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ALP Program Report

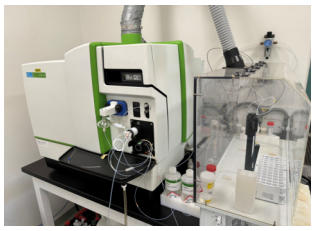
Robert O. Miller, PhD, ALP Technical Director, Windsor, CO
Christopher Czyryca, Collaborative Testing Services, Inc, Sterling, VA

ALP Overview

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 52.
- Sixty Laboratories provided soil pH (1:1) H_2O results and medians ranged from 4.43 - 7.94.
- Soil M3-P ICP for Cycle 52 ranged from 9.8 to 168 mg kg^{-1} with MAD values ranging 1.2 - 8.5 mg kg^{-1} across the five soils.
- Soil M3-K values ranged from 76 - 328 mg kg^{-1} for the five ALP soils of PT Cycle 52.
- Botanical P concentrations ranged from 0.09 to 0.62 % across the four PT samples.
- Botanical K concentrations ranged from 1.28 to 7.14 % for cycle 52.
- Botanical total Mo, ranged from 0.07 - 4.19 mg kg^{-1} for 26 reporting labs.

The Agriculture Laboratory Proficiency (ALP) Program spring 2023 Round Cycle 52 was completed December 6, 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.

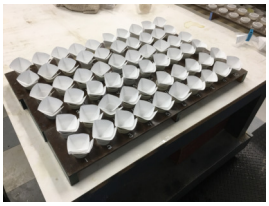
Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 52 were: SRS-2311 Cecil clay loam, collected Anderson Cty SC; SRS-2312 Winooski silt loam Litchfield Cty, CT; SRS-2313 a Pivot Loamy sand collected from Holt Cty, NE; SRS-2314 is Aridic Haploxeroll collected near Osoyoos, BC, Canada; and SRS-2315 a Nevee silt loam collected in Crook Cty, WY. Physio-chemical properties of the SRS materials ranges: pH (1:1) H_2O 4.43 - 7.94; SMP Buf 6.64 - 7.54 mg kg^{-1}; Bray P1 (1:10) 1.0 - 137 mg kg^{-1}; M3-K 76 - 328 mg kg^{-1}; M3-Ca 487 - 11,211 mg kg^{-1}; DTPA-Zn 0.27 - 32.3 mg kg^{-1}; SOM-LOI 1.54 – 5.64%; CEC 5.9 - 13.0 cmol kg^{-1}; clay 7.1 - 32.1%; extractable Cl 3.4 - 27.1 mg kg^{-1}; and NO_3-N 13.5 - 145 mg kg^{-1}.

Standard Reference Botanical (SRB) materials for Cycle 52 were: SRB-2309 canola composite from IA; SRB-2310 lime leaf composite from CA; SRB-2311 pistachio leaf composite from CA and SRB-2312 chicory leaf composite from CO. SRB median analytes concentrations: NO_3-N 15 - 2,193 mg kg^{-1}; Dumas N 1.79 - 3.59 %; wet digestion total P 0.094 - 0.62 %; total K 1.29 - 7.15 %; total Ca 1.46 - 3.62 %; total S 0..17 - 0.59 %, total B 35.3 - 139 mg kg^{-1}; and Zn 11.7 - 49.5 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2307 a water sample collected from a domestic well Gates Mills, OH; SRW-2308 was collected from a stream Ponca, NE; and SRW-2309 from a canal near North Platte, NE. SRW median concentrations: pH 8.14 - 8.81; EC 0.58 - 0.92 dSm^{-1}; SAR 0.43 - 2.15; Ca 2.57 - 4.11 mmolc L^{-1}; Na 0.94 - 3.42 mmolc L^{-1}; HCO_3 0.31 - 7.05 mmolc L^{-1} ; and NO_3 0.01 - 1.61 mmolc L^{-1}.

Soil Homogeneity Evaluation



SRS material homogeneity was evaluated based on soil test codes pH (1:1) H_2O, buffer pH Adams Evans, EC (1:1), P Olsen, K Olsen, NO_3-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 H_2O. Homogeneity was also evaluated on SRB and SRW matrix samples.

"..soil pH, Buf pH A&E, Olsen P and SOM-WB analysis Stdev values for Cycle 52 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation 2023, Cycle 52.

Sample	pH (1:1) H_2O		EC (dS m^{-1})		P Olsen (mg kg^{-1})		SOM-WB (%)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-2311	5.19	*0.01*	0.58	*0.02*	3.3	*0.9*	2.78	*0.15*
SRS-2312	6.87	*0.03*	0.21	*0.005*	18.8	*1.6*	3.49	*0.18*
SRS-2313	4.48	*0.01*	1.20	*0.01*	20.0	*1.5*	1.87	*0.11*
SRS-2314	6.72	*0.01*	1.41	*0.01*	59.9	*4.7*	3.87	*0.20*
SRS-2315	7.98	*0.01*	0.80	*0.02*	3.4	*0.4*	2.04	*0.13*

[1] Statistics based on five randomly selected soil replicates, each analyzed in triplicate ALP Cycle

2023 Cycle 52 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis inter-lab MAD values for Cycle 52 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 52 ranged from 0.78 to 2.71% SOC. SRS-2311 had an abnormally low extractable M3-Ca (Test code 140) of 487 mg kg^{-1}, likely associated with an acid soil and CEC dominated by 1:1 clay minerals. M3-Ca MAD values ranged 42 - 1048 mg kg^{-1} and M3-Mg MAD values ranged 9 to 32 mg kg^{-1} for the five soils. For soils SRS-2312 and SRS-2313 M3-P colorimetric intra-lab standard deviations were consistently 30 - 70% lower than values for the M3-P ICP method. Extractable M-3 Zn concentrations ranged from 0.88 mg kg^{-1} for SRS-2314 to 63.4 mg kg^{-1} for SRS-2314 collected from a vine yard in British Columbia, Canada.

Across the four botanical samples Dumas combustion N MAD values averaged 0.045% nitrogen with intra-lab median *s* of 0.053%, 0.045%, 0.047% and 0.039%, respectively. Botanical sample SRB-2310 had a very low median Mo with a concentration of 0.078 mg kg^{-1} and with a MAD of 0.044 mg kg^{-1}. The Chicori composite sample SRB-2312 had higher median concentrations of Cl, N, P, K, S, Mn, Mo, Al, As, Cd, and Co and relative to the other three botanical samples. Consistent with past ALP cycles, Cycle 52 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 0.811, 0.584 and 0.919 dSm^{-1}, respectively. Median Mg values ranged from 0.21 - 4.11 mmolc L^{-1} across the three ALP water samples with MAD values ranging 0.044 to 0.100 mmolc L^{-1}. Sample SRW-2307 had B 0.13 mg kg^{-1} with a MAD of 0.012 mg kg^{-1} .

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

Sixty laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 4.43 - 7.94. Lab results were ranked low to high based on sample SRS-2313 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally across labs all soils showed good consistency across labs. Labs #7, #26, #42, #45 and #60 showed inconsistency across SRS-2311, SRS-2312 and SRS-2315 soils. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

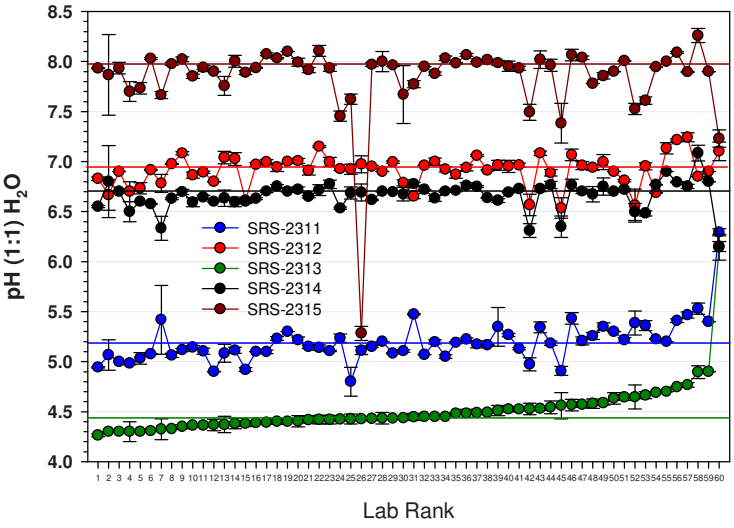


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2023 Cycle

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.019 to 0.024 pH units, the lowest noted for SRS-2313. Five labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #2, #15, #25, #39, and #52 exceeded 0.10 pH units for SRS-2311. Soil SRS-2313 was the least variable with respect to intra-lab variance.

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

Bray P1 results were reported by twenty-nine labs. M3-P ICP was reported by 44 labs. Median soil Bray P1 values ranged from 1.0 - 137 mg kg^{-1} PO_4-P; Olsen P 3.6 to 53.4 mg kg^{-1} P; Bray P2 ranged from 11.8 to 241 mg kg^{-1} P; and M1-P from 1.9 to 152 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-2315, median M3-P ICP concentrations are shown in indicated in Figure 2. Soil SRS-2314, highest in concentration was variable between labs. Soils SRS-2311 and SRS-2315 had near identical concentrations of 10 mg kg^{-1} P. Soils SRS-2312 and SRS-2313 had similar M3-P ICP concentrations. Lab #1, #42, #43 and #44 had inconsistent results across all five soils. Labs #22, #32 and #38 had high intra-lab variances for SRS-2314.

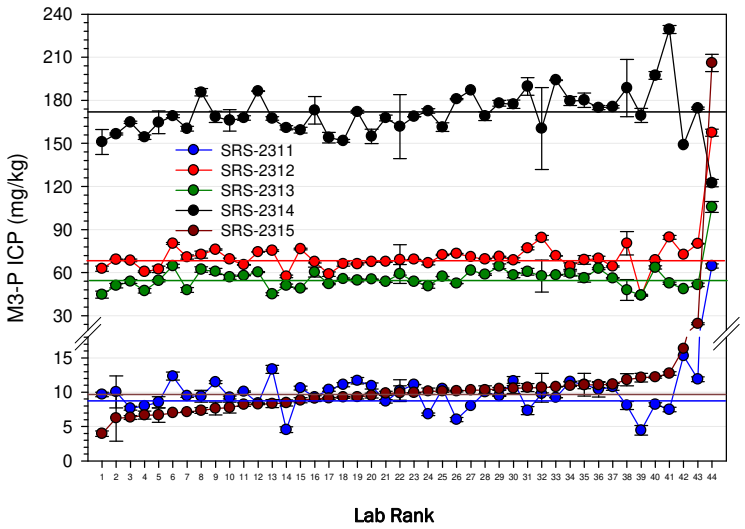


Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2023 Cycle 52.

Seven labs reported M3-P Spec median concentrations ranging 8.3 - 144 mg kg^{-1} P. Ten laboratories reported Bray P2, seven labs for M1-P and two results for Modified Morgan P, with medians ranging from 0.6 - 73.2 mg kg^{-1} PO_4-P. Modified Kelowna was reported by two laboratories ranging from 4.4 - 101 mg kg^{-1} P and total P (US-EPA 503) ranged 312 - 889 mg kg^{-1} P with the highest concentration noted for SRS-2314.

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-2311 (see Figure 3). Soil SRS-2313 and SRS-2314 were the most inconsistent across labs. The source of the variability is unknown. Laboratory #43 showed high bias on all five soils. Across all soils labs #1, #35, #41 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 median intra-lab *s* values were lowest for soil SRS-2311, with a median intra-lab value of 1.5 mg kg^{-1} K and highest for SRS-2314 with a value of 3.6 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 five labs which exceeded 15 mg kg^{-1} K on SRS-2313. Across cycle 52 soils ten labs were flagged for poor precision. Poor precision is attributed to extraction and/or analysis instrument operation.

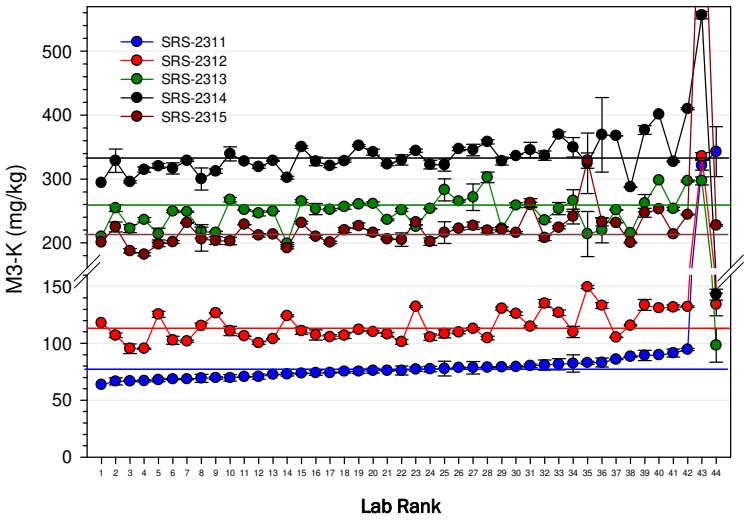


Figure 3. M3-K distribution plots for SRS materials, ALP 2023 Cycle 52.

SRS - SOM-LOI

Forty-five laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 1.45 to 5.64%. Results were ranked based on sample SRS-2313 (see Figure 4). Labs #1-#3 showed consistent low bias on all five soils. Lab #45 had consistent high bias. Labs #4, #8, #42 and #44 were inconsistent across the five soils. Source of bias is likely related to muffle furnace operation and/or method compliance.

SOM-LOI precision across the five soils indicates high median intra-lab precision *s* values ranging from 0.026 to 0.058% SOM-LOI, highest for SRS-2311. Across labs, *s* values for SRS-2313 ranged from 0.005 - 0.302%. Across soils low precision was noted for several laboratories. Specifically *s* for labs #1, #2, #6, #15, #28 and #45, exceeded 0.12% SOM-LOI for SRS-2312. Lab #1 had poor precision on SRS-2311. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

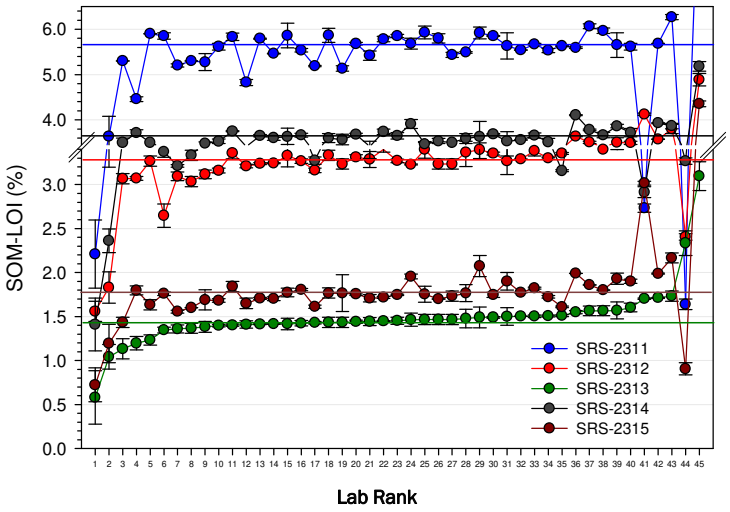


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2023 Cycle 52.

SRS - Magnesium

Forty-one laboratories provided ALP results for soil M3-Mg (test code 161) results. Results were ranked low to high based on sample SRS-2313 (see Figure 5). Soil SRS-2311 and SRS-2313 were the most inconsistent across labs. The source of the variability is unknown. Laboratory #41 showed high bias on all five soils and labs #24 and #39 were inconsistent. Source of inconsistency is likely related to extraction, analysis instrument and/or method compliance.

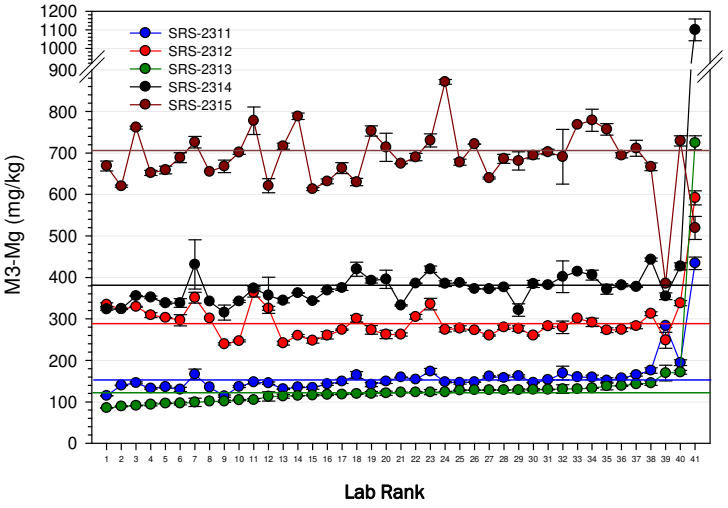


Figure 5. M3-Mg distribution plots for SRS materials, ALP 2023 Cycle 52.

M3-Mg median intra-lab *s* values ranged from 2.0 - 8.8 mg kg^{-1}, highest for SRS-2315 and lowest for SRS-2313. Across soils low precision was noted for several laboratories. Specifically s for labs #7, #12, #19, #32, and #42, exceeded 20 mg kg^{-1}. Across the five cycle 52 soils eleven labs were flagged for poor precision. Poor precision is attributed to extraction and/or analysis instrument operation.

SRB - NO_3-N

Twenty-seven laboratories provided ALP results for NO_3-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-2312 (see Figure 6). The data plot shows labs #8, #12, #23, #24 and #26 were inconsistent on one of four samples.

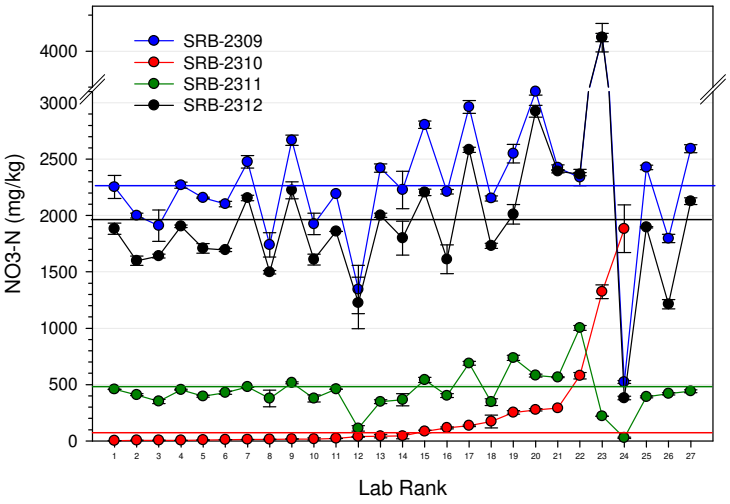


Figure 6. Nitrate distribution plots for SRB materials, ALP 2023, Cycle 52.

Botanical NO_3-N (test code 202) results for Cycle 52 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 3.1 to 36.5 mg kg^{-1} across the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-2309 ranged from 4 – 94 mg kg^{-1}; SRB-2310 ranged from 3 - 60 mg kg^{-1}, SRB-2311 ranged from 2 – 74 mg kg^{-1} and SRB-2312 ranged from 6 - 318 mg kg^{-1}. Lab #12 had consistently high standard deviations for two of four samples. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty-nine laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and eight labs for TKN (Test code 209) for Cycle 52. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2310 (see Figure 7). Labs #1, #3, #37 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-2309, was 0.023% N, SRB-2310 was 0.014% N, SRB-2311 was 0.022% N, and SRB–2312 was 0.018% N. Labs #2, #21, and #28 had consistently high standard deviations on three of four PT samples. TKN median intra-lab *s* values for SRB-2309 was 0.031%, SRB-2310 0.016%, SRB-2311 0.029% and SRB-2312 0.019% TKN nitrogen, respectively.

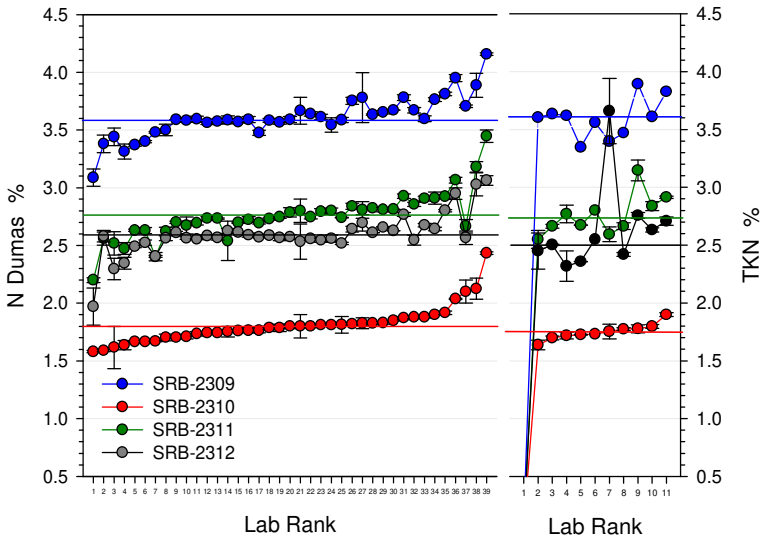


Figure 7. N distribution lab plots for SRB materials, ALP 2023 Cycle 52.

SRB - Phosphorus

Forty-nine laboratories provided results for cycle 52 phosphorus (P) (test code 212). Botanical results median values are designated by horizontal lines for each botanical material and lab results are ranked low to high based on sample SRB-2310 (see Figure 8). Consistent high bias was noted for labs #48 - #49. Labs #1, #37, #38, and #47 showed inconsistency, 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 0.017 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-2309; ranged from 0.002 - 0.087% P; SRB-2310 ranged from 0.0004 – 0.025 % P and SRB-2311 0.002 - 0.065 % P; and SRB-2312 0.002 - 0.027 % P. Six labs were flagged for poor precision for botanical P for Cycle 52.

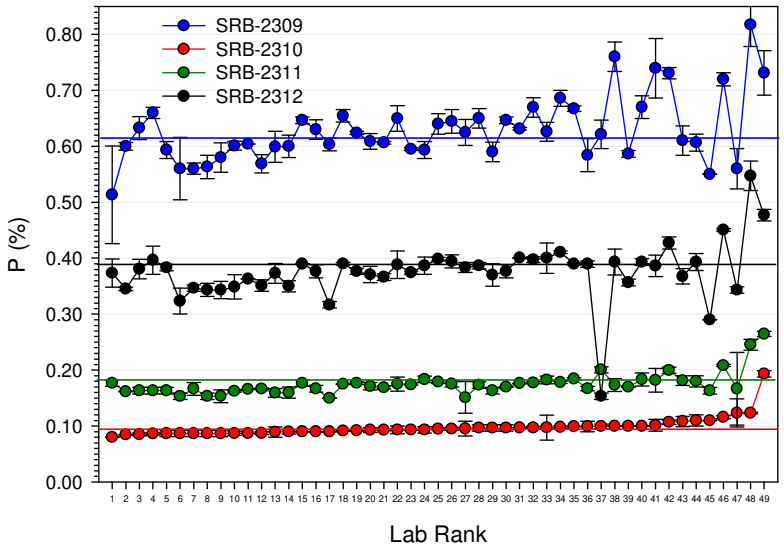


Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2023 Cycle 52.

SRB - Potassium

Forty-nine 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-2310 (see Figure 9). Labs #37, #43, #48 and #49 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 0.025 to 0.175 % K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2309, ranged from 0.006 - 0.157 % K; SRB-2310, 0.002 - 0.57 % K; SRB-2311, 0.003 - 0.226 % K; and SRS-2312, 0.010 - 1.18 % K. Lab #23 had high standard deviations exceeding 0.20 % K on two of four proficiency samples. Across all samples ten labs were flagged for poor K precision for ALP cycle 52.

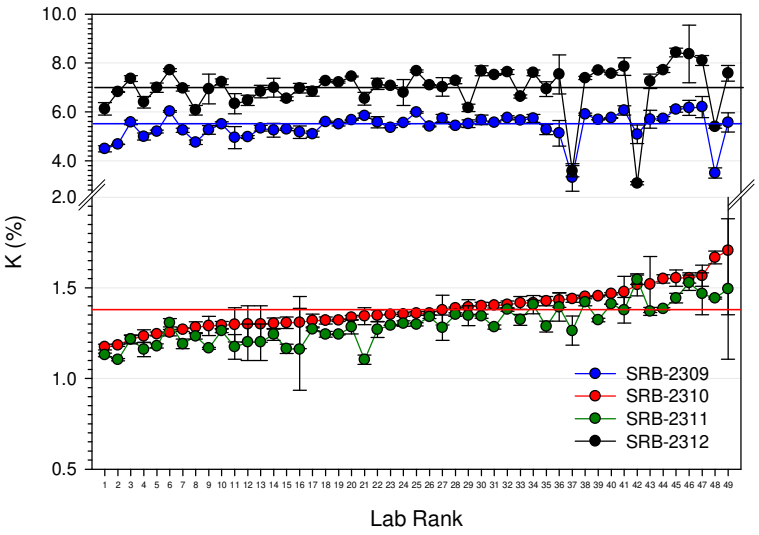


Figure 9. Potassium lab plot for SRB materials, ALP 2023 Cycle 52.

SRB - Molybdenum

Twenty-six laboratories provided ALP results for molybdenum (Mo) (test code 224). Samples SRB-2310 and SRB-2311 were likely at the method detection limits of most PT program respondence. 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-2309 (see Figure 10). Across samples labs #25 and #26 exhibited high bias. Lab #1, and #2 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

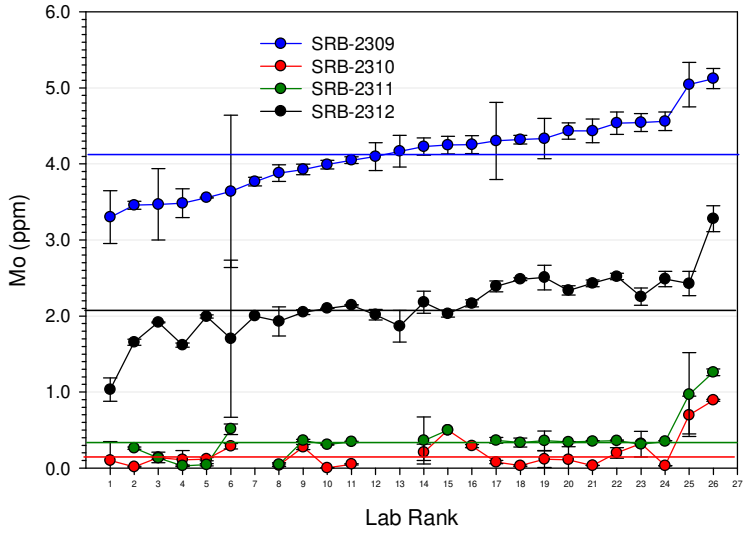
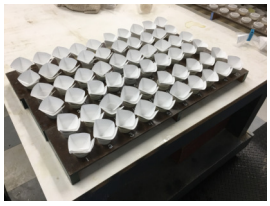


Figure 10. Molybdenum (code 224) lab plots for SRB materials, ALP 2023 Cycle 52.

Botanical Mo results indicate moderate precision, with median intra-lab standard deviation (*s*) values ranged from 0.015 to 0.12 mg kg^{-1} Mo across the four botanical samples. Individual lab intra-lab *s* values for SRB-2309; ranged from 0.005 - 0.992 mg kg^{-1} Mo; and SRB-2312 ranged from 0.005 – 1.03 mg kg^{-1} Mo. Lab #6 had consistently high standard deviations for two of four PT samples.

SRW - Water EC



Seventeen laboratories provided ALP results for water pH (test code 302) and EC. Lab results were ranked low to high based on sample SRW-2308 (see Figure 11). Sample SRW-2309 had the highest EC in Cycle 52. Lab #1 had consistently low bias 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 0.003, 0.002 and 0.003 dSm^{-1}, for the three water samples respectively. Precision for sample SRW-2308 was the most consistent across the seventeen participating laboratories. Intra-lab *s* values for lab #3 exceeded 0.045 dSm^{-1} on SRW-2309. 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.

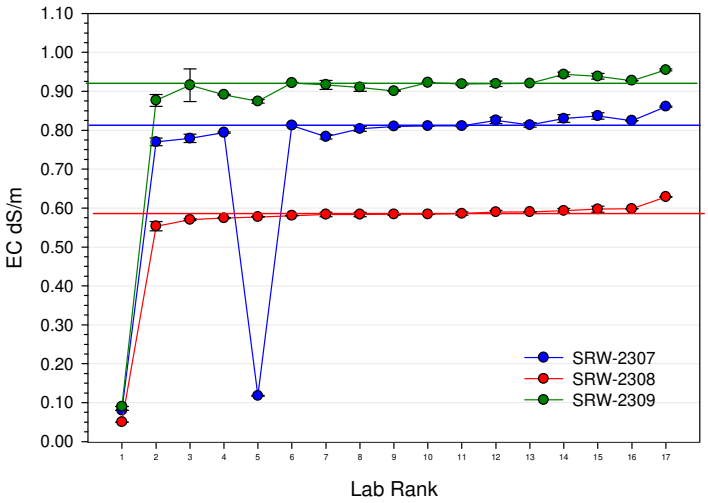


Figure 11 . Water EC distribution plots for SRW PT samples, ALP 2023 Cycle 52.

SRW - Mg

Seventeen laboratories provided ALP results for water Mg (test code 304). Lab results were ranked low to high based on sample SRW-2308 (see Figure 12) lowest in Mg concentration. Median values are designated by horizontal lines. Labs #15, #16 and #17 showed bias and inconsistency on all three Proficiency samples, and is likely a result of a calibration error.

Magnesium precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.027, 0.006, and 0.066 mmolc L^{-1} for SRW-2307, SRW-2308, and for SRW-2309, respectively. Water Mg precision was excellent for all individual labs with only labs #11, and #12 exceeding 0.07 mmolc L^{-1} Mg on sample SRW-2307. Six labs were flagged for poor precision on ALP Cycle 52 for Mg content.

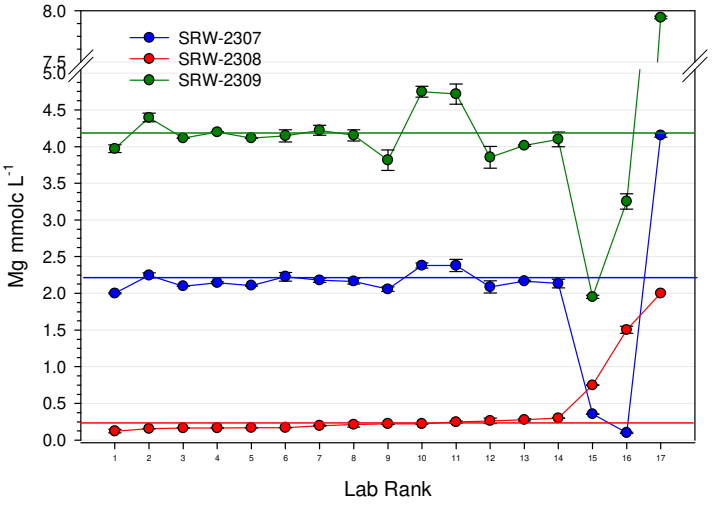


Figure 12. Water Mg distribution plots for SRW PT samples, ALP 2023 Cycle 52.

Announcements

- 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 pulverized to minus 0.20 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 and botanical test codes later this year to follow the Ag Gateway Modus method codes. 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.

- The ALP program has collaborated with ALTA and the Iowa Nutrient Research and Education Council (IA-NREC) in coordinating a double-blind soil analysis proficiency program for labs serving Iowa. The ISLPP (Iowa Soil Laboratory Performance Program) coordinated three double blind tests of Iowa labs in 2023. Results will be presented in an ALTA webinar in January 2024.

- MASTPAWG will have their 2024 meeting the February 20-21, 2024, in Raleigh, NC. Topics include lab analysis, soil carbon analysis, a virtual lab tour and plant analyses. 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 52. Since 2005 ALP has completed the analysis of 260 soils, 180 plant samples and 168 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 52. 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 53 Ship

March 18, 2024

"When the well's dry, we know the worth of water. "

– Ben Franklin, 1746

ALP
Agricultural Laboratory Proficiency Program