

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

## **Report of the Inter-laboratory Comparison Project 1999**

**on Soil**

1<sup>st</sup> Attempt

November 2001  
Acid Deposition and Oxidant Research Center

## Contents

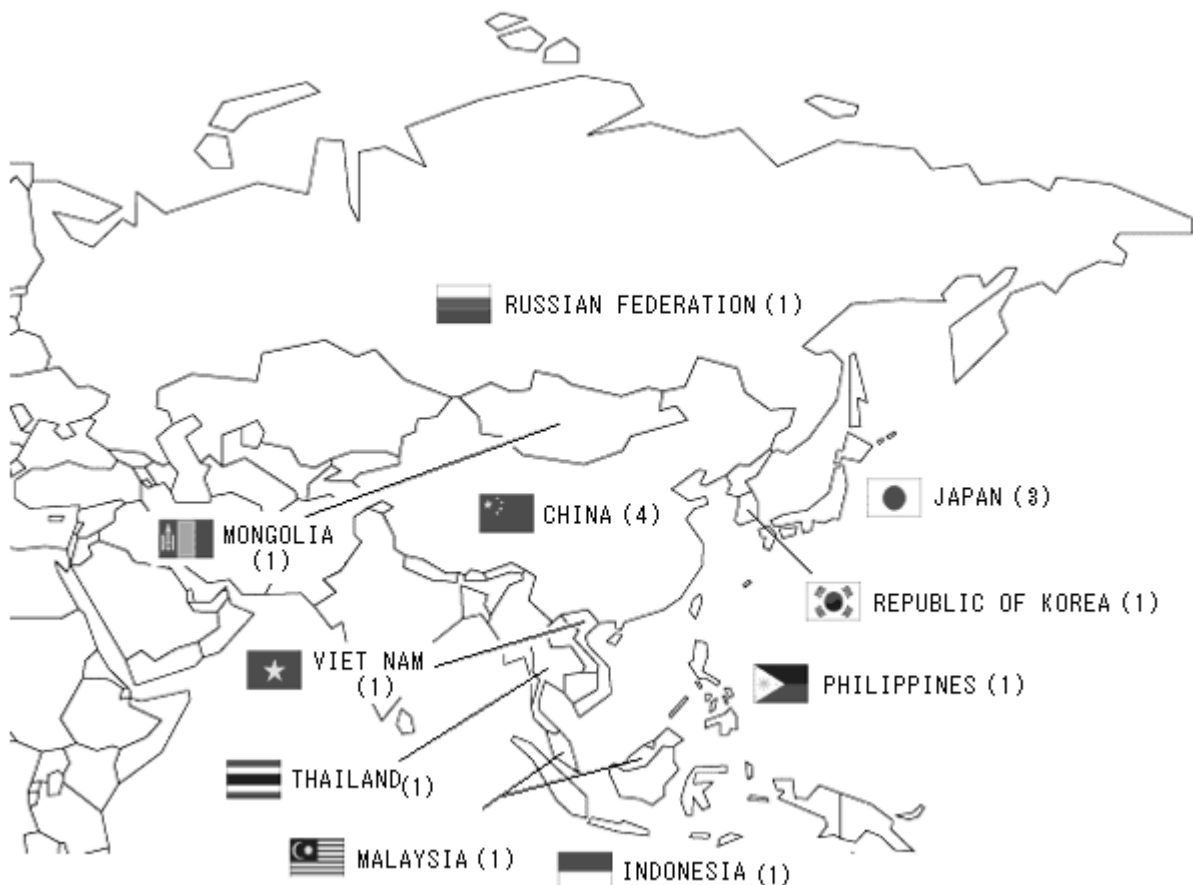
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## 1. INTRODUCTION

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 is one of the activities on the QA/QC programs, and the results can be used for estimation of data quality on the monitoring.

As the 1<sup>st</sup> project, INC dispatched two soil samples, Sample No. 991 and 992, to laboratories for soil monitoring in the participating countries in December 1999. 15 laboratories of 10 countries have participated in the 1<sup>st</sup> project. In these laboratories, chemical properties of the soil samples were analyzed, and the data were submitted to (I)NC. NC received the results from the last participating laboratory in February 2001, and analyzed the data statistically.

In this report, the data from various laboratories were analyzed 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 for the future activities of EANET.



**Figure 1. Laboratories participating in this Inter-laboratory comparison project of EANET**

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

## 2. PROCEDURE

### 2.1. Dispatched Soil Samples

The characteristics of the samples were as follows:

#### Sample No. 991: Acrisols

The soil was collected from forest area in Aichi Prefecture Agricultural Research Center, Toyohashi Research and Extension Station.

#### Sample No. 992: Gleysols

The soil was collected from test field in Akita Agricultural Experimental Station, Ogata Experimental Farm (Ogata Village, Akita Prefecture).

The soil samples are air-dried for 1-2 weeks, sieved, mixed well, bottled by 500 grams, and sterilized using radioisotope (20kGy.). Chemical characteristics of these samples were not informed for fair evaluation of the program.

The real values of parameters were unknown since the natural soils were used for the samples. Five bottles for each sample were analyzed, and variations of analytical parameters among bottles were checked (Appendix 5).

### 2.2. Parameters

All the participating laboratories were expected to measure the mandatory parameters and hopefully recommended parameters (Table 1).

**Table 1. Parameters to be measured**

Parameters	Unit	Criterion
a) pH (H <sub>2</sub> O) and pH (KCl)		M
b) Exchangeable Base Cations (Ca, Mg, K and Na)	cmol(+) kg <sup>-1</sup>	M
c) Cation Exchangeable Capacity (CEC)	cmol(+) kg <sup>-1</sup>	M
d) Exchangeable Acidity	cmol(+) kg <sup>-1</sup>	O*
e) Exchangeable Al, H	cmol(+) kg <sup>-1</sup>	O*
f) Effective Cation Exchangeable Capacity (ECEC)	cmol(+) kg <sup>-1</sup>	O*
g) Total Carbon Content	g kg <sup>-1</sup>	O
i) Total Nitrogen Content	g kg <sup>-1</sup>	O
j) Available Phosphate	P mg g <sup>-1</sup>	O
k) Sulfate	S mg g <sup>-1</sup>	O

M: Mandatory items; O: Optional items; \*: Recommended items. ECEC could be calculated as sum of Exchangeable cations

“Exchangeable” were abbreviated to “Ex-“ in the following 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 “Monitoring

Guidelines and Technical Manuals for Soil and Vegetation Monitoring (Environment Agency, Government of Japan, 1997)". More detailed information on some parameters and alternative available methods, which were later adopted in the Technical Manual for Soil and Vegetation Monitoring in East Asia (2<sup>nd</sup> ISAG, 2000), were also attached to the instruction.

For the estimation of analytical quality in the respective laboratory, all the parameters were analyzed twice on within-laboratory-reproducibility condition that part or all of analyst, time, and instrument are different. Thus, all the analytical procedures were repeated twice in each laboratory.

For the accurate analysis, the moisture contents of the samples were measured shortly before soil analysis because data should be expressed on basis of oven-dry soil. Moisture contents were analyzed with three replicates, and the average was used for calculation of all the parameters.

#### **2.4. Statistical analysis**

Data obtained from repeat analyses in the participating laboratories were statistically analyzed according to the following procedures described in the Technical Manual for Soil and Vegetation Monitoring in East Asia (2<sup>nd</sup> ISAG, 2000). Data with 1 decimal place of mandatory and recommended parameters (except ECEC) 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 ( $S_R$ ) and Sum of square within-laboratory ( $S_{RW}$ ).

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

Based on the above equation, Inter-laboratories variance and Within-laboratory-reproducibility 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

Basic statistics calculated from the laboratory averages are shown in Table 2.1 and 2.2, and especially coefficients of variation (CVs) among laboratories were shown in Figure 2. For calculation of the statistics, verified data by Cochran and Grubbs methods were used.

In pH (H<sub>2</sub>O) and pH (KCl), CV was lowest (ca. 5%). Simple procedures for pH may be one of the reasons for small variation although value of pH was log scale and relatively stable parameters. The results of Exchangeable basic cations (Na, K, Mg, Ca) and Ex-H were varied (CV, 40-110%). The sample with larger value has smaller variation; in Ex-Na, Ex-Ca, CEC and Ex-acidity, samples No. 992, 992, 992, and 991 have smaller CV, respectively.

It was suggested that analytical procedures (complexity) and concentration level of sample could affect on variation among laboratories.

**Table 2.1. Statistics of Verified data: Soil Sample No.991**

Statistics	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex--Acidity	Ex-Al	Ex-H
			cmol (+)/kg							
Number of laboratories	13	13	11	13	14	13	9	11	11	9
Total average	4.6	3.9	0.2	0.2	0.4	0.4	10.7	5.7	4.9	0.5
Maximum	4.9	4.2	0.5	0.3	0.7	0.9	19.0	6.8	6.4	1.1
Minimum	4.1	3.6	0.0	0.0	0.0	0.0	3.8	4.3	1.0	0.1
Standard deviation	0.2	0.2	0.2	0.1	0.2	0.3	4.9	0.7	1.8	0.3
CV (%)	5.3	4.0	113.6	56.0	50.0	79.1	45.4	12.0	36.1	72.7

Data has been verified by the methods of Cochran and Grubbs, and outliers have been removed.

**Table 2.2. Statistics of Verified data: Soil Sample No.992**

Statistics	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex--Acidity	Ex-Al	Ex-H
			cmol (+)/kg							
Number of laboratories	14	12	12	14	13	14	9	12	9	10
Total average	7.1	5.7	1.0	1.4	4.5	21.4	38.6	0.1	0.0	0.1
Maximum	7.6	6.0	1.8	2.9	6.7	33.2	50.5	0.3	0.0	0.2
Minimum	6.6	5.4	0.1	0.0	0.1	0.1	27.8	0.0	0.0	0.0
Standard deviation	0.3	0.2	0.4	0.7	2.4	11.1	7.6	0.1	0.0	0.1
CV (%)	4.7	3.3	42.9	49.4	53.2	52.0	19.6	88.3	0.0	82.0

Data has been verified by the methods of Cochran and Grubbs, and outliers have been removed.

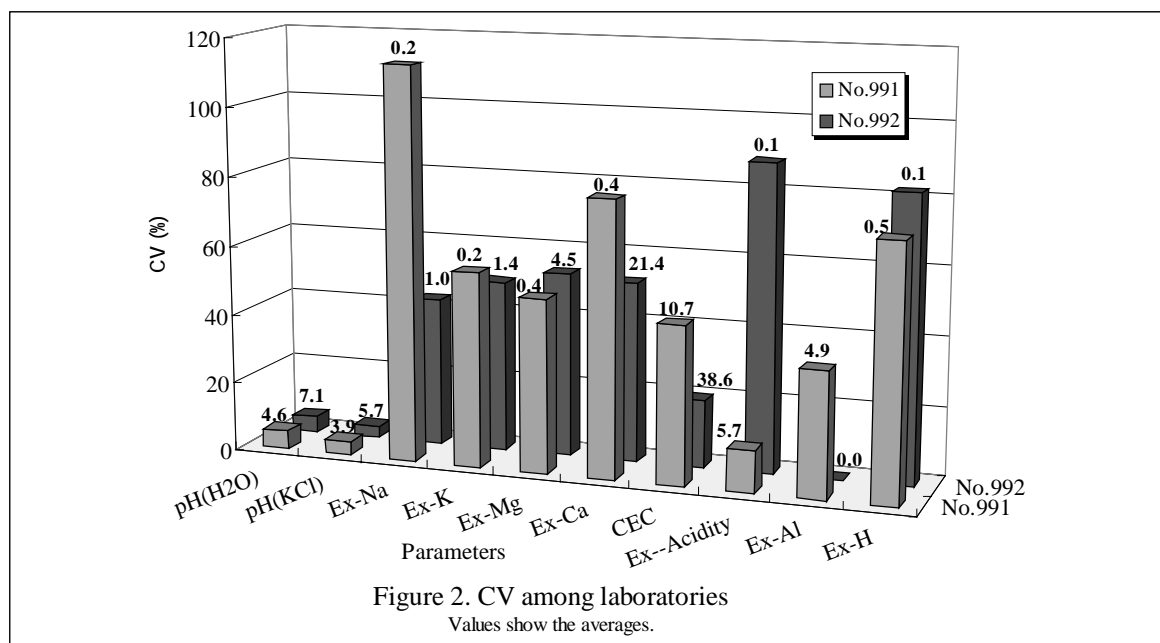


Figure 2. CV among laboratories  
Values show the averages.

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

### 3.1. Verification of data

#### 1) Detection of outliers

The average and range (difference) of values in the respective laboratory, which were calculated from two data of repeat analysis, were shown in Figure 3.1 to Figure 7.2 for each parameter. The outliers judged by Cochran and Grubbs methods were marked with asterisk c and g.

Laboratories, which have remarkably large range, were judged as outliers by Cochran method (examination of the evenness of within-laboratory precision): e.g. “1412” for pH (H<sub>2</sub>O) and “1804” for pH (KCl) in No. 991 (Figure 3.1.b)). Then, laboratories, which have remarkably large average, were judged as outliers by Grubbs method (examination of the average value in each laboratory): e.g. “1B20” for both pH (H<sub>2</sub>O) and pH (KCl) in No.991 (Figure 3.1.a)). For other parameters, a few outliers were also detected.

The results of verification were shown in Table 3.1 and 3.2.

#### 2) Analytical condition

Information on analytical conditions and staff in the respective laboratory was shown in Table 4.1 to 5.2.

Concerning extractants for the exchangeable cations, most laboratories used same extractants according to the Technical Manual, except the laboratory “1714” (Table 4.1). For elemental analyses of Ex-Na and K, Flame Emission Photometry (FEP) or Atomic Absorption Spectrometry (AAS) were used. For Ex-Mg and Ca, AAS were used in most laboratories although the laboratories, “1714” and “1711” used Titration method (Table 4.2). For CEC, titration methods were majority, however, Spectrophotometry and Ion chromatography were also used. Ex-acidity, Al and H were analyzed by Titration method in most laboratories although Ex-Al was analyzed by AAS in one laboratory. Temperatures for measurement of pH were varied from 18 to 28.5 °C, and most were around 20 °C. Concerning the number of staff, one to three staffs were in charge of measurement (Table 5.1). In the laboratories “1B20”, “1804” and “1427”, all the parameters might be repeated by two persons, and it seems that same persons might analyze all the parameters in 9 laboratories. The years of experiences were varied, and some of staffs have 1 year or less than 1 year experiences (Table 5.2).

The implication between analytical conditions and outliers was not clarified. However, for CEC, data of the laboratory “1806” with different methods (Spectrophotometry), were outliers, and it was suggested that methodologies or operations were not equivalent for other laboratories. The data of the laboratory “1714” with different extractant were also outliers because of its low reproducibility in the laboratory. At least, in these cases, analytical conditions may be important factor for within-laboratory and inter-laboratories reproducibility.

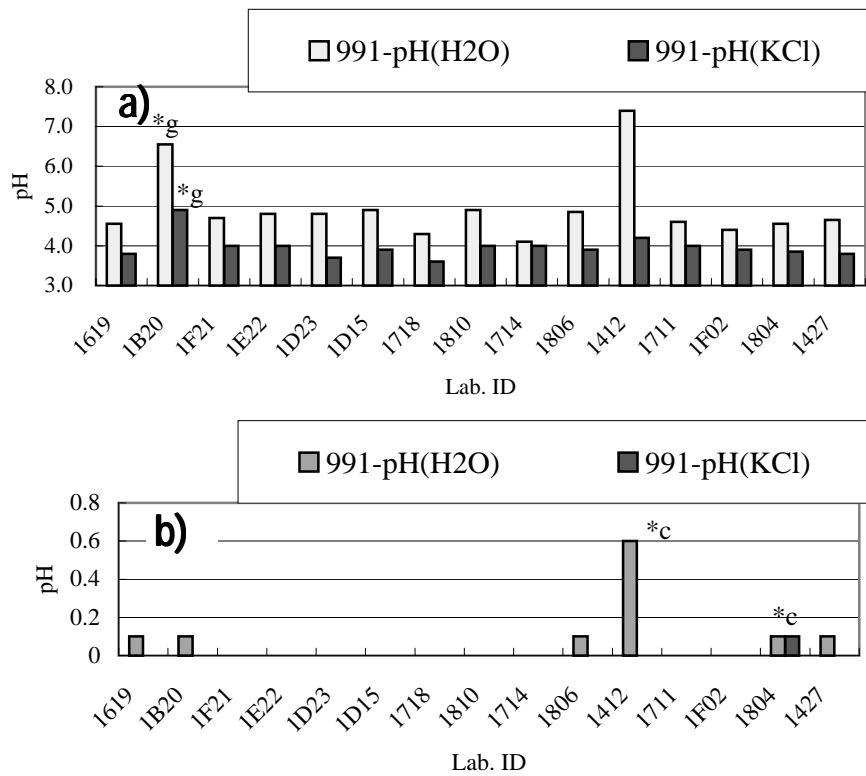


Figure 3.1. Laboratory average a) and range b) of pH(H<sub>2</sub>O) and pH(KCl) for No.991

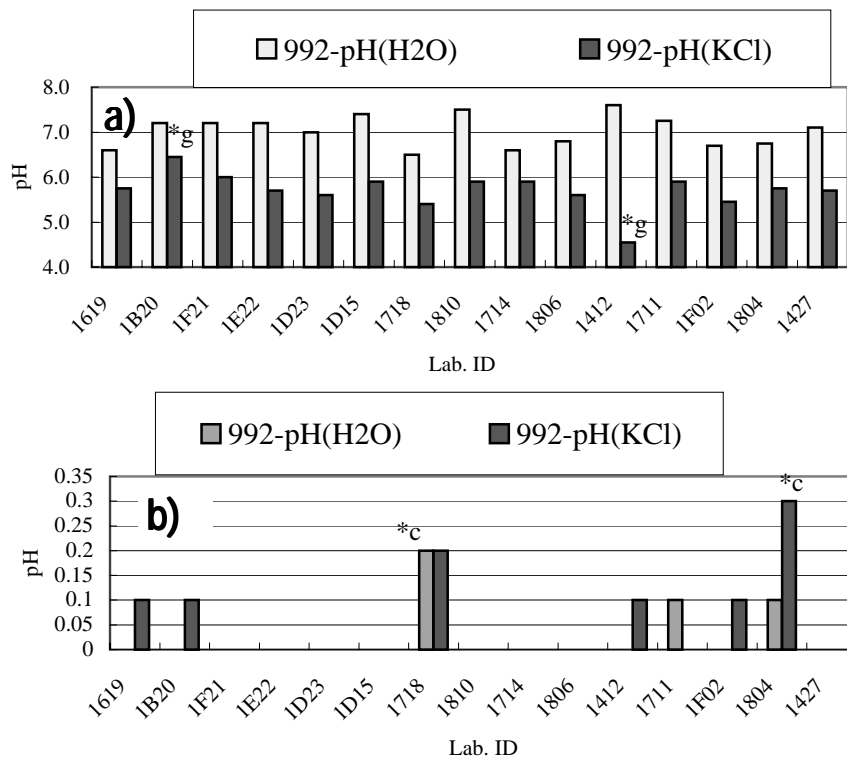


Figure 3.2. Laboratory average a) and range b) of pH(H<sub>2</sub>O) and pH(KCl) for No.992

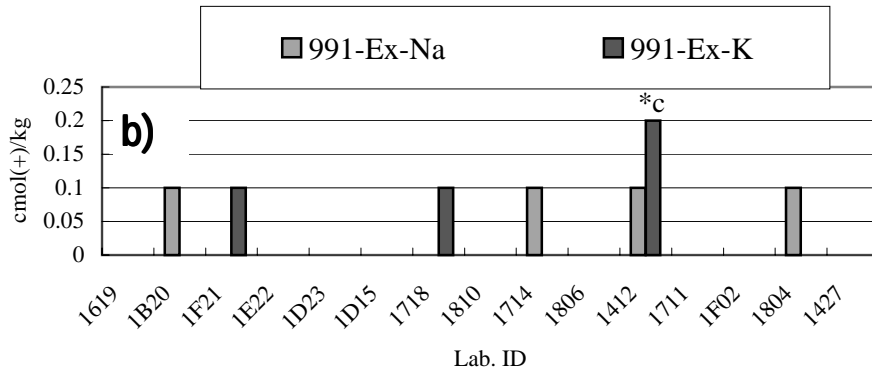
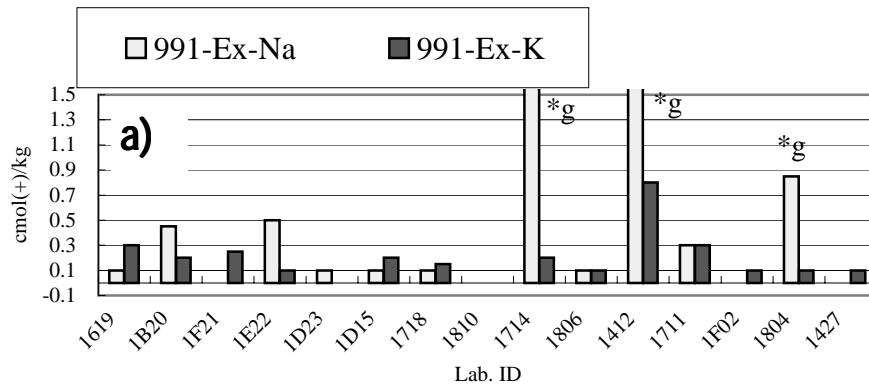


Figure 4.1. Laboratory average a) and range b) of Ex-Na and K for No.991

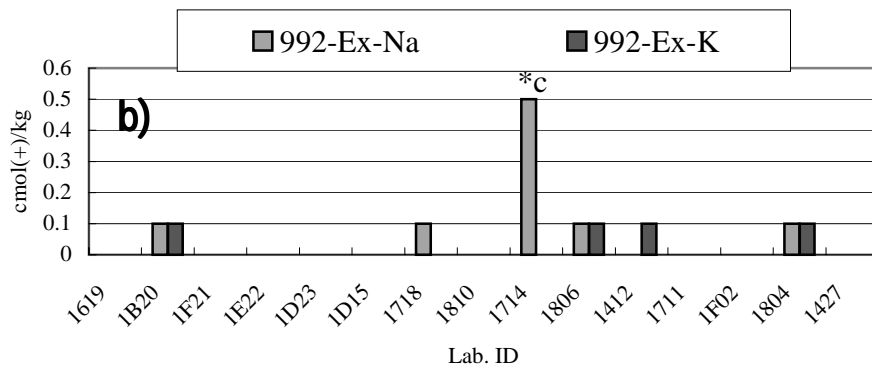
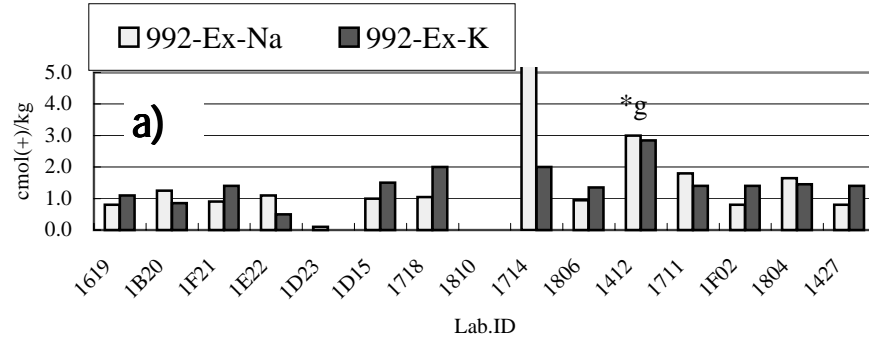


Figure 4.2. Laboratory average a) and range b) of Ex-Na and K for No.992

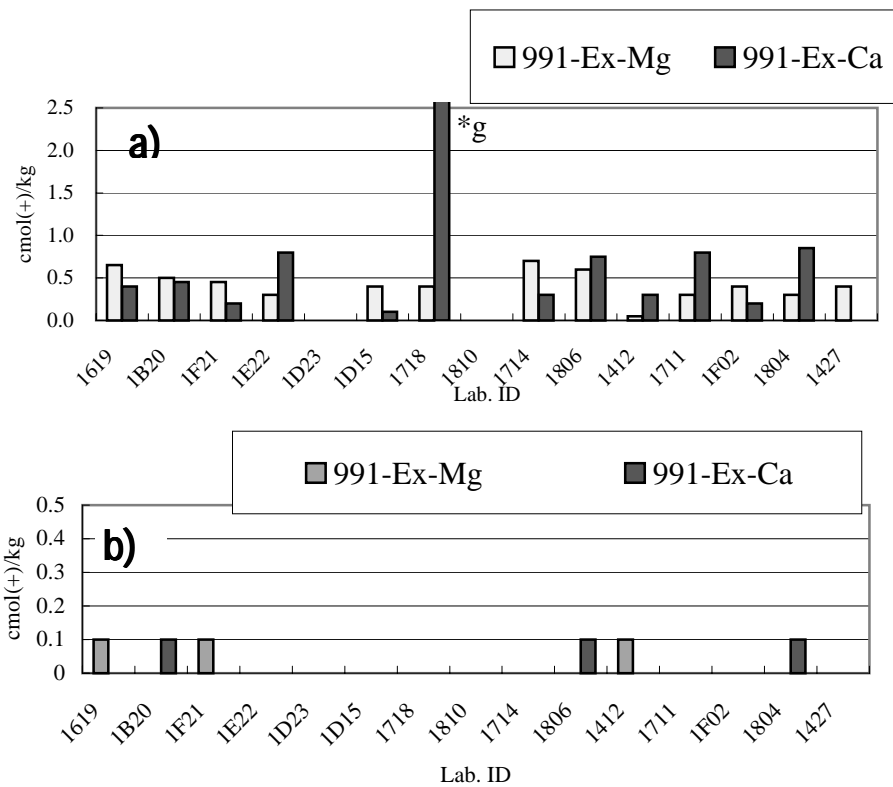


Figure 5.1. Laboratory average a) and range b) of Ex-Mg and Ca for No.991

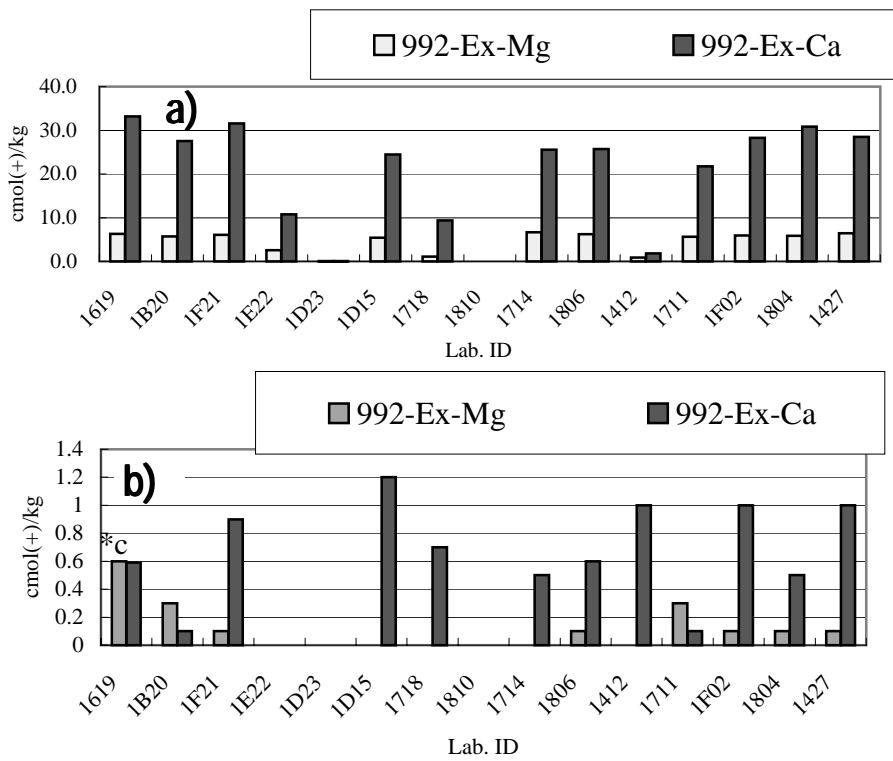


Figure 5.2. Laboratory average a) and range b) of Ex-Mg and Ca for No.992

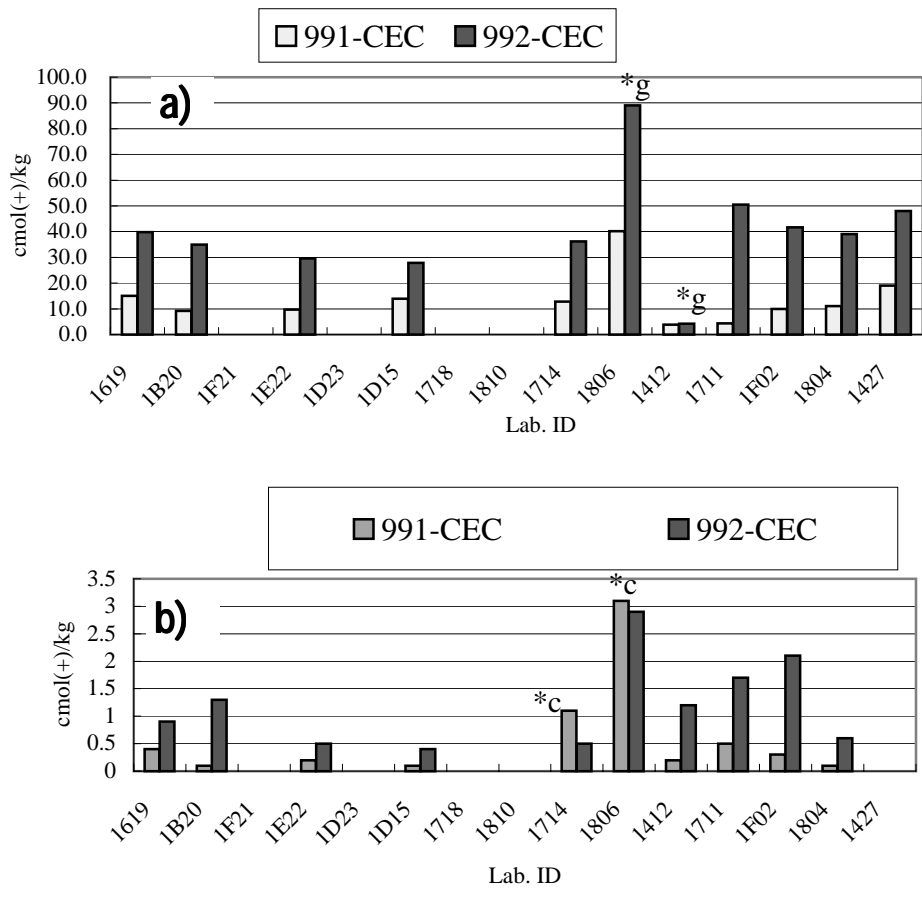


Figure 6. Laboratory average a) and range b) of CEC for No.991 and 992

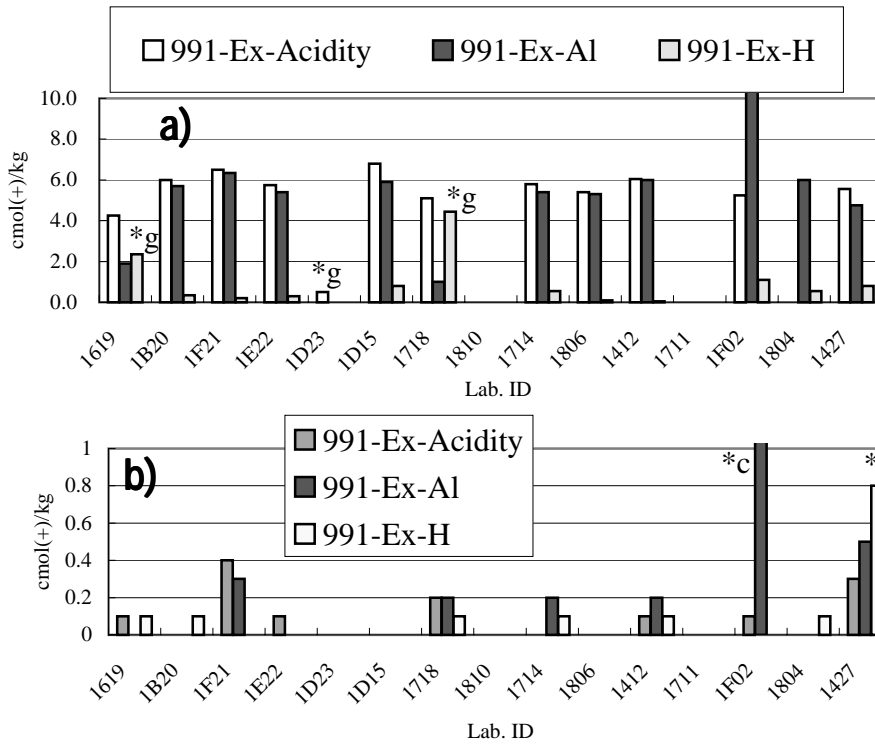


Figure 7.1. Laboratory average a) and range b) of Ex-Acidity, Al and H for No.991

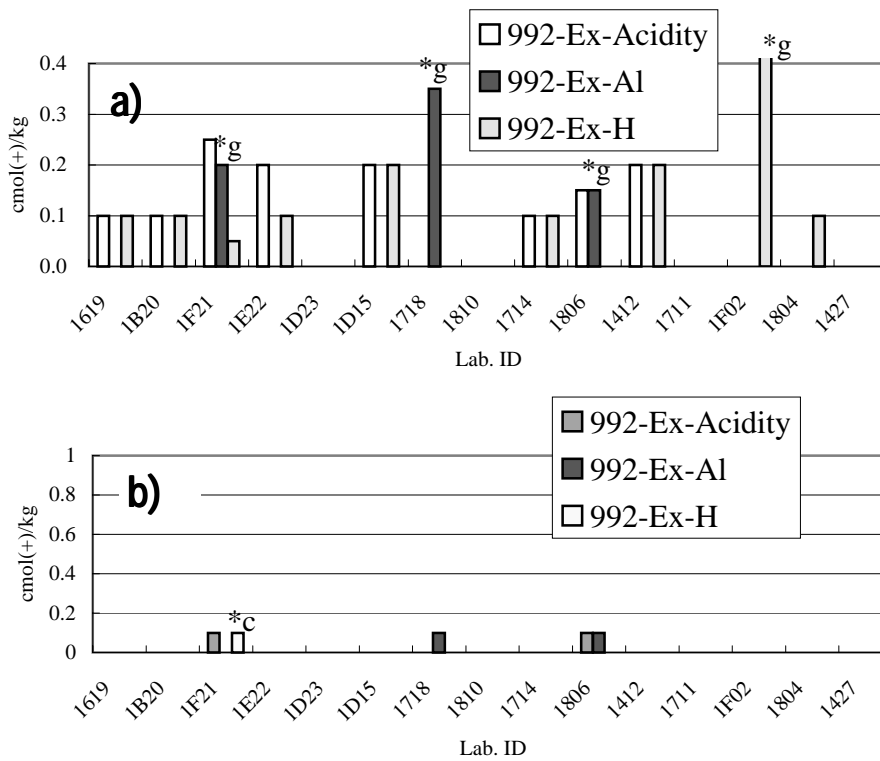


Figure 7.2. Laboratory average a) and range b) of Ex-Acidity, Al and H for No.992

**Table 3.1. Data tested by Grubbs' and Cochran's methods: Soil Sample No.991**

ID		pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H
				cmol (+)/kg							
1619	1st	4.6	3.8	0.1	0.3	0.6	0.4	14.8	4.3	1.9	2.4*g
	2nd	4.5	3.8	0.1	0.3	0.7	0.4	15.2	4.2	1.9	2.3*g
1B20	1st	6.6*g	4.9*g	0.5	0.2	0.5	0.4	9.2	6.0	5.7	0.3
	2nd	6.5*g	4.9*g	0.4	0.2	0.5	0.5	9.3	6.0	5.7	0.4
1F21	1st	4.7	4.0	0.0	0.3	0.5	0.2	ND	6.3	6.2	0.2
	2nd	4.7	4.0	0.0	0.2	0.4	0.2	ND	6.7	6.5	0.2
1E22	1st	4.8	4.0	0.5	0.1	0.3	0.8	9.6	5.7	5.4	0.3
	2nd	4.8	4.0	0.5	0.1	0.3	0.8	9.8	5.8	5.4	0.3
1D23		4.8	3.7	0.1	0.0	0.0	0.0	ND	0.5*g	ND	ND
1D15	1st	4.9	3.9	0.1	0.2	0.4	0.1	14.0	6.8	5.9	0.8
	2nd	4.9	3.9	0.1	0.2	0.4	0.1	13.9	6.8	5.9	0.8
1718	1st	4.3	3.6	0.1	0.1	0.4	5.9*g	ND	5.2	1.1	4.4*g
	2nd	4.3	3.6	0.1	0.2	0.4	5.9*g	ND	5.0	0.9	4.5*g
1810	1st	4.9	4.0	ND	ND	ND	ND	ND	ND	ND	ND
	2nd	4.9	4.0	ND	ND	ND	ND	ND	ND	ND	ND
1714	1st	4.1	4.0	4.0*g	0.2	0.7	0.3	12.2*c	5.8	5.3	0.6
	2nd	4.1	4.0	4.1*g	0.2	0.7	0.3	13.3*c	5.8	5.5	0.5
1806	1st	4.8	3.9	0.1	0.1	0.6	0.8	38.6*c	5.4	5.3	0.1
	2nd	4.9	3.9	0.1	0.1	0.6	0.7	41.7*c	5.4	5.3	0.1
1412	1st	7.1*c	4.2	2.6*g	0.7*c	0.1	0.3	3.9	6.0	5.9	0.1
	2nd	7.7*c	4.2	2.5*g	0.9*c	0.0	0.3	3.7	6.1	6.1	0.0
1711	1st	4.6	4.0	0.3	0.3	0.3	0.8	4.6	ND	ND	ND
	2nd	4.6	4.0	0.3	0.3	0.3	0.8	4.1	ND	ND	ND
1F02	1st	4.4	3.9	0.0	0.1	0.4	0.2	9.8	5.3	52.3*c	1.1
	2nd	4.4	3.9	0.0	0.1	0.4	0.2	10.1	5.2	50.6*c	1.1
1804	1st	4.5	3.9*c	0.9*g	0.1	0.3	0.8	11.0	ND	6.0	0.6
	2nd	4.6	3.8*c	0.8*g	0.1	0.3	0.9	11.1	ND	6.0	0.5
1427	1st	4.7	3.8	0.0	0.1	0.4	0.0	19.0	5.7	4.5	1.2*c
	2nd	4.6	3.8	0.0	0.1	0.4	0.0	19.0	5.4	5.0	0.4*c

Note: Asterisk shows outliers judged by the methods of Grubbs and Cochran.

**Table 3.2. Data tested by Grubbs' and Chocran's method: Soil Sample No.992**

ID		pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H
				cmol (+)/kg							
1619	1st	6.6	5.8	0.8	1.1	6.0*c	32.9	39.3	0.1	0.0	0.1
	2nd	6.6	5.7	0.8	1.1	6.6*c	33.5	40.2	0.1	0.0	0.1
1B20	1st	7.2	6.4*g	1.3	0.9	5.6	27.6	34.3	0.1	0.0	0.1
	2nd	7.2	6.5*g	1.2	0.8	5.9	27.5	35.6	0.1	0.0	0.1
1F21	1st	7.2	6.0	0.9	1.4	6.1	32.0	ND	0.3	0.2*g	0.0*c
	2nd	7.2	6.0	0.9	1.4	6.0	31.1	ND	0.2	0.2*g	0.1*c
1E22	1st	7.2	5.7	1.1	0.5	2.6	10.8	29.3	0.2	0.0	0.1
	2nd	7.2	5.7	1.1	0.5	2.6	10.8	29.8	0.2	0.0	0.1
1D23		7.0	5.6	0.1	0.0	0.1	0.1	ND	0.0	ND	ND
1D15	1st	7.4	5.9	1.0	1.5	5.4	23.9	27.6	0.2	0.0	0.2
	2nd	7.4	5.9	1.0	1.5	5.4	25.1	28.0	0.2	0.0	0.2
1718	1st	6.4*c	5.3	1.1	2.0	1.1	9.7	ND	0.0	0.4*g	0.0
	2nd	6.6*c	5.5	1.0	2.0	1.1	9.0	ND	0.0	0.3*g	0.0
1810	1st	7.5	5.9	ND	ND	ND	ND	ND	ND	ND	ND
	2nd	7.5	5.9	ND	ND	ND	ND	ND	ND	ND	ND
1714	1st	6.6	5.9	27.6*c	2.0	6.7	25.8	36.5	0.1	0.0	0.1
	2nd	6.6	5.9	28.1*c	2.0	6.7	25.3	36.0	0.1	0.0	0.1
1806	1st	6.8	5.6	1.0	1.4	6.2	25.4	87.6*g	0.2	0.2*g	0.0
	2nd	6.8	5.6	0.9	1.3	6.3	26.0	90.5*g	0.1	0.1*g	0.0
1412	1st	7.6	4.5*g	3.0*g	2.9	0.9	2.3	4.8*g	0.2	0.0	0.2
	2nd	7.6	4.6*g	3.0*g	2.8	0.9	1.3	3.6*g	0.2	0.0	0.2
1711	1st	7.2	5.9	1.8	1.4	5.8	21.7	51.3	ND	ND	ND
	2nd	7.3	5.9	1.8	1.4	5.5	21.8	49.6	ND	ND	ND
1F02	1st	6.7	5.4	0.8	1.4	6.0	28.8	42.7	0.0	0.0	0.9*g
	2nd	6.7	5.5	0.8	1.4	5.9	27.8	40.6	0.0	0.0	0.9*g
1804	1st	6.7	5.9*c	1.7	1.4	5.8	30.6	39.3	ND	0.0	0.1
	2nd	6.8	5.6*c	1.6	1.5	5.9	31.1	38.7	ND	0.0	0.1
1427	1st	7.1	5.7	0.8	1.4	6.4	28.0	48.0	0.0	0.0	0.0
	2nd	7.1	5.7	0.8	1.4	6.5	29.0	48.0	0.0	0.0	0.0

Note: Asterisk shows outliers judged by the methods of Grubbs and Cochran.

**Table 4.1. Analytical conditions-1**

ID	Extractant used for the analysis						
	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al, H
1619	A	A	A	A	B	D	D
1B20	A	A	A	A	B	D	D
1F21	A	A	A	A	-	D	D
1E22	A	A	A	A	B	+	D
1D23	+	+	+	+	-	+	-
1D15	A	A	A	A	B	D	D
1718	A	A	A	A	+	D	D
1810	-	-	-	-	-	-	-
1714	A	A	A	A	C	D	D
1806	A	A	A	A	B	D	D
1412	+	+	A	A	+	+	+
1711	A	A	A	A	B	-	-
1F02	A	A	A	A	B	D	D
1804	A	A	A	A	B	-	D
1427	A	A	A	A	B	D	D

Note: -, Not determined; +, No information; A, 1M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0); B, 1M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0)/10% KCl; C, 1M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0)/10% NaCl (acidified); D, 1M KCl. Shadow cells mean outliers for No.991 and/or 992.

**Table 4.2. Analytical conditions-2**

ID	Analytical methods							Temperature (°C)	
	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	pH 1st analysis	pH 2nd analysis
1619	AAS	AAS	AAS	AAS	Titration	Titration	Titration	18	18
1B20	AAS	AAS	AAS	AAS	Titration	Titration	Titration	21.5	21.5
1F21	AAS	AAS	AAS	AAS	-	Titration	Titration	18	18
1E22	FEP	FEP	AAS	AAS	Titration	Titration	AAS	20.8	20.8
1D23	+	+	+	+	+	+	+	+	+
1D15	AAS	AAS	AAS	AAS	Titration	Titration	Titration	19.2±2	19.5±2
1718	FEP	FEP	AAS	AAS	-	Titration	Titration	28.3	28.3
1810	-	-	-	-	-	-	-	20	20
1714	FEP	FEP	Titration	Titration	Titration	Titration	Titration	28.5	28.5
1806	AAS	AAS	AAS	AAS	Spectrophotometry	Titration	Titration	22	22
1412	+	+	AAS	AAS	+	+	+	24.6	24.6
1711	FEP	FEP	Calc.	Titration	Titration	-	-	18	18
1F02	AAS	AAS	AAS	AAS	Titration	Titration	Titration	24.5	24.5
1804	FEP	FEP	AAS	AAS	Titration	-	Titration	18.6-19.6	18.6-19.6
1427	AAS	AAS	AAS	AAS	IC	Titration	Titration	22	22

Note: -, Not determined; +, No information; AAS, Atomic absorption spectrometry; FEP, Flame (emission) photometry; Calc., Calculation from Ex-Ca and hardness; IC, Ion chromatography. Shadow cells mean outliers for No.991 and/or 992.

**Table 5.1. Staff in charge of measurement**

ID	Total	Moisture content	pH	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al, H
1619	3	A	B	C	C	C	C	C	B	B
1B20	2	A, B	A, B	A, B	A, B	A, B	A, B	A, B	A, B	A, B
1F21	3	A	B	C	C	C	C	-	A	A
1E22	1	A	A	A	A	A	A	A	A	A
1D23	?	+	+	+	+	+	+	+	+	+
1D15	?	+	+	+	+	+	+	+	+	+
1718	1	A	A	A	A	A	A	-	A	A
1810	1?	+	A	-	-	-	-	-	-	-
1714	1	A	A	A	A	A	A	A	A	A
1806	1	A	A	A	A	A	A	A	A	A
1412	2?	A, B	A, B	+	+	B	B	+	+	+
1711	2	A	B	B	B	B	B	B	-	-
1F02	1	A	A	A	A	A	A	A	A	A
1804	2	A, B	A, B	A, B	A, B	A, B	A, B	A, B	-	A, B
1427	2	A, B	A, B	A, B	A, B	A, B	A, B	A, B	A, B	A, B

Note: -, Not determined; +, No information; "A", "B", and "C" represent individual staffs in each laboratory who are in charge of measurement. Shadow cells mean outliers for No.991 and/or 992.

**Table 5.2. Years of experience of staff**

ID	Moisture content	pH	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al, H
1619	8	14	14	14	14	14	14	14	14
1B20	1	1	1	1	1	1	1	1	1
1F21	0.2		5	5	5	5		0.2	0.2
1E22	10	10	10	10	10	10	10	10	10
1D23	+	+	+	+	+	+	-	+	-
1D15	+	+	+	+	+	+	+	+	+
1718	1	1	1	1	1	1	-	1	1
1810	+	5	-	-	-	-	-	-	-
1714	23	23	23	23	23	23	23	23	23
1806	3	3	3	3	3	3	3	3	3
1412	+	+	+	+	+	+	+	+	+
1711	1	1	1	1	1	1	1	-	-
1F02	3	3	3	3	3	3	3	3	3
1804	6, 1	6, 1	6, 1	6, 1	6, 1	6, 1	6, 1	-	6, 1
1427	9, 0	9, 0	9, 0	9, 0	9, 0	9, 0	9, 0	9, 0	9, 0

Note: -, Not determined; +, No information. Shadow cells mean outliers for No.991 and/or 992.

### 3.2. Analysis of variance and estimation of precision

For the verified data, not including the outliers judged by Cochran and Grubbs methods, “within-laboratory-precision” and “inter-laboratories-precision” were estimated (Table 6.1 and 6.2. For detailed information of analysis of variance (ANOVA), see Appendix 3 and 4). For the statistical analysis, data of the laboratory “1D23” was not used since only single set of the data was reported (Statistics in Table 2.1 and 2.2 included the data of “1D23”).

#### 1) Within-laboratory-precision

Within-laboratory standard deviations were relatively small in all the parameter, especially in pH (H<sub>2</sub>O) and pH (KCl): the CVs were less than 1%. In general, in the parameters with high concentration, the within-laboratory-precision was high: the CVs were relatively low for Ex-basic cations in No.991 and for Ex-acidity in No. 992.

In this result, the within-laboratory-precision was remarkably lower than the inter-laboratories precision. It was suggested that the results might include data not only in the within-laboratory-reproducibility condition, but also in the repeatability condition. In the future program, instructions and reporting format for the repeat analysis should be elaborated in order to obtain accurate information of the analytical conditions.

#### 2) Inter-laboratories-precision

Inter-laboratories-precision was relatively high in pH (H<sub>2</sub>O) and pH (KCl): CVs were around 5%. In other parameters, the precision was very low even if variation among the bottles also could affect on the Inter-laboratories-reproducibility (Appendix 5).

Environmental factors of the laboratories, such as place, person, and instruments/apparatus, could affect the data variation. However, 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. In the future program of the inter-laboratory comparison for soil analysis, effect of each analytical step on the variation among laboratories should be evaluated.

### 3.3. Calculation of permissible tolerance

Permissible tolerances were also shown in Table 6.1 and 6.2.

In pH (H<sub>2</sub>O) and pH (KCl), within-laboratory-reproducibility limits were around 0.1, and it could be a reference value in the repeat analysis of same sample. In the concentration level of No.992, within-laboratory-reproducibility limit might be available for Ex-base cations. For Ex-acidity, in the concentration level of No.991, the limit also might be available.

Concerning the reproducibility limit, inter-laboratories-precision should be improved and the discussion should be carried out.

**Table 6.1. Estimation of precision and determination of permissible tolerance: The verified data of No.991**

		pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H
				cmol (+)/kg							
Statistics	Number of data	24	24	20	24	26	24	18	22	22	18
	Number of laboratories	12	12	10	12	13	12	9	11	11	9
	Total sum	110.6	94.2	3.3	4.2	10.9	10.3	192.1	124.9	107.4	8.0
	Total average	4.6	3.9	0.2	0.2	0.4	0.4	10.7	5.7	4.9	0.4
Estimated precision	Within-laboratory standard deviation ( $s_{RW}$ )	0.04	0.00	0.02	0.03	0.03	0.04	0.18	0.12	0.14	0.05
	Inter-laboratories standard deviation ( $s_R$ )	0.25	0.15	0.19	0.08	0.17	0.30	4.87	0.70	1.76	0.34
	Within-laboratory precision CV (%)	0.9	0.0	13.6	16.5	8.1	8.2	1.7	2.2	3.0	10.6
	Inter-laboratories precision CV (%)	5.4	3.8	112.5	44.8	40.9	69.8	45.6	12.3	36.1	77.2
Permissible tolerance	Within-laboratory-reproducibility limit ( $R_w$ )	0.11	0.000	0.06	0.08	0.10	0.10	0.52	0.34	0.40	0.13
	Reproducibility limit (R)	0.70	0.42	0.52	0.22	0.48	0.84	13.63	1.95	4.93	0.96

Note: Data of the laboratory "1D23" was not used for the above analysis since only single set of the data was reported.

**Table 6.2. Estimation of precision and determination of permissible tolerance: The verified data of No.992**

		pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H
				cmol (+)/kg							
Statistics	Number of data	26	22	22	26	24	26	18	22	18	20
	Number of laboratories	13	11	11	13	12	13	9	11	9	10
	Total sum	183.8	126.4	24.2	38.4	117.3	598.8	694.8	2.6	0.0	1.8
	Total average	7.1	5.7	1.1	1.5	4.9	23.0	38.6	0.1	0.0	0.1
Estimated precision	Within-laboratory standard deviation ( $s_{RW}$ )	0.03	0.05	0.04	0.04	0.10	0.52	0.78	0.03	0.00	0.00
	Inter-laboratories standard deviation ( $s_R$ )	0.34	0.20	0.34	0.57	2.09	9.66	7.56	0.09	0.00	0.07
	Within-laboratory precision CV (%)	0.4	0.9	3.9	2.7	2.0	2.2	2.0	25.5	0.0	0.0
	Inter-laboratories precision CV (%)	4.9	3.4	31.0	38.9	42.8	41.9	19.6	76.3	0.0	82.0
Permissible tolerance	Within-laboratory-reproducibility limit ( $R_w$ )	0.08	0.146	0.12	0.11	0.27	1.45	2.17	0.08	0.00	0.00
	Reproducibility limit (R)	0.96	0.55	0.95	1.61	5.85	27.05	21.16	0.25	0.00	0.21

Note: Data of the laboratory "1D23" was not used for the above analysis since only single set of the data was reported.

#### 4. ACKNOWLEDGMENT

ADORC wishes to thank Dr. Tomoyuki Hakamata for support on the preparation of the soil sample and useful advice on the statistical analysis of the data. ADORC thanks also “Aichi Prefecture Agricultural Research Center, Toyohashi Research and Extension Station” and “Akita Agricultural Experimental Station, Ogata Experimental Farm” for their cooperation on the soil sampling.

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

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## **APPENDIX 1: Participating laboratories**

### **1. CHINA**

Laboratories in the following four cities:

1) Chong qing

2) Xi'an

3) Xiamen

4) Zhuhai

### **2. INDONESIA**

Environmental Management Centre (EMC)

### **3. JAPAN**

1) Agricultural Experimental Station, Shimane Prefecture

2) Gifu Prefectural Research Institute of Health and Environment

3) Ecological Impact Research Department, Acid Deposition and Oxidant Research Center

### **4. Republic of KOREA**

Soil Environmental Laboratory, National Institute of Environmental Research

### **5. MALAYSIA**

Department of Environmental Sciences, Universiti Putra Malaysia

### **6. MONGOLIA**

Central Laboratory of Environmental Monitoring

### **7. PHILIPPINES**

Department of Soil Science, University of the Philippines, Los Banos

### **8. RUSSIA**

Limnological Institute Russian Academy of Science/Siberian Branch

### **9. THAILAND**

King Mongkut's University of Technology Thonburi

### **10. VIET NAM**

Water and Atmospheric Environmental Research Center, Institute of Meteorology and Hydrology

**APPENDIX 2.1. Original data: Soil Sample No.991**

ID		Moisture content	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H	ECEC	T-C	T-N	Available phosphate	Sulphate
		%														P-mg/kg	S-mg/kg
cmol (+)/kg														g/kg	g/kg	P-mg/kg	S-mg/kg
1619	1st	6.1	4.6	3.8	0.1	0.3	0.6	0.4	14.8	4.3	1.9	2.4	5.7	2.93	0.51	0.90	85.70
	2nd	6.1	4.5	3.8	0.1	0.3	0.7	0.4	15.2	4.2	1.9	2.3	5.7	2.99	0.50	1.04	84.90
1B20	1st	5.9	6.6	4.9	0.5	0.2	0.5	0.4	9.2	6.0	5.7	0.3	7.6				
	2nd	5.9	6.5	4.9	0.4	0.2	0.5	0.5	9.3	6.0	5.7	0.4	7.6				
1F21	1st	5.9	4.7	4.0	0.0	0.3	0.5	0.2	ND	6.3	6.2	0.2	7.3	4.16	0.63		13.21
	2nd		4.7	4.0	0.0	0.2	0.4	0.2	ND	6.7	6.5	0.2	7.5	4.18	0.61		12.71
1E22	1st	5.3	4.8	4.0	0.5	0.1	0.3	0.8	9.6	5.7	5.4	0.3	7.4	4.68	0.56	0.00	94.00
	2nd	5.3	4.8	4.0	0.5	0.1	0.3	0.8	9.8	5.8	5.4	0.3	7.5	4.67	0.53	0.00	94.00
1D23		5.4	4.8	3.7	0.1	0.0	0.0	0.0	ND	0.5	ND	ND	0.6				
1D15	1st	5.8	4.9	3.9	0.1	0.2	0.4	0.1	14.0	6.8	5.9	0.8	7.6				
	2nd		4.9	3.9	0.1	0.2	0.4	0.1	13.9	6.8	5.9	0.8	7.6				
1718	1st	4.4	4.3	3.6	0.1	0.1	0.4	5.9	ND	5.2	1.1	4.4	11.7				
	2nd		4.3	3.6	0.1	0.2	0.4	5.9	ND	5.0	0.9	4.5	11.6				
1810	1st	6.0	4.9	4.0	ND	ND	ND	ND	ND	ND	ND	ND					
	2nd	6.0	4.9	4.0	ND	ND	ND	ND	ND	ND	ND	ND					
1714	1st	4.9	4.1	4.0	4.0	0.2	0.7	0.3	12.2	5.8	5.3	0.6	11.0	0.66			
	2nd		4.1	4.0	4.1	0.2	0.7	0.3	13.3	5.8	5.5	0.5	11.1	0.67			
1806	1st	5.8	4.8	3.9	0.1	0.1	0.6	0.8	38.6	5.4	5.3	0.1	7.0	2.80	0.60	0.00	0.56
	2nd		4.9	3.9	0.1	0.1	0.6	0.7	41.7	5.4	5.3	0.1	6.9	2.90	0.80	0.00	0.67
1412	1st	5.1	7.1	4.2	2.6	0.7	0.1	0.3	3.9	6.0	5.9	0.1	9.7	57.90	7.46	8.03	13.78
	2nd		7.7	4.2	2.5	0.9	0.0	0.3	3.7	6.1	6.1	0.0	9.8	59.73	8.25	4.83	13.00
1711	1st	4.1	4.6	4.0	0.3	0.3	0.3	0.8	4.6	ND	ND	ND					
	2nd		4.6	4.0	0.3	0.3	0.3	0.8	4.1	ND	ND	ND					
1F02	1st	5.3	4.4	3.9	0.0	0.1	0.4	0.2	9.8	5.3	52.3	1.1	6.0				
	2nd		4.4	3.9	0.0	0.1	0.4	0.2	10.1	5.2	50.6	1.1	5.9				
1804	1st	6.4	4.5	3.9	0.9	0.1	0.3	0.8	11.0	ND	6.0	0.6	8.7	3.24	0.54	0.01	0.41
	2nd		4.6	3.8	0.8	0.1	0.3	0.9	11.1	ND	6.0	0.5	8.6	3.29	0.54	0.01	0.41
1427	1st	5.6	4.7	3.8	0.0	0.1	0.4	0.0	19.0	5.7	4.5	1.2	6.2				
	2nd		4.6	3.8	0.0	0.1	0.4	0.0	19.0	5.4	5.0	0.4	5.9				

Note: ND, not determined; Ex-, Exchangeable; T-C, Total carbon; T-N, Total Nitrogen. ECEC was calculated as sum of Ex-cations

**APPENDIX 2.2.Original data: Soil Sample No.992**

ID		Moisture content	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H	ECEC	T-C	T-N	Available phosphate	Sulphate
		%														P-mg/kg	S-mg/kg
cmol (+)/kg														g/kg	g/kg	P-mg/kg	S-mg/kg
1619	1st	8.7	6.6	5.8	0.8	1.1	6.0	32.9	39.3	0.1	0.0	0.1	40.9	17.20	1.81	42.90	13.90
	2nd	8.8	6.6	5.7	0.8	1.1	6.6	33.5	40.2	0.1	0.0	0.1	42.1	17.10	1.78	42.50	13.60
1B20	1st	8.3	7.2	6.4	1.3	0.9	5.6	27.6	34.3	0.1	0.0	0.1	35.5				
	2nd	8.3	7.2	6.5	1.2	0.8	5.9	27.5	35.6	0.1	0.0	0.1	35.5				
1F21	1st	8.2	7.2	6.0	0.9	1.4	6.1	32.0	ND	0.3	0.2	0.0	40.7	18.95	1.83	29.56	17.73
	2nd		7.2	6.0	0.9	1.4	6.0	31.1	ND	0.2	0.2	0.1	39.6	19.01	1.85	29.70	17.23
1E22	1st	7.0	7.2	5.7	1.1	0.5	2.6	10.8	29.3	0.2	0.0	0.1	15.2	18.87	1.74	118.00	18.00
	2nd	7.0	7.2	5.7	1.1	0.5	2.6	10.8	29.8	0.2	0.0	0.1	15.2	18.82	1.74	118.00	18.00
1D23		7.7	7.0	5.6	0.1	0.0	0.1	0.1	ND	0.0	ND	ND	0.3				
1D15	1st	8.1	7.4	5.9	1.0	1.5	5.4	23.9	27.6	0.2	0.0	0.2	32.0				
	2nd		7.4	5.9	1.0	1.5	5.4	25.1	28.0	0.2	0.0	0.2	33.2				
1718	1st	5.8	6.4	5.3	1.1	2.0	1.1	9.7	ND	0.0	0.4	0.0	13.9				
	2nd		6.6	5.5	1.0	2.0	1.1	9.0	ND	0.0	0.3	0.0	13.1				
1810	1st	8.3	7.5	5.9	ND	ND	ND	ND	ND	ND	ND	ND					
	2nd	8.5	7.5	5.9	ND	ND	ND	ND	ND	ND	ND	ND					
1714	1st	6.8	6.6	5.9	27.6	2.0	6.7	25.8	36.5	0.1	0.0	0.1	62.2	3.54			
	2nd		6.6	5.9	28.1	2.0	6.7	25.3	36.0	0.1	0.0	0.1	62.2	3.57			
1806	1st	8.0	6.8	5.6	1.0	1.4	6.2	25.4	87.6	0.2	0.2	0.0	34.2	16.60	2.10	1.11	0.05
	2nd		6.8	5.6	0.9	1.3	6.3	26.0	90.5	0.1	0.1	0.0	34.6	15.80	1.90	1.08	0.03
1412	1st	7.4	7.6	4.5	3.0	2.9	0.9	2.3	4.8	0.2	0.0	0.2	9.3	71.82	14.10	84.40	4.32
	2nd		7.6	4.6	3.0	2.8	0.9	1.3	3.6	0.2	0.0	0.2	8.2	70.15	16.13	94.70	7.50
1711	1st	5.4	7.2	5.9	1.8	1.4	5.8	21.7	51.3	ND	ND	ND					
	2nd		7.3	5.9	1.8	1.4	5.5	21.8	49.6	ND	ND	ND					
1F02	1st	7.3	6.7	5.4	0.8	1.4	6.0	28.8	42.7	0.0	0.0	0.9	37.0				
	2nd		6.7	5.5	0.8	1.4	5.9	27.8	40.6	0.0	0.0	0.9	35.9				
1804	1st	8.5	6.7	5.9	1.7	1.4	5.8	30.6	39.3	ND	0.0	0.1	39.6	54.30	1.99	0.12	0.06
	2nd		6.8	5.6	1.6	1.5	5.9	31.1	38.7	ND	0.0	0.1	40.2	54.70	1.95	0.12	0.06
1427	1st	8.0	7.1	5.7	0.8	1.4	6.4	28.0	48.0	0.0	0.0	0.0	36.6				
	2nd		7.1	5.7	0.8	1.4	6.5	29.0	48.0	0.0	0.0	0.0	37.7				

Note: ND, not determined; Ex-, Exchangeable; T-C, Total carbon; T-N, Total Nitrogen. ECEC was calculated as sum of Ex-cations

**APPENDIX 3.1. ANOVA , estimation of precision and determination of permissible tolerance: The verified data of No.991**

		pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H
				cmol (+)/kg							
Statistics	Number of data	24	24	20	24	26	24	18	22	22	18
	Number of laboratories	12	12	10	12	13	12	9	11	11	9
	Total sum	110.6	94.2	3.3	4.2	10.9	10.3	192.1	124.9	107.4	8.0
	Total average	4.6	3.9	0.2	0.2	0.4	0.4	10.7	5.7	4.9	0.4
ANOVA	Total sum of square (S <sub>T</sub> )	1.38	0.48	0.63	0.15	0.72	1.99	379.62	9.86	62.33	1.90
	Sum of square inter-laboratories (S <sub>R</sub> )	1.36	0.48	0.62	0.14	0.71	1.97	379.31	9.69	62.10	1.88
	Sum of square within-laboratory (S <sub>RW</sub> = S <sub>T</sub> - S <sub>R</sub> )	0.02	0.00	0.01	0.01	0.01	0.01	0.30	0.16	0.23	0.02
	Total degree of freedom (Φ <sub>T</sub> )	23	23	19	23	25	23	17	21	21	17
	Inter-laboratories degree of freedom (Φ <sub>R</sub> )	11	11	9	11	12	11	8	10	10	8
	Within-laboratory-reproducibility degree of freedom (Φ <sub>RW</sub> )	12	12	10	12	13	12	9	11	11	9
	Inter-laboratories variance (V <sub>R</sub> = S <sub>R</sub> /Φ <sub>R</sub> )	0.12	0.04	0.07	0.01	0.06	0.18	47.41	0.97	6.21	0.24
Within-laboratory-reproducibility Variance (V <sub>RW</sub> = S <sub>RW</sub> /Φ <sub>RW</sub> )	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.01	0.02	0.00	
Estimated precision	Laboratory component of variance (s <sub>b</sub> <sup>2</sup> = (V <sub>R</sub> - V <sub>RW</sub> )/2)	0.06	0.02	0.03	0.01	0.03	0.09	23.69	0.48	3.09	0.12
	Within-laboratory standard deviation (s <sub>RW</sub> = SQRT(V <sub>RW</sub> ))	0.04	0.00	0.02	0.03	0.03	0.04	0.18	0.12	0.14	0.05
	Inter-laboratories standard deviation (s <sub>R</sub> = SQRT(s <sub>b</sub> <sup>2</sup> + s <sub>RW</sub> <sup>2</sup> /2))	0.25	0.15	0.19	0.08	0.17	0.30	4.87	0.70	1.76	0.34
	Within-laboratory precision CV (%)	0.9	0.0	13.6	16.5	8.1	8.2	1.7	2.2	3.0	10.6
	Inter-laboratories precision CV (%)	5.4	3.8	112.5	44.8	40.9	69.8	45.6	12.3	36.1	77.2
Permissible tolerance	Within-laboratory-reproducibility limit (R <sub>w</sub> = D (2, 0.95) s <sub>RW</sub> )	0.11	0.000	0.06	0.08	0.10	0.10	0.52	0.34	0.40	0.13
	Reproducibility limit (R = D (2, 0.95) s <sub>R</sub> )	0.70	0.42	0.52	0.22	0.48	0.84	13.63	1.95	4.93	0.96

Note: ANOVA was carried out according to the Annex II of the Technical Manual for Soil and Vegetation Monitoring in East Asia (2000). Data of the laboratory "1D23" was not used for the above analysis since only single set of the data was reported.

**APPENDIX 3.2. ANOVA , estimation of precision and determination of permissible tolerance: The verified data of No.992**

		pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H
				cmol (+)/kg							
Statistics	Number of data	26	22	22	26	24	26	18	22	18	20
	Number of laboratories	13	11	11	13	12	13	9	11	9	10
	Total sum	183.8	126.4	24.2	38.4	117.3	598.8	694.8	2.6	0.0	1.8
	Total average	7.1	5.7	1.1	1.5	4.9	23.0	38.6	0.1	0.0	0.1
ANOVA	Total sum of square (S <sub>T</sub> )	2.84	0.81	2.34	7.95	96.23	2243.50	919.32	0.17	0.00	0.10
	Sum of square inter-laboratories (S <sub>R</sub> )	2.83	0.78	2.32	7.93	96.11	2240.01	913.91	0.16	0.00	0.10
	Sum of square within-laboratory (S <sub>RW</sub> = S <sub>T</sub> - S <sub>R</sub> )	0.01	0.03	0.02	0.02	0.11	3.49	5.41	0.01	0.00	0.00
	Total degree of freedom (Φ <sub>T</sub> )	25	21	21	25	23	25	17	21	17	19
	Inter-laboratories degree of freedom (Φ <sub>R</sub> )	12	10	10	12	11	12	8	10	8	9
	Within-laboratory-reproducibility degree of freedom (Φ <sub>RW</sub> )	13	11	11	13	12	13	9	11	9	10
	Inter-laboratories variance (V <sub>R</sub> = S <sub>R</sub> /Φ <sub>R</sub> )	0.24	0.08	0.23	0.66	8.74	186.67	114.24	0.02	0.00	0.01
Within-laboratory-reproducibility Variance (V <sub>RW</sub> = S <sub>RW</sub> /Φ <sub>RW</sub> )	0.00	0.00	0.00	0.00	0.01	0.27	0.60	0.00	0.00	0.00	
Estimated precision	Laboratory component of variance (s <sub>b</sub> <sup>2</sup> = (V <sub>R</sub> - V <sub>RW</sub> )/2)	0.12	0.04	0.12	0.33	4.36	93.20	56.82	0.01	0.00	0.01
	Within-laboratory standard deviation (s <sub>RW</sub> = SQRT(V <sub>RW</sub> ))	0.03	0.05	0.04	0.04	0.10	0.52	0.78	0.03	0.00	0.00
	Inter-laboratories standard deviation (s <sub>R</sub> = SQRT(s <sub>b</sub> <sup>2</sup> + s <sub>RW</sub> <sup>2</sup> /2))	0.34	0.20	0.34	0.57	2.09	9.66	7.56	0.09	0.00	0.07
	Within-laboratory precision CV (%)	0.4	0.9	3.9	2.7	2.0	2.2	2.0	25.5	0.0	0.0
	Inter-laboratories precision CV (%)	4.9	3.4	31.0	38.9	42.8	41.9	19.6	76.3	0.0	82.0
Permissible tolerance	Within-laboratory-reproducibility limit (R <sub>w</sub> = D (2, 0.95) s <sub>RW</sub> )	0.08	0.146	0.12	0.11	0.27	1.45	2.17	0.08	0.00	0.00
	Reproducibility limit (R = D (2, 0.95) s <sub>R</sub> )	0.96	0.55	0.95	1.61	5.85	27.05	21.16	0.25	0.00	0.21

Note: ANOVA was carried out according to the Annex II of the Technical Manual for Soil and Vegetation Monitoring in East Asia (2000). Data of the laboratory "1D23" was not used for the above analysis since only single set of the data was reported.

**APPENDIX 4.1. ANOVA , estimation of precision and determination of permissible tolerance: All the data of No.991**

		pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H
				cmol (+)/kg							
Statistics	Number of data	28	28	26	26	26	26	22	22	24	24
	Number of laboratories	14	14	13	13	13	13	11	11	12	12
	Total sum	138.5	111.7	18.2	5.8	10.9	22.1	297.9	124.9	210.3	23.2
	Total average	4.9	4.0	0.7	0.2	0.4	0.9	13.5	5.7	8.8	1.0
ANOVA	Total sum of square (S <sub>T</sub> )	21.49	2.29	35.70	0.89	0.72	57.25	1950.49	9.86	4039.54	35.29
	Sum of square inter-labotatories (S <sub>R</sub> )	21.28	2.28	35.68	0.86	0.71	57.23	1944.78	9.69	4037.86	34.94
	Sum of square within-labotatory (S <sub>RW</sub> = S <sub>T</sub> - S <sub>R</sub> )	0.20	0.00	0.02	0.03	0.01	0.02	5.71	0.16	1.67	0.35
	Total degree of freedom (Φ <sub>T</sub> )	27	27	25	25	25	25	21	21	23	23
	Inter-laboratories degree of freedom (Φ <sub>R</sub> )	13	13	12	12	12	12	10	10	11	11
	Within-laboratory-reproducibility degree of freedom (Φ <sub>RW</sub> )	14	14	13	13	13	13	11	11	12	12
	Inter-laboratories variance (V <sub>R</sub> = S <sub>R</sub> /Φ <sub>R</sub> )	1.64	0.18	2.97	0.07	0.06	4.77	194.48	0.97	367.08	3.18
Within-laboratory-reproducibility Variance (V <sub>RW</sub> = S <sub>RW</sub> /Φ <sub>RW</sub> )	0.01	0.00	0.00	0.00	0.00	0.00	0.52	0.01	0.14	0.03	
Estimated precision	Laboratory component of variance (s <sub>b</sub> <sup>2</sup> = (V <sub>R</sub> - V <sub>RW</sub> )/2)	0.81	0.09	1.49	0.03	0.03	2.38	96.98	0.48	183.47	1.57
	Within-laboratory standard deviation (s <sub>RW</sub> = SQRT(V <sub>RW</sub> ))	0.12	0.02	0.04	0.05	0.03	0.03	0.72	0.12	0.37	0.17
	Inter-laboratories standard deviation (s <sub>R</sub> = SQRT(s <sub>b</sub> <sup>2</sup> + s <sub>RW</sub> <sup>2</sup> /2)	0.90	0.30	1.22	0.19	0.17	1.54	9.86	0.70	13.55	1.26
	Within-laboratory precision CV (%)	2.4	0.5	5.6	21.5	8.1	4.0	5.3	2.2	4.3	17.7
	Inter-laboratories precision CV (%)	18.3	7.4	174.2	84.7	40.9	181.7	72.8	12.3	154.6	130.4
Permissible tolerance	Within-laboratory-reproducibility limit (R <sub>w</sub> = D (2, 0.95) s <sub>RW</sub> )	0.34	0.05	0.11	0.13	0.10	0.10	2.02	0.34	1.05	0.48
	Reproducibility limit (R = D (2, 0.95) s <sub>R</sub> )	2.53	0.83	3.41	0.53	0.48	4.32	27.61	1.95	37.93	3.53

Note: ANOVA was carried out according to the Annex II of the Technical Manual for Soil and Vegetation Monitoring in East Asia (2000). Data of the laboratory "1D23" was not used for the above analysis since only single set of the data was reported.

**APPENDIX 4.2. ANOVA , estimation of precision and determination of permissible tolerance: All the data of No.992**

		pH(H <sub>2</sub> O)	pH(KCl)	Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Acidity	Ex-Al	Ex-H
				cmol (+)/kg							
Statistics	Number of data	28	28	26	26	26	26	22	22	24	24
	Number of laboratories	14	14	13	13	13	13	11	11	12	12
	Total sum	196.8	159.9	85.9	38.4	129.9	598.8	881.3	2.6	1.4	3.7
	Total average	7.0	5.7	3.3	1.5	5.0	23.0	40.1	0.1	0.1	0.2
ANOVA	Total sum of square (S <sub>T</sub> )	3.46	4.69	1314.53	7.95	100.09	2243.50	8334.53	0.17	0.30	1.32
	Sum of square inter-labotatories (S <sub>R</sub> )	3.43	4.60	1314.38	7.93	99.79	2240.01	8324.20	0.16	0.29	1.31
	Sum of square within-labotatory (S <sub>RW</sub> = S <sub>T</sub> - S <sub>R</sub> )	0.03	0.09	0.15	0.02	0.29	3.49	10.33	0.01	0.01	0.00
	Total degree of freedom (Φ <sub>T</sub> )	27	27	25	25	25	25	21	21	23	23
	Inter-laboratories degree of freedom (Φ <sub>R</sub> )	13	13	12	12	12	12	10	10	11	11
	Within-laboratory-reproducibility degree of freedom (Φ <sub>RW</sub> )	14	14	13	13	13	13	11	11	12	12
	Inter-laboratories variance (V <sub>R</sub> = S <sub>R</sub> /Φ <sub>R</sub> )	0.26	0.35	109.53	0.66	8.32	186.67	832.42	0.02	0.03	0.12
Within-laboratory-reproducibility Variance (V <sub>RW</sub> = S <sub>RW</sub> /Φ <sub>RW</sub> )	0.00	0.01	0.01	0.00	0.02	0.27	0.94	0.00	0.00	0.00	
Estimated precision	Laboratory component of variance (s <sub>b</sub> <sup>2</sup> = (V <sub>R</sub> - V <sub>RW</sub> )/2)	0.13	0.17	54.76	0.33	4.15	93.20	415.74	0.01	0.01	0.06
	Within-laboratory standard deviation (s <sub>RW</sub> = SQRT(V <sub>RW</sub> ))	0.05	0.08	0.11	0.04	0.15	0.52	0.97	0.03	0.03	0.02
	Inter-laboratories standard deviation (s <sub>R</sub> = SQRT(s <sub>b</sub> <sup>2</sup> + s <sub>RW</sub> <sup>2</sup> /2)	0.36	0.42	7.40	0.57	2.04	9.66	20.40	0.09	0.11	0.24
	Within-laboratory precision CV (%)	0.7	1.4	3.2	2.7	3.0	2.2	2.4	25.5	49.5	13.2
	Inter-laboratories precision CV (%)	5.2	7.4	224.0	38.9	40.8	41.9	50.9	76.3	196.3	158.6
Permissible tolerance	Within-laboratory-reproducibility limit (R <sub>w</sub> = D (2, 0.95) s <sub>RW</sub> )	0.13	0.22	0.30	0.11	0.42	1.45	2.71	0.08	0.08	0.06
	Reproducibility limit (R = D (2, 0.95) s <sub>R</sub> )	1.02	1.18	20.72	1.61	5.71	27.05	57.12	0.25	0.32	0.68

Note: ANOVA was carried out according to the Annex II of the Technical Manual for Soil and Vegetation Monitoring in East Asia (2000). Data of the laboratory "1D23" was not used for the above analysis since only single set of the data was reported.

**APPENDIX 5. Variation on chemical properties among bottles**

Sample No.	Serial No.	pH (H <sub>2</sub> O)	pH (KCl)	cmol(+)/kg							
				Ex-Na	Ex-K	Ex-Mg	Ex-Ca	CEC	Ex-Al (AA)	Ex-Al (T)	Ex-H
No.991	991-001	4.8	3.8	0.04	0.08	0.45	0.24	7.97	5.44	5.91	0.60
	991-002	4.9	3.8	0.03	0.08	0.44	0.21	11.15	5.40	5.99	0.34
	991-020	4.9	3.8	0.03	0.09	0.44	0.21	8.50	5.34	6.04	0.30
	991-026	4.9	3.8	0.02	0.07	0.42	0.20	7.70	5.27	5.86	0.26
	991-030	4.8	3.8	0.02	0.07	0.43	0.21	6.77	5.25	5.77	0.40
	Mean	4.8	3.8	0.03	0.08	0.44	0.21	8.42	5.34	5.91	0.38
	Standard deviation	0.0	0.0	0.01	0.01	0.01	0.02	1.65	0.08	0.11	0.13
	CV (%)	1.0	0.4	29.88	10.73	2.62	7.09	19.61	1.53	1.80	35.11
No.992	992-001	7.1	5.6	0.83	1.49	5.77	29.33	21.99	0.13	0.00	0.22
	992-002	7.2	5.6	0.84	1.49	5.77	29.95	21.59	0.14	0.00	0.22
	992-020	7.2	5.6	0.84	1.49	5.75	29.40	22.28	0.13	0.00	0.22
	992-026	7.3	5.6	0.85	1.47	5.74	29.47	21.59	0.11	0.00	0.22
	992-030	7.3	5.7	0.84	1.48	5.77	29.53	21.46	0.09	0.00	0.22
	Mean	7.2	5.6	0.84	1.48	5.76	29.54	21.78	0.12	0.00	0.22
	Standard deviation	0.1	0.0	0.01	0.01	0.01	0.24	0.34	0.02	0.00	0.00
	CV (%)	1.0	0.7	0.84	0.60	0.25	0.82	1.57	16.67	0.00	0.00

Note: Al (AA) and Al (T) mean analytical results by atomic absorption spectrometry and titration, respectively.