

ALP Program Report



Robert O. Miller, PhD, ALP Technical Director, Windsor, CO

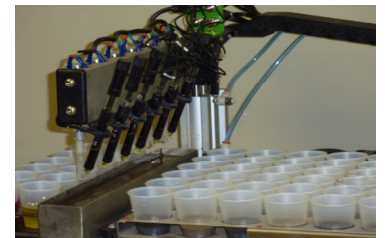
Christopher Czzyryca, Collaborative Testing Services, Inc, Sterling, VA

ALP Overview

Special points of interest:

- An assessment homogeneity of all ALP proficiency materials indicate were highly uniform for Cycle 55.
- Sixty-five laboratories provided soil pH (1:1) H₂O results, medians ranged from 4.85 - 6.87.
- Soil M3-P ICP for Cycle 55 ranged from 8.9 to 44.1 mg kg⁻¹ with intra-lab stdev MAD values ranging 2.2 - 5.2 mg kg⁻¹ across the five soils.
- Soil M3-K values ranged from 41 - 500 mg kg⁻¹ for the five ALP soils of PT Cycle 55.
- Results for botanical CI indicate a range in concentrations with SRB-2409, having a median concentration of 1.48 %.
- Botanical N by combustion was reported by 38 labs, with six labs showing high bias across all PT materials for Cycle 55.

The Agriculture Laboratory Proficiency (ALP) Program spring 2024 Round Cycle 55 was completed November 15, 2024, with results from one-hundred sixteen labs enrolled from the US, Canada, South Africa, Italy, Guatemala and Philippines. Proficiency samples consisted of five soils, four botanical and three water samples. Analytical methods are base on those published by AOAC, regional soil work groups, the Soil Plant Analysis Council and Forestry Canada. ALP has completed nineteen years of service to Ag laboratory industry.



Data was compiled for each method (test code) and proficiency material. Data analysis of each material include: the number results; grand median value; median absolute deviation (MAD), 95% Confidence Interval; method intra-lab standard deviation (*s*); lab mean, and standard deviation. Additional information on methods and statistical protocols can be found at the program web site.

Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 55 were: SRS-2411 Chenango gravely loam, collected Chautauqua Cty, NY; SRS-2412 collected near Three Bridges, ON Canada; SRS-2413 a Maymen stony loam collected from Santa Cruz Cty, CA; SRS-2414 is Moody silty clay loam collected Rock Cty, MN; and SRS-2415 a Grigsby fine sandy loam collected Breathitt Cty KY. Chemical properties of the SRS materials ranges: pH (1:1) H₂O 4.85 - 6.87; SMP Buf 6.00 - 7.20 mg kg⁻¹; Bray P1 (1:10) 8.3 - 25.3 mg kg⁻¹; SO₄-S 4.7 - 31.0 mg kg⁻¹; M3-K 75 - 305 mg kg⁻¹; M3-Ca 778 - 3947 mg kg⁻¹; DTPA-Zn 0.66 - 2.49 mg kg⁻¹; SOM-LOI 2.8 - 7.42%; CEC 8.3 - 24.1 cmol kg⁻¹; clay 13.3 - 32.0% and NO₃-N 1.3 - 203 mg kg⁻¹.

Standard Reference Botanical (SRB) materials for Cycle 55 were: SRB-2409 broccoli leaf composite from CA; SRB-2410 corn plant composite from MN; SRB-2411 cherry leaves composite from Poland and SRB-2412 Kernza forage composite from CO. SRB median analytes concentrations: NO₃-N 50 - 1980 mg kg⁻¹; Dumas N 0.97 - 2.96 %; wet digestion total P 0.116 - 0.535 %; total K 1.70 - 3.48 %; total Ca 0.22 - 2.31 %; total S 0.087 - 1.05 %, total B 6.8 - 49.1 mg kg⁻¹; and Zn 5.1 - 36.6 mg kg⁻¹.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2407 a water sample collected from an Fall River, CO; SRW-2408 collected well Akron, CO, and SRW-2409 from a domestic well in, Forsyth, NY. SRW median concentrations: pH 6.95 - 8.08; EC 0.034 - 1.21 dSm⁻¹; SAR 0.25 - 11.6; Ca 0.15 - 6.84 mmolc L⁻¹; Na 0.082 - 4.93 mmolc L⁻¹; HCO₃ 0.21 - 3.85 mmolc L⁻¹; and NO₃ 0.015 - 0.54 mmolc L⁻¹.

Inside this issue:

2024 Cycle 55 PT homogeneity	2
SRS Results: pH, P, K, SOM	3
SRS Sikora Buffer pH	5
SRB CI results	5
SRB: N, P, K and Zn	6
SRW Results: EC an Na	8
Announcements	9

Homogeneity Evaluations



“..soil pH, Buf pH A&E, Olsen P and SOM-WB analysis Stdev values for Cycle 55 met homogeneity standards.”

SRS material homogeneity was evaluated based on soil test codes pH (1:1) H₂O, buffer pH Adams Evans, EC (1:1), P Olsen, K Olsen, NO₃-N, SOM-WB and DTPA-Zn on analysis of six jars of each PT soil, each in analyzed in triplicate by an independent laboratory. Homogeneity results were within acceptable limits for all soils, with the lowest noted for pH H₂O, Table 1. Proficiency soil antecedent moisture contents were: 6.2 ± 0.2%, 8.1 ± 0.1%, 2.1 ± 0.1%, 3.6 ± 0.1% and 1.5 ± 0.1%, respectively.

Homogeneity was also evaluated on SRB and SRW matrix samples. Botanical results indicate all samples were well homogenized for N, P, Zn and C, with RSD values less than 0.5% of N and C on three of botanical samples, Table 2. Water results for EC, Ca, NO₃ and NH₄ were well homogenized with RSD values for EC less than 1% for all three of the PT samples, Table 3.

Table 1. ALP soils homogeneity evaluation Cycle 55, 2024.

Sample	pH (1:1) H ₂ O		EC (dS m ⁻¹)		P Olsen (mg kg ⁻¹)		SOM-WB (%)	
	Mean ¹	Std	Mean	Std	Mean	Std	Mean	Std
SRS-2411	5.26	0.01	0.28	0.006	11.7	0.50	6.22	0.07
SRS-2412	6.82	0.02	1.68	0.028	10.0	0.60	8.68	0.31
SRS-2413	4.83	0.03	0.25	0.005	1.7	0.44	4.67	0.19
SRS-2414	5.00	0.01	0.29	0.018	9.3	0.50	4.99	0.16
SRS-2415	5.61	0.02	0.70	0.024	3.1	0.36	3.00	0.14

¹ Statistics based on five randomly selected soil replicates, each analyzed in triplicate.

Table 2. ALP botanical homogeneity evaluation Cycle 55, 2024.

Sample	N (%)		P (%)		Zn (mg kg ⁻¹)		C (%)	
	Mean ¹	Std	Mean	Std	Mean	Std	Mean	Std
SRB-2409	3.03	0.016	0.403	0.002	20.5	0.10	46.6	0.27
SRB-2410	1.66	0.014	0.537	0.004	35.5	0.58	41.7	0.09
SRB-2411	2.19	0.012	0.229	0.003	15.8	0.50	43.4	0.33
SRB-2412	1.04	0.006	0.111	0.002	5.07	0.26	44.2	0.07

¹ Statistics based on three randomly selected botanical replicates analyzed.

Table 3. ALP water homogeneity evaluation Cycle 55, 2024.

Sample	EC (dS m ⁻¹)		Ca (meq L ⁻¹)		NO ₃ (meq L ⁻¹)		NH ₄ (meq L ⁻¹)	
	Mean ¹	Std	Mean	Std	Mean	Std	Mean	Std
SRW-2407	0.032	0.0048	0.142	0.021	0.012	0.004	0.24	0.05
SRW-2408	1.18	0.014	6.92	0.082	0.524	0.026	2.85	0.16
SRW-2409	0.502	0.006	0.221	0.024	0.014	0.005	0.32	0.04

¹ Statistics based on three randomly selected soil replicates, each analyzed in triplicate.

SRS - pH (1:1)_{H2O}

Sixty-five laboratories provided ALP results for soil pH (1:1) H₂O (test code 116). Soils ranged from acid to alkaline, median range 4.85 - 6.85. Lab results were ranked low to high based on sample SRS-2413 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally across labs all soils showed good consistency across labs. Labs #1 through #3 showed low bias across all four soils. Labs #12 #48, #64 and #65 were inconsistent for Cycle 55. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.035 to 0.069 pH units, the lowest noted for SRS-2414. Eight labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #5, #43, #48, and #64 exceeded 0.10 pH units for SRS-2412. Soil SRS-2408 was the least variable with respect to intra-lab variance.

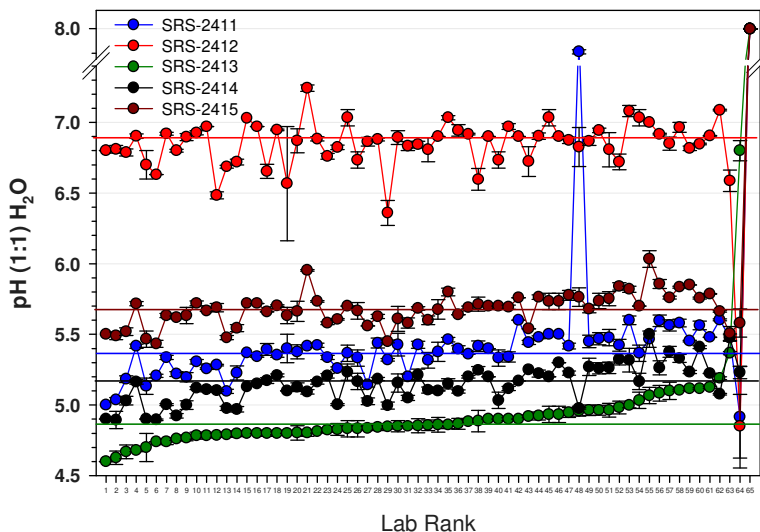


Figure 1. pH (1:1) H₂O distribution plots for SRS materials, ALP 2024 Cycle 55.

SRS - Phosphorus: Bray P1, M3-P, Olsen P

Bray P1 results were reported by thirty labs. Olsen-P was reported by 44 labs and M3-P ICP was reported by 48 labs. Median soil Bray P1 values ranged from 5.4 - 25.3 mg kg⁻¹ PO₄-P; Olsen P 2.4 to 10.9 mg kg⁻¹ P; Bray P2 ranged from 12 to 75 mg kg⁻¹ P; and M1-P from 4.5 to 39 mg kg⁻¹ P, across the five soils. Ranking lab results based on sample SRS-2408, median Bray P1 concentrations are shown in indicated in Figure 2. Soil SRS-2412, moderate in concentration was variable between labs. Soils SRS-2411 and SRS-2414 had near identical concentrations of approximately 25 mg kg⁻¹ P. Lab #2, #29 and #30 had inconsistent results across all five soils. Lab #1 had Bray P1 low bias for all five soils.

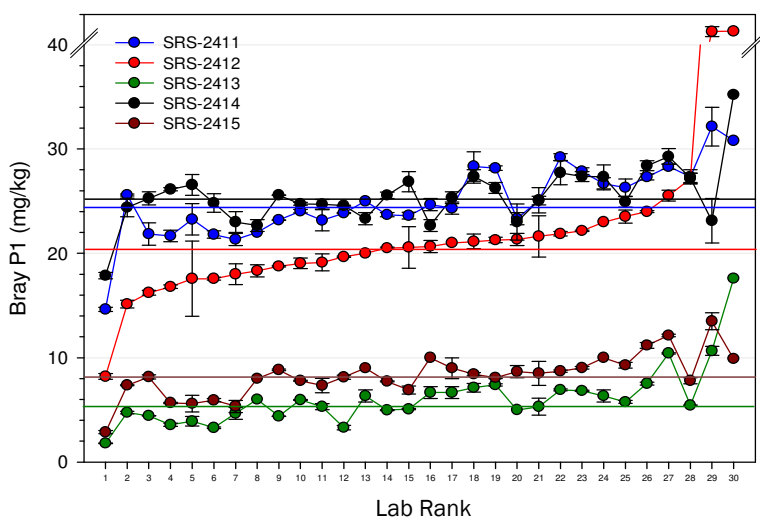


Figure 2. Bray P1 distribution plots for SRS materials, ALP 2024 Cycle 55.

Three labs reported saturated paste PO₄ with median concentrations of 0.05 - 0.14 mmol_c l⁻¹. Eight labs reported M3-P Spec median concentrations ranging 5.7 - 23.3 mg kg⁻¹ P. Two laboratories reported Bray P 1:7 with medians ranging from 4.1 - 20 mg kg⁻¹ PO₄-P. Three results for Modified Morgan P, with medians ranging from 0.7 - 6.4 mg kg⁻¹ PO₄-P. Modified Kelowna was reported by two laboratories ranging from 2.5 - 17.1 mg kg⁻¹ P and total P (US-EPA 513) ranged 196 - 1154 mg kg⁻¹ P with the highest concentration noted for SRS-2411.

SRS - Potassium

Forty-five laboratories provided ALP results for soil M-3 K (test code 159) results. Results were ranked low to high based on sample SRS-2413 (see Figure 3). Soil SRS-2412 and SRS-2415 were the most inconsistent across labs. The source of the variability is for SRS-2411 is likely associated with higher coarse sand. Lab #46 had high bias on all soils. Across all soils labs #1, #32 and #43 were inconsistent across soils. Source of inconsistency is likely related to extraction, analysis instrument and/or method compliance.

M3-K intra-lab *s* values were lowest for soil SRS-2412, with a median intra-lab value of 0.90 mg kg⁻¹ K and highest for SRS-2413 with a value of 4.46 mg kg⁻¹. M3-K within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 200 mg kg⁻¹ K. Precision was poor (based on intra-lab *s*) for three labs which exceeded 10 mg kg⁻¹ K on SRS-2411. Across the five soils for Cycle 55 twelve labs were flagged for poor intra-lab precision. Poor precision is attributed to extraction and/or analysis instrument operation.

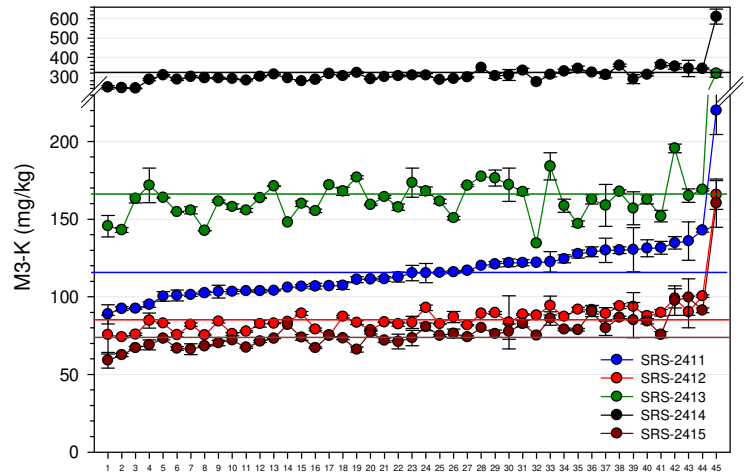


Figure 3. Extractable M3-K distribution plots for SRS materials, ALP 2024 Cycle 55.

SRS - SOM-LOI

Forty-two laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 2.80 to 7.42%. Results were ranked based on sample SRS-2415 (see Figure 4) and had high consistency. Lab #1 and #2 had consistent low bias across all soils. Labs #7, #12, and #35 were inconsistent across the five soils. Source of bias is likely related to muffle furnace operation and/or method compliance.

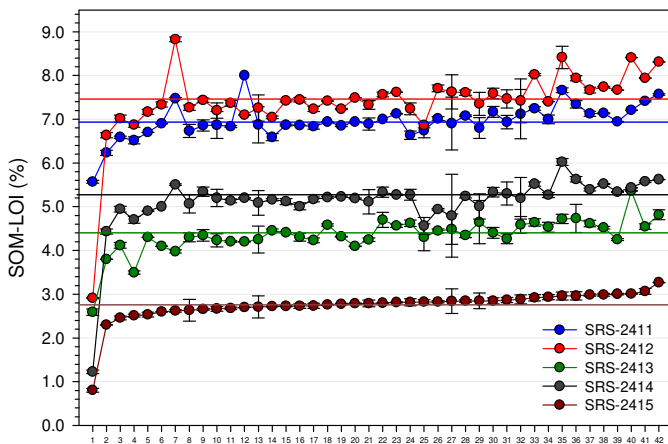


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2024 Cycle 55.

SOM-LOI precision across the five soils indicates high median intra-lab precision *s* values ranging from 0.090 to 0.20% SOM-LOI, highest for SRS-2414. Across labs, *s* values for SRS-2411 ranged from 0.006 - 0.57%. Across soils low precision was noted for several laboratories. Specifically *s* for labs #10, #13, #29, #32, and #27 exceeded 0.10% SOM-LOI for SRS-2408. Lab #27 had poor precision on all Cycle 55 samples. Poor precision may be associated with the muffle furnace and heating time.

ALP Soil Sikora Buffer pH

Thirty-one laboratories provided ALP results for soil Sikora buffer pH (test code 123) results. Results were ranked low to high based on sample SRS-2413 (see Figure 5). Soil SRS-2411 was the most inconsistent across laboratories. Laboratories #29 through #31 showed high bias on all soils. Across all soils labs #3, #6, #21 and #23 were inconsistent across three of five soils and the source likely related to extraction, analysis instrument and/or method compliance.

Soil Sikora Buffer pH intra-lab *s* values were lowest for soil SRS-2412, with a median intra-lab value of 0.02 and highest for SRS-2413 with a value of 0.05 mg kg⁻¹. Generally Sikora Buffer pH within-lab precision across the ALP soil materials indicates very good precision. Precision was poor (based on intra-lab *s*) for three labs for SRS-2411 with a median Sikora Buffer pH of 6.34 and five labs having lab *s* values exceeding 0.05 pH units. Lab #23 Had poor precision on four of five cycle 55 soils. Across the five soils for cycle 55 seven labs were flagged for poor precision.

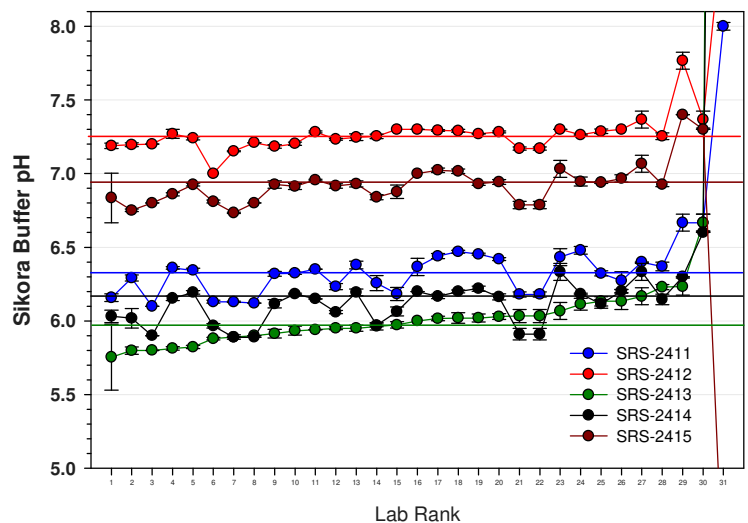


Figure 5. Soil NO₃-N distribution plots for SRS materials, ALP 2024 Cycle 55.

SRB - Chloride

Eighteen laboratories provided ALP results for botanical extractable Cl (test codes 208). Median values are designated by horizontal lines for each of the four botanical materials labs based on sample SRB-2408 (see Figure 6). Lab #1 had low bias results for three materials and Lab #18 had high bias across all 4 botanical materials. The data plot shows labs #2, #12, #15 and #16 were inconsistent on two of four samples.

Botanical Cl (test code 208) results for Cycle 55 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 0.021 to 0.047 % across the four samples. Cl intra-lab *s* values for SRB-2409 ranged from 0.014 - 0.127 %; SRB-2410 ranged from 0.012 - 0.053 %, SRB-2411 ranged from 0.007 - 0.104 % and SRB-2412 ranged from 0.007 - 0.026 %. Labs #3 and 15 had consistently high standard deviations for samples SRB-2411 lowest in Cl content Labs #13 and #14 had poor precision on SRB-2410. Seven of 18 labs were flagged for poor precision across the four samples.

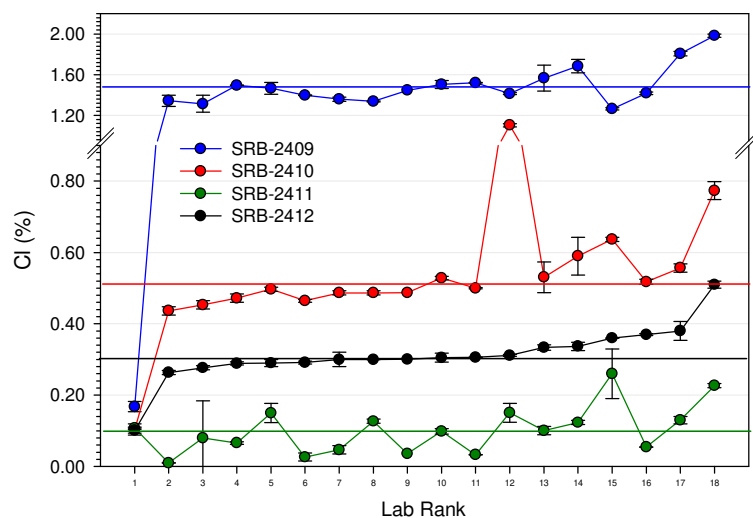


Figure 6. Nitrate distribution plots for SRB materials, ALP 2024, Cycle 55.

2024 Volume 3

SRB - Combustion Nitrogen and TKN

Thirty-eight laboratories provided ALP results for botanical combustion (Dumas) nitrogen (test code 210) and eight labs for TKN (Test code 209) for Cycle 55. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2412 (see Figure 7). Lab #1 had consistently low bias and labs #38 had consistent high bias for Dumas N. TKN results were very inconsistent across all four samples.

Combustion N results indicate very high intra-lab precision across all labs for all samples. Intra-lab median N lab *s* values were 0.060% N for SRB-2409; 0.058 % N for SRB-2410; 0.062% for SRB-2411; and 0.023% for SRB-2412. Lab #1, #23, and #38 had consistently high standard deviations on three of four PT samples. TKN median intra-lab *s* values for SRB-2409 were 0.051%, SRB-2410 0.020%, SRB-2411 0.017% and SRB-2412 0.026% TKN nitrogen, respectively.

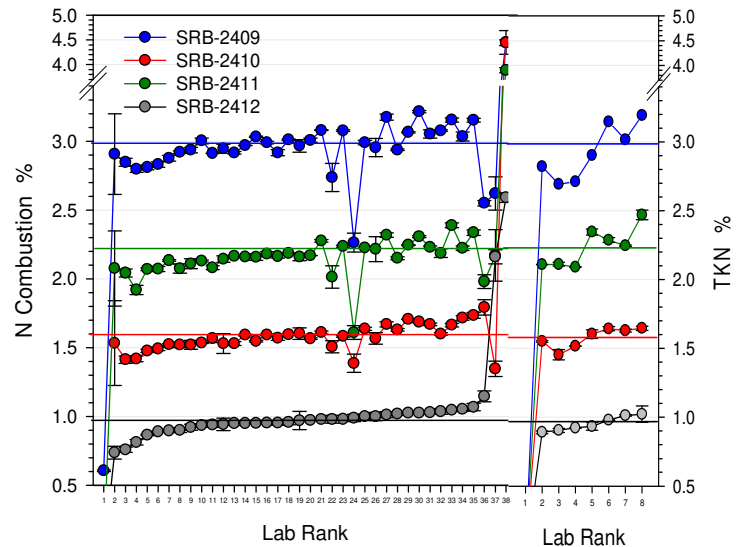


Figure 7. N distribution lab plots for SRB materials, ALP 2024 Cycle 55.

SRB - Phosphorus

Forty-four laboratories provided ALP results for Cycle 55 phosphorus (P) (test code 212). Botanical results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-2411 (see Figure 8). Labs #1, #41, #43 and #44 showed inconsistency. Source of inconsistency is likely related to sample digestion, analysis instrument and/or test code method compliance.

Botanical P results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged 0.004 to 0.017 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-2409; ranged from 0.001 - 0.0151% P; SRB-2410 ranged from 0.001 - 0.045 % P and SRB-2411 0.001 - 0.021 % P; and SRB-2412 0.001 - 0.014 % P. Ten labs were flagged for poor precision for botanical P for Cycle 55.

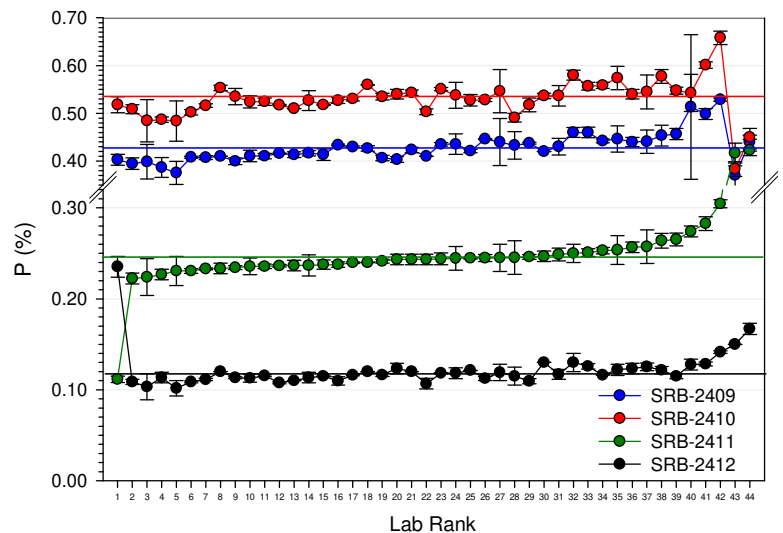


Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2024 Cycle 55.

SRB - Potassium

Forty-three laboratories provided ALP results for potassium (K) (test code 213). Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-2412 (see Figure 9). Labs #3, #38, and #43 were inconsistent. Source of bias is related sample digestion, analysis instrument and/or method compliance.

Botanical K results indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 0.049 to 0.110 % K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2409, ranged from 0.003 - 0.155 % K; SRB-2401, 0.006 - 0.415 % K; SRB-2411, 0.002 - 0.234 % K; and SRS-2412, 0.002 - 0.161 % K. Lab #270 had high standard deviations exceeding 0.20 % K on two of four samples. Across samples nine labs were flagged for poor K precision for Cycle 55.

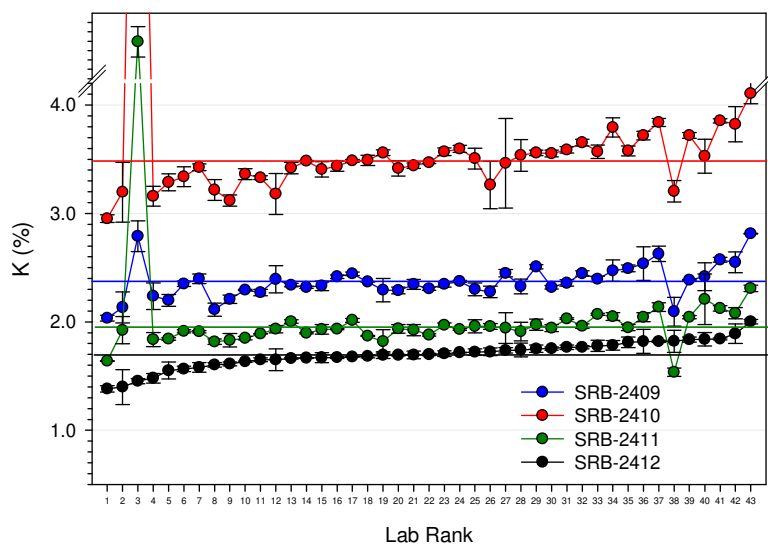


Figure 9. Potassium lab plot for SRB materials, ALP 2024 Cycle 55.

SRB - Zinc

Forty laboratories provided ALP results for zinc (Zn) (test code 215). Result median values are designated by horizontal lines for each botanical material and individual labs results are ranked low to high based on sample SRB-2412 (see Figure 10). Across samples labs #2 had low bias on all samples. Labs #5, #30 and #39 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Zn results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.91 to 2.56 mg kg⁻¹ Zn for across the four botanical proficiency samples. Individual lab intra-lab *s* values for SRB-2409; ranged from 0.02 - 31 mg kg⁻¹ % Zn; SRB-2401 ranged from 0.02 - 5.5 mg kg⁻¹ Zn; SRB-2411 0.02 - 4.0 mg kg⁻¹ % Zn; and SRB-2412 0.02 - 2.7 % Zn. Lab #4 had consistently high standard deviations for three samples.

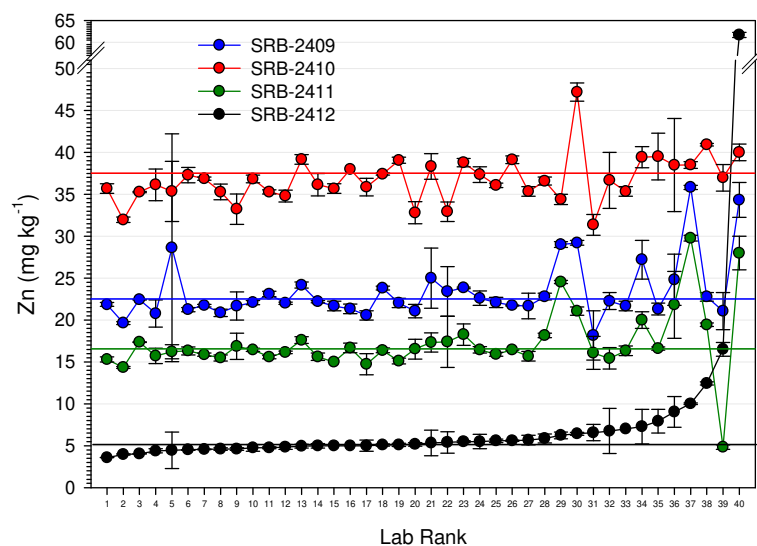
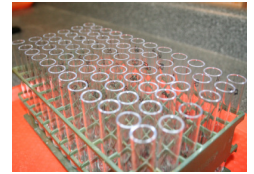


Figure 10. Zinc (code 215) lab plots for SRB materials, ALP 2024 Cycle 55.

SRW - Water EC

Twenty-three laboratories provided ALP results for water pH (test code 302) and EC. Lab results were ranked low to high based on sample SRW-2407 (see Figure 11). Sample SRW-2409 had the highest EC in for Cycle 55. Labs #14 and #23 indicated inconsistency across samples. Source of bias is likely associated with EC probe performance and/or calibration.



EC precision across the three water materials indicates very high precision, with intra-lab median s values of 0.003, 0.030 and 0.012 dSm^{-1} , for the three water samples, respectively. Precision for sample SRW-2409 was the most consistent across the twenty-three participating laboratories. Intra-lab s values for lab #20 exceeded 0.100 dSm^{-1} on SRW-2408. Highest precision was noted for lab #7 with intra-lab s values of < than 0.003 dSm^{-1} for all three samples. Four labs were flagged for precision for EC.

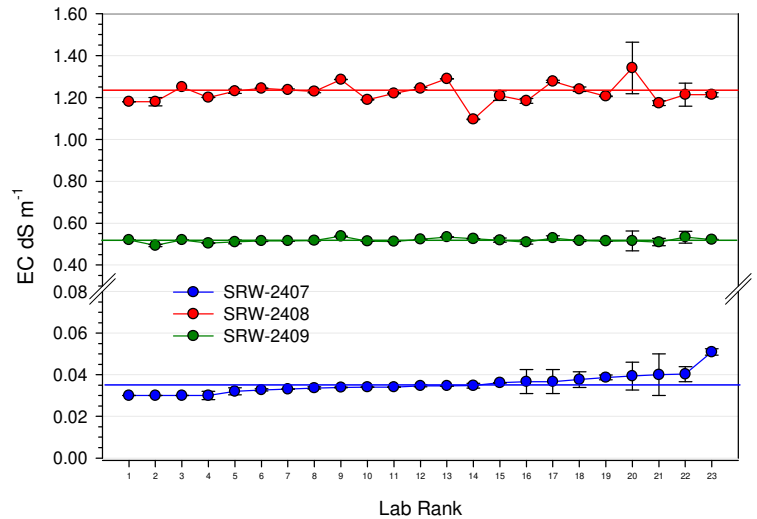


Figure 11. Water EC distribution plots for SRW materials, ALP 2024 Cycle 55.

SRW - Na

Twenty-three laboratories provided ALP results for water Na (test code 304). Lab results were ranked low to high based on sample SRW-2407 (see Figure 12). Median values are designated by horizontal lines. Lab #23 showed consistent high bias on all samples, and is likely a result of a calibration error.

Sodium precision across the three water solution matrices indicates excellent precision, with intra-lab s values of 0.019, 0.052, and 0.122 mmolc L^{-1} for SRW-2407, SRW-2408, and for SRW-2409, respectively. Water Na precision was excellent for all individual labs with only labs #3, #14, and #23 exceeding 0.07 mmolc L^{-1} Na on sample SRW-2407. Six labs was flagged for poor precision on Na for ALP Cycle 55.

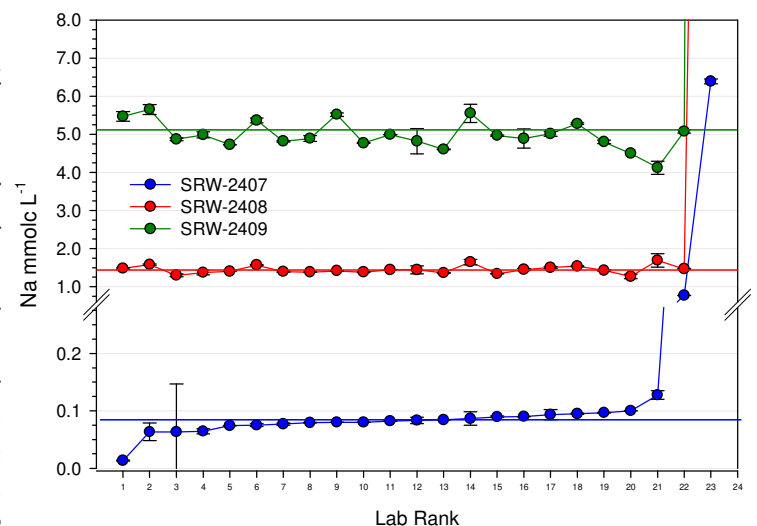


Figure 12. Water Na distribution plots for SRW materials, ALP 2024 Cycle 55.

Announcements

- ▶ The ALP program soil carbon proficiency program will initiate in January 2025. Test parameter include, total Soil Carbon (SC), soil organic carbon (SOC), soil inorganic carbon (SIC), pH and moisture content. The program will consist three cycles per year each with four soils. The soil carbon proficiency program will be required for labs seeking ALTA-SAC certification.
- ▶ ALTA has established a additional proficiency program, Enhanced Quality Assurance (EQA) program. EQA is based on double blind testing of lab participants using ALP standard reference soils. For more information visit ALTA.Ag .
- ▶ The 18th International Symposium on Soil and Plant Analyses (ISPPA) will be held in June 9-13, 2025 in Durham, North Carolina. Topics include soil, plant and water analysis, soil health, proximal sensors and plant nutrition. More information and enrollment can found at: <https://www.isspasymposium.org/>
- ▶ ALP has secured new proficiency soil materials from New York, Georgia, Nebraska, Iowa, Illinois and Alaska for the 2025 proficiency program.
- ▶ ALP has standard reference soils and botanical tissue materials available for purchase. For more information on these contact the ALP Technical Director, Robert.Miller@cts-interlab.com.

Summary

ALP is has provided nineteen years of service with the completion of Cycle 55. Since 2005 ALP has completed the analysis of 275 soils, 192 plant samples and 177 water samples providing comprehensive proficiency data on inter and intra laboratory performance across a range of analytical methods.

We thank all laboratories who participated in Cycle 55. As the coordinators of the program we appreciate your consideration and participation in the proficiency program. We continually seek feedback from laboratory participants to improve the service and function of the program. Please forward all comments to info@cts-interlab.com.

Cycle 56 Ship
March 15, 2024

**“Everything is theoretically impossible,
until it is done . ”**

– Robert A. Heinlein, 1978

