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ALP Program Report

2022 Fall - Cycle 49

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ALP Overview

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 49.
- Sixty-one Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.36 - 7.56.
- Soil Bray P for Cycle 49 ranged from 9.5 to 137 mg kg^{-1} with MAD values ranging 0.8 - 11.2 mg kg^{-1} across the five soils.
- Soil M3-K values ranged from 94 - 925 mg kg^{-1} for the five ALP soils of PT Cycle 49.
- Botanical N by combustion was reported by 34 labs, with three labs showing high bias values on for one PT material with > 3.0% N for Cycle 49.
- Botanical Total P, ranged from 0.110 - 1.16% with three of thirty-eight labs noted for inconsistency across the four samples.

The Agriculture Laboratory Proficiency (ALP) Program fall 2022 Round Cycle 49 was completed November 22, 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.

Inside this issue:

Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 49 were: SRS-2211 a loamy sand, from near Osoyoos, BC, Canada; SRS-2212 Cecil sandy clay loam collected Rowan Cty, NC; SRS-2213 a Delco loam collected from Power Cty ID; SRS-2214 is a Capac-Marlette loam collected in Clinton Cty, MI; and SRS-2215 a Goldridge fine sandy loam collected in Sonoma Cty, CA. Chemical properties of SRS materials ranged: pH (1:1) H_2O 5.36 - 7.56; SMP Buf 6.60 - 7.51 mg kg^{-1}; Bray P1 (1:1) 9.5 - 131 mg kg^{-1}; SO_4-S 7.2 - 100 mg kg^{-1}; M3-K 93.6 - 925 mg kg^{-1}; M3-Ca 781 - 4060 mg kg^{-1}; DTPA-Zn 0.71 - 3.81 mg kg^{-1}; SOM-LOI 1.39 – 3.18%; CEC 6.0 - 10.5 cmol kg^{-1}; sand 34.4 - 85.1% and NH_4-N 1.6 - 34.4 mg kg^{-1}.

Standard Reference Botanical (SRB) materials for Cycle 49 were: SRB-2209 millet flour from Canada; SRB-2210 mango leaf composite from Sri Lanka; SRB-2211 blueberry leaf composite from Washington State; and SRB-2212 a basil Leaves composite, Colorado. SRB median analytes ranged: NO_3-N 13.6 - 4370 mg kg^{-1}; Dumas N 1.48 - 6.29%; wet digestion total P 0.11 - 1.16%; total K 0.26 - 4.08%; total Ca 0.013 - 1.21%; total S 0.13 - 0.56%, total B 1.5 - 33.2 mg kg^{-1}; and total Cl 0.045 - 0.167%.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2207 is an irrigation well water collected Weld County, CO: SRW-2208 is a well water collected Denton, NE; and SRW-2209 was collected from an from an irrigation well Madison County, NE. SRW median concentrations: pH 7.63 - 8.47; EC 0.23 - 1.83 dSm^{-1}; SAR 0.30 - 1.71; Ca 1.6 - 8.43 mmolc L^{-1}; Na 0.31 - 4.85 mmolc L^{-1}; HCO_3 1.9 - 5.39 mmolc L^{-1}; and NO_3 0.22 - 0.61 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 49 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation 2022, Cycle 49.

Sample	pH (1:1) H_2O		EC (1:1) (dS m^{-1})		Olsen P (mg kg^{-1})		SOM-WB (%)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-2211	6.95	*0.02*	0.57	*0.02*	42.9	*2.0*	1.54	*0.08*
SRS-2212	5.52	*0.03*	0.53	*0.02*	4.7	*0.5*	3.17	*0.16*
SRS-2213	7.56	*0.03*	2.38	*0.02*	19.8	*1.0*	1.56	*0.07*
SRS-2214	7.24	*0.02*	0.61	*0.02*	53.5	*2.9*	3.87	*0.16*
SRS-2215	4.94	*4.94*	0.53	*0.04*	6.0	*0.6*	1.95	*0.08*

[1] Statistics based on five randomly selected soil replicates, each analyzed in triplicate ALP Cycle 49.

2022 Cycle 49 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis median intra-lab standard deviation values for Cycle 49 averaged 0.055 pH units across the five soils. Median. Soil Organic C values for the Cycle 49 ranged from 0..862 to 1.896% SOC. SRS-2209 had an abnormally high extractable M3-B (Test code 169) of 2.41 dSm^{-1}. M3-K MAD values ranged 7.3 - 25.8 mg kg^{-1} and M3-Mg MAD values ranged 7.5 to 17.7 mg kg^{-1} for the five soils. For ALP soil SRS-2215 M3-P the colorimetric intra-lab standard deviation was lower than values for the M3-ICP method. The lower M3-P colorimetric within lab standard deviation maybe related to the low Bray P1 content and/or cropping history of the collection site, a field in Sonoma Cty, California.

Across the four botanical samples Dumas combustion N MAD values averaged 0.045% nitrogen with intra-lab median *s* of 0.032%, 0.043%, 0.046% and 0.059%, respectively. Botanical sample SRB-2208 had a low median Cu with a concentration of 5.81 mg kg^{-1} and with a MAD of 0.40 mg kg^{-1}. The mango leaf composite sample SRB-2210 had low median concentrations of S, Zn, Mo, Cd, Co and Ni relative to the other three botanical samples. Consistent with past ALP cycles for 2022, Cycle 49 intra-lab relative variability results were lowest for combustion N than other macro elements across the four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC Median values ranged from 1.82, 0.771 and 0.233 dSm^{-1}, respectively. Na values ranged from 0.31 - 4.85 molc L^{-1} across the three ALP water samples with MAD values ranging 0.017 to 0.233 molc L^{-1}. Sample SRW-2207 had Cl 0.126 molc L^{-1} with a MAD of 0.113 molc L^{-1}.

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

Sixty-one laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.36 - 7.56. Lab results were ranked low to high based on sample SRS-2215 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-2211 and SRS-2212 showed good consistency across labs. Labs #1 #61 showed consistent high bias on all soils. Lab #13, #16 and #52 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.

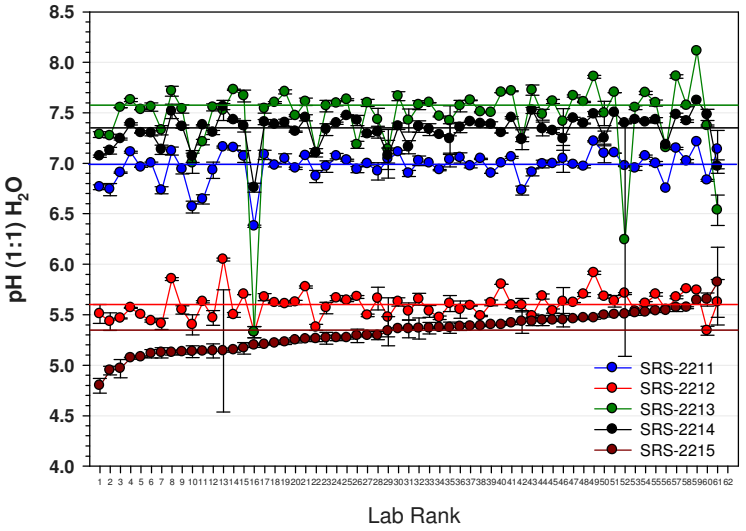

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2022 Cycle 49.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.017 to 0.026 pH units, the lowest noted for SRS-2211. Eight labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #13, #29, #33 #42, and #61 exceeded 0.10 pH units for SRS-2215. Soil SRS-2212 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-four labs. M3-P ICP was reported by 39 labs. Median soil Bray P1 values ranged from 9.5 - 137 mg kg^{-1} PO_4-P; Olsen P 7.5 to 54.8 mg kg^{-1} P; Bray P2 ranged from 14 to 486 mg kg^{-1} P; and M1-P from 5.3 to 416 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-2212, median Olsen P concentrations are shown in indicated in Figure 2. Soil SRS-2214, highest in concentration was variable between labs, where as SRS-2213 was highly consistent. Soils. Lab #1 had consistently low bias across four of five soils and labs # 38 and #39 had consistent high bias on four of five soils. Labs #21, #23, #30 and #33 were inconsistent across soils three of five soils.

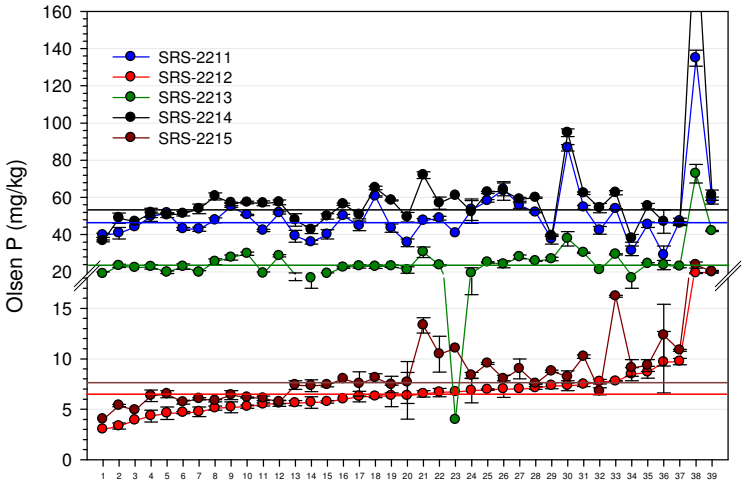

Figure 2. Olsen P distribution plots for SRS materials, ALP 2022 Cycle 49.

Six labs reported M3-P Spec median concentrations ranging 7.6 - 152 mg kg^{-1} P. Thirty-nine laboratories reported M3-P ICP with medians ranging 7.2–172 mg kg^{-1} P and two results for Modified Morgan P, with medians ranging from 3.2 - 223 mg kg^{-1} PO_4-P. Modified Kelowna was reported by two laboratories with median concentrations ranging from 6.4 - 102 mg kg^{-1} P and total P (US-EPA 503) ranged 345 - 1033 mg kg^{-1} P with the lowest concentration noted for SRS-2215.

SRS - Potassium

Thirty-three laboratories provided ALP results for soil M-3 K (test code 159) results. Results were ranked low to high based on sample SRS-2214 (see Figure 3) lowest in M3-K concentration. Lab results for lab #39 showed high bias for all soils. Labs #1, #2, #3, #11, and #24 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-2215, with a median intra-lab value of 1.1 mg kg^{-1} K and highest for SRS-2213 with a value of 8.9 mg kg^{-1}. M3-K within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 250 mg kg^{-1} K. Precision was poor (based on intra-lab *s*) for two labs which exceeded 25 mg kg^{-1} K on SRS-2212. Labs #18 and #30 had poor precision on three of five soils for Cycle 49. Poor precision is attributed to extraction and/or analysis instrument operation.

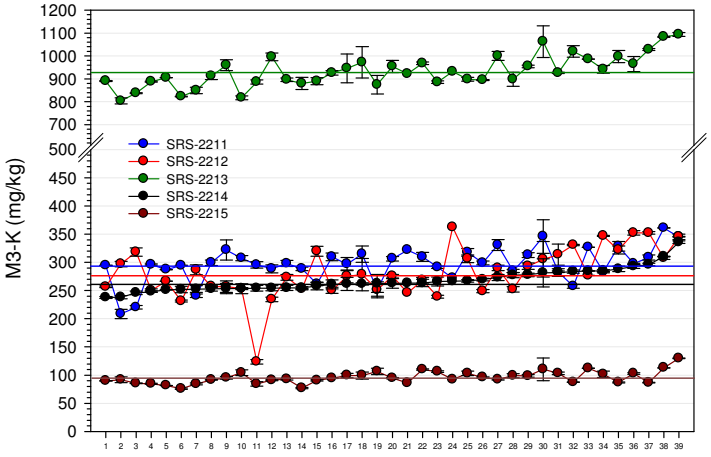

Figure 3. Extractable K distribution plots for SRS materials, ALP 2022 Cycle 49.

SRS - SOM-LOI

Forty-two laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 1.56 to 4.60%. Results were ranked based on sample SRS-2211 (see Figure 4). Samples SRS-2212 and SRS-2214 had high consistency. Labs #1 — #3 had low bias across all soils. Labs #16, #41 and #42 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 0.023 to 0.052% SOM-LOI, highest for SRS-2215. Across soils low precision was noted for several laboratories. Specifically *s* for labs #12, #35 #41, and #42, exceeded 0.20% SOM-LOI for SRS-2212. Seven labs were flagged for poor intra precision. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

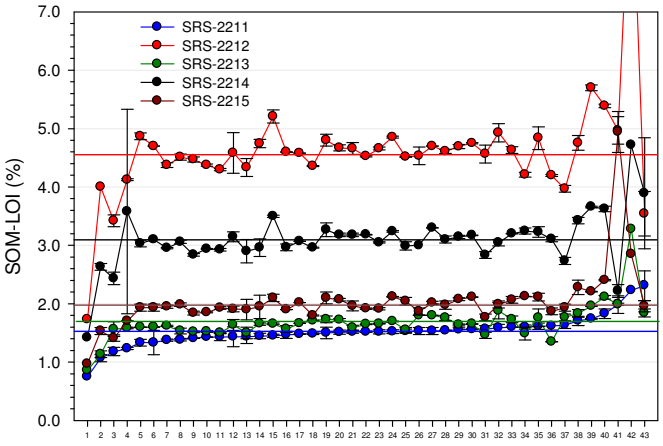

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2022 Cycle 49.

SRS M3-S

Thirty laboratories provided ALP results for soil M3-S (test code 163). Results were ranked low to high based on sample SRS-2215 (see Figure 5). Soil SRS-2211 was the most consistent across labs. Lab #30 had consistent high bias and #1 low bias on four of five soils. Across soils, labs #25, #28, # and #29 were inconsistent across soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

Soil M3-S median intra-lab *s* values were lowest for ALP soil SRS-2215 and SRS-2212, averaging 0.6 mg kg^{-1} and highest for SRS-2013 with a value of 3.3 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of labs #25, #27 and #28 on three of five soils. Intra-lab precision was very good for labs #2, #3, and #4, on all five soils with intra-lab s < 0.6 mg kg^{-1}. The high level of precision is likely associated with sample extraction, ICP instrument calibration and laboratory quality control quality assurance. Nine laboratories were flagged for poor precision over the five proficiency soils.

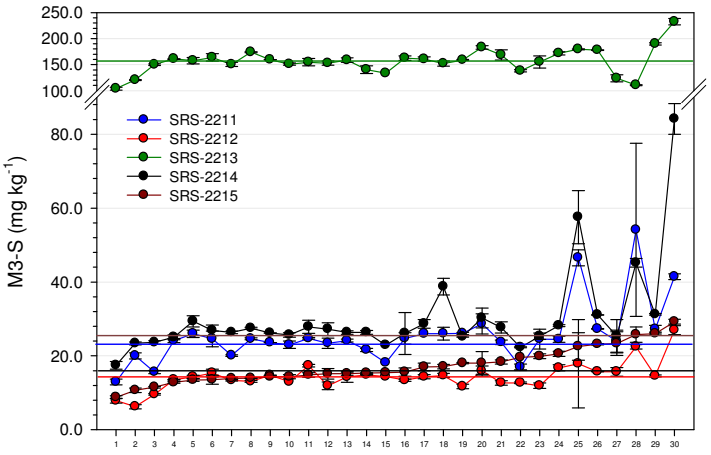

Figure 5. M3-S distribution plots for SRS materials, ALP 2022 Cycle 49.

SRB - NO_3-N

Twenty-two laboratories provided ALP results for NO_3-N by cadmium reduction, ISE and other (test codes 202, 203 and 204). Lab analysis values for cadmium reduction are designated by horizontal lines for each of the four botanical materials labs based on sample SRB-2209 (see Figure 6). Labs #15 had extreme high results for three of four PT samples. Labs #10, #13, and #15 were inconsistent across the four samples.

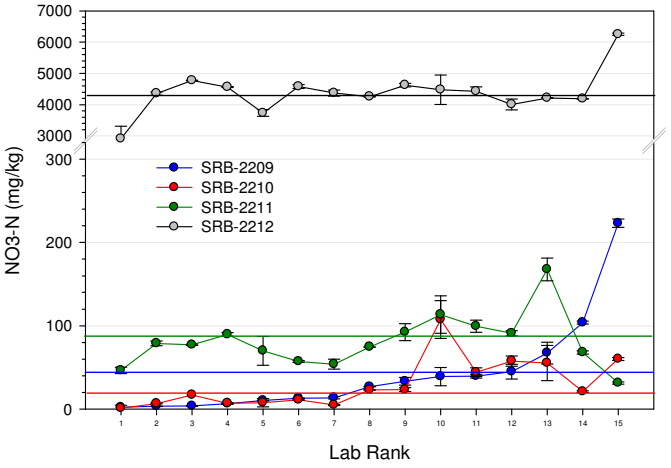

Figure 6. Nitrate distribution plots for SRB materials, ALP 2022, Cycle 49.

Botanical NO_3-N (test code 202) results for Cycle 49 indicate poor precision, with intra-lab median standard deviation (*s*) values ranging from 1.0 to 3.0 mg kg^{-1} on thee three samples with less 300 mg kg^{-1} NO_3-N. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-2209 ranged from 0.3 – 13 mg kg^{-1}; SRB-2210 ranged from 0.2 - 23 mg kg^{-1}, SRB-2211 ranged from 0.7 – 22 mg kg^{-1} and SRB-2212 ranged from 4.3 - 473 mg kg^{-1}. Lab #5, #10 and #13 had consistently high standard deviations for three of four samples. Seven labs were flagged for poor precision across the four samples.

SRB - Dumas Nitrogen and TKN

Thirty-four laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and eight labs for TKN (Test code 209) for Cycle 49. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2210 (see Figure 7). Labs #1, #33 and #34 were inconsistent for SRB-2209 and SRS-2204 relative to SRB-2208. It is note worthy that TKN was inconsistent and lower than Dumas for SRB-2212.

Dumas N results indicate very high intra-lab precision across all labs for all samples. Individual lab Dumas N median lab *s* values for SRB-2209, was 0.015 N, SRB-2210 was 0.012% N, SRB-2211 was 0.015% N, and SRB–2212 was 0.031% N. Lab #12, #20 and #31 had consistently high standard deviations on three of four PT samples. Lab TKN median *s* values for SRB-2209 was 0.017%, SRB-2210 was 0.013% TKN, SRB-2211 was 0.011% TKN nitrogen and SRB-2212 was 0.032% TKN nitrogen.

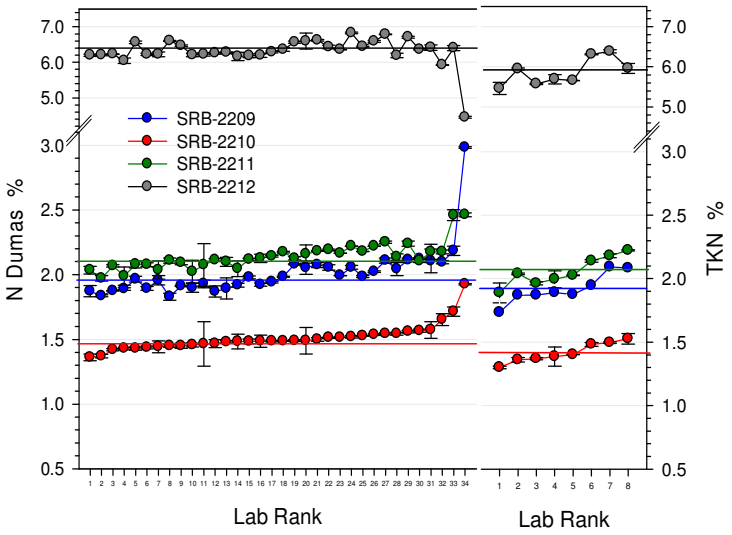

Figure 7. N distribution lab plots for SRB materials, ALP 2022 Cycle 49.

SRB - Phosphorus

Forty-two laboratories provided ALP results for Cycle 49 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-2210 (see Figure 8). Consistent high bias was noted for labs #37 and #38. Labs #1 and #28 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 0.016 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-2209; ranged from 0.001 - 0.033% P; SRB-2210 ranged from 0.001 – 0.025 % P and SRB-2211 0.001 - 0.010 % P; and SRB-2212 0.004 - 0.131 % P. Lab #22 and #31 had a high standard deviation exceeding 0.100 % P on SRB-2212 PT sample. Six lab results were flagged for poor precision for botanical P for Cycle 49.

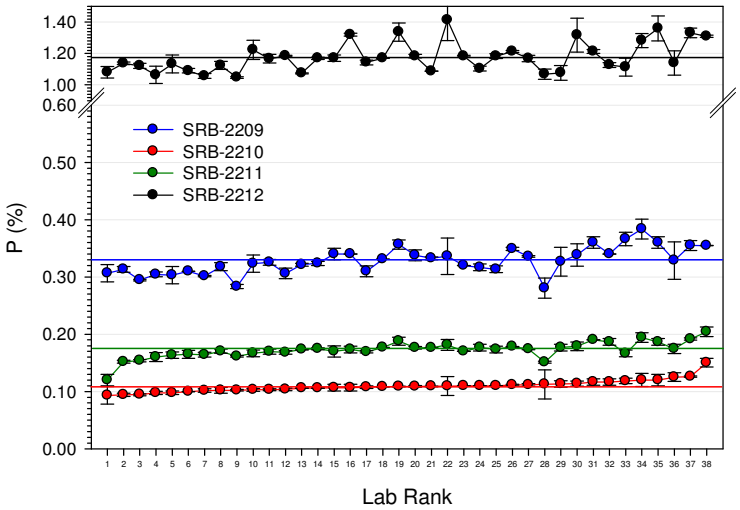

Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2022 Cycle

SRB - Potassium

Thirty-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-2209 lowest in concentration (see Figure 9). Labs #3, #22, #30, and #37 were inconsistent across the four botanical samples. 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 0.006 to 0.040 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2209, ranged from 0.001 - 0.065 % K; SRB-2210, 0.001 - 0.094 % K; SRB-2211, 0.001 - 0.064 % K; and SRS-2212, 0.003 - 0.443 % K. Lab #31 had high standard deviations exceeding 0.07 %K on three of four samples. Six lab results were flagged for poor botanical K precision Cycle 49.

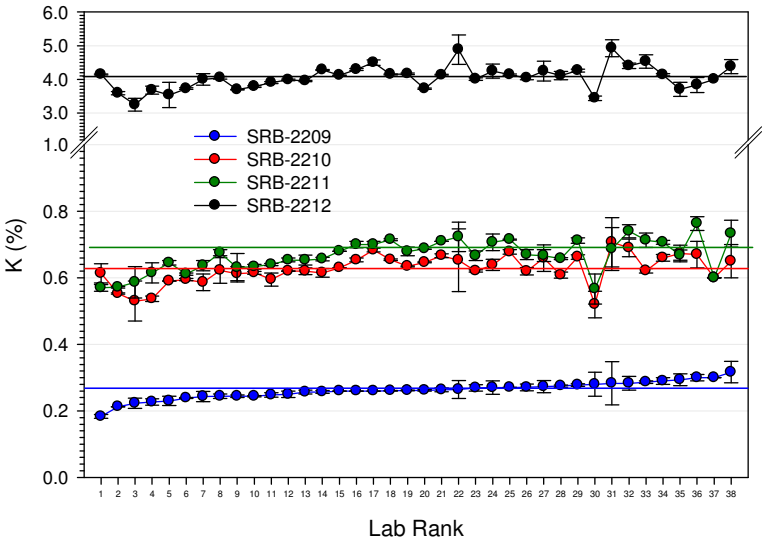

Figure 9. Potassium lab plot for SRB materials, ALP 2022 Cycle 49.

SRB - Calcium

Thirty-six laboratories provided ALP results for calcium (Ca) (test code 214). 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-2209 (see Figure 10). Across samples labs #30—37 exhibited high bias for SRS-2209. Labs #1, #21, and #25 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Ca results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.001 to 0.038 % Ca for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2209; ranged from 0.001 - 0.053 % Ca; SRB-2210 ranged from 0.010 – 0.361 % Ca; SRB-2211 0.003 - 0.046 % Ca; and SRB-2212 0.006 - 0.241 % Ca. Lab #13 had consistently high standard deviations for three samples. Six lab results were flagged for poor precision for botanical Ca for Cycle 49.

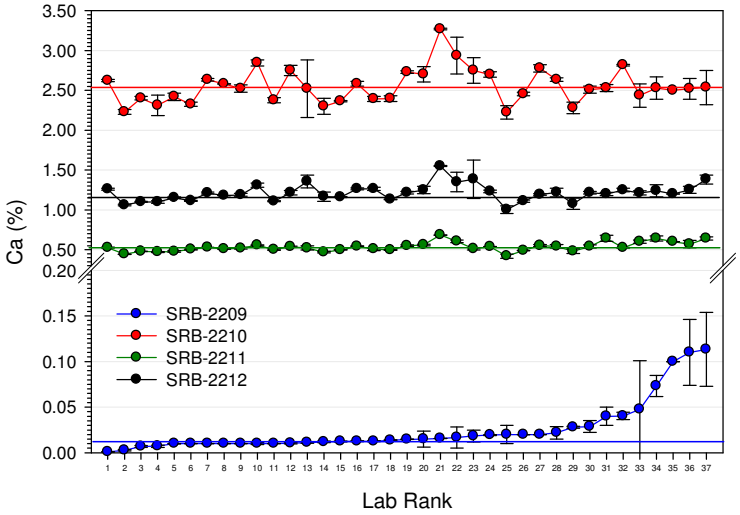

Figure 10. Calcium (code 214) lab plots for SRB materials, ALP 2022 Cycle 49.

SRW - Water EC

Seventeen laboratories provided ALP results for water EC (test code 302). Lab result were ranked low to high based on sample SRW-2209 (see Figure 11). Sample SRW-2207 had the highest EC in Cycle 49. Lab #3 indicated inconsistency on sample SRW-2207 and SRW-2208. Source of bias and inconsistency 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 standard deviation values of 0.012, 0.006 and 0.0004 dSm^{-1}, respectively. Precision for sample SRW-2207 was the most consistent across the seventeen participating laboratories. Intra-lab s values for labs #3, #10 and #12 exceeded 0.04 dSm^{-1} on SRW-2207. Highest precision was noted for lab #11 with intra-lab s values of < than 0.002 dSm^{-1} for all three water samples.

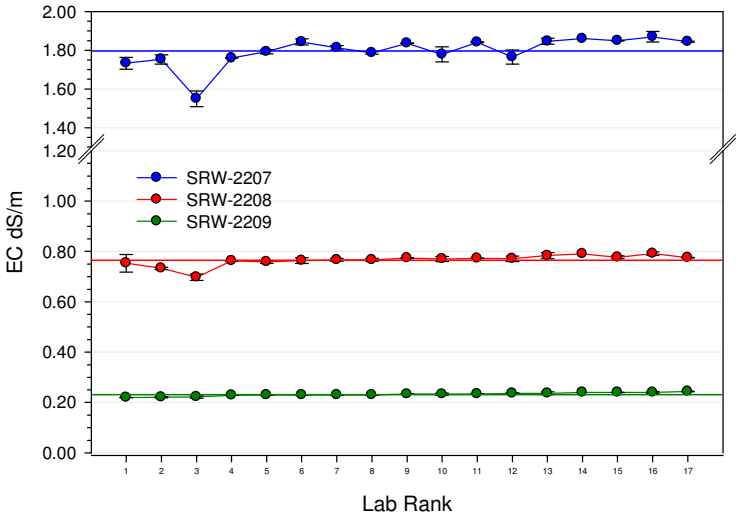

Figure 11 . Water EC distribution plots for SRW materials, ALP 2022 Cycle 49.

SRW - Ca Results

Seventeen laboratories provided ALP results for water Ca (test code 303). Lab results were ranked low to high based on sample SRW-2209 (see Figure 12) lowest in Ca concentration. Median values are designated by horizontal lines. Lab #1 showed low bias and #7 showed consistent high bias on all three samples, and is likely a result of a calibration error.

Ca precision across the three water solution matrices indicates excellent precision, with intra-lab s values of 0.091, 0.042, and 0.051 meq L^{-1} for SRW-2207, SRW-2208, and for SRW-2209, respectively. Water Ca precision was excellent for all individual labs with only labs #3, #8 and #13 exceeding 0.35 meq L^{-1} Ca on sample SRW-2207. Five labs were flagged for poor precision across all three samples for Cycle 49.

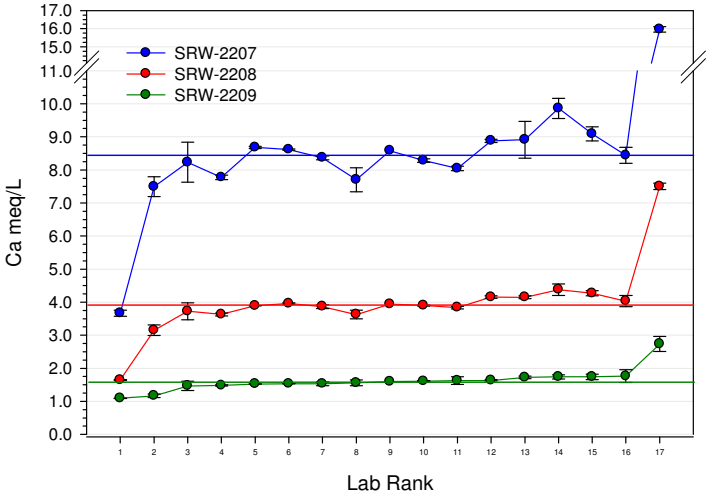

Figure 12. Water Ca distribution plots for SRW materials, ALP 2022 Cycle 49.

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 soil method codes for reporting soil proficiency test results later this year. More information can be found www.aggateway.org/Portals/.

- Mid-Atlantic Soil and Plant Analysis Working Group (MASTPAWG), Will be held February 22-23, Embassy Suites by Hilton Raleigh Crabtree, North Carolina. To register visit: https://www.eventbrite.com/e/mid-atlantic-soil-plant-analysis-working-group-mastpawg-registration-445440613867

- The Agricultural Laboratory Testing Association (ALTA) will have their winter meeting March 1, 2023, in Lafayette, Indiana. Topics included presentations on optimizing Mehlich 3 ICP-OES soil analysis, report on FRST lime project and development of LIBS for soil and plant analysis. For more information can be found at ALTA.Ag.

- The 17th International Symposium on Soil and Plant Analysis (ISSPA) will be in Concepción, Chile the March 17-21, 2023. The symposium will cover recent developments in laboratory analysis/recommendations. https://isspa2023.cl/venue-isspa-2023/

- 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 49. Since 2005 ALP has completed the analysis of 245 soils, 160 plant samples and 140 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 49. 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 50 Ship

March 15, 2023

"An expert is a person who has made all the mistakes that can be made in a very narrow field." – Neils Bohr, 1870

ALP
Agricultural Laboratory Proficiency Program