

Report of the Inter-laboratory Comparison Project 2018 (Draft)

Chapter 4: 20th Inter-laboratory Comparison Project on Soil

Network Center for EANET

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Description of Soil Samples

- Sample No.181s: Cambisols
- Sample No.182s: Cambisols
- The soil No.181s and No.182s were collected in *Cryptomeria japonica* plantation in Niigata Prefecture, Japan.
- Thirteen laboratories of 6 countries participated in the 20th project.

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Analyzed Soil Chemical Properties

Parameters	Unit	No. 181s and No. 182s
a) Moisture Content	wt %	M
b) pH (H ₂ O)	-	M
c) pH (KCl)	-	M
d) Exchangeable Ca	cmol _c kg ⁻¹	M
e) Exchangeable Mg	cmol _c kg ⁻¹	M
f) Exchangeable K	cmol _c kg ⁻¹	M
g) Exchangeable Na	cmol _c kg ⁻¹	M
h) Exchangeable Acidity	cmol _c kg ⁻¹	M
i) Exchangeable Al	cmol _c kg ⁻¹	M
j) Exchangeable H	cmol _c kg ⁻¹	M

M: Mandatory items

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Assessing Repeatability and Reproducibility

- **Repeatability**
Triplicate analysis under the same condition.
- **Reproducibility**
Twice analyses--- on different days,
by different analysts, or
using different instruments.

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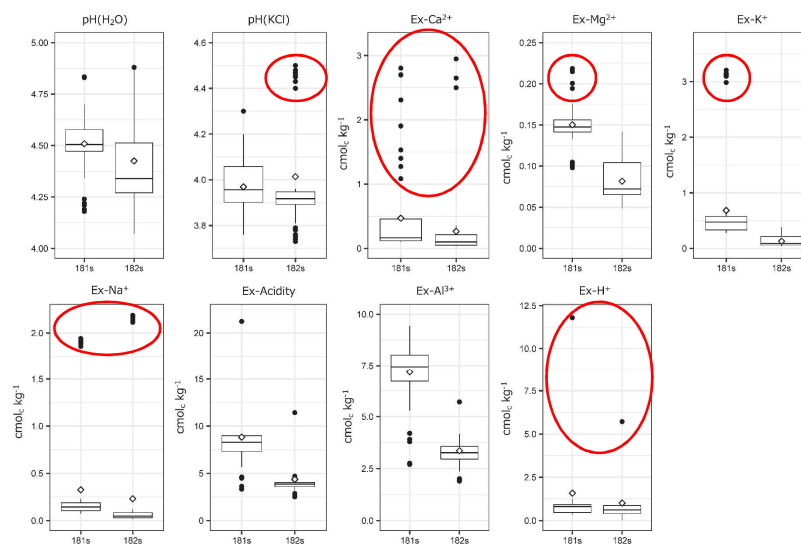
Standardization of Methods / Procedures

- **Atomic absorption spectrometry (AAS) method** should be used basically for analysis of Ex-Ca, Mg, K and Na.
- **Titration method** should be used for analysis of EX-acidity, Al and H.
- **Calibration curve method** should be used for determination of Ex-Ca²⁺, Mg²⁺, K⁺ and Na⁺.
- **1M CH₃COONH₄ (pH 7.0) solution** should be used to prepare each standard solution as the solvent.
- **Sr** should be added to the samples and each standard solution for analysis of Ex-Ca²⁺, Mg²⁺, K⁺ and Na⁺.
- **Digital reporting forms** were provided by excel files to avoid possible easy mistakes.

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Data Variation among 13 Laboratories



Outstanding outliers were found in almost all items.

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Data Verification by Cochran and Grubbs tests - 181s											
No. 181s											
Country	Lab.	Repeat analysis	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
cmol kg ⁻¹											
China	CN01	1st	4.3	3.8	3.20 c	0.10 g	0.72	1.91 g	4.12 c	3.57 c	0.55
		2nd	4.4	3.8	3.01 c	0.10 g	0.73	1.90 g	4.63 c	3.99 c	0.64
	CN02	1st	4.5	4.0	0.20	0.15	0.48	0.17	8.28	7.89	0.39
		2nd	4.5	4.1	0.19	0.15	0.48	0.17	8.24	7.85	0.39
	CN03	1st	4.5	3.9	0.16	0.14	0.44	0.18	5.75	5.40	0.35
		2nd	4.5	3.9	0.15	0.14	0.42	0.19	5.78	5.42	0.37
	CN04	1st	4.5	3.9	0.12	0.14	0.30	0.09	8.00 c	6.80 c	1.21
		2nd	4.5	3.9	0.12	0.14	0.29	0.08	8.28 c	7.06 c	1.22
Indonesia	ID01	1st	4.4	3.8	0.14	0.15	0.34	0.11	7.99	7.14	0.85
		2nd	4.4	3.8	0.14	0.15	0.33	0.10	8.03	7.21	0.82
	ID04	1st	4.5	3.9	0.24	0.19 c	0.42	0.20	7.37	6.58	0.79
		2nd	4.5	3.9	0.23	0.21 c	0.43	0.21	7.32	6.54	0.78
Mongolia	MN01	1st	4.7	4.0	NA	NA	NA	NA	21.24 g	9.44	11.80 g
		2nd	4.6	4.0	NA	NA	NA	NA	21.24 g	9.44	11.80 g
Philippines	PH01	1st	4.5	4.0	1.91 c	0.14	3.15 c	3.52 c	8.55 c	7.49	0.45
		2nd	4.5	3.9	1.25 c	0.14	4.07 c	0.08 c	8.70 c	7.51	0.53
Russia	RU01	1st	4.2	3.9	0.47 g	0.16 c	0.28	0.10	7.29	6.75	0.53
		2nd	4.2	3.9	0.48 g	0.17 c	0.29	0.11	7.24	6.82	0.41
Vietnam	VN01	1st	4.6	4.1	0.10	0.15	0.57	0.14	8.94	7.87 c	0.91
		2nd	4.6	4.1	0.10	0.15	0.57	0.14	8.98	7.64 c	0.85
	VN02	1st	4.5	4.1	NA	NA	NA	NA	9.06	8.17	0.81
		2nd	4.5	4.1	NA	NA	NA	NA	9.04	8.21	0.77
	VN04	1st	4.6	4.2	0.10	0.15	0.57	0.14	8.76	7.58	1.16
		2nd	4.6	4.2	0.10	0.15	0.57	0.14	8.79	7.59	1.16
	VN05	1st	4.8	4.0	NA	NA	NA	NA	9.04	8.13	0.81
		2nd	4.8	4.0	NA	NA	NA	NA	9.06	8.17	0.77

The outliers were determined by Cochran and Grubbs tests, and were indicated by "c" and "g" signs, respectively. 7

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Data Verification by Cochran and Grubbs tests - 182s											
No. 182s											
Country	Lab.	Repeat analysis	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
cmol kg ⁻¹											
China	CN01	1st	4.2	3.8	3.30 c	0.05	0.25	2.14 c	2.66	1.96	0.71
		2nd	4.2	3.8	2.99 c	0.05	0.24	2.19 c	2.78	2.09	0.69
	CN02	1st	4.3	3.9	0.10	0.11	0.10	0.05	3.82	3.11	0.72
		2nd	4.3	3.9	0.11	0.11	0.10	0.05	3.89	3.14	0.75
	CN03	1st	4.3	3.9	0.08	0.08	0.11	0.09	3.80	2.63	1.17
		2nd	4.3	3.9	0.08	0.08	0.11	0.09	3.80	2.63	1.17
	CN04	1st	4.3	3.9	0.04	0.06	0.05	0.02	3.72	2.89	0.83
		2nd	4.3	3.9	0.04	0.06	0.05	0.02	3.87	2.97	0.90
Indonesia	ID01	1st	4.2	3.7	0.05	0.07	0.07	0.03	3.51	3.15	0.36
		2nd	4.2	3.8	0.05	0.07	0.06	0.03	3.51	3.17	0.35
	ID04	1st	4.3	3.9	0.09	0.13	0.23	0.09	3.40	2.97	0.41
		2nd	4.3	3.9	0.09	0.12	0.24	0.10	3.46	2.85	0.55
Mongolia	MN01	1st	4.4	3.9	NA	NA	NA	NA	11.42 g	5.71 g	5.71 g
		2nd	4.4	3.8	NA	NA	NA	NA	11.42 g	5.71 g	5.71 g
Philippines	PH01	1st	4.3	3.9	0.04 c	0.07	0.14 c	0.02	3.60 c	3.98 c	0.25
		2nd	4.3	3.8	0.07 c	0.08	0.36 c	0.03	3.89 c	3.67 c	0.31
Russia	RU01	1st	4.1	3.9	0.31 c	0.11	0.06	0.03	3.60	3.28	0.29
		2nd	4.1	3.9	0.35 c	0.10	0.06	0.03	3.65	3.20	0.44
Vietnam	VN01	1st	4.9	4.5	0.21	0.07	0.09	0.07	4.30	3.57	0.65
		2nd	4.8	4.5	0.21	0.07	0.09	0.07	4.33	3.64	0.64
	VN02	1st	4.9	4.5	NA	NA	NA	NA	3.89	3.38	0.41
		2nd	4.9	4.5	NA	NA	NA	NA	3.89	3.35	0.49
	VN04	1st	4.8	4.4	0.21	0.07	0.09	0.07	4.64	3.84	0.92
		2nd	4.8	4.5	0.21	0.07	0.09	0.07	4.68	3.84	0.88
	VN05	1st	4.5	3.9	NA	NA	NA	NA	3.87	3.35	0.41
		2nd	4.5	3.9	NA	NA	NA	NA	3.89	3.35	0.49

The outliers were determined by Cochran and Grubbs tests, and were indicated by "c" and "g" signs, respectively. 8

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Statistical Summary of Verified Data

Statistics	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol _c kg ⁻¹						
No. 181s									
Number of Laboratories	13	13	7	7	9	8	9	10	12
Total average	4.5	4.0	0.15	0.15	0.46	0.14	8.05	7.47	0.73
Median	4.5	3.9	0.14	0.15	0.43	0.14	8.26	7.54	0.79
Maximum	4.8	4.2	0.23	0.15	0.73	0.20	9.05	9.44	1.21
Minimum	4.2	3.8	0.10	0.14	0.29	0.09	5.77	5.41	0.36
Standard deviation	0.2	0.1	0.05	0.01	0.15	0.04	1.10	1.09	0.28
CV (%) ⁺¹	4.4	2.5	33.3	6.7	32.6	28.6	13.7	14.6	38.4
No. 182s									
Number of Laboratories	13	13	7	10	9	9	11	11	12
Total average	4.4	4.0	0.11	0.08	0.11	0.05	3.77	3.11	0.62
Median	4.3	3.9	0.09	0.07	0.09	0.05	3.80	3.16	0.56
Maximum	4.9	4.5	0.21	0.13	0.24	0.09	4.66	3.84	1.17
Minimum	4.1	3.8	0.04	0.05	0.05	0.02	2.72	2.02	0.28
Standard deviation	0.3	0.3	0.07	0.02	0.07	0.03	0.49	0.49	0.27
CV (%) ⁺¹	6.8	7.5	63.6	25.0	63.6	60.0	13.0	15.8	43.5

Verified average and CV (%) were calculated to evaluate the analyzed value in each laboratory

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Analysis of Variance for Verified Data

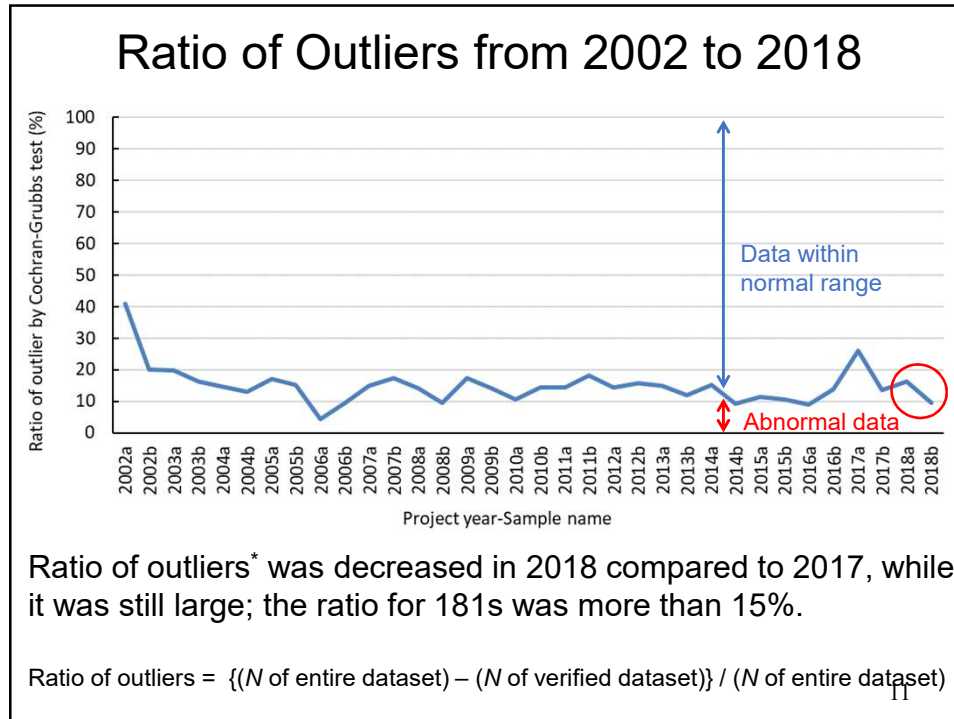
Statistics	No. 181s								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Inter-laboratories precision CV (%)	3.4	3.1	33.91	4.21	32.06	29.29	13.67	14.58	38.19
Within-laboratory precision CV (%)	0.4	0.7	3.12	1.16	1.44	3.72	0.31	0.39	5.39
Repeatability precision CV (%)	0.6	0.5	7.80	2.66	2.44	6.76	0.72	1.55	11.48
Reproducibility limit (R = D(2, 0.95)*s _R)	0.4	0.3	0.14	0.02	0.41	0.12	3.08	3.05	0.78
Within-laboratory-reproducibility limit (R _w = D(2, 0.95)*s _{R,w})	0.1	0.1	0.01	0.00	0.02	0.01	0.07	0.08	0.11
Repeatability limit (r = D(3, 0.95)*s _r)	0.1	0.1	0.04	0.01	0.04	0.03	0.19	0.38	0.28
Statistics	No. 182s								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Inter-laboratories precision CV (%)	5.7	6.5	64.29	29.08	63.19	53.13	13.06	15.78	43.45
Within-laboratory precision CV (%)	0.4	0.5	0.99	5.43	3.04	6.94	1.25	1.56	8.52
Repeatability precision CV (%)	0.6	0.6	20.63	5.92	6.80	20.38	3.02	3.19	15.18
Reproducibility limit (R = D(2, 0.95)*s _R)	0.7	0.7	0.20	0.07	0.20	0.08	1.38	1.37	0.75
Within-laboratory-reproducibility limit (R _w = D(2, 0.95)*s _{R,w})	0.0	0.1	0.00	0.01	0.01	0.01	0.13	0.14	0.15
Repeatability limit (r = D(3, 0.95)*s _r)	0.1	0.1	0.08	0.02	0.03	0.04	0.38	0.33	0.31

In pH, inter-laboratories, within-laboratory and repeatability precision were larger than previous year (<5% in 2017 → < 7% in 2018).

In exchangeable cations and acidity, inter-laboratories precision was still large (4 - 64%), whereas within-laboratory and repeatability precisions were relatively small (< 21%).

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Summary

- In 20th Inter-laboratory Comparison Project on soil, 13 laboratories from 6 countries have participated.
- CVs of inter-laboratories precision for pH were small but became larger compared to 2017.
- CVs of within-laboratory precision were enough small in all properties.
- Ratio of outliers appeared at usual range.

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Recommendation

- **Extremely-large variations in Ex-base cations** might be produced by error of the calculation or the data handling (e.g. copy and paste). Analyst needs to recheck the both reporting procedures before submitting the data.
- **Reducing the outliers** will be considered firstly, especially in exchangeable base and acid cations. The condition of standard solution, extraction solution (potassium chloride and ammonium acetate), dilution rate and calculation will be checked.
- **Easy mistakes should be avoided** by careful reporting process. NC will not make inquiries about obviously strange values, because reporting is a part of QA/QC process.

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