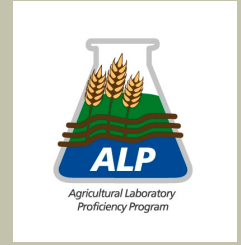


ALP Program Report



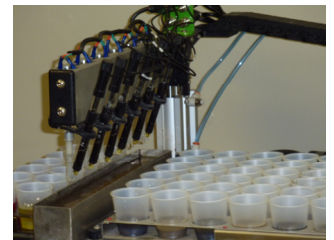
Robert O. Miller, PhD, ALP Technical Director, Windsor, CO
Christopher Czzyryca, Collaborative Testing Services, Inc, Sterling, VA

ALP Overview

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 51.
- Sixty Laboratories provided soil pH (1:1) H₂O results and medians ranged from 5.02 - 7.72.
- Soil M3-P ICP for Cycle 51 ranged from 7.4 to 70.8 mg kg⁻¹ with MAD values ranging 0.7 - 6.8 mg kg⁻¹ across the five soils.
- Soil M3-K values ranged from 95 - 231 mg kg⁻¹ for the five ALP soils of PT Cycle 51.
- Botanical N by combustion was reported by 38 labs, with four labs showing inconsistency across the three PT materials for Cycle 51.
- Botanical Total B, ranged from 1.5 - 27 mg kg⁻¹ with four of forty-three labs noted for inconsistency across the four samples.

The Agriculture Laboratory Proficiency (ALP) Program spring 2023 Round Cycle 51 was completed August 24, 2023, with results from one-hundred eight 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 seventeen 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 51 were: SRS-2306 Mainly Orthic sandy loam, collected Saskatchewan, Canada; SRS-2307 Mayodan sandy loam collected Chesterfield Cty VA; SRS-2308 a Gilford fine sandy loam collected from Cass Cty IN; SRS-2309 is Hayden-Stordem loam collected in Boone Cty, IA; and SRS-2310 a Ipano-Ticell loam collected in Cascade Cty, MT. Chemical properties of the SRS materials ranges: pH (1:1) H₂O 5.02 - 7.72; SMP Buf 6.25 - 7.50 mg kg⁻¹; Bray P1 (1:10) 5.3 - 51.9 mg kg⁻¹; M3-K 95 - 231 mg kg⁻¹; M3-Ca 700 - 5280 mg kg⁻¹; DTPA-Zn 0.23 - 4.95 mg kg⁻¹; SOM-LOI 1.24 - 4.67%; CEC 7.7 - 13.3 cmol kg⁻¹; clay 10.3 - 25.9% and NO₃-N 8.8 - 115 mg kg⁻¹.

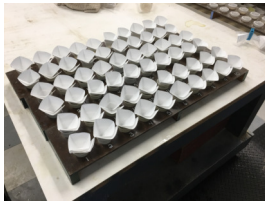
Standard Reference Botanical (SRB) materials for Cycle 51 were: SRB-2305 artichoke leaf composite from CA; SRB-2306 kale leaf composite from CA; SRB-2307 corn stalk composite from CT and SRB-2308 potato petiole composite from WA. SRB median analytes concentrations: NO₃-N 300 - 19,600 mg kg⁻¹; Dumas N 0.29 - 4.06 %; wet digestion total P 0.05 - 0.43 %; total K 0.30 - 10.8 %; total Ca 0.12 - 1.27 %; total S 0.06 - 0.27 %, total B 1.5 - 27 mg kg⁻¹; and Zn 4.0 - 44.5 mg kg⁻¹.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2304 a water sample collected from a domestic well Severance, CO; SRW-2305 was collected Wilmont, SD; and SRW-2306 from a domestic water supply Foley, AL. SRW median concentrations: pH 7.60 - 7.98; EC 0.11 - 0.87 dSm⁻¹; SAR 0.27 - 0.76; Ca 0.50 - 6.65 mmolc L⁻¹; Na 0.44 - 1.17 mmolc L⁻¹; HCO₃ 0.62 - 5.62 mmolc L⁻¹; and NO₃ 0.01 - 0.06 mmolc L⁻¹.

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Soil Homogeneity Evaluation



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 and SOM-WB 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. Homogeneity was also evaluated on SRB and SRW matrix samples.

Table 1. ALP soils homogeneity evaluation 2023, Cycle 51.

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-2306	7.66	0.02	0.82	0.01	11.6	0.8	1.21	0.07
SRS-2307	4.94	0.02	0.22	0.01	28.9	1.8	5.27	0.18
SRS-2308	5.11	0.02	0.72	0.02	30.9	2.5	2.38	0.15
SRS-2309	6.38	0.03	0.95	0.01	14.7	1.8	2.02	0.10
SRS-2310	7.59	0.01	1.85	0.03	2.7	0.3	1.49	0.14

¹ Statistics based on six randomly selected soil replicates, each analyzed in triplicate ALP Cycle 51.

*“...soil pH, Buf pH
A&E, Olsen P and
SOM-WB analysis Stdev
values for Cycle 51 met
homogeneity standards.”*

2023 Cycle 51 Observations

Results for soil pH (1:1) H₂O (test code 115) analysis inter-lab MAD values for Cycle 51 averaged 0.07 pH units across the five soils. Median within lab pH standard deviation was 0.04 pH units. Soil Organic C values for the Cycle 51 ranged from 1.04 to 2.52% SOC. SRS-2307 had an abnormally low extractable M3-Ca (Test code 140) of 700 mg kg⁻¹, likely associated with loamy sand soil texture and low CEC. M3-Ca MAD values ranged 51 - 297 mg kg⁻¹ and M3-Mg MAD values ranged 6.9 to 27 mg kg⁻¹ for the five soils. For soils SRS-2307 and SRS-2308 M3-P colorimetric intra-lab standard deviations were consistently 40% - 70% lower than values for the M3-P ICP method. Extractable Cl concentrations ranged from 4.0 mg kg⁻¹ for SRS-2306 to 278 mg kg⁻¹ for SRS-2310, collected, a wheat field in Cascade Morrow county, Montana.

Across the four botanical samples Dumas combustion N MAD values averaged 0.038% nitrogen with intra-lab median s of 0.046%, 0.039%, 0.030% and 0.287%, respectively. Botanical sample SRB-2307 had a very low median B with a concentration of 1.5 mg kg⁻¹ and with a MAD of 0.56 mg kg⁻¹. The potato petiole composite sample SRB-2308 had higher median concentrations of NO₃-N, N, P, K, Ca, Mg, S, Cl, Zn, Mn, Cu, Mo, Ba, Cd, Ni, and Sr and relative to the other three botanical samples. Consistent with past ALP cycles, Cycle 51 intra-lab relative variability results were lowest for total P than other macro elements across all three of four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC median values were 0.118, 0.578 and 0.875 dSm⁻¹, respectively. Median Mg values ranged from 0.10 - 3.04 mmolc L⁻¹ across the three ALP water samples with MAD values ranging 0.017 to 0.120 mmolc L⁻¹. Sample SRW-2306 had B 0.16 mg kg⁻¹ with a MAD of 0.014 mg kg⁻¹.

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

Sixty-one laboratories provided ALP results for soil pH (1:1) H₂O (test code 115). Soils ranged from acid to alkaline, median range 5.03 - 7.72. Lab results were ranked low to high based on sample SRS-2307 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally across labs all soils showed good consistency across labs. Labs #9, #29, #45, #60 and #61 showed inconsistency across SRS-2306, SRS-2309 and SRS-2310 soils. 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 0.037 to 0.049 pH units, the lowest noted for SRS-2308. Twelve labs had poor precisions, with standard deviations exceeding consensus median intra-lab s. Specifically s for labs #15, #28, #29, #47, and #61 exceeded 0.06 pH units for SRS-2306. Soil SRS-2307 was the least variable with respect to intra-lab variance.

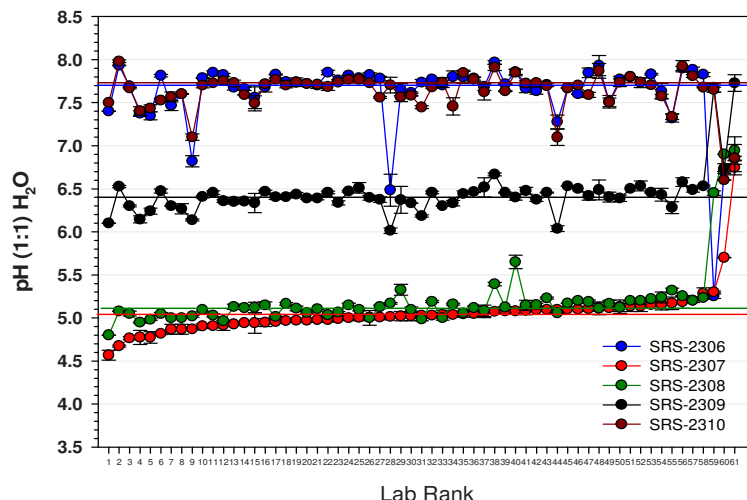


Figure 1. pH (1:1) H₂O distribution plots for SRS materials, ALP 2023 Cycle

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

Bray P1 results were reported by thirty-one-nine labs. M3-P ICP was reported by 45 labs. Median soil Bray P1 values ranged from 5.3 - 52.0 mg kg⁻¹ PO₄-P; Olsen P 4.5 to 31.5 mg kg⁻¹ P; Bray P2 ranged from 48 to 97.2 mg kg⁻¹ P; and M1-P from 8.3 to 43.3 mg kg⁻¹ P, across the five soils. Ranking lab results based on sample SRS-2307, median M3-P ICP concentrations are shown in indicated in Figure 2. Soil SRS-2306, moderate in concentration was variable between labs. Soils SRS-2307 and SRS-2308 had near identical concentrations of 75 mg kg⁻¹ P. Soils SRS-2306 and SRS-2309 had similar Bray P1 concentrations. Lab #1, #44 and #45 had in consistent results across all five soils. Labs #11, #21 and #44 had high intra-lab variances for SRS-2309.

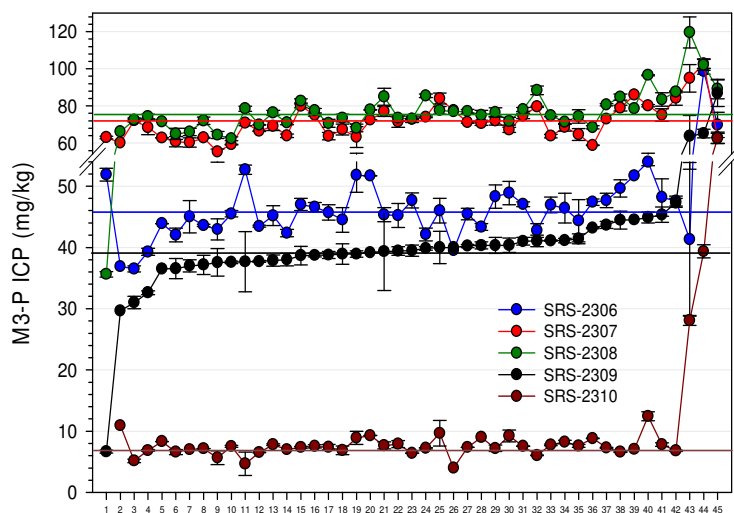


Figure 2. Bray P1 distribution plots for SRS materials, ALP 2023 Cycle 51.

Six labs reported M3-P Spec median concentrations ranging 8.3 - 57.7 mg kg⁻¹ P. Nine laboratories reported Bray P2, five labs for M1-P and two results for Modified Morgan P, with medians ranging from 3.7 - 29.0 mg kg⁻¹ PO₄-P. Modified Kelowna was reported by two laboratories ranging from 3.0 - 37.2 mg kg⁻¹ P and total P (US-EPA 513) ranged 312 - 512 mg kg⁻¹ P with the highest concentration noted for SRS-2302.

SRS - Potassium

Forty-three laboratories provided ALP results for soil M-3 K (test code 159) results. Results were ranked low to high based on sample SRS-2307 (see Figure 3). Soil SRS-2308 and SRS-2310 were the most inconsistent across labs. The source of the variability is unknown. Laboratory #43 showed low bias on four of five soils. Across all soils labs #1, #22, #34 and #41 were inconsistent across the five soils for M3-K. 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-2307, with a median intra-lab value of $3.2 \text{ mg kg}^{-1} \text{ K}$ and highest for SRS-2310 with a value of 11.7 mg kg^{-1} . M3-K within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than $200 \text{ mg kg}^{-1} \text{ K}$. Precision was poor (based on intra-lab s) for four labs which exceeded $10 \text{ mg kg}^{-1} \text{ K}$ on SRS-2306. Across the five soils for cycle 51 six labs were flagged for poor precision. Poor precision is attributed to extraction and/or analysis instrument operation.

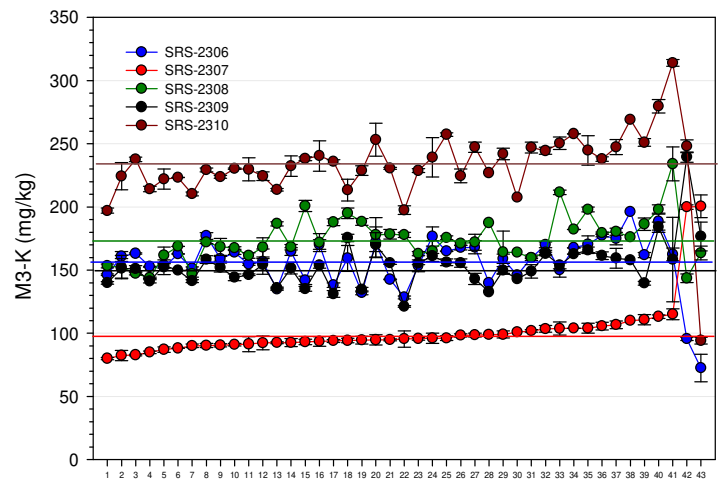


Figure 3. Extractable K distribution plots for SRS materials, ALP 2023 Cycle 51.

SRS - SOM-LOI

Forty-three laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 1.07 to 4.43%. Results were ranked based on sample SRS-2310 (see Figure 4). Sample SRS-2308 had high consistency. Lab #1 had consistent low bias. Labs #12, #8, #42 and #43 were inconsistent across the five soils. Source of bias is likely related to muffle furnace operation and/or method compliance.

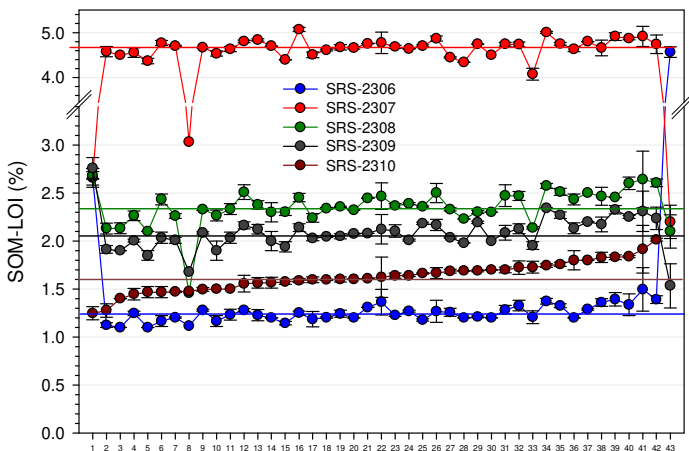


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2023 Cycle 51.

SOM-LOI precision across the five soils indicates high median intra-lab precision s values ranging from 0.023 to 0.042% SOM-LOI, highest for SRS-2308. Across labs, s values for SRS-2306 ranged from 0.006 - 0.226%. Across soils low precision was noted for several laboratories. Specifically s for labs #22, #41, and #42, exceeded 0.10% SOM-LOI for SRS-2310. Lab #41 had poor precision on SRS-2308. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

ALP soil comparison

ALP soil proficiency sample SRS-2306 was previously submitted four years ago in cycle 39 as SRS-1906. A limited comparison of results are shown in Table 2. Results indicate 94% of the 96 analysis methods evaluated, were within the inter-lab measurement error as measured by the MAD. For specific analyses, pH, SOM-LOI and clay, median values were reproducible within two significant digits. Only results for extractable Mn and Fe (all methods) showed higher values after four years of storage.

These results verify ALP botanical proficiency statistical analysis results across laboratories, as measured by the median and inter-lab MAD, are stable for periods of seven years with no changes in the concentration of total and/or extractable analytical results. In addition measurements of intra-lab precision show improvement over time.

Table 2. ALP soil result comparison, SRS-1906 vs SRS-2304.

Analysis	Unit	SRB-1906 ¹		SRB-2306	
		Median	MAD	Median	MAD
pH 1:1 H ₂ O		7.70	0.07	7.72	0.09
NO ₃ -N (Cd-Rd)	mg kg ⁻¹	93.4	7.4	92.9	4.4
NH ₄ -N	mg kg ⁻¹	2.2	0.6	2.7	0.5
P-Olsen	mg kg ⁻¹	12.5	1.5	13.3	1.4
K-AmmAc	mg kg ⁻¹	130	8.1	143	12
Ca-AmmAc	mg kg ⁻¹	2990	405	3060	407
Zn-DTPA	mg kg ⁻¹	0.22	0.05	0.23	0.03
Mn-DTPA	mg kg ⁻¹	4.1	1.5	9.6	1.2
Cl	mg kg ⁻¹	3.9	0.9	4.1	1.0
SOM-LOI	%	1.28	0.06	1.24	0.05
Clay	%	10.8	2.2	10.4	2.0

¹ ALP SRS-1906, soil sample collected Arcola, Saskatchewan, Canada.

SRB - NO₃-N

Twenty-eight laboratories provided ALP results for NO₃-N by cadmium reduction and ISE (test codes 202, 203 and 204). Median values are designated by horizontal lines for each of the four botanical materials labs based on sample SRB-2307 (see Figure 5). Labs #26, #27 and #28 had high bias results for all four materials. The data plot shows labs #1, #4, #14 and #23 were inconsistent on one of four samples.

Botanical NO₃-N (test code 202) results for Cycle 51 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 28 to 1224 mg kg⁻¹ across the four samples. Individual lab NO₃-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-2305 ranged from 2 – 80 mg kg⁻¹; SRB-2306 ranged from 4 - 104 mg kg⁻¹, SRB-2307 ranged from 2 – 183 mg kg⁻¹ and SRB-2308 ranged from 58 - 4130 mg kg⁻¹. Lab #1 had consistently high standard deviations for two of four samples. Four labs were flagged for poor precision.

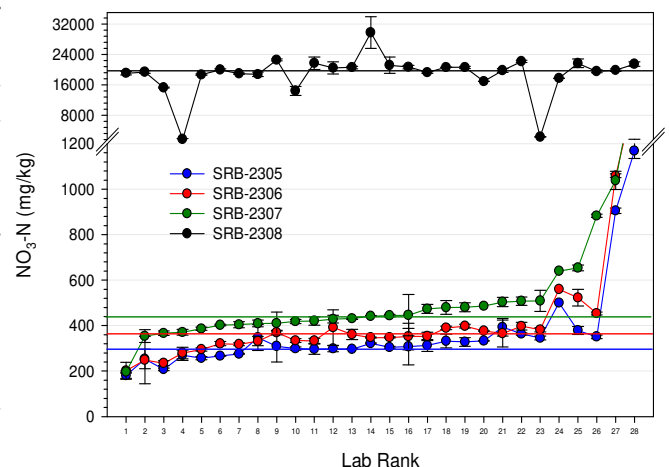


Figure 5. Nitrate distribution plots for SRB materials, ALP 2023, Cycle 51.

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SRB - Dumas Nitrogen and TKN

Thirty-eight laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and eight labs for TKN (Test code 209) for Cycle 51. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2307 (see Figure 7). Labs #2, #16, #42, #32 and #38 were inconsistent for across the four samples. Its note worthy that TKN was inconsistent and lower than Dumas for SRB-2304.

Dumas N results indicate very high intra-lab precision across all labs for all samples. Lab intra-lab median N lab s values for SRB-2305, was 0.015% N, SRB-2306 was 0.014% N, SRB-2307 was 0.011% N, and SRB-2308 was 0.023% N. Lab #2 #16, and #27 had consistently high standard deviations on three of four PT samples. TKN median intra-lab s values for SRB-2305 was 0.008%, SRB-2306 0.012%, SRB-2307 0.004% and SRB-2308 0.041% TKN nitrogen, respectively.

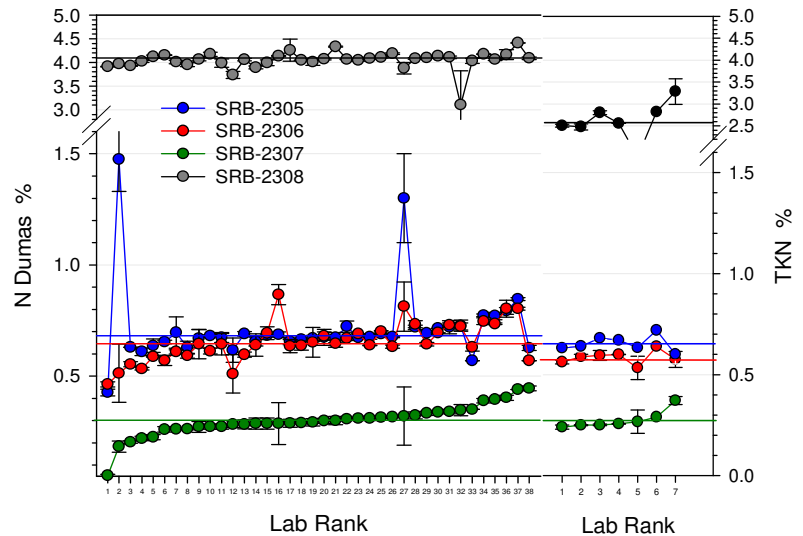


Figure 7. N distribution lab plots for SRB materials, ALP 2023 Cycle 51.

SRB - Phosphorus

Forty-seven laboratories provided ALP results for Cycle 51 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-2307 (see Figure 8). Consistent high bias was noted for labs #46 - #47. Labs #1, #2, #32 and #46 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 0.001 to 0.026 % P for test code 212 across the four botanical samples. Individual lab intra-lab s values for SRB-2305; ranged from 0.001 - 0.021% P; SRB-2306 ranged from 0.001 - 0.019 % P and SRB-2307 0.001 - 0.018 % P; and SRB-2308 0.001 - 0.040 % P. Six labs were flagged for poor precision for botanical P for Cycle 51.

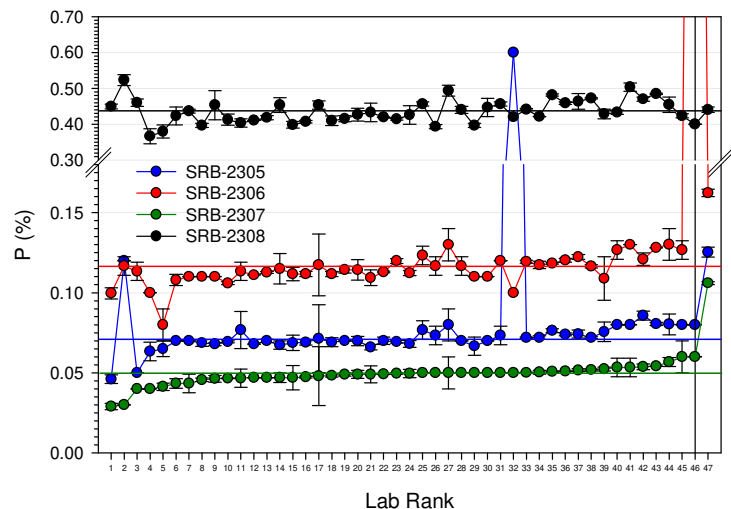


Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2023 Cycle 51.

SRB - Potassium

Forty-eight 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-2307 (see Figure 9). Labs #2, #7, #12, and #40 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 0.015 to 0.045 % K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2305, ranged from 0.01 - 0.157 % K; SRB-2306, 0.01 - 0.288 % K; SRB-2307, 0.01 - 0.164 % K; and SRS-2308, 0.01 - 1.81 % K. Labs #23 had high standard deviations exceeding 0.20 % K on two of four samples. Across samples four labs were flagged for poor K precision for Cycle 51.

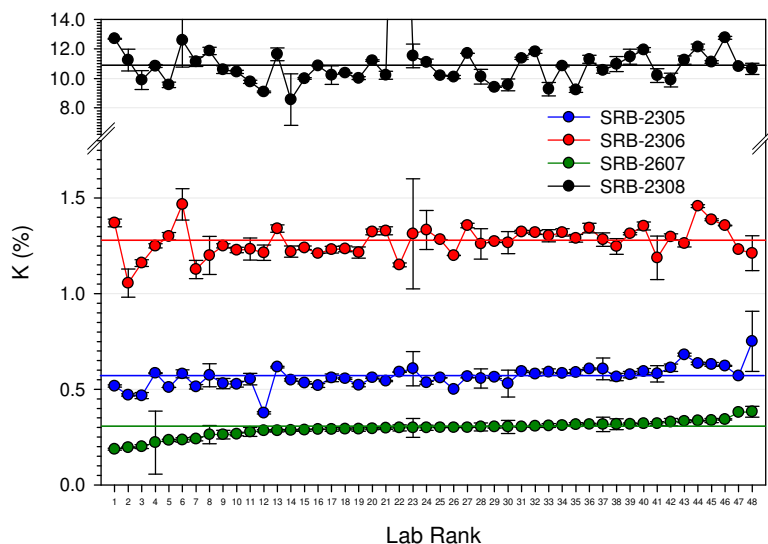


Figure 9. Potassium lab plot for SRB materials, ALP 2023 Cycle 51.

SRB - Boron

Forty-three laboratories provided ALP results for Boron (B) (test code 219). 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-2307 (see Figure 10). Across samples labs #42 and #43 exhibited high bias. Labs #1, and #31 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical B results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 2.1 to 7.4 mg kg⁻¹B for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2305; ranged from 0.1 - 2.3 mg kg⁻¹ B; SRB-2306 ranged from 0.1 - 2.5 mg kg⁻¹ B; SRB-2307 0.2 - 0.70 mg kg⁻¹B; and SRB-2308 0.5 - 5.6 mg kg⁻¹ B. Lab #19 had consistently high standard deviations for three samples.

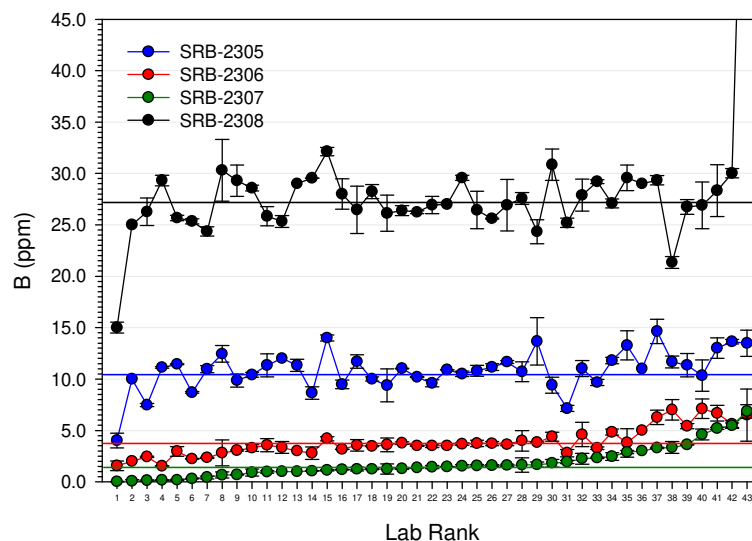


Figure 10. Boron (code 219) lab plots for SRB materials, ALP 2023 Cycle 51.

SRW - Water EC

Twenty laboratories provided ALP results for water pH (test code 302) and 19 for EC. Lab results were ranked low to high based on sample SRW-2304 (see Figure 11). Sample SRW-2303 had the highest EC in Cycle 51. Lab #1 and #10 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 0.013, 0.009 and 0.013 dSm^{-1} , for the three water samples respectively. Precision for sample SRW-2304 was the most consistent across the nineteen participating laboratories. Intra-lab s values for lab #9 exceeded 0.057 dSm^{-1} on SRW-2304. Highest precision was noted for lab #10 with intra-lab s values of < than 0.001 dSm^{-1} for all three samples. Three labs were flagged for precision for EC.

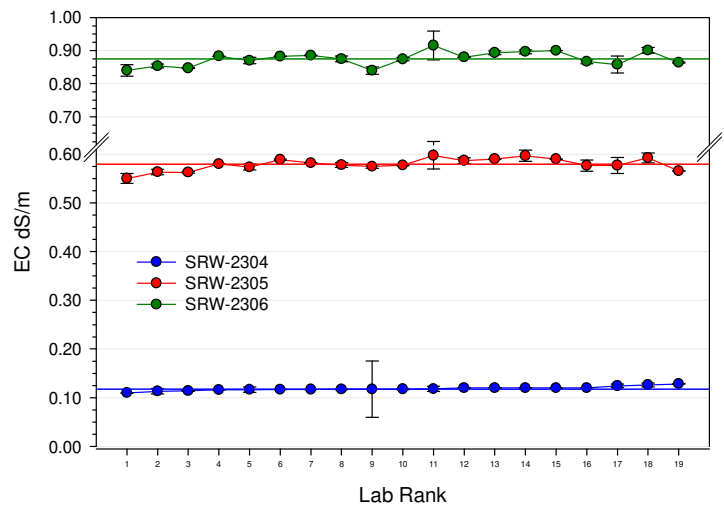


Figure 11 . Water EC distribution plots for SRW materials, ALP 2023 Cycle 51.

SRW - Ca

Eighteen laboratories provided ALP results for water Ca (test code 303). Lab results were ranked low to high based on sample SRW-2304 (see Figure 12) lowest in Ca concentration. Median values are designated by horizontal lines. Lab #18 showed consistent high bias on all three Proficiency samples, and is likely a result of a calibration error.

Calcium precision across the three water solution matrices indicates excellent precision, with intra-lab s values of 0.075, 0.041, and 0.069 mmolc L^{-1} for SRW-2304, SRW-2305, and for SRW-2306, respectively. Water Ca precision was excellent for all individual labs with only labs #2, and #16 exceeding 0.05 $\text{mmolc L}^{-1}\text{Ca}$ on sample SRW-2304. Two labs were flagged for poor precision on ALP Cycle 51 for HCO_3 content.

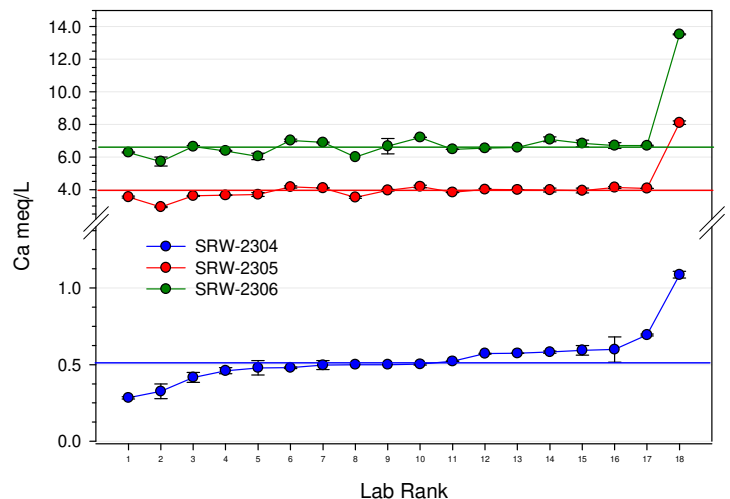


Figure 12. Water Ca distribution plots for SRW materials, ALP 2023 Cycle 51.

Announcements

- ▶ The ALP Program has been collaborating over the past 18 months with Ag Gateway on the next revision of the Modus method codes for soil, plant and manure analyses. ALP will be adopting the new method codes for reporting soil proficiency test results for cycle 53 in 2024. More information can be found www.aggateway.org/Portals/.
- ▶ ALP will initiate a soil carbon proficiency testing program in January 2024. Test parameter include, total Soil Carbon (SC), soil organic carbon (SOC), soil inorganic carbon (SIC), pH and moisture content. Soils will be powder crushed to minus 0.3 mm and moisture stabilized. The program will consist three cycles per year each with four soils. The soil carbon proficiency program will be required for labs seeking ALTA-SC certification.
- ▶ ALP will be updating proficiency soil test codes later this year. Specific parameter/methods which currently have no reported proficiency data will be deprecated. Additional tests codes will be instituted based on comments of laboratory participants.
- ▶ ALTA will have their winter meeting the 1st week of February, in The Dells Wisconsin. Topics include presentations on lab analysis, soil carbon analysis, Modus soil and plant codes and the new ISLPP program serving Iowa. For more information can be found at ALTA.Ag.
- ▶ ALP has standard reference soils and plant tissue samples available for purchase. For more information on these methods contact the ALP Technical Director, Robert.Miller@cts-interlab.com.

Summary

ALP is has provided seventeen years of service with the completion of Cycle 51. Since 2005 ALP has completed the analysis of 255 soils, 176 plant samples and 165 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 51. 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 52 Ship
September 19, 2023

**“One thing that you can't
fake is chemistry.”**

**– Blake Shelton,
2022**

