data.

In ADORC, different methods were applied/treated for analysis for Ex-base cations (see Appendix 3.1). Calibration curve method and standard additional method were carried out for AAS. Although the results were not so different for Ex-Mg, K and Na, the data by calibration curve method were smaller than ones by standard additional method, especially for Ex-Ca. In the standard additional method, the sample solution was used as a matrix for preparation of the standard solution. Thus, the standard solution had similar matrix to the sample solution and the effect of other ions and a matrix of the solution could be cancelled. As the results, the larger values were detected. The similar values were obtained by ICP-AES. ICP-AES would also be affected by matrix of the sample solution, and therefore, in this analysis, extractant (ammonium acetate) was used for preparation of standard solution to make similar matrix to the sample solution. For canceling effect of matrix, it might be useful to prepare the standard solution by the extractant.

4) Date of analysis

Date of analysis in the respective laboratories and days used for the analysis were shown in Table 4.5. All the laboratories carried out the analysis from March to June, and the most of them did it from March and April. There were no significant implication between date of analysis and the data. Days used for the analysis was only one or two days in most laboratories. Interval between the first and second analysis of the repeat analysis was varied from 0 (in a same day) to 77 days, however the interval might not affect the results of repeat analysis (within-laboratory reproducibility) in these laboratories.

Table3. Data verified by Cochran-Grubbs methods

Laboratory	Ca	Mg	K	Na	Ex-acidity	Al	H
	cmol(+)/kg						
cn01	0.88	0.13	0.08	0.09	2.20	1.77	0.43
	0.88	0.13	0.08	0.09	2.22	1.77	0.45
cn02	0.79	0.10	0.07	0.06	2.13	1.98	0.15
	0.80	0.10	0.07	0.06	2.14	1.97	0.16
cn03	0.81	0.10	0.08	0.05	0.13*g	0.12*g	0.01
	0.81	0.10	0.08	0.05	0.13*g	0.13*g	0.01
cn04	0.48	0.07	0.07	0.06	1.76	1.38	0.39
	0.48	0.07	0.07	0.06	1.76	1.38	0.38
id01	0.24	0.10	0.08	0.07	2.42	1.98*c	0.37
	0.25	0.10	0.08	0.07	2.37	2.08*c	0.35
id02	0.83*c	0.14*c	0.09	0.00	1.99	1.91	0.09
	0.87*c	0.20*c	0.06	0.00	2.01	1.90	0.11
jp01	0.62*c	0.08*c	0.21*g	0.05	2.36	1.99	0.37
	0.71*c	0.30*c	0.23*g	0.05	2.34	1.97	0.36
my01	0.96*c	0.07	0.07	0.05	2.25	1.78	0.48
	0.69*c	0.08	0.10	0.05	2.23	1.76	0.47
mn01					2.68	1.92	0.77
					2.75	1.95	0.80
ph01	0.74*c	0.09	0.08	0.07*c	1.57		
	0.61*c	0.09	0.09	0.06*c	1.59		
ph02	1.17	0.05	0.18*g	0.07	2.47	2.24	0.23
	1.17	0.05	0.18*g	0.07	2.54	2.28	0.27
kr01	0.41	0.09	0.08	0.08	2.29	1.75*c	0.54
	0.42	0.09	0.08	0.08	2.23	1.68*c	0.56
ru01	0.63	0.10	0.10*g	0.08	2.88	2.88	0.00
	0.63	0.10	0.10*g	0.08	2.88	2.88	0.00
ru02	0.75	0.09	0.08	0.08	2.32	2.02	0.31
	0.75	0.09	0.08	0.08	2.32	2.02	0.31
th01	0.73*c	0.13	0.09	0.09*c	2.17	1.97	0.20
	0.66*c	0.13	0.09	0.10*c	2.20	1.98	0.22
vn01	0.98	0.29*g	0.08	0.14	1.25	1.18	0.07
	0.98	0.28*g	0.08	0.14	1.28	1.15	0.13

The outliers judged by Cochran and Grubbs methods were marked with asterisk c and g, respectively.

Table 4.1. Number and experience of analyst

Lab.	Exchangeable base cations			Exchangeable acidity		
	Number of analyst	Years of experience		Number of analyst	Years of experience	
		Chemical	Soil		Chemical	Soil
cn01	1	18	17	1	17	16
cn02	2	6	3	1	3	3
cn03	1	4	2	1	11	3
cn04	1	5	5	1	5	5
id01	1	10	7	1	10	7
id02	2	30/21	30/21	1	5	5
jp01	1	3	3	1	3	3
my01	1	5	3	1	5	3
mn01	-	-	-	1	8	8
ph01	2	13/6	10/1	1	5	1
ph02	1	25	25	1	25	25
kr01	1	6	4	1	6	4
ru01	2	4/13	4/2	1	4	4
ru02	1	7	3	1	7	3
th01	1	2	2	1	2	2
vn01	1	+	1	1	+	1

Table 4.2. Analytical instrument

Lab.	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-Acidity	Ex-Al
cn01	AAS	AAS	AAS	AAS	Titration	Titration
cn02	AAS	AAS	AAS	AAS	Titration	Titration
cn03	AAS	AAS	AAS	AAS	Titration	Titration
cn04	AAS	AAS	FEP	FEP	Titration	ICP-AES
id01	AAS	AAS	AAS	AAS	Titration	AAS
id02	AAS	AAS	FEP	FEP	Titration	AAS
jp01	AAS	AAS	FEP	FEP	Titration	Titration
my01	AAS/ICP-AES*1	AAS/ICP-AES*1	AAS/ICP-AES*1	AAS/ICP-AES*1	Titration	ICP-AES
mn01	-	-	-	-	Titration	Titration
ph01	AAS/AAS*2	AAS/AAS*2	AAS/AAS*2	AAS/AAS*2	Titration	-
ph02	AAS	AAS	FEP	AAS	Titration	Titration
kr01	AAS	AAS	AAS	AAS	Titration	Titration
ru01	AAS	AAS	FEP	FEP	Titration	Titration
ru02	AAS	AAS	FEP	FEP	Titration	Others (photometry)
th01	AAS	AAS	AAS	AAS	Titration	Titration
vn01	Titration	Calculation*3	FEP	FEP	Titration	Titration

Note: AAS, Atomic absorption Spectrometry; FEP, Flame (emission) photometry; ICP-AES, Inductively Coupled Plasma Atomic Emission Spectroscopy. *1. The 1st and 2nd analyses were carried out by different instruments, AAS and ICP-AES, respectively. *2. The 1st and 2nd analyses were carried out by different makes of AAS. *3. Calculation from Ca and hardness

Table 4.3. Years in use of instruments

Lab.	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-Al
cn01	4	4	4	4	-
cn02	12	12	12	12	-
cn03	16	16	16	16	-
cn04	1	1	2	2	5
id01	9	9	9	9	2
id02	33	33	33	33	7
jp01	16	16	16	16	-
my01	12/8*1	12/8*1	12/8*1	12/8*1	8
mn01	-	-	-	-	-
ph01	2/3*2	2/3*2	2/3*2	2/3*2	-
ph02	5	5	12	5	-
kr01	3	3	3	3	-
ru01	17	17	17	17	-
ru02	22	22	18	18	1
th01	5	5	5	5	-
vn01	-	-	6	6	-

Note: *1. The 1st and 2nd analyses were carried out by different instruments, AAS and ICP-AES, respectively.
*2. The 1st and 2nd analyses were carried out by different makes of AAS.

Table 4.4 a) Analytical condition for AAS and FEP

Laboratory	Ex-Ca		Ex-Mg		Ex-K		Ex-Na		Ex-Al	
	BG Correction	Added solution[*1]	BG Correction	Added solution	BG Correction	Added solution	BG Correction	Added solution	BG Correction	Added solution
cn01	no	added	no	added	no	not added	no	not added	-	-
cn02	D2	added	D2	added	D2	added	D2	added	-	-
cn03	Zeeman	added	Zeeman	added	Zeeman	added	Zeeman	added	-	-
cn04	+	added□Sr□	+	added□Sr□	+	+	+	+	-	-
id01	Zeeman	added□Sr□	Zeeman	added□Sr□	Zeeman	added□Sr□	Zeeman	added□Sr□	no	added
id02	no	added	no	added	no	added	no	added	Zeeman	not added
jp01	Zeeman	added□Sr□	Zeeman	added□Sr□	Zeeman	not added	Zeeman	not added	-	-
my01	no	not added	no	not added	no	not added	no	not added	-	-
mn01	-	-	-	-	-	-	-	-	-	-
ph01	D2	added(La)	D2	not added	no	added (Cs)	no	not added	-	-
ph02	no	added(Sr)	no	not added	no	not added	no	not added	-	-
kr01	no	not added	no	not added	no	not added	no	not added	-	-
ru01	D2	not added	D2	not added	D2	not added	D2	not added	-	-
ru02	no	not added	no	not added	no	not added	no	not added	-	-
th01	no	not added	no	not added	no	not added	no	not added	-	-
vn01	-	-	-	-	+	+	+	+	-	-

Note: +, No information in the report; -, other methods were used; BG, Background. *1. La, Sr, or Cs solution was added for the analysis. In some laboraotory, added solution was not reported.

Table 4.4 b) Effect of La, Sr, or Cs solution

Addition of La, Sr, or Cs	Ex-Ca	Ex-Mg	Ex-K	Ex-Na
Not added	0.66 (0.13)	0.09 (0.02)	0.12 (0.03)	0.07 (0.01)
Added	0.73 (0.13)	0.11 (0.02)[1]	0.08 (0.01)*	0.05 (0.02)**

Note: Value in parenthesis shows 95% confidence interval. 1. Jp01 were excluded for the calculation. *, Significant difference by ANOVA, $P < 0.05$. **, $P < 0.01$.

Table 4.5. Date of analysis

Lab.	Ex-Ca			Ex-Mg			Ex-K/Ex-Na			Ex-Acidity		
	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	26-Mar	2	7	26-Mar	2	7	26-Mar	2	7	26-Mar	2	7
	2-Apr	2		2-Apr	2		2-Apr	2		2-Apr	2	
cn02	6-Mar	2	6	6-Mar	2	6	18-Mar	1	2	4-Mar	1	3
	12-Mar	2		12-Mar	2		20-Mar	1		7-Mar	1	
cn03	26-Feb	1	1	26-Feb	1	1	26-Feb	1	1	Not Rep.	1	0
	27-Feb	1		27-Feb	1		27-Feb	1		Not Rep.	1	
cn04	13-Mar	1	0	13-Mar	1	0	13-Mar	1	0	14-Mar	1	0
	13-Mar	1		13-Mar	1		13-Mar	1		14-Mar	29	
id01	19-Feb	1	0	19-Feb	1	0	19-Feb	1	0	20-Feb	1	0
	19-Feb	1		19-Feb	1		19-Feb	1		20-Feb	1	
id02	7-Feb	1	14	7-Feb	1	14	7-Feb	1	14	7-Mar	1	1
	21-Feb	1		21-Feb	1		21-Feb	1		8-Mar	1	
jp01	13-Feb	1	6	13-Feb	1	6	13-Feb	1	6	20-Feb	1	1
	19-Feb	1		19-Feb	1		19-Feb	1		21-Feb	1	
my01	27-Mar	1	1	27-Mar	1	1	27-Mar	1	1	27-Mar	1	1
	28-Mar	1		28-Mar	1		28-Mar	1		28-Mar	1	
mn01	-	-	-	-	-	-	-	-	-	25-Feb	1	2
	-	-	-	-	-	-	-	-	-	26-Feb	1	
ph01	4-Apr	2	77	4-Apr	2	77	4-Apr	2	77	20-Mar	1	5
	20-Jun	1		20-Jun	1		20-Jun	1		25-Mar	1	
ph02	7-Mar	1	1	7-Mar	1	1	11-Mar	1	1	15-Mar	1	1
	8-Mar	1		8-Mar	1		12-Mar	1		16-Mar	1	
kr01	8-Apr	1	2	8-Apr	1	2	8-Apr	1	2	8-Apr	1	2
	10-Apr	1		10-Apr	1		10-Apr	1		10-Apr	1	
ru01	10-Mar	1	3	10-Mar	1	3	10-Mar	1	3	18-Mar	1	1
	13-Mar	1		13-Mar	1		13-Mar	1		19-Mar	1	
ru02	4-Apr	3	21	4-Apr	3	21	8-Apr	5	17	10-Apr	2	6
	25-Apr	2		25-Apr	2		25-Apr	2		16-Apr	2	
th01	7-May	14	0	26-Apr	3	0	26-Apr	3	0	23-Apr	2	0
	7-May	14		26-Apr	3		26-Apr	3		23-Apr	2	
vn01	8-Mar	1	0	8-Mar	1	0	8-Mar	1	0	8-Mar	1	0
	8-Mar	1		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.

3.3. Analysis of variance and estimation of precision

For the entire data and verified data, " repeatability-precision", "within-laboratory-precision" and "inter-laboratories-precision" were estimated (Table 5).

1) Repeatability-precision

Repeatability standard deviations were relatively small for the most parameters even for the entire data, and the CVs of the most parameters were less than 10%. Especially for Ex-Acidity and Al, the CVs were less than 3% in the entire data, and less than 2% in the verified data. CV of Ex-H was relatively large even in the verified data. Ex-H was done as the calculation value from Ex-Acidity and Al, and it may be one of the factors for the large variation.

The analysis was carried out three times under the same condition. Process on dilution of the sample, and stability of the instruments might affect the results. These 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 the most parameters even in the entire data, and the CVs of the most parameters were less than 10%. Especially the CVs of Ex-Acidity and Al were less than 2% in both the entire data and verified data. Especially in the verified data, CVs of Ex-Ca and Al were less than 1%.

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 even in the verified data; even in the verified data, CVs were 25 - 46%. Only CV of Ex-K was 7.3%. CVs of Ex-Acidity and Al were around 20%.

In the same soil type, Andosol, of the second project, the inter-laboratory precision (CV) of soil analysis was about 50% for Ex-base cations; CVs of Ex-Ca, Mg, K, and Na were 45.72%, 52.75%, 51.89%, and 51.10%, respectively. The inter-laboratories precisions (CVs) for Ex-Acidity, Al and H were 31.45%, 62.67%, and 75.07%, respectively. As described above, these precisions of soil analysis included effect of processes on soil extraction and instrumental analysis. In this third project, the precision on instrumental analysis was estimated. Comparing these precisions and the results of this project, it was suggested that process on instrumental analysis had relatively large effect on the inter-laboratories-precision.

To improve the inter-laboratory precision, standard operating procedures should be elaborated based on the discussion on analytical condition.

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. However, repeatability limits for Ex-Ca and H were relatively large and significant larger than within-laboratory reproducibility limit. Repeatability precision should be improved.

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

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

(Entire data)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	15	15	15	15	16	15	15
Number of Data	90	90	90	90	96	90	90
Total sum	65.22	10.66	8.71	6.28	197.61	161.27	26.99
Total average	0.72	0.12	0.10	0.07	2.06	1.79	0.30
Sum of square inter-laboratories (S_R)	4.35	0.29	0.16	0.08	38.21	29.92	3.88
Sum of square within-laboratory (S_{RW})	0.16	0.08	0.00	0.00	0.03	0.03	0.01
Sum of square repeatablility (S_r)	0.12	0.27	0.00	0.00	0.08	0.10	0.13
Total sum of square (S_T)	4.63	0.63	0.16	0.08	38.32	30.05	4.02
Inter-laboratories degree of freedom (ϕ_R)	14	14	14	14	15	14	14
Within-laboratory degree of freedom (ϕ_{RW})	15	15	15	15	16	15	15
Repeatability degree of freedom (ϕ_r)	60	60	60	60	64	60	60
Total degree of freedom (ϕ_T)	89	89	89	89	95	89	89
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.311	0.020	0.011	0.005	2.547	2.137	0.277
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.011	0.005	0.000	0.000	0.002	0.002	0.001
Repeatability variance ($V_r = S_r/\phi_r$)	0.002	0.004	0.000	0.000	0.001	0.002	0.002
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.050	0.003	0.002	0.001	0.424	0.356	0.046
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.003	0.000	0.000	0.000	0.000	0.000	0.000
Repeatability component of variance ($s_r^2 = V_r$)	0.002	0.004	0.000	0.000	0.001	0.002	0.002
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.228	0.058	0.043	0.030	0.652	0.597	0.215
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.059	0.042	0.008	0.002	0.025	0.026	0.016
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.045	0.067	0.004	0.006	0.036	0.040	0.046
Inter-laboratories precision CV (%)	31.41	49.23	44.55	42.83	31.65	33.31	71.67
Within-laboratory precision CV (%)	8.19	35.07	8.46	2.76	1.22	1.44	5.33
Repeatability precision CV (%)	6.20	56.30	4.62	8.27	1.74	2.23	15.37
Reproducibility limit ($R_W = D(2, 0.95)*s_R$)	0.64	0.16	0.12	0.08	1.82	1.67	0.60
Within-laboratory-reproducibility limit ($R = D(2, 0.95)*s_{Rw}$)	0.17	0.12	0.02	0.01	0.07	0.07	0.04
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.13	0.19	0.01	0.02	0.10	0.11	0.13
(Verified data)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	10	12	12	13	15	12	15
Number of Data	60	72	72	78	90	72	90
Total sum	42.94	6.81	5.71	5.33	196.83	138.05	26.99
Total average	0.72	0.09	0.08	0.07	2.19	1.92	0.30
Sum of square inter-laboratories (S_R)	4.15	0.04	0.00	0.07	14.41	11.77	3.88
Sum of square within-laboratory (S_{RW})	0.00	0.00	0.00	0.00	0.03	0.01	0.01
Sum of square repeatablility (S_r)	0.11	0.00	0.00	0.00	0.08	0.03	0.13
Total sum of square (S_T)	4.26	0.04	0.01	0.07	14.52	11.81	4.02
Inter-laboratories degree of freedom (ϕ_R)	9	11	11	12	14	11	14
Within-laboratory degree of freedom (ϕ_{RW})	10	12	12	13	15	12	15
Repeatability degree of freedom (ϕ_r)	40	48	48	52	60	48	60
Total degree of freedom (ϕ_T)	59	71	71	77	89	71	89
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.461	0.003	0.000	0.006	1.029	1.070	0.277
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.000	0.000	0.000	0.000	0.002	0.001	0.001
Repeatability variance ($V_r = S_r/\phi_r$)	0.003	0.000	0.000	0.000	0.001	0.001	0.002
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.077	0.001	0.000	0.001	0.171	0.178	0.046
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	-0.001	0.000	0.000	0.000	0.000	0.000	0.000
Repeatability component of variance ($s_r^2 = V_r$)	0.003	0.000	0.000	0.000	0.001	0.001	0.002
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.277	0.023	0.006	0.032	0.414	0.422	0.215
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.003	0.002	0.008	0.001	0.026	0.013	0.016
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.052	0.005	0.002	0.006	0.037	0.026	0.046
Inter-laboratories precision CV (%)	38.75	24.61	7.31	46.26	18.94	22.02	71.67
Within-laboratory precision CV (%)	0.39	2.16	10.68	2.14	1.19	0.69	5.33
Repeatability precision CV (%)	7.24	5.43	2.97	8.28	1.69	1.34	15.37
Reproducibility limit ($R_W = D(2, 0.95)*s_R$)	0.78	0.07	0.02	0.09	1.16	1.18	0.60
Within-laboratory-reproducibility limit ($R = D(2, 0.95)*s_{Rw}$)	0.01	0.01	0.02	0.00	0.07	0.04	0.04
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.15	0.01	0.01	0.02	0.10	0.07	0.13

4. DISCUSSION

4.1. Improvement of inter-laboratories precision

As described above, since the instrumental analysis may have relatively large effect on the total precision of soil analysis, inter-laboratories precision in the instrumental analysis should be improved. Based on the results of this project, the following points could be noted for the improvement of the precision.

1) Addition of La or Sr solution for AAS analysis of Ex-Ca

   La or Sr solution may affect sensitivity of the instrument, and the solution should be applied for the AAS analysis.

2) Preparation of standard solution

   A soil extract contents of the most constituent ions and extractant (ammonium acetate) itself is relatively higher concentration in the solution. The matrix and the other ions than the targets may affect sensitivity of the instrument. In order to avoid the effect, it is better to use the sample solution for preparation of standard solution (standard additional method). At least, the standard solution should be prepared by using the extractant for making similar matrix to the extract.

3) Instrument for Ex-K and Na

   The results of FEP and AAS were a little different in the analysis of Ex-K and Na. As one of the trials, standardization of instruments for Ex-K and Na should be discussed: All the laboratories would use AAS if the lamps were available, or all the laboratories would use FEP.

4.2. From 1999 to 2001

The soil samples were dispatched in 1999 and 2000, and the precision all of procedures of soil analysis was estimated. According to these results, it was suggested that precision on each step of the procedures should be evaluated. In 2001, through the 3^{rd} project, it was clarified that instrumental analysis was the important step for the precision on the soil analysis. As described above, a few factors, which could affect the precision of the instrumental analysis, were also clarified.

The operating procedures will be elaborated in detail in the next project taking into account the above points to improve the inter-laboratories precision.

5. ACKNOWLEDGMENT

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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

1) Environmental Management Center	**id01**
2) Center for Soil and Agro-Climate Research and Development	**id02**

3. JAPAN

Agricultural Experimental Station, Shimane Prefecture	**jp01**

4. MALAYSIA

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

6. MONGOLIA

Central Laboratory of Environmental Monitoring	**mn01**

7. PHILIPPINES

1) Environmental Management Bureau	**ph01**
2) Department of Soil Science, University of the Philippines, Los Banos:	**ph02**

8. Republic of KOREA

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

9. RUSSIA

1) Limnological Institute Russian Academy of Science/Siberian Branch	**ru01**
2) Primorskgidromet	**ru02**

10. THAILAND

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

11. VIET NAM

Institute of Meteorology and Hydrology, Hydro-Meteorological Service	**vn01**

APPENDIX 2.1. Entire data of Ex-base cations

Laboratory	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
	cmol(+)/kg											
	Lab. average	Average	Raw data	Lab. average	Average	Raw data	Lab. average	Average	Raw data	Lab. average	Average	Raw data
cn01	0.88	0.88 (0.02)	0.89	0.14	0.13 (0.00)	0.13	0.08	0.08 (0.00)	0.08	0.09	0.09 (0.00)	0.09
			0.87			0.13			0.08			0.09
			0.88			0.13			0.08			0.09
		0.88 (0.00)	0.88		0.14 (0.01)	0.13		0.08 (0.00)	0.08		0.09 (0.00)	0.09
			0.88			0.14			0.08			0.09
			0.88			0.14			0.08			0.09
cn02	0.80	0.79 (0.01)	0.79	0.10	0.10 (0.00)	0.10	0.07	0.07 (0.00)	0.07	0.06	0.06 (0.00)	0.06
			0.79			0.10			0.07			0.06
			0.80			0.10			0.07			0.06
		0.80 (0.01)	0.79		0.10 (0.00)	0.10		0.07 (0.00)	0.07		0.06 (0.00)	0.06
			0.80			0.10			0.07			0.06
			0.80			0.10			0.07			0.06
cn03	0.81	0.81 (0.00)	0.81	0.10	0.10 (0.00)	0.10	0.08	0.08 (0.00)	0.08	0.05	0.05 (0.01)	0.05
			0.81			0.10			0.08			0.06
			0.81			0.10			0.08			0.05
		0.81 (0.00)	0.81		0.10 (0.00)	0.10		0.08 (0.00)	0.08		0.05 (0.01)	0.06
			0.81			0.10			0.08			0.05
			0.81			0.10			0.08			0.05
cn04	0.48	0.48 (0.02)	0.48	0.07	0.07 (0.00)	0.07	0.07	0.07 (0.00)	0.07	0.06	0.06 (0.00)	0.06
			0.49			0.07			0.07			0.06
			0.47			0.07			0.07			0.06
		0.48 (0.02)	0.47		0.07 (0.00)	0.07		0.07 (0.00)	0.07		0.06 (0.00)	0.06
			0.49			0.07			0.07			0.06
			0.48			0.07			0.07			0.06
id01	0.25	0.24 (0.00)	0.24	0.10	0.10 (0.00)	0.10	0.08	0.08 (0.00)	0.08	0.07	0.07 (0.01)	0.07
			0.24			0.10			0.08			0.07
			0.24			0.10			0.08			0.08
		0.25 (0.00)	0.25		0.10 (0.00)	0.10		0.08 (0.00)	0.08		0.07 (0.01)	0.08
			0.25			0.10			0.08			0.07
			0.25			0.10			0.08			0.07
id02	0.85	0.83 (0.09)	0.81	0.17	0.14 (0.00)	0.14	0.08	0.09 (0.00)	0.09	0.00	0.00 (0.00)	0.00
			0.81			0.14			0.09			0.00
			0.87			0.14			0.09			0.00
		0.87 (0.16)	0.94		0.20 (0.03)	0.21		0.06 (0.00)	0.06		0.00 (0.00)	0.00
			0.87			0.19			0.06			0.00
			0.81			0.19			0.06			0.00
jp01	0.67	0.62 (0.01)	0.62	0.19	0.08 (0.00)	0.08	0.22	0.21 (0.00)	0.21	0.05	0.05 (0.00)	0.05
			0.61			0.08			0.21			0.05
			0.62			0.08			0.21			0.05
		0.71 (0.01)	0.71		0.30 (0.90)	0.09		0.23 (0.01)	0.23		0.05 (0.00)	0.05
			0.71			0.09			0.22			0.05
			0.72			0.72			0.23			0.05
my01	0.83	0.96 (0.04)	0.94	0.08	0.07 (0.00)	0.07	0.09	0.07 (0.01)	0.08	0.05	0.05 (0.00)	0.05
			0.97			0.07			0.07			0.05
			0.96			0.07			0.07			0.05
		0.69 (0.00)	0.69		0.08 (0.01)	0.07		0.10 (0.00)	0.10		0.05 (0.00)	0.05
			0.69			0.08			0.10			0.05
			0.69			0.08			0.10			0.05
mn01												
ph01	0.68	0.74 (0.06)	0.73	0.09	0.09 (0.00)	0.09	0.09	0.08 (0.00)	0.08	0.07	0.07 (0.00)	0.07
			0.73			0.09			0.08			0.07
			0.77			0.09			0.08			0.07
		0.61 (0.02)	0.61		0.09 (0.00)	0.09		0.09 (0.00)	0.09		0.06 (0.01)	0.06
			0.62			0.09			0.09			0.07
			0.60			0.09			0.09			0.06
ph02	1.17	1.17 (0.51)	1.27	0.05	0.05 (0.02)	0.05	0.18	0.18 (0.04)	0.17	0.07	0.07 (0.01)	0.06
			0.93			0.04			0.17			0.07
			1.30			0.06			0.20			0.07
		1.17 (0.26)	1.10		0.05 (0.00)	0.05		0.18 (0.03)	0.17		0.07 (0.05)	0.08
			1.12			0.05			0.19			0.05
			1.29			0.05			0.19			0.09
kr01	0.42	0.42 (0.01)	0.41	0.09	0.09 (0.01)	0.09	0.08	0.08 (0.01)	0.07	0.08	0.08 (0.02)	0.07
			0.42			0.10			0.08			0.08
			0.42			0.09			0.08			0.09
		0.42 (0.00)	0.42		0.09 (0.01)	0.09		0.08 (0.01)	0.07		0.08 (0.02)	0.07
			0.42			0.09			0.08			0.08
			0.42			0.10			0.08			0.09
ru01	0.63	0.63 (0.01)	0.63	0.11	0.11 (0.01)	0.10	0.10	0.10 (0.00)	0.10	0.08	0.08 (0.00)	0.08
			0.63			0.11			0.10			0.08
			0.62			0.11			0.10			0.08
		0.63 (0.00)	0.63		0.11 (0.01)	0.10		0.10 (0.00)	0.10		0.08 (0.00)	0.08
			0.63			0.11			0.10			0.08
			0.63			0.11			0.10			0.08
ru02	0.75	0.75 (0.00)	0.75	0.09	0.09 (0.00)	0.09	0.08	0.08 (0.00)	0.08	0.08	0.08 (0.00)	0.08
			0.75			0.09			0.08			0.08
			0.75			0.09			0.08			0.08
		0.75 (0.00)	0.75		0.09 (0.00)	0.09		0.08 (0.00)	0.08		0.08 (0.00)	0.08
			0.75			0.09			0.08			0.08
			0.75			0.09			0.08			0.08
th01	0.70	0.73 (0.05)	0.74	0.13	0.13 (0.04)	0.12	0.09	0.09 (0.00)	0.09	0.09	0.09 (0.02)	0.09
			0.75			0.12			0.09			0.08
			0.71			0.15			0.09			0.10
		0.66 (0.02)	0.66		0.13 (0.01)	0.13		0.09 (0.01)	0.09		0.09 (0.01)	0.09
			0.65			0.12			0.08			0.10
			0.67			0.13			0.09			0.09
vn01	0.98	0.98 (0.01)	0.98	0.29	0.29 (0.04)	0.29	0.08	0.08 (0.00)	0.08	0.14	0.14 (0.00)	0.14
			0.98			0.30			0.08			0.14
			0.99			0.27			0.08			0.14
		0.98 (0.02)	0.97		0.28 (0.02)	0.28		0.08 (0.00)	0.08		0.14 (0.01)	0.14
			0.98			0.29			0.08			0.15
			0.99			0.27			0.08			0.14

APPENDIX 2.2. Entire data of Ex-Acidity, Al, and H

Laboratory	Ex-Acidity			Ex-Al			Ex-H		
	cmol(+)/kg								
	Lab. average	Average	Raw data	Lab. average	Average	Raw data	Lab. average	Average	Raw data
cn01	2.21	2.20 (0.00)	2.20	1.77	1.77 (0.03)	1.76	0.44	0.43 (0.03)	0.44
			2.20			1.78			0.42
			2.20			1.76			0.44
		2.22 (0.04)	2.23		1.77 (0.03)	1.76		0.45 (0.04)	0.47
			2.20			1.78			0.44
			2.23			1.76			0.45
cn02	2.14	2.13 (0.00)	2.13	1.98	1.98 (0.01)	1.98	0.16	0.16 (0.01)	0.16
			2.13			1.98			0.15
			2.13			1.97			0.16
		2.14 (0.03)	2.15		1.97 (0.01)	1.97		0.16 (0.01)	0.16
			2.13			1.97			0.16
			2.13			1.98			0.15
cn03	0.13	0.13 (0.00)	0.13	0.13	0.12 (0.01)	0.12	0.01	0.01 (0.00)	0.01
			0.13			0.12			0.01
			0.13			0.13			0.01
		0.13 (0.00)	0.13		0.13 (0.00)	0.13		0.01 (0.00)	0.01
			0.13			0.13			0.01
			0.13			0.13			0.01
cn04	1.76	1.76 (0.01)	1.77	1.38	1.38 (0.02)	1.38	0.39	0.39 (0.04)	0.39
			1.76			1.39			0.37
			1.76			1.37			0.40
		1.76 (0.00)	1.76		1.38 (0.01)	1.39		0.38 (0.02)	0.37
			1.76			1.38			0.39
			1.76			1.38			0.38
id01	2.40	2.42 (0.14)	2.42	2.03	1.98 (0.33)	1.83	0.37	0.37 (0.20)	0.38
			2.48			2.03			0.45
			2.37			2.08			0.29
		2.37 (0.00)	2.37		2.08 (0.19)	2.15		0.36 (0.30)	0.22
			2.37			2.00			0.40
			2.37			2.10			0.45
id02	2.00	1.99 (0.03)	2.00	1.91	1.91 (0.01)	1.90	0.10	0.09 (0.03)	0.10
			2.00			1.91			0.10
			1.98			1.91			0.08
		2.01 (0.01)	2.01		1.90 (0.01)	1.90		0.11 (0.02)	0.11
			2.01			1.91			0.10
			2.02			1.90			0.12
jp01	2.35	2.36 (0.06)	2.33	1.98	1.99 (0.09)	1.99	0.37	0.37 (0.08)	0.34
			2.36			1.96			0.40
			2.38			2.03			0.36
		2.34 (0.04)	2.32		1.97 (0.08)	1.95		0.37 (0.06)	0.37
			2.35			2.01			0.34
			2.35			1.96			0.39
my01	2.24	2.25 (0.01)	2.25	1.77	1.78 (0.16)	1.71	0.48	0.48 (0.15)	0.54
			2.25			1.79			0.47
			2.26			1.84			0.42
		2.23 (0.09)	2.21		1.76 (0.09)	1.74		0.47 (0.01)	0.47
			2.21			1.74			0.47
			2.27			1.80			0.48
mn01	2.72	2.68 (0.16)	2.75	1.94	1.92 (0.14)	1.85	0.79	0.77 (0.30)	0.90
			2.62			1.95			0.67
			2.68			1.95			0.73
		2.75 (0.00)	2.75		1.95 (0.00)	1.95		0.80 (0.00)	0.80
			2.75			1.95			0.80
			2.75			1.95			0.80
ph01	1.58	1.57 (0.04)	1.56						
			1.59						
			1.56						
		1.59 (0.07)	1.59						
			1.62						
			1.56						
ph02	2.51	2.47 (0.23)	2.43	2.26	2.24 (0.00)	2.24	0.25	0.23 (0.23)	0.19
			2.57			2.24			0.33
			2.40			2.24			0.16
		2.54 (0.31)	2.67		2.28 (0.09)	2.31		0.27 (0.22)	0.36
			2.54			2.28			0.26
			2.42			2.24			0.18
kr01	2.26	2.29 (0.06)	2.26	1.72	1.75 (0.17)	1.67	0.55	0.54 (0.12)	0.59
			2.30			1.77			0.52
			2.30			1.80			0.50
		2.23 (0.07)	2.26		1.68 (0.16)	1.75		0.56 (0.11)	0.52
			2.23			1.63			0.61
			2.20			1.65			0.55
ru01	2.88	2.88 (0.00)	2.88	2.88	2.88 (0.00)	2.88	0.00	0.00 (0.00)	0.00
			2.88			2.88			0.00
			2.88			2.88			0.00
		2.88 (0.00)	2.88		2.88 (0.00)	2.88		0.00 (0.00)	0.00
			2.88			2.88			0.00
			2.88			2.88			0.00
ru02	2.32	2.32 (0.10)	2.30	2.02	2.02 (0.07)	2.00	0.31	0.31 (0.03)	0.30
			2.37			2.05			0.32
			2.30			2.00			0.30
		2.32 (0.10)	2.30		2.02 (0.07)	2.00		0.31 (0.03)	0.30
			2.30			2.00			0.30
			2.37			2.05			0.32
th01	2.19	2.17 (0.04)	2.19	1.98	1.97 (0.04)	1.98	0.21	0.20 (0.04)	0.21
			2.16			1.98			0.18
			2.16			1.95			0.21
		2.20 (0.04)	2.22		1.98 (0.06)	2.00		0.22 (0.04)	0.22
			2.19			1.95			0.24
			2.19			1.98			0.21
vn01	1.27	1.25 (0.01)	1.25	1.17	1.18 (0.04)	1.16	0.10	0.07 (0.05)	0.09
			1.24			1.19			0.05
			1.25			1.19			0.08
		1.28 (0.06)	1.25		1.15 (0.02)	1.14		0.13 (0.04)	0.11
			1.28			1.15			0.13
			1.30			1.16			0.14

APPENDIX 3.1. Results of Ex-base cations in ADORC

				Ex-Ca		Ex-Mg		Ex-K		Ex-Na		Dilution rate
Date	Instrument	Methods	Sr	cmol(+)/kg								
23-Mar	AAS	Calibration curve methods[*1]	Added	0.76	0.78	0.10	0.1	0.09	0.09	0.07	0.06	10
					0.76		0.1		0.09		0.07	5
					0.75		0.1		0.09		0.07	3.33
					0.78		0.1		0.09		0.07	2.5
					0.76		0.1		0.09		0.07	2
					0.76		0.1		0.09		0.07	1.67
					0.75				0.09			1.25
25-Mar	AAS	Calibration curve methods[*1]	Added	0.76	0.78	0.10	0.10	0.09	0.09	0.07	0.06	10
					0.76		0.10		0.09		0.07	5
					0.75		0.10		0.09		0.07	3.33
					0.77		0.10		0.09		0.07	2.5
					0.76		0.10		0.09		0.07	2
					0.76		0.10		0.09		0.07	1.67
					0.75		-		-		-	1.25
		Standard additional methods[*2]	Added	0.93	0.91	0.12	0.12	0.10	0.10	0.09	0.09	2.5
					0.95		-		0.10		-	2
					0.94		-		-		-	1.67
19-Sep	ICP-AES	Calibration curve methods[*3]	-	0.90	0.93	0.11	0.11	0.10	0.10	0.08	0.08	1[*4]
					0.89		0.11		0.10		0.08	1[*4]
					0.88		0.11		0.10		0.09	1[*4]
29-Sep	ICP-AES	Calibration curve methods[*3]	-	0.86	0.85	0.10	0.11	0.10	0.10	0.07	0.07	1[*4]
					0.87		0.10		0.10		0.07	1[*4]
					0.87		0.09		0.10		0.07	1[*4]
		Total average		0.84		0.11		0.10		0.08		

Note: *1. HCl was also added for stability of ionization. *2. Sample was used for preparation of standard solution. *3. Ammonium acetate was used for preparation of standard solution. *4. Ex-Ca was diluted by five times.

APPENDIX 3.2. Results of Ex-Acidity, Al and H in ADORC

Date	Ex-Acidity		Ex-Al		Ex-H	
	cmol(+)/kg					
30-Dec-01	2.89	2.85	2.40	2.27	0.49	0.58
		2.92		2.39		0.53
		2.93		2.43		0.49
		2.96		2.47		0.49
		2.83		2.40		0.44
		2.86		2.43		0.43
4-Jan-02	2.97	2.91	2.39	2.30	0.58	0.61
		2.92		2.39		0.53
		2.99		2.40		0.59
		2.99		2.40		0.59
		3.00		2.41		0.58
		3.01		2.45		0.55
11-Jan-02	3.04	2.99	2.50	2.41	0.54	0.58
		3.04		2.60		0.44
		3.02		2.55		0.47
		3.08		2.52		0.56
		3.07		2.49		0.58
		3.02		2.43		0.59
18-Jan-02	2.98	2.99	2.55	2.59	0.44	0.41
		3.03		2.52		0.51
		3.01		2.62		0.39
		2.93		2.52		0.41
		2.96		2.49		0.46
25-Jan-02	3.15	3.12	2.44	2.43	0.71	0.69
		3.11		2.40		0.72
		3.18		2.45		0.72
		3.17		2.47		0.70
		-		-		-
		-		-		-
Total average	3.01 (0.12)		2.46 (0.08)		0.55 (0.13)	

Note: Value in parenthesis shows 95% confidence interval.

Corrigenda

A few editorial mistakes were found in the Report of the Inter-laboratory Comparison Project on Soil in the previous years, 1999 and 2000. These mistakes were not directly related to the results and evaluation of the data. Please refer the following correction for the previous reports

1) Report of the Inter-laboratory Comparison Project on Soil 1999

Page/chapter/line	Mistake	Correction
General	AAS: Atomic *adsorption* spectrometry	AAS: Atomic *absorption* spectrometry

2) Report of the Inter-laboratory Comparison Project on Soil 2000

Page/chapter/line	Mistake	Correction
General	AAS: Atomic *adsorption* spectrometry	AAS: Atomic *absorption* spectrometry
Page 2/subchapter 2.1/line 2 and 5	**Sample No. *001:* Andosols** The soil was collected from chestnuts forest area in Tochigi Prefectural Forest Research Center (Utsunomiya City, Tochigi Prefecture). **Sample No. *002:* Cambisols** The soil was collected from forest area in the University Forest in Aichi, The University of Tokyo (Seto City, Aichi Prefecture).	**Sample No. *002:* Andosols** The soil was collected from chestnuts forest area in Tochigi Prefectural Forest Research Center (Utsunomiya City, Tochigi Prefecture). **Sample No. *001:* Cambisols** The soil was collected from forest area in the University Forest in Aichi, The University of Tokyo (Seto City, Aichi Prefecture).