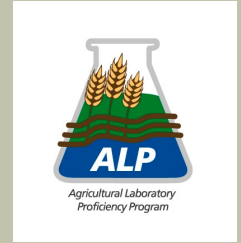


ALP Program Report



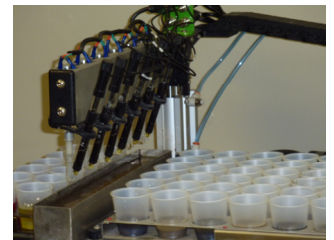
Robert O. Miller, PhD, ALP Technical Director, Windsor, CO
 Christopher Czuryca, Collaborative Testing Services, Inc, Sterling, VA

ALP Overview

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 50.
- Sixty-four Laboratories provided soil pH (1:1) H₂O results and medians ranged from 4.89 - 6.79.
- Soil M3-P ICP for Cycle 50 ranged from 36.7 to 112 mg kg⁻¹ with MAD values ranging 2.6 - 9.2 mg kg⁻¹ across the five soils.
- Soil M3-K values ranged from 78 - 582 mg kg⁻¹ for the five ALP soils of PT Cycle 50.
- Botanical N by combustion was reported by 43 labs, with three labs showing inconsistency across the three PT materials for Cycle 50.
- Botanical Total Mn, ranged from 34 - 204 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 50 was completed May 10, 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 50 were: SRS-2301 a loam, collected Ontario, Canada; SRS-2302 Quincy loamy fine sand collected Morrow Cty OR; SRS-2303 a Hambrook sandy loam collected from Caroline Cty DE; SRS-2304 is a Pickwick silt loam collected in Washington Cty, AR; and SRS-2305 a Marshall silty clay loam collected in Cass Cty, IA. Chemical properties of the SRS materials ranges: pH (1:1) H₂O 4.89 - 6.79; SMP Buf 6.69 - 7.09 mg kg⁻¹; Bray P1 (1:10) 29.5 - 85.7 mg kg⁻¹; M3-K 78 - 582 mg kg⁻¹; M3-Ca 435 - 3118 mg kg⁻¹; DTPA-Zn 0.80 - 2.93 mg kg⁻¹; SOM-LOI 1.51 - 4.39%; CEC 2.7 - 20.1 cmol kg⁻¹; clay 5.0 - 29.7% and NO₃-N 3.5 - 240 mg kg⁻¹.

Standard Reference Botanical (SRB) materials for Cycle 50 were: SRB-2301 celery leaf composite from CA; SRB-2303 tomato leaf composite from CO; SRB-2303 parsley leaf composite from CA; and SRB-2304 corn leaf composite from SD. SRB median analytes ranged: NO₃-N 487 - 3067 mg kg⁻¹; Dumas N 2.12 - 4.13%; wet digestion total P 0.27 - 0.56%; total K 1.89 - 2.77%; total Ca 1.22 - 4.54%; total S 0.25 - 1.82 %, total B 28.9 - 62.2 mg kg⁻¹; and total Cl 0.60 - 3.23 %.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2301 a water sample collected from a domestic well Albion, NE; SRW-2302 was collected Niwott, CO; and SRW-2303 from a domestic water supply Severance, CO. SRW median concentrations: pH 7.61 - 7.79; EC 0.11 - 0.70 dSm⁻¹; SAR 0.26 - 0.89; Ca 0.52 - 3.84 mmolc L⁻¹; Na 0.39 - 1.40 mmolc L⁻¹; HCO₃ 0.76 - 4.43 mmolc L⁻¹; and NO₃ 0.01 - 3.34 mmolc L⁻¹.

Inside this issue:

Soil homogeneity evaluation	2
2023 Cycle 50 observations	2
SRS Results: pH, P, K, SOM	3
ALP Botanical comparison	5
SRB NO ₃ -N results	5
SRB: N, P, Mg and Mn	6
SRW Results	8
Announcements	9

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 50.

Sample	pH (1:1) H ₂ O		EC (dS m ⁻¹)		NO ₃ -N (mg kg ⁻¹)		SOM-WB (%)	
	Mean ¹	Std	Mean	Std	Mean	Std	Mean	Std
SRS-2301	6.81	0.02	0.63	0.008	60.2	2.2	4.29	0.10
SRS-2302	6.13	0.01	1.60	0.012	185.2	6.0	1.58	0.16
SRS-2303	6.15	0.05	0.11	0.017	3.2	2.4	1.80	0.14
SRS-2304	4.85	0.01	1.02	0.017	127.0	5.0	1.30	0.05
SRS-2305	5.71	0.01	1.83	0.020	256.2	3.8	2.33	0.09

¹ Statistics based on six randomly selected soil replicates, each analyzed in triplicate ALP Cycle 50.

*“..soil pH, Buf pH
A&E, Olsen P and
SOM-WB analysis Stdev
values for Cycle 50 met
homogeneity standards.”*

2023 Cycle 50 Observations

Results for soil pH (1:1) H₂O (test code 115) analysis inter-lab MAD values for Cycle 50 averaged 0.07 pH units across the five soils. Median within lab pH standard deviation was 0.05 pH units. Soil Organic C values for the Cycle 50 ranged from 0.653 to 2.141% SOC. SRS-2303 had an abnormally low extractable M3-Ca (Test code 140) of 435 mg kg⁻¹, likely associated with loamy sand soil texture and low CEC. M3-Ca MAD values ranged 40 - 281 mg kg⁻¹ and M3-Mg MAD values ranged 4.3 to 40.7 mg kg⁻¹ for the five soils. For soils SRS-2304 and SRS-2305 M3-P colorimetric intra-lab standard deviations were consistently 50 - 60% lower than values for the M3-P ICP method. M3-P colorimetric within lab standard deviation for SRS-2304 were similar to M3-P and may be related to the high sand content of the collection site, a corn field in Morrow county, Oregon.

Across the four botanical samples Dumas combustion N MAD values averaged 0.078% nitrogen with intra-lab median s of 0.048%, 0.035%, 0.037% and 0.043%, respectively. Botanical sample SRB-2302 had a very low median Cu with a concentration of 5.2 mg kg⁻¹ and with a MAD of 0.62 mg kg⁻¹. The celery leaf composite sample SRB-2301 had higher median concentrations of NO₃-N, N, Na, Al, Cu, Mo, Ni, Pb and Ba and relative to the other three botanical samples. Consistent with past ALP cycles, Cycle 50 intra-lab relative variability results were lowest for total P than other macro elements across all four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC median values were 0.475, 0.110 and 0.704 dSm⁻¹, respectively. Median Mg values ranged from 0.149 - 1.18 mmolc L⁻¹ across the three ALP water samples with MAD values ranging 0.025 to 0.061 mmolc L⁻¹. Sample SRW-2302 had Cl 0.134 mmolc L⁻¹ with a MAD of 0.013 mmolc L⁻¹.

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

Sixty-four laboratories provided ALP results for soil pH (1:1) H₂O (test code 115). Soils ranged from acid to alkaline, median range 4.89 - 6.78. Lab results were ranked low to high based on sample SRS-2304 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-2304 and SRS-2305 showed good consistency across labs. Labs #59, #60, #61 and #62 showed consistent high bias on two of five soils. Labs #3, #5, #44, #57 #61, #62, #63 and #64 results were inconsistent across 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 0.015 to 0.041 pH units, the lowest noted for SRS-2305. Twelve labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #1, #12, #22, #55, and #62 exceeded 0.10 pH units for SRS-2303. Soil SRS-2304 was the least variable with respect to intra-lab variance.

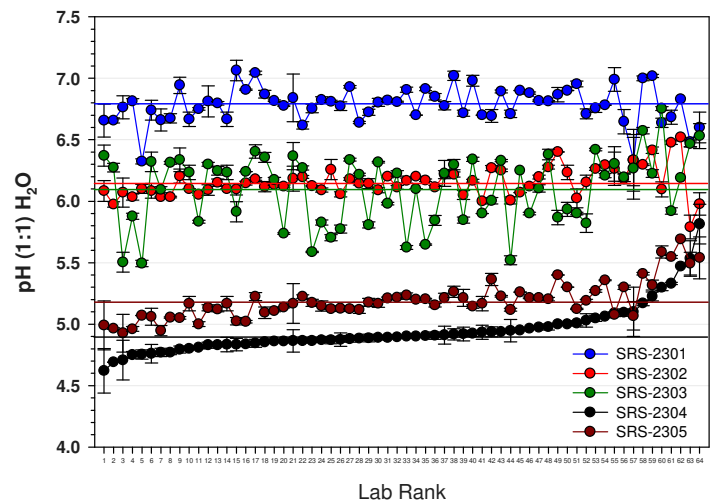


Figure 1. pH (1:1) H₂O distribution plots for SRS materials, ALP 2023 Cycle 50.

SRS - Phosphorus: Bray P1, M3-P Bray P2,

Bray P1 results were reported by twenty-nine labs. M3-P ICP was reported by 51 labs. Median soil Bray P1 values ranged from 29.5 - 85.7 mg kg⁻¹ PO₄-P; Olsen P 14.1 to 37.8 mg kg⁻¹ P; Bray P2 ranged from 45.8 to 286 mg kg⁻¹ P; and M1-P from 25.3 to 245.9 mg kg⁻¹ P, across the five soils. Ranking lab results based on sample SRS-2302, median Bray P1 concentrations are shown in indicated in Figure 2. Soil SRS-2303, highest in concentration was variable between labs. Soils SRS-2304 and SRS-2305 had near identical concentrations of 30 mg kg⁻¹ P; soils SRS-2302 and SRS-2303 had similar Bray P1 concentrations. Lab #2 had consistently low bias across all five soils. Labs #1, #22 and #25 were inconsistent across all five soils.

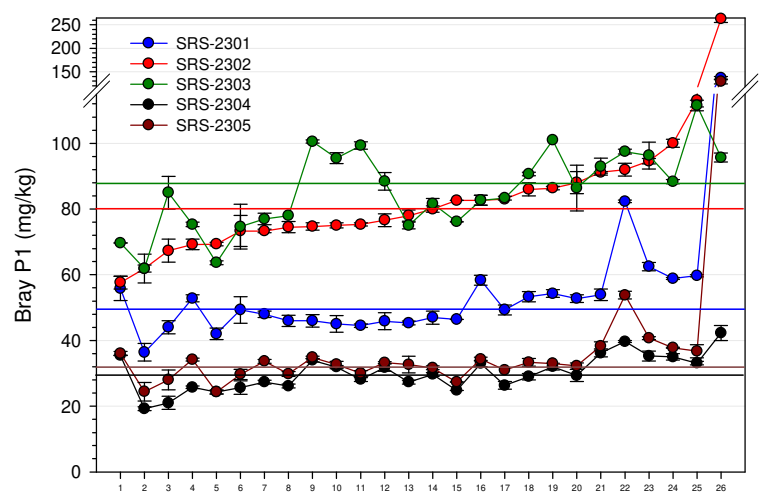


Figure 2. Bray P1 distribution plots for SRS materials, ALP 2023 Cycle 50.

Six labs reported M3-P Spec median concentrations ranging 25.4 - 78.4 mg kg⁻¹ P. Nine laboratories reported Bray P2 with medians ranging 45–286 mg kg⁻¹ P and three results for Modified Morgan P, with medians ranging from 1.1 - 22.1 mg kg⁻¹ PO₄-P. Modified Kelowna was reported by two laboratories ranging from 22.7 - 63.2 mg kg⁻¹ P and total P (US-EPA 503) ranged 302 - 1003 mg kg⁻¹ P with the highest concentration noted for SRS-2302.

SRS - Potassium

Forty-four laboratories provided ALP results for soil M-3 K (test code 159) results. Results were ranked low to high based on sample SRS-2303 (see Figure 3). Soil SRS-2301 and SRS-2305 were the most inconsistent across labs. The source of the variability is unknown. Laboratory #1 showed low bias on soils with $< 150 \text{ mg kg}^{-1} \text{ K}$. Across all soils labs #6, #14, #36 and #44 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-2303, with a median intra-lab value of $4.3 \text{ mg kg}^{-1} \text{ K}$ and highest for SRS-2303 with a value of 25.3 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 five labs which exceeded $10 \text{ mg kg}^{-1} \text{ K}$ on SRS-2301. Labs #6, #25 and # 46 had poor precision on three of five soils with M3-K values $< 150 \text{ mg kg}^{-1} \text{ K}$ for Cycle 50. Poor precision is attributed to extraction and/or analysis instrument operation.

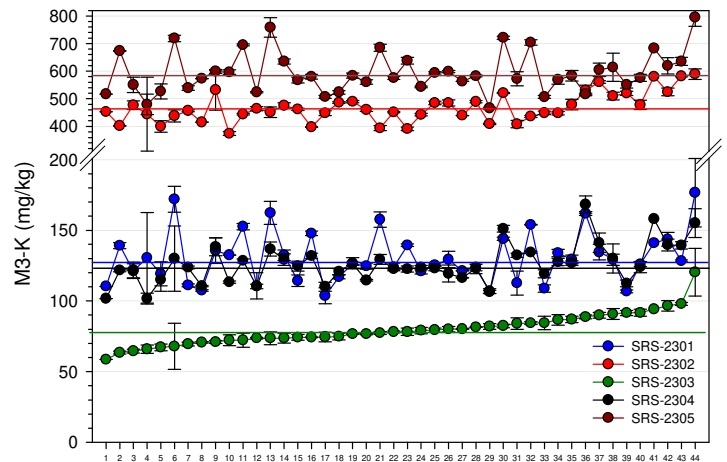


Figure 3. Extractable K distribution plots for SRS materials, ALP 2023 Cycle 50.

SRS - SOM-LOI

Forty-five laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 1.48 to 4.40%. Results were ranked based on sample SRS-2304 (see Figure 4). Sample SRS-2301 had high consistency. Lab #1 had consistent low bias. Labs #2, #5, #25 and #39 were inconsistent across the five soils. Source of bias is likely related to muffle furnace operation and/or method compliance.

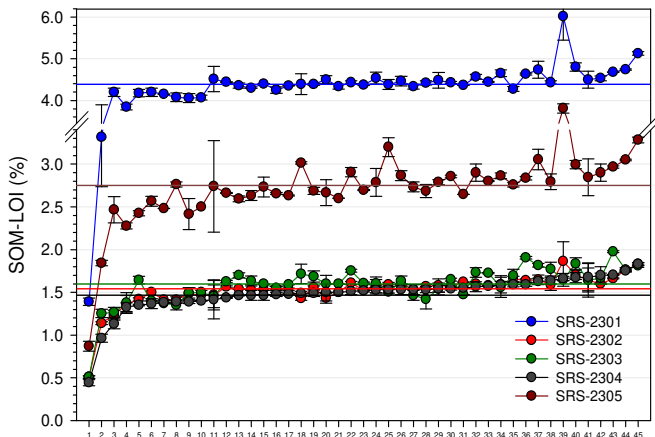


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2023 Cycle 50.

SOM-LOI precision across the five soils indicates high median intra-lab precision s values ranging from 0.058 to 0.157% SOM-LOI, highest for SRS-2301. Across labs, s values for SRS-2301 ranged from 0.006 - 0.579%. Across soils low precision was noted for several laboratories. Specifically s for labs #11, #39, and #41, exceeded 0.10% SOM-LOI for SRS-2302. Lab #2 had poor precision on SRS-2301. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

ALP botanical comparison

ALP botanical proficiency sample SRB-2204 was previously submitted seven years ago in cycle 29 as SRB-1603. A limited comparison of results are shown in Table 2. Results indicate 93% of the 43 analysis methods evaluated, were within the inter-lab measurement error as measured by the MAD. For specific analyses, N, P, S, Zn, and As, median values were reproducible within two significant digits. ALP SRB-2304 median results for Cl, K, Ca, Mg, B, Mo, Ba, Ni and Sr were reproducible within < 4% of the original values.

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-1603 vs SRS-2304.

Analysis	Unit	SRB-1603 ¹		SRB-2304	
		Median	MAD	Median	MAD
Dry Matter	%	93.8	0.40	97.0	0.40
NO ₃ -N (Cd-Rd)	mg kg ⁻¹	448	31	488	47
N-Dry Comb.	%	2.182	0.063	2.125	0.052
P	%	0.277	0.012	0.276	0.002
K	%	2.882	0.152	2.772	0.109
S	%	0.253	0.020	0.250	0.010
Zn	mg kg ⁻¹	51.6	3.3	51.0	2.4
Mn	mg kg ⁻¹	60.3	3.4	59.8	2.8
Mo	mg kg ⁻¹	0.553	0.053	0.502	0.075
Ni	mg kg ⁻¹	2.11	0.15	2.06	0.19
Pb	mg kg ⁻¹	0.201	0.06	0.215	0.018

¹ ALP SRB-1603, a corn leaf sample collected 2015 in Colorado, USA.

SRB - NO₃-N

Twenty-five 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-2304 (see Figure 6). Lab #25 had high bias results for all four materials. The data plot shows labs #1, #4, and #21 were inconsistent on three of four samples.

Botanical NO₃-N (test code 202) results for Cycle 50 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 12 to 85 mg kg⁻¹ across the four samples. Individual lab NO₃-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-2301 ranged from 6 – 362 mg kg⁻¹; SRB-2302 ranged from 4 - 419 mg kg⁻¹, SRB-2303 ranged from 2 - 122 mg kg⁻¹ and SRB-2304 ranged from 2 - 62 mg kg⁻¹. Lab #1 had consistently high standard deviations for two of four samples. Four labs were flagged for poor precision.

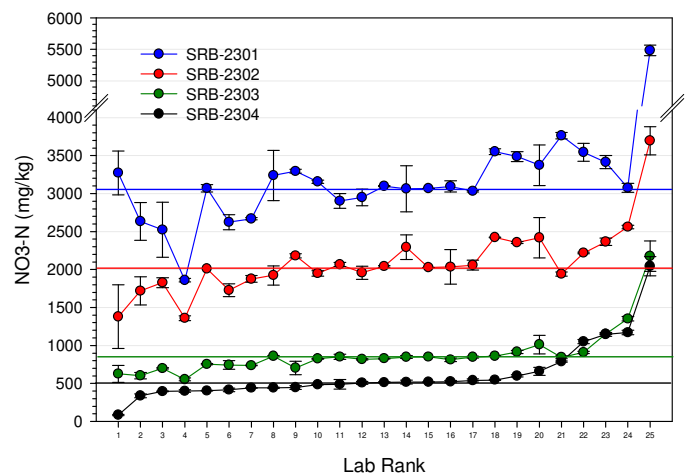


Figure 6. Nitrate distribution plots for SRB materials, ALP 2023, Cycle 50.

2023 Volume 1

SRB - Dumas Nitrogen and TKN

Forty-three laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and eight labs for TKN (Test code 209) for Cycle 50. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2304 (see Figure 7). Labs #1, #9, #42 and #43 were inconsistent for SRB-2302 and SRS-2303 relative to SRB-2301. 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-2301, was 0.024% N, SRB-2302 was 0.015% N, SRB-2303 was 0.021% N, and SRB-2304 was 0.012% N. Lab #1 and #42 had consistently high standard deviations on three of four PT samples. TKN median intra-lab s values for SRB-2301 was 0.057%, SRB-2302 0.050%, SRB-2303 0.020% and SRB-2304 0.026% TKN nitrogen, respectively.

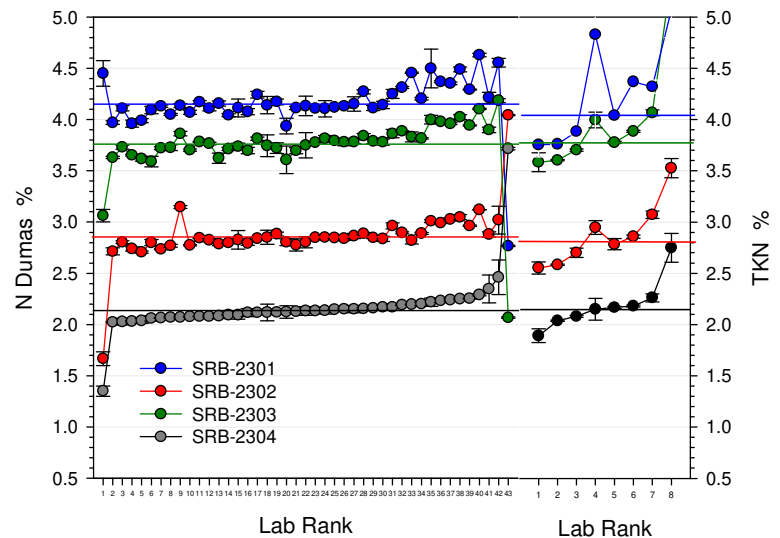


Figure 7. N distribution lab plots for SRB materials, ALP 2023 Cycle 50.

SRB - Phosphorus

Forty-seven laboratories provided ALP results for Cycle 50 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-2302 (see Figure 8). Consistent high bias was noted for labs #44 - #47. Labs #1, #2 and #5 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 0.003 to 0.012 % P for test code 2102 across the four botanical samples. Individual lab intra-lab s values for SRB-2301; ranged from 0.001 - 0.041% P; SRB-2302 ranged from 0.001 - 0.026 % P and SRB-2303 0.001 - 0.023 % P; and SRB-2304 0.001 - 0.062 % P. Lab #5 had a high standard deviation exceeding 0.041 % P on SRB-2301 PT sample. Six labs were flagged for poor precision for botanical P for Cycle 50.

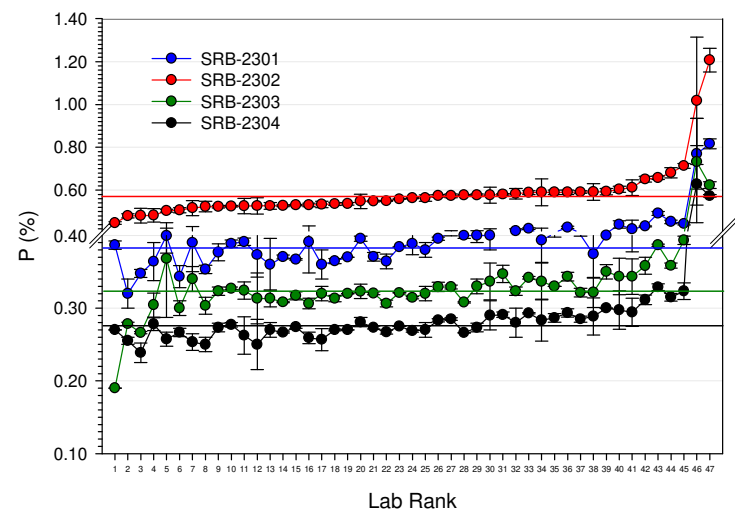


Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2023 Cycle

SRB - Magnesium

Forty-seven laboratories provided ALP results for magnesium (Mg) (test code 215). Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-2303 (see Figure 9). Labs #1, #2, #21, #42, #43 and #45 were inconsistent. Source of bias is related sample digestion, analysis instrument and/or method compliance.

Botanical Mg results indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 0.015 to 0.045 % Mg for test code 215 across the four samples. Individual lab intra-lab *s* values were: SRB-2301, ranged from 0.001 - 0.108 % Mg; SRB-2302, 0.001 - 0.121 % Mg; SRB-2303, 0.002 - 0.042 % Mg; and SRS-2304, 0.001 - 0.084 % Mg. Labs #6 and #44 had high standard deviations exceeding 0.05 % Mg on two of four samples. Across samples seven labs were flagged for poor Mg precision for Cycle 50.

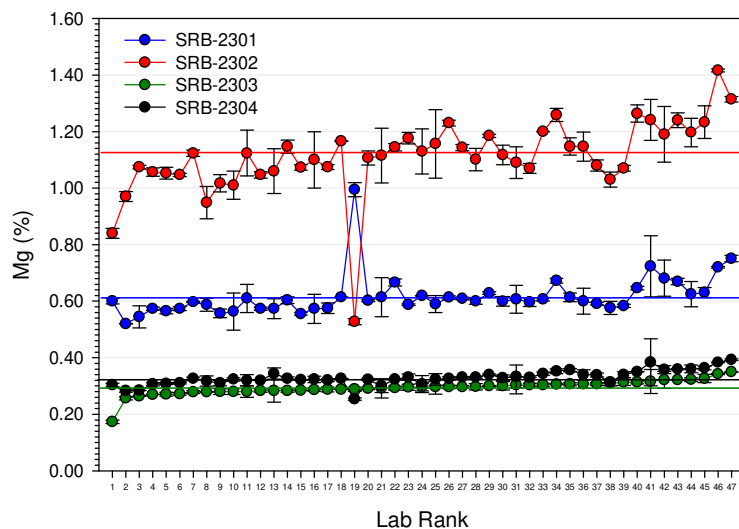


Figure 9. Magnesium lab plot for SRB materials, ALP 2023 Cycle 50.

SRB - Manganese

Forty-six laboratories provided ALP results for Manganese (Mn) (test code 221). 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-2302 (see Figure 10). Across samples labs #39 and #40 exhibited high bias. Labs #2, and #4 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Mn results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 2.1 to 7.4 mg kg⁻¹ Mn for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2301; ranged from 0.6 - 14.8 mg kg⁻¹ Mn; SRB-2302 ranged from 0.1 - 5.3 mg kg⁻¹ Mn; SRB-2303 0.2 - 24.4 mg kg⁻¹ Mn; and SRB-2304 0.2 - 6.7 mg kg⁻¹ Mn. Lab #23 had consistently high standard deviations for three samples.

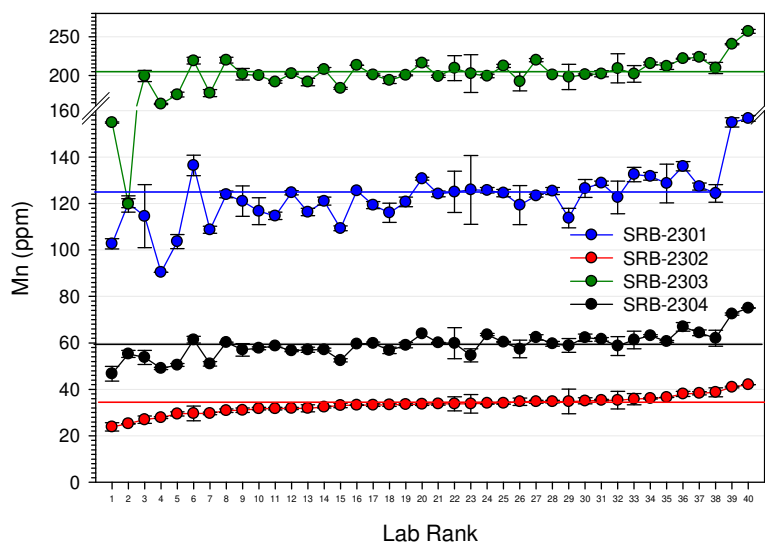
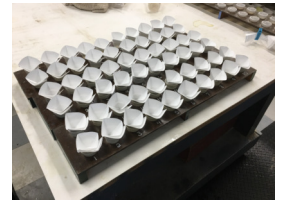


Figure 10. Manganese (code 221) lab plots for SRB materials, ALP 2023 Cycle 50.

SRW - Water EC

Nineteen laboratories provided ALP results for water EC (test code 302). Lab results were ranked low to high based on sample SRW-2302 (see Figure 11). Sample SRW-2303 had the highest EC in Cycle 50. Lab #12 indicated inconsistency across samples. Lab #19 had high bias on SRW-2301. 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 0.007, 0.006 and 0.008 dSm^{-1} , for the three water samples respectively. Precision for sample SRW-2302 was the most consistent across the nineteen participating laboratories. Intra-lab s values for lab #19 exceeded 0.025 dSm^{-1} on SRW-2302. Highest precision was noted for lab #7 with intra-lab s values of $< 0.0010 \text{ dSm}^{-1}$ for all three samples. Five labs were flagged for precision for EC.

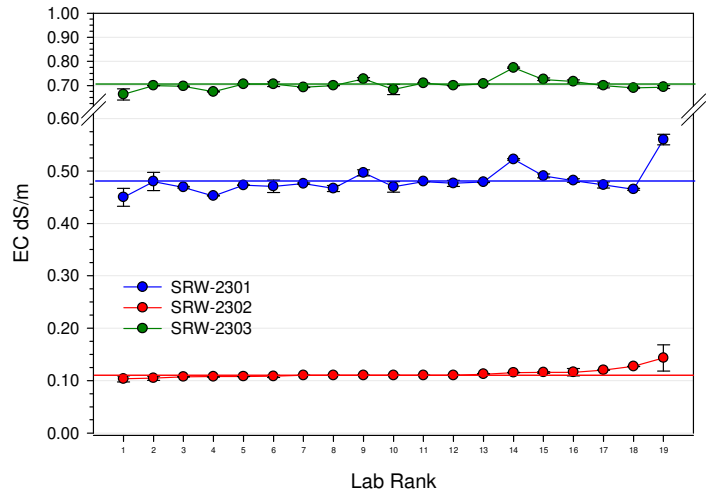


Figure 11. Water EC distribution plots for SRW materials, ALP 2023 Cycle 50.

SRW - HCO_3

Fifteen laboratories provided ALP results for water HCO_3 (test code 311). Lab results were ranked low to high based on sample SRW-2301 (see Figure 12) moderate in HCO_3 concentration. Median values are designated by horizontal lines. Lab #15 showed consistent high bias on all three Proficiency samples, and is likely a result of a calibration error.

HCO_3 precision across the three water solution matrices indicates excellent precision, with intra-lab s values of 0.075, 0.041, and $0.069 \text{ mmolc L}^{-1}$ for SRW-2301, SRW-2302, and for SRW-2303, respectively. Water HCO_3 precision was excellent for all individual labs with only labs #1, #9 and #10 exceeding $0.10 \text{ mmolc L}^{-1} \text{ HCO}_3$ on sample SRW-2301. Three labs were flagged for poor precision on ALP Cycle 50 for HCO_3 content.

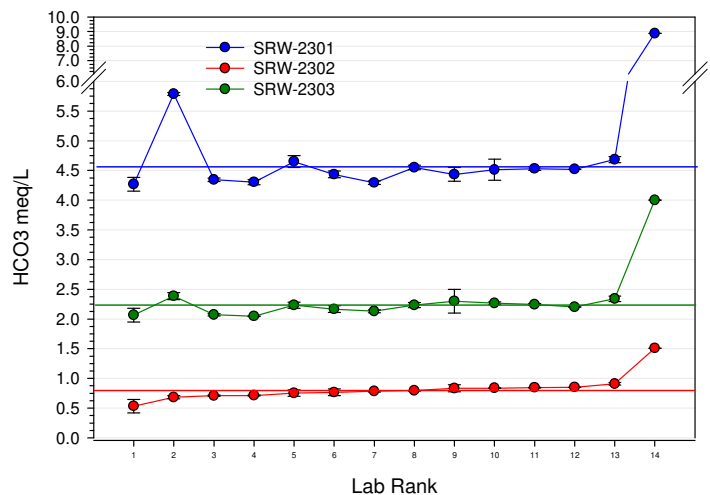


Figure 12. Water HCO_3 distribution plots for SRW materials, ALP 2023 Cycle 50.

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 later this year. More information can be found www.aggateway.org/Portals/.
- ▶ The 2023 SERA-IEG 6 annual meeting will be held June 5-7, 2023 in Auburn, AL. Topics include, update on public lab testing across the southeast region, and update on SERA-6 activities. For more information contact Jessica Davis at Auburn University, jld0084@auburn.edu.
- ▶ ALTA will have their summer meeting August 28-29, 2023, in Bloomington, Illinois. Topics include presentations on lab analysis, soil carbon analysis, a consultants perspective on using plant-tissue analysis and the new ISLPP program serving Iowa. For more information can be found at ALTA.Ag.
- ▶ ALP will be updating the list of 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.
- ▶ 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 50. Since 2005 ALP has completed the analysis of 250 soils, 168 plant samples and 159 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 50. 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 51 Ship
June 22, 2023

**“In any team sport, the best teams have
consistency and chemistry. ”**

– Roger Staubach, 1979

