2022 Volume 1

12 May 2022

ALP Program Report

2022 Spring - Cycle 47

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ALP Overview

The Agriculture Laboratory Proficiency (ALP) Program fall 2022 Round Cycle 47 was completed May 17, 2022, with results from one-hundred seven 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 fifteen 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.

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 47.
- Sixty-two Laboratories provided soil pH (1:1) H_2O results and medians ranged from 4.49 - 7.86.
- Soil M3-P ICP for Cycle 47 ranged from 15.5 to 90 mg kg^{-1} with MAD values ranging 1.6 - 7.8 mg kg^{-1} across the five soils.
- Soil M3-K values ranged from 96 - 296 mg kg^{-1} for the five ALP soils of PT Cycle 47.
- Botanical N by combustion was reported by 43 labs, with three labs showing high bias values on for two PT materials with > 2.5% N for Cycle 47.
- Botanical Total P, ranged from 0.140 - 0.447% with four of forty-three labs noted for inconsistency across the four samples.

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Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 47 were: SRS-2201 a sandy loam, collected Prince Edward Island, Canada; SRS-2202 Cotaco loam collected Raleigh Cty WV; SRS-2203 a Danvers-Shaak clay collected from Yellowstone Cty MT, Canada; SRS-2204 is a Webster clay loam collected in Worth Cty, IA; and SRS-2205 a Bruella sandy loam collected in Sacramento Cty, CA. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 4.49 - 7.86; SMP Buf 6.18 - 7.47 mg kg^{-1}; Bray P1 (1:10) 10.2 - 90.6 mg kg^{-1}; M3-K 96 - 296 mg kg^{-1}; M3-Ca 335 - 7201 mg kg^{-1}; DTPA-Zn 0.16 - 3.35 mg kg^{-1}; SOM-LOI 2.00 – 6.90%; CEC 6.2 - 27.3 cmol kg^{-1}; clay 10.0 - 39.2% and NO_3-N 2.5 - 115 mg kg^{-1}.

Standard Reference Botanical (SRB) materials for Cycle 47 were: SRB-2201 chives leaf composite from CA; SRB-2202 barley grass composite from OR; SRB-2203 almond leaf composite from CA; and SRB-2204 potato petiole composite from ID. SRB median analytes ranged: NO_3-N 176 - 18590 mg kg^{-1}; Dumas N 1.92 - 4.46%; wet digestion total P 0.14 - 0.447%; total K 1.02 - 10.09%; total Ca 0.33 - 3.98%; total S 0.16 - 0.48 %, total B 3.7 - 40.3 mg kg^{-1}; and total Cl 0.18 - 2.67 %.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2201 a water sample collected from a domestic well near Mt Princeton, CO: SRW-2202 was collected near Fairplay, CO; and SRW-2203 from a domestic water supply Severance, CO. SRW median concentrations: pH 7.68 - 8.19; EC 0.17 - 1.05 dSm^{-1}; SAR 0.28 - 1.19; Ca 0.93 - 4.02 mmolc L^{-1}; Na 0.23 - 2.61 mmolc L^{-1}; HCO_3 0.94 - 4.4 mmolc L^{-1}; and NO_3 0.01 - 0.085 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 47 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation 2022, Cycle 47.

Sample	pH (1:1) H_2O		Olsen P (mg kg^{-1})		NO_3-N (mg kg^{-1})		SOM-WB (%)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-2201	4.49	*0.02*	33.2	*2.3*	135	*1.3*	3.89	*0.28*
SRS-2202	5.48	*0.02*	17.3	*1.0*	141	*1.2*	4.55	*0.22*
SRS-2203	7.80	*0.02*	3.8	*0.3*	63.5	*0.5*	1.25	*0.19*
SRS-2204	6.15	*0.02*	4.7	*0.2*	10.8	*0.3*	7.29	*0.26*
SRS-2205	7.09	*0.02*	18.1	*0.5*	2.4	*0.05*	1.81	*0.09*

[1] Statistics based on six randomly selected soil replicates, each analyzed in triplicate ALP Cycle 47.

2022 Cycle 47 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis inter-lab MAD values for Cycle 47 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 47 ranged form 0.821 to 3.947% SOC. SRS-2201 had an abnormally low extractable M3-Ca (Test code 140) of 315 mg kg^{-1}, likely associated with sandy loam soil series and low CEC. M3-Ca MAD values ranged 29 - 616 mg kg^{-1} and M3-Mg MAD values ranged 3.6 to 73 mg kg^{-1} for the five soils. For soils SRS-2204 and SRS-2205 M3-P colorimetric intra-lab standard deviations were consistently 20 - 40% lower than values for the M3-ICP method. The higher M3-P colorimetric within lab standard deviation for SRSR-2204 maybe related to the higher clay content and/or cropping history of the collection site, a corn field in in Worth county, Iowa.

Across the four botanical samples Dumas combustion N MAD values averaged 0.056% nitrogen with intra-lab median *s* of 0.041%, 0.036%, 0.036% and 0.045%, respectively. Botanical sample SRB-2202 had a very low median B with a concentration of 3.7 mg kg^{-1} and with a MAD of 0.43 mg kg^{-1}. The potato leaf composite sample SRB-2204 had higher median concentrations of NO_3-N, NH_4-N, K, Na, Cu, and Ba and relative to the other three botanical samples. Consistent with past ALP cycles for 2022, cycle 47 intra-lab relative variability results were lowest for combustion N 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 ranged from 0.175, 0.179 and 1.054 dSm^{-1}, respectively. Mg values ranged from 0.178 - 5.47 molc L^{-1} across the three ALP water samples with MAD values ranging 0.020 to 0.23 molc L^{-1}. Sample SRW-2203 had Cl 0.54 molc L^{-1} with a MAD of 0.02 molc L^{-1}.

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

Sixty-two laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 4.49 - 7.86. Lab results were ranked low to high based on sample SRS-2201 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-2201 and SRS-2202 showed good consistency across labs. Labs #1 #2, #4 and #5 showed consistent high bias on all soils. Labs #6, #45, and #62 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.

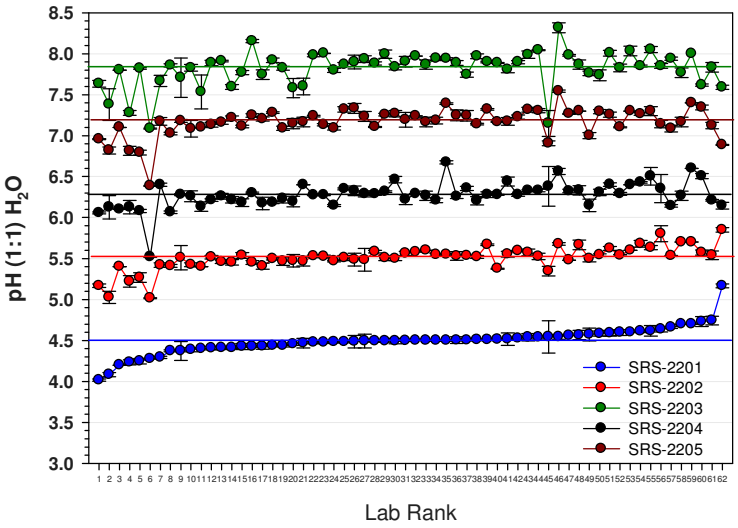


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2022 Cycle 47.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.015 to 0.031 pH units, the lowest noted for SRS-2201. Five labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #2, #9, #11, #20, and #45 exceeded 0.10 pH units for SRS-2203. Soil SRS-2201 was the least variable with respect to intra-lab variance.

SRS - Phosphorus: Bray P1, Bray P2, Olsen, Modified Morgan, M1, and M3

Bray P1 results were reported by twenty-six labs. M3-P ICP was reported by 41 labs. Median soil Bray P1 values ranged from 10 - 79 mg kg^{-1} PO_4-P; Olsen P 4.9 to 35 mg kg^{-1} P; Bray P2 ranged from 44 to 118 mg kg^{-1} P; and M1-P from 2.7 to 41.8 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-2201, median Bray P1 concentrations are shown in indicated in Figure 2. Soil SRS-2201, highest in concentration was highly variable between labs. Soils SRS-2204 and SRS-2205 had near identical concentrations of 11 mg kg^{-1} P; soils SRS-2202 and SRS-2205 had similar Bray P1 concentrations. Lab #1 had consistently low bias across all five soils. Labs #13 #18 and #24 were inconsistent across soils three of five soils.

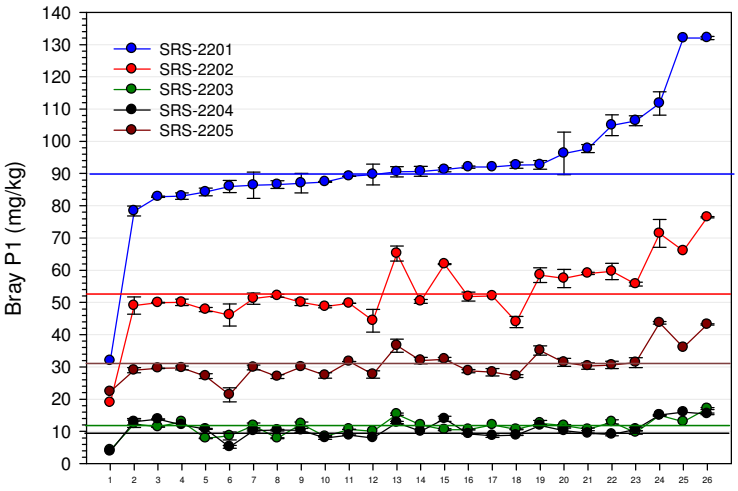


Figure 2. Bray P1 distribution plots for SRS materials, ALP 2022 Cycle 47.

Six labs reported M3-P Spec median concentrations ranging 3 - 79 mg kg^{-1} P. Nine laboratories reported Bray P2 with medians ranging 44–118 mg kg^{-1} P and three results for Modified Morgan P, with medians ranging from 1.5 - 12.7 mg kg^{-1} PO_4-P. Modified Kelowna was reported by two laboratories ranging from 7.6 - 60 mg kg^{-1} P and total P (US-EPA 503) ranged 392 - 667 mg kg^{-1} P with the highest concentration noted for SRS-2201.

SRS - Potassium

Forty laboratories provided ALP results for soil M-3 K (test code 159) results. Results were ranked low to high based on sample SRS-2203 (see Figure 3). Soil SRS-2201 and SRS-2204 were the most inconsistent across labs #1 - #36. The source of the variability is unknown. Labs #1, #37 and #38 were inconsistent across the five soils for M3-K. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

M3-K intra-lab *s* values were lowest for soil SRS-2201, with a median intra-lab value of 1.6 mg kg^{-1} K and highest for SRS-2203 with a value of 4.4 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 12 mg kg^{-1} K on SRS-2203. Labs #30 and # 39 had poor precision on three of four soils for cycle 47. Poor precision is attributed to extraction and/or analysis instrument operation.

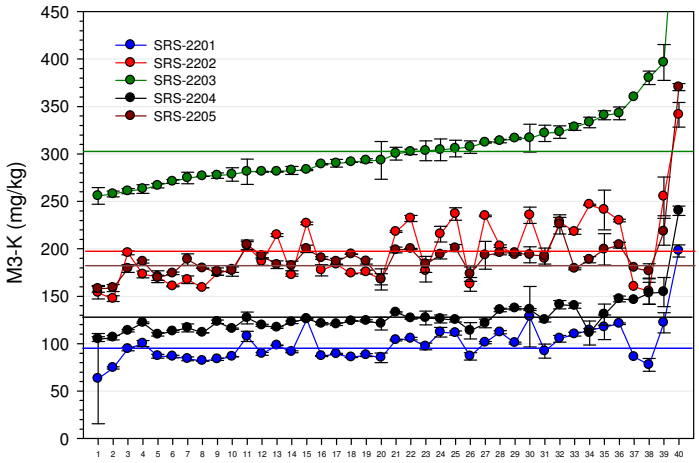


Figure 3. Extractable K distribution plots for SRS materials, ALP 2022 Cycle 47.

SRS - SOM-LOI

Forty-three laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 1.36 to 5.20%. Results were ranked based on sample SRS-2202 (see Figure 4). Sample SRS-2201 had high consistency. Labs #2 , #31, #39 and #43 had inconsistency 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 intra-lab precision, with median *s* values ranging from 0.028 to 0.058% SOM-LOI, highest for SRS-2204. Across labs, *s* values for SRS-2201 ranged from 0.007 - 0.554%. Across soils low precision was noted for several laboratories. Specifically *s* for labs #18, #130, #32, #37 and #43, exceeded 0.20% SOM-LOI for SRS-2102. Lab #30 had poor precision on three of five soils. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

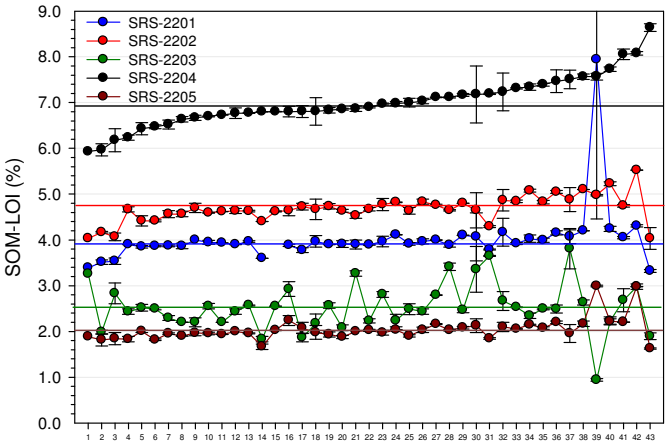


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2022 Cycle 47.

SRS - pH method comparison

A comparison was made of two soil pH methods, pH 1:1 H_2O and pH 1:1 0.01 M $CaCl_2$ (test codes 116 and 118) for cycle 47 (see Figure 5). Sixty-two labs reported results for the pH 1:1 H_2O and sixteen for pH 1:1 0.01 M $CaCl_2$. pH method medians differences range from 0.16 to 0.59 pH units, with the pH 1:1 0.01 M $CaCl_2$ consistently lower. For soil SRS-2203, pH 1:1 H_2O had higher intra-lab variability resulting in a MAD of 0.066 pH units, whereas the value for pH 1:1 0.01 M $CaCl_2$ was 0.035 pH units.

Across laboratories intra-lab precision, as noted by the length of the error bars, is consistently narrower for the pH 1:1 0.01 M $CaCl_2$ method.

Overall, there was greater inter-lab and intra-lab consistency for the soil pH 1:1 0.01 M $CaCl_2$ method.

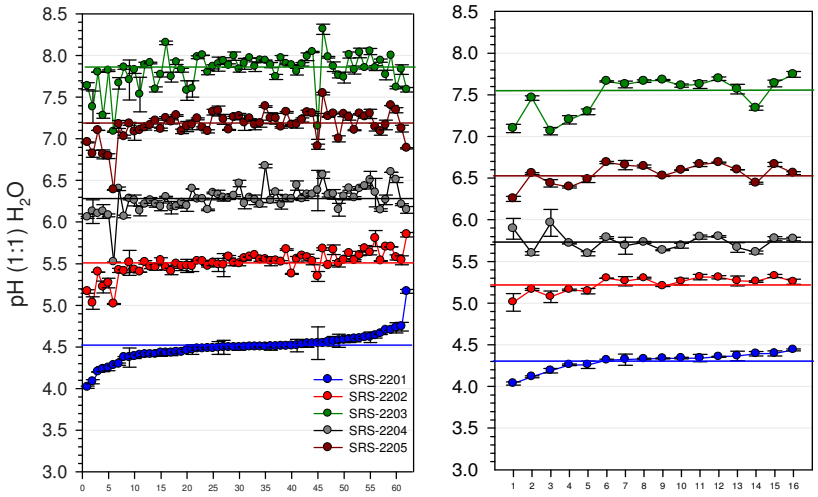


Figure 5. Comparison of two soil pH methods, Cycle 47.

SRB - NO_3-N

Twenty-six 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-2201 (see Figure 6). Lab #5 had extreme high results for SRS-2203. The data plot shows labs #24—#26 were bias high on three of four samples.

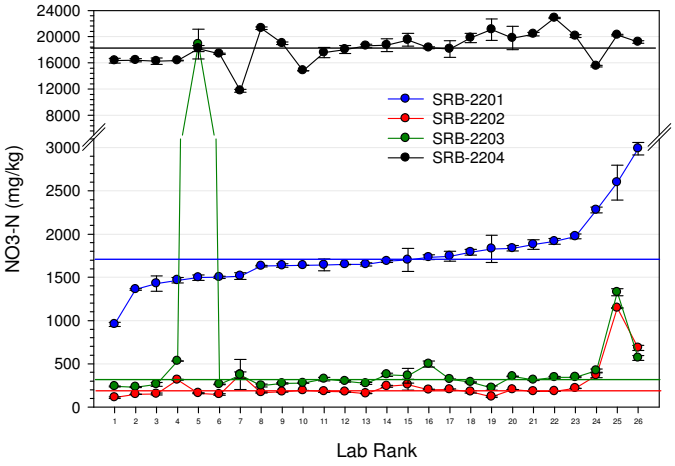


Figure 6. Nitrate distribution plots for SRB materials, ALP 2022, Cycle 47.

Botanical NO_3-N (test code 202) results for cycle 47 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 7.2 to 283 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-2201 ranged from 2.0 – 201 mg kg^{-1}; SRB-2202 ranged from 1.0 - 174 mg kg^{-1}, SRB-2203 ranged from 4 – 2253 mg kg^{-1} and SRB-2204 ranged from 86 1615 mg kg^{-1} Lab #15 had consistently high standard deviations for two of four samples. Three labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Forty-two laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and seven labs for TKN (Test code 209) for Cycle 47. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2201 (see Figure 7). Labs #5, #32 and #36 were inconsistent for SRB-2202 and SRS-2203 relative to SRB-2201. It is note worthy that TKN was inconsistent and lower than Dumas for SRB-2204.

Dumas N results indicate very high precision across all labs for all samples. Individual lab Dumas median N lab *s* values for SRB-2201, was 0.016% N, SRB-2202 was 0.015% N, SRB-2203 was 0.012% N, and SRB–2204 was 0.020% N. Lab #5 and #19 had consistently high standard deviations on three of four PT samples. Lab TKN median *s* values for SRB-2201 was 0.037%, SRB-2202 was 0.011% TKN, SRB-2203 was 0.035% TKN nitrogen and SRB-2204 was 0.049% TKN nitrogen.

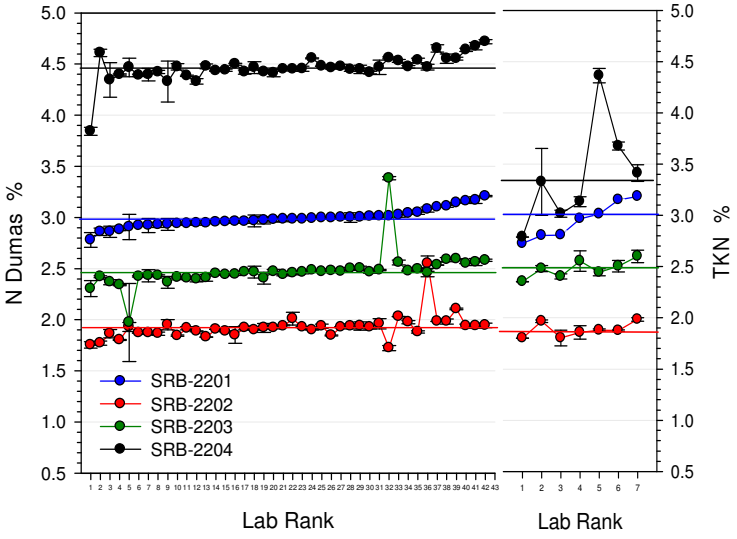


Figure 7. N distribution lab plots for SRB materials, ALP 2022 Cycle 47.

SRB - Phosphorus

Forty-five laboratories provided ALP results for Cycle 47 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-2201 (see Figure 8). Consistent high bias was noted for labs #42 - #45. Labs #9, #38 and #40 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-2201; ranged from 0.001 - 0.041% P; SRB-2202 ranged from 0.001 – 0.026 % P and SRB-2203 0.001 - 0.023 % P; and SRB-2204 0.001 - 0.062 % P. Lab #5 had a high standard deviation exceeding 0.041 % P on SRB-2201 PT sample. One lab was flagged for poor precision for botanical P for Cycle 47.

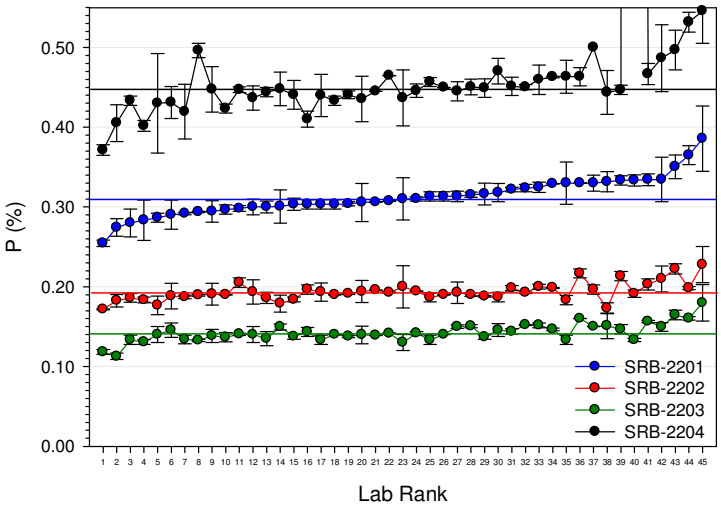


Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2022 Cycle

SRB - Potassium

Forty-five 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-2201 (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 K results indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 0.015 to 0.168 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2201, ranged from 0.001 - 0.303 % K; SRB-2202, 0.001 - 0.152 % K; SRB-2203, 0.002 - 0.322 % K; and SRS-2204, 0.001 - 0.901 % K. Lab #6 had high standard deviations exceeding 0.30 %K on three of four samples. One lab was flagged for poor K precision for Cycle 47.

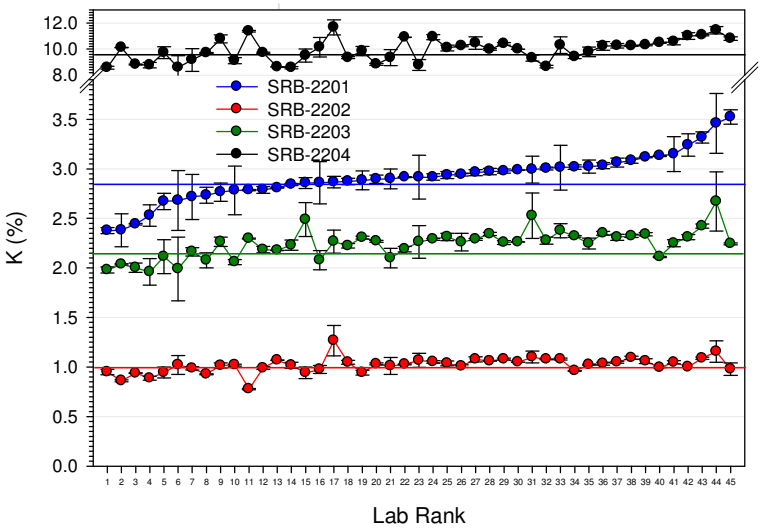


Figure 9. Potassium lab plot for SRB materials, ALP 2022 Cycle 47.

SRB - Magnesium

Forty-four laboratories provided ALP results for Magnesium (Mg) (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-2201 (see Figure 10). Across samples labs #43 and #44 exhibited high bias. Labs #4, #8, and #23 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Mg results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.002 to 0.011 % Mg for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2201; ranged from 0.001 - .028 % Mg; SRB-2202 ranged from 0.002 – 0.010 % Mg; SRB-2203 0.001 - 0.095 % Mg; and SRB-2204 0.001 - 0.040 % Mg. Lab #8 had consistently high standard deviations for three samples. One lab was flagged for poor Mg precision for Cycle 47.

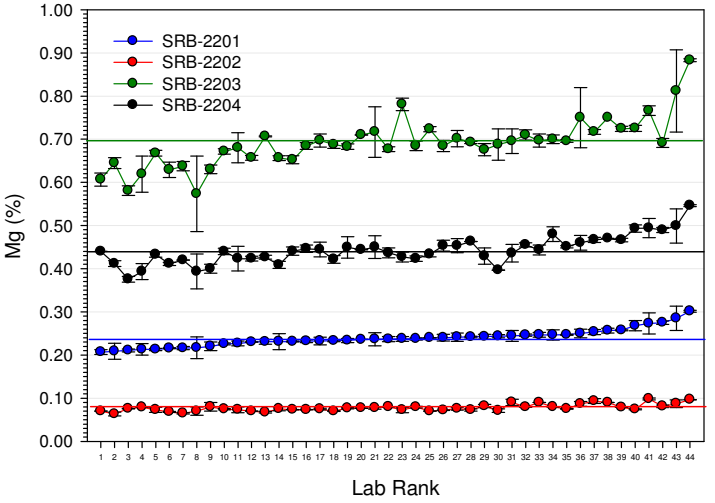
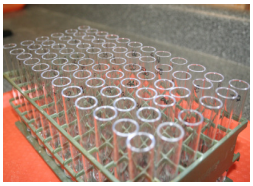


Figure 10. Magnesium (code 215) lab plots for SRB materials, ALP 2022 Cycle 47.

SRW - Water EC



Fourteen laboratories provided ALP results for water EC (test code 302). Lab result were ranked low to high based on sample SRW-2201 (see Figure 11). Sample SRW-2203 had the highest EC in Cycle 47. Lab #12 indicated in consistency across samples. Lab #14 had high bias on a;; three 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 Std values of 0.0003, 0.0004 and 0.003 dSm^{-1}, respectively. Precision for sample SRW-2201 was the most consistent across the fourteen participating laboratories. Intra-lab *s* values for lab #8 exceeded 0.006 dSm^{-1} on SRW-2202. Highest precision was noted for lab #10 with intra-lab *s* values of < than 0.0006 dSm^{-1} for all three samples.

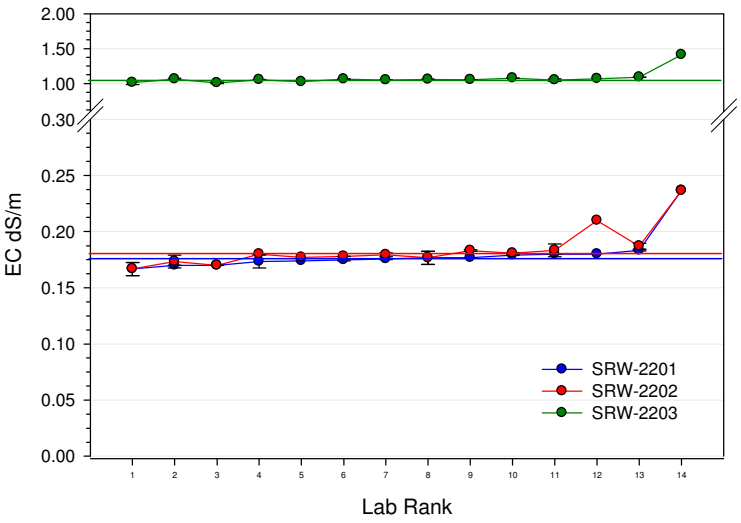


Figure 11 . Water EC distribution plots for SRW materials, ALP 2022 Cycle 47.

SRW - Mg Results

Fifteen laboratories provided ALP results for water Ma (test code 303). Lab results were ranked low to high based on sample SRW-2201 (see Figure 12) lowest in Na concentration. Median values are designated by horizontal lines. Labs #15 showed consistent high bias on two of thee samples, and is likely a result of a calibration error.

Na precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.005, 0.003, and 0.033 meq L^{-1} for SRW-2201, SRW-2202, and for SRW-2203, respectively. Water Mg precision was excellent for all individual labs with only labs #2 and #10 exceeding 0.05 meq L^{-1} Mg on two of the three samples. Two labs were flagged for poor precision on ALP Cycle 47 for Mg content.

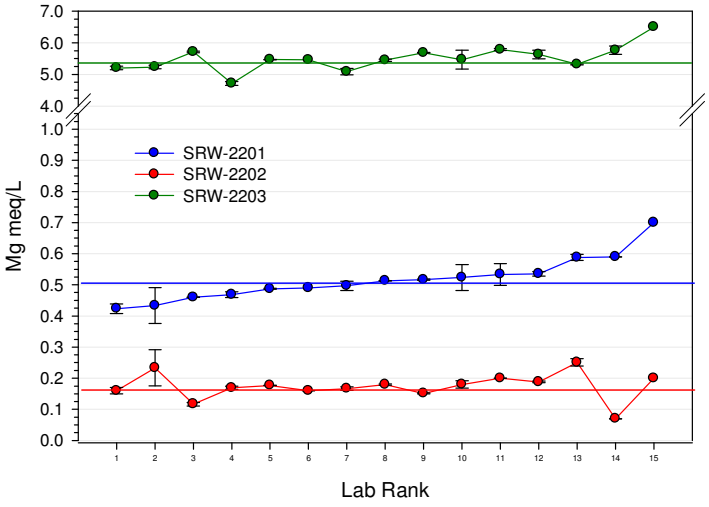


Figure 12. Water Mg distribution plots for SRW materials, ALP 2022 Cycle 47.

Announcements

- The ALP Program has been collaborating over the past year 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 2022 SERA-IEG 6 annual meeting will be held June 6-8, 2022 in Nashville, TN. Topics include, update on public lab testing in the region, hemp testing, a lab workshop on soil scooping and lab quality management. For more information contact Robert Florence at the University of Tennessee, RobertF@utk.edu.

- The Agricultural Laboratory Testing Association (ALTA) is planning a webinar on the 2nd edition of "Recommended Methods of Manure Analysis, 2nd edition", June 28, 2022. For more information contact the ALTA secretary, gfisher@unitedsoilsinc.com.

- ALTA will have their summer meeting August 29, 2022, in Des Moines, Iowa. Topics include presentations on optimizing Mehlich 3 ICP-OES soil analysis, consultants perspective on using plant-tissue analysis and development of LIBS for soil and plant analysis. 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 47. Since 2005 ALP has completed the analysis of 235 soils, 152 plant samples and 134 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 47. 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 48 Ship

June 22, 2022

"Science is the word we use to describe a method of organizing our curiosity"

– Tim Minchin, 2013

ALP
Agricultural Laboratory Proficiency Program