2022 Volume 2

31August 2022

ALP Program Report

2022 Summer - Cycle 48

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ALP Overview

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 48.
- Sixty-one Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.37 - 8.30.
- Soil Bray P for Cycle 48 ranged from 2.0 to 26.9 mg kg^{-1} with MAD values ranging 0.8 - 2.1 mg kg^{-1} across the five soils.
- Soil M3-K values ranged from 74 - 535 mg kg^{-1} for the five ALP soils of PT Cycle 48.
- Botanical N by combustion was reported by 37 labs, with three labs showing high bias values on for two PT materials with > 2.5% N for Cycle 48.
- Botanical Total P, ranged from 0.098 - 0.039% with two of forty labs noted for inconsistency across the four samples.

The Agriculture Laboratory Proficiency (ALP) Program fall 2022 Round Cycle 48 was completed August 31, 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.

Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 48 were: SRS-2206 a clay, from Division #2, near Lethbridge, AB, Canada; SRS-2207 Maury-Urban land complex, loam collected Davidson Cty, TN; SRS-2208 a Harkey very fine sandy loam collected from Eddy Cty NM; SRS-2209 is a Thurman loamy fine sand collected in Madison Cty, NE; and SRS-2210 a Volusia Channery silt loam collected in Wayne Cty, PA. Chemical properties of SRS materials ranged: pH (1:1) H_2O 5.37 - 8.30; Sikora Buf 6.81 - 7.16 mg kg^{-1}; Bray P1 (1:10) 2.0 - 26.9 mg kg^{-1}; M3-K 74 - 535 mg kg^{-1}; M3-Ca 1035 - 8714 mg kg^{-1}; DTPA-Zn 0.41 - 1.00 mg kg^{-1}; SOM-LOI 0.89 – 3.37%; CEC 5.8 - 28.5 cmol kg^{-1}; clay 11.0 - 43.7% and NO_3-N 5.4 - 34.3 mg kg^{-1}.

Standard Reference Botanical (SRB) materials for Cycle 48 were: SRB-2205 grape blade composite from CA; SRB-2206 corn a V6 plant composite from WI; SRB-2207 banana leaf composite from Sri Lanka; and SRB-2208 a spruce needle composite, Colorado. SRB median analytes ranged: NO_3-N 23.3 - 4283 mg kg^{-1}; Dumas N 1.10 - 3.71%; wet digestion total P 0.098 - 0.39%; total K 0.37 - 2.49%; total Ca 0.63 - 2.00%; total S 0.92 - 0.32%, total Cu 2.4 - 23.9 mg kg^{-1}; and total Cl 0.047 - 0.25%.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2204 is an irrigation water sample provided by Nick Ward, Kearney, NE: SRW-2205 is an artificial water matrix sample; and SRW-2206 was collected from an from an irrigation ditch Tinmath, CO. SRW median concentrations: pH 7.70 - 7.96; EC 0.33 - 1.41 dSm^{-1}; SAR 0.60 - 1.79; Ca 1.4 - 5.57 mmolc L^{-1}; Na 0.69 - 3.50 mmolc L^{-1}; HCO_3 1.16 - 5.37 mmolc L^{-1}; and NO_3 0.037 - 7.91 mmolc L^{-1}.

Inside this issue:

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 48 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation 2022, Cycle 48.

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-2206	7.21	*0.01*	10.9	*0.4*	20.9	*2.1*	3.49	*0.10*
SRS-2207	5.80	*0.03*	8.1	*0.7*	38.4	*3.8*	3.25	*0.09*
SRS-2208	8.11	*0.01*	8.3	*0.5*	21.9	*2.0*	1.92	*0.14*
SRS-2209	5.21	*0.03*	4.3	*0.3*	5.5	*0.8*	1.28	*0.08*
SRS-2210	6.76	*0.02*	7.6	*0.6*	19.4	*0.7*	1.08	*0.11*

[1] Statistics based on six randomly selected soil replicates, each analyzed in triplicate ALP Cycle 48.

2022 Cycle 48 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis median intra-lab standard deviation values for Cycle 48 averaged 0.025 pH units across the five soils. Median. Soil Organic C values for the cycle 48 ranged from 0.482 to 3.815% SOC. SRS-2209 had an abnormally low extractable EC 1:1 (Test code 114) of 0.096 dSm^{-1}, likely associated with loamy sand soil series and low NO_3-N. M3-K MAD values ranged 4.3 - 26.9 mg kg^{-1} and M3-Mg MAD values ranged 70.7 to 40.3 mg kg^{-1} for the five soils. For ALP soil SRS-2207 M3-P the colorimetric intra-lab standard deviation was consistently 80% lower than values for the M3-ICP method. The lower M3-P colorimetric within lab standard deviation for SRSR-2207 maybe related to the low Bray P2 content and/or cropping history of the collection site, a field in Davidson Cty, Tennessee.

Across the four botanical samples Dumas combustion N MAD values averaged 0.056% nitrogen with intra-lab median *s* of 0.048%, 0.044%, 0.043% and 0.037%, respectively. Botanical sample SRB-2208 had a low median Cu with a concentration of 2.72 mg kg^{-1} and with a MAD of 0.27 mg kg^{-1}. The banana leaf composite sample SRB-2207 had low median concentrations of NO_3-N, NH_4-N, Cl, SO_4-S, Na and Ni relative to the other three botanical samples. Consistent with past ALP cycles for 2022, cycle 48 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 0.33, 1.10 and 1.39 dSm^{-1}, respectively. Na values ranged from 0.69 - 3.49 molc L^{-1} across the three ALP water samples with MAD values ranging 0.026 to 0.128 molc L^{-1}. Sample SRW-2204 had Cl 0.148 molc L^{-1} with a MAD of 0.015 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 5.37 - 8.30. Lab results were ranked low to high based on sample SRS-2209 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-2206 and SRS-2209 showed good consistency across labs. Labs #1 #2, #4 and #5 showed consistent high bias on all soils. Labs #13, #26, #35 and #58 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.

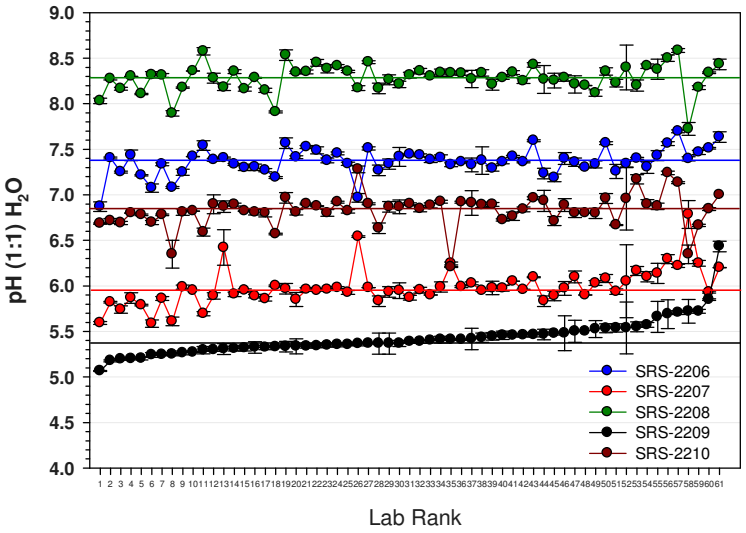

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2022 Cycle 48.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.023 to 0.028 pH units, the lowest noted for SRS-2206. Eleven labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #13, #52 #55, and #58 exceeded 0.10 pH units for SRS-2207. Soil SRS-2206 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-three labs. M3-P ICP was reported by 40 labs. Median soil Bray P1 values ranged from 2 - 23 mg kg^{-1} PO_4-P; Olsen P 5.5 to 13.3 mg kg^{-1} P; Bray P2 ranged from 24 to 92 mg kg^{-1} P; and M1-P from 11.8 to 67.4 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-2210, median Bray P1 concentrations are shown in indicated in Figure 2. Soil SRS-2210, highest in concentration was variable between labs, where as SRS-2208 was highly consistent. Soils. Lab #1 had consistently low bias across all five soils and lab #23 has consistent high bias on four of five soils. Labs #9, #10, #11 , #14 and #19 were inconsistent across soils three of five soils.

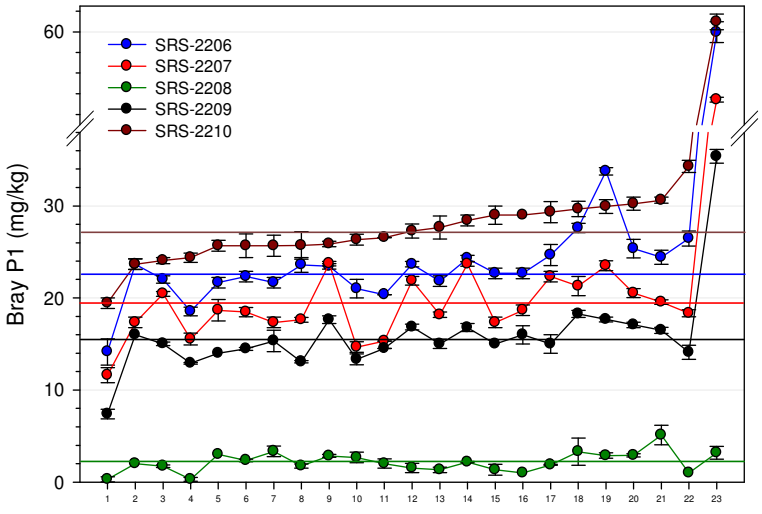

Figure 2. Bray P1 distribution plots for SRS materials, ALP 2022 Cycle 48.

Six labs reported M3-P Spec median concentrations ranging 15.6 - 41.8 mg kg^{-1} P. Nine laboratories reported Bray P2 with medians ranging 24.4–92 mg kg^{-1} P and three results for Modified Morgan P, with medians ranging from 1.4 - 32 mg kg^{-1} PO_4-P. Modified Kelowna was reported by two laboratories with median concentrations ranging from 11.1 - 24.5 mg kg^{-1} P and total P (US-EPA 503) ranged 193 - 555 mg kg^{-1} P with the lowest concentration noted for SRS-2209.

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-2209 (see Figure 3) lowest in M3-K concentration. Lab results for lab #40 showed high bias for all soils. Labs #1, #2, #3, #19, #23 and #39 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-2210, with a median intra-lab value of 1.4 mg kg^{-1} K and highest for SRS-2206 with a value of 5.6 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 20 mg kg^{-1} K on SRS-2208. Labs #11 and # 23 had poor precision on three of five soils for cycle 48. Poor precision is attributed to extraction and/or analysis instrument operation.

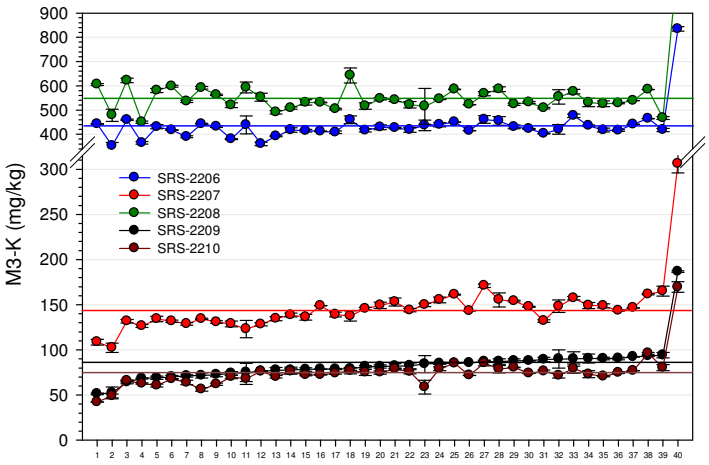

Figure 3. Extractable K distribution plots for SRS materials, ALP 2022 Cycle 48.

SRS - SOM-LOI

Forty-four laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 1.24 to 4.10%. Results were ranked based on sample SRS-2206 (see Figure 4). Sample SRS-2206 had high consistency. Labs #1 and #2 had low bias across all soils. Labs #3, #8 and #44 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 0.026 to 0.057% SOM-LOI, highest for SRS-2206. Across soils low precision was noted for several laboratories. Specifically *s* for labs #2, #4, #5, and #35, exceeded 0.20% SOM-LOI for SRS-2207. Lab #5 had poor precision on four of five soils. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

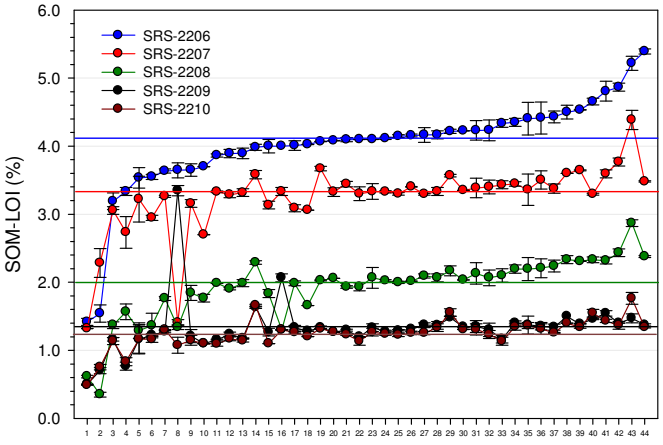

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2022 Cycle 48.

ALP Soil comparison

ALP proficiency soil SRS-2206 was previously submitted four years ago in cycle 37 as SRS-1812. A limited comparison of results are shown in Table 2. Results indicate more than 99% of the analysis methods evaluated, were within the inter-lab measurement error as measured by the MAD. For specific analyses, EC, NO_3-N, K, Cl, SOM-LOI and SOC the median values were reproducible to two significant digits. Only results for DTPA extractable Mn indicated an increase in concentration, likely associated with oxidation of Mn^{+2} to Mn^{+4} while the soil was in storage.

These results verify air dried (moisture content < 3%) proficiency soils, are stable for periods of four years with no changes in the concentration of total and/or extractable analytical results; and ALP soil proficiency statistical median and MAD results are highly reproducible.

Table 2. ALP soil result comparison, SRS-1822 vs SRS-2206.

		SRS-1812		SRS-2206	
Analysis	Unit	Median	MAD	Median	MAD
EC (1:1)	dS/m	0.647	0.076	0.643	0.040
pH (1:1) H_2O		7.25	0.06	7.37	0.07
NO_3-N	mg kg^{-1}	19.2	1.2	19.0	0.90
Bray-P	mg kg^{-1}	21.2	1.5	23.0	1.4
M3-P ICP	mg kg^{-1}	27.2	1.7	29.2	1.3
K $_{NH4Ac}$	mg kg^{-1}	423	19	425	26
M3-K	mg kg^{-1}	419	15	422	16
DTPA-Mn	mg kg^{-1}	62.8	2.9	81.8	6.9
Cl	mg kg^{-1}	21.5	1.4	21.8	1.8
SOM-LOI	%	4.15	0.23	4.10	0.24
SOC	%	1.963	0.067	1.984	0.113

ALP SRS-1812, a clay soil collected near Lethbridge, AB, Canada.

SRB - NO_3-N

Twenty-three laboratories provided ALP results for NO_3-N by cadmium reduction and ISE (test codes 202 and 203). Median values are designated by horizontal lines for each of the four botanical materials labs based on sample SRB-2205 (see Figure 6). Labs #20-#23 had extreme high results for three of four PT samples. Lab # 16 was inconsistent across the four samples.

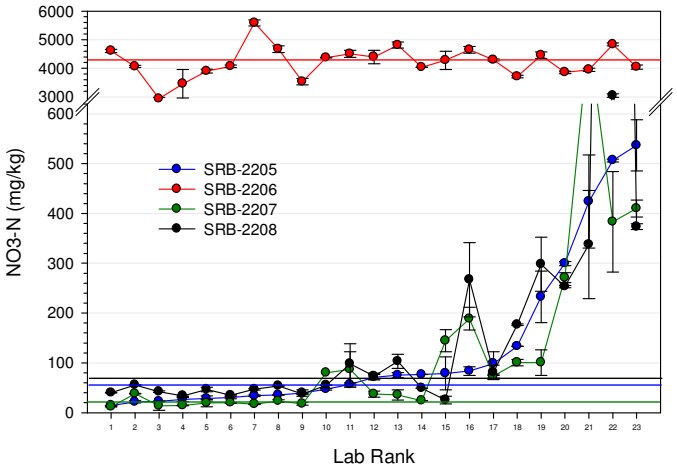

Figure 6. Nitrate distribution plots for SRB materials, ALP 2022, Cycle 48.

Botanical NO_3-N (test code 202) results for cycle 48 indicate poor precision, with intra-lab median standard deviation (s) values ranging from 14 to 36 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-2204 ranged from 0.1 – 51 mg kg^{-1}; SRB-2205 ranged from 15 - 494 mg kg^{-1}, SRB-2206 ranged from 0.6 – 134 mg kg^{-1} and SRB-2208 ranged from 0.3—108 mg kg^{-1} Lab #18, #22 and #23 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-seven laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and seven labs for TKN (Test code 209) for Cycle 48. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2208 (see Figure 7). Labs #1, #17 and #24 were inconsistent for SRB-2205 and SRS-2204 relative to SRB-2208. It is note worthy that TKN was inconsistent and lower than Dumas for SRB-2206.

Dumas N results indicate very high precision across all labs for all samples. Individual lab Dumas median N lab *s* values for SRB-2205, was 0.015 N, SRB-2206 was 0.018% N, SRB-2207 was 0.012% N, and SRB–2208 was 0.011% N. Lab #2 and #3 had consistently high standard deviations on three of four PT samples. Lab TKN median *s* values for SRB-2205 was 0.061%, SRB-2206 was 0.038% TKN, SRB-2207 was 0.026% TKN nitrogen and SRB-2208 was 0.015% TKN nitrogen.

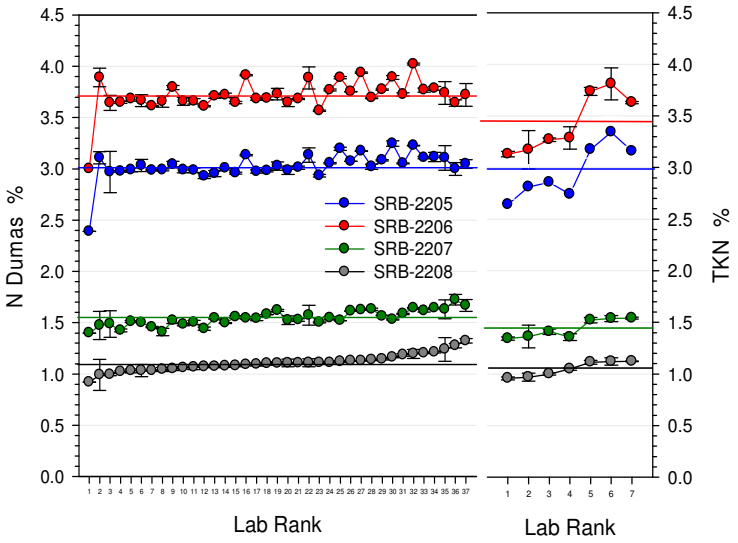

Figure 7. N distribution lab plots for SRB materials, ALP 2022 Cycle 48.

SRB - Phosphorus

Forty-two laboratories provided ALP results for Cycle 48 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-2207 (see Figure 8). Consistent high bias was noted for labs #41 and #42. Labs #10, and #23 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 0.004 to 0.014 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-2205; ranged from 0.001 - 0.044% P; SRB-2206 ranged from 0.001 – 0.061 % P and SRB-2207 0.001 - 0.021 % P; and SRB-2208 0.001 - 0.036 % P. Lab #10 had a high standard deviation exceeding 0.041 % P on SRB-2206 PT sample. Seven lab results were flagged for poor precision for botanical P for cycle 48.

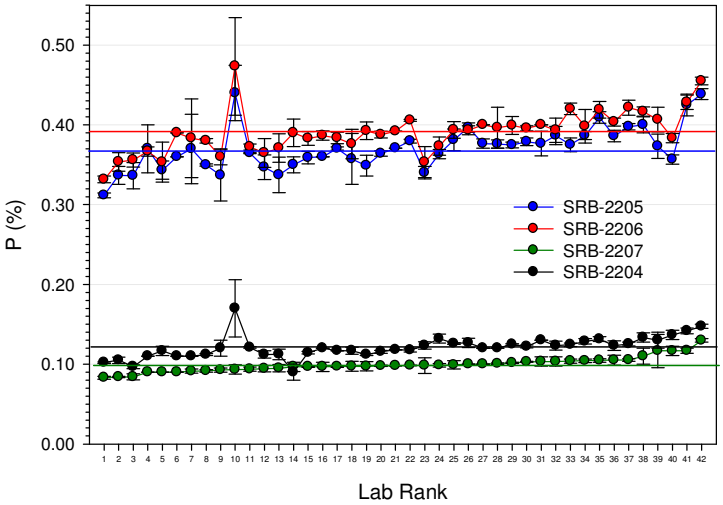

Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2022 Cycle

SRB - Potassium

Forty-two 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-2208 lowest in concentration (see Figure 9). Labs #1, #6, #21, #27, and #38 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 0.021 to 0.061 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2205, ranged from 0.001 - 0.144 % K; SRB-2206, 0.008 - 0.200 % K; SRB-2207, 0.006 - 0.127 % K; and SRS-2208, 0.003 - 0.127 % K. Lab #42 had high standard deviations exceeding 0.07 %K on three of four samples. Five lab results were flagged for poor botanical K precision cycle 48.

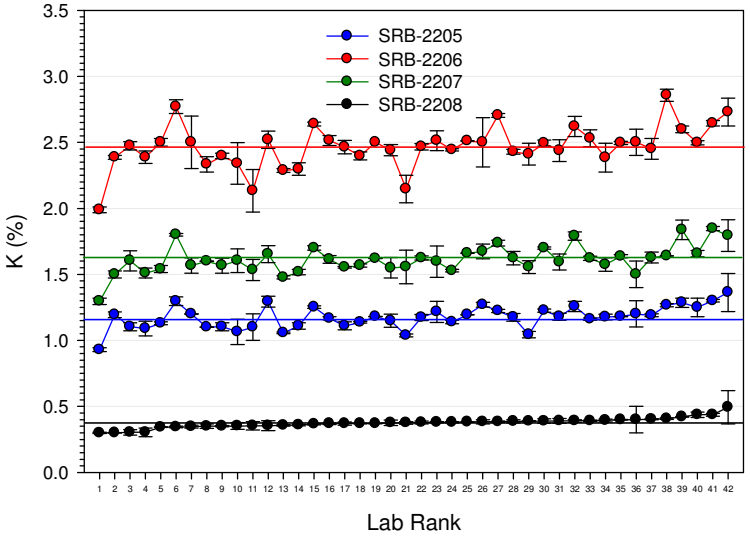

Figure 9. Potassium lab plot for SRB materials, ALP 2022 Cycle 48.

SRB - Manganese

Forty 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-2208 (see Figure 10). Across samples lab #40 exhibited high bias. Labs #1, #2, #9 and #28 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 1.6 to 27.2 mg kg^{-1} Mn for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2205; ranged from 0.19 - 22.0 mg kg^{-1} Mn; SRB-2206 ranged from 0.28 – 6.5 mg kg^{-1} Mn; SRB-2207 08 - 102 mg kg^{-1} Mn; and SRB-2208 0.10 - 5.4 mg kg^{-1} Mn. Lab #39 had consistently high standard deviations for three samples. Six lab results were flagged for poor precision for botanical Mn for cycle 48..

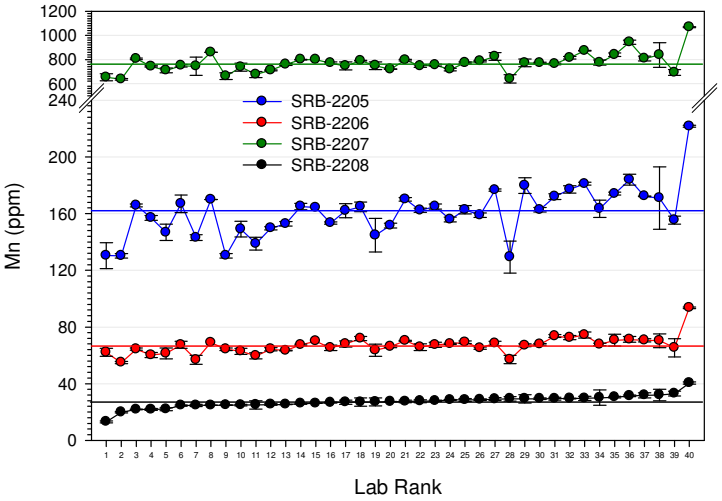

Figure 10. Manganese (code 221) lab plots for SRB materials, ALP 2022 Cycle 48.

SRW - Water EC

Fifteen laboratories provided ALP results for water EC (test code 302). Lab result were ranked low to high based on sample SRW-2204 (see Figure 11). Sample SRW-2206 had the highest EC in cycle 48. Lab #2 indicated inconsistency on sample SRW-2206. Lab #15 had high bias on all 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 0.003, 0.007 and 0.012 dSm^{-1}, respectively. Precision for sample SRW-2204 was the most consistent across the fifteen participating laboratories. Intra-lab *s* values for lab #10 exceeded 0.015 dSm^{-1} on SRW-2205. Highest precision was noted for lab #12 with intra-lab *s* values of < than 0.002 dSm^{-1} for all three samples.

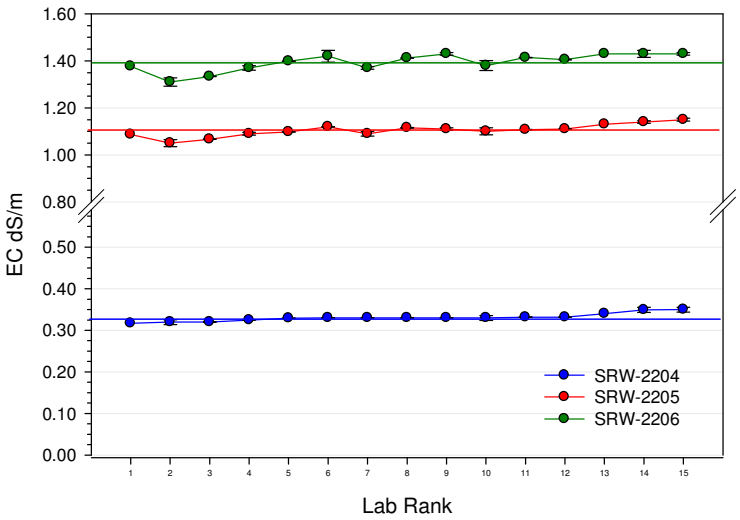

Figure 11 . Water EC distribution plots for SRW materials, ALP 2022 Cycle 48.

SRW - Na Results

Sixteen laboratories provided ALP results for water Na (test code 303). Lab results were ranked low to high based on sample SRW-2204 (see Figure 12) lowest in Na concentration. Median values are designated by horizontal lines. Labs #16 showed consistent high bias on all three 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 0.030, 0.0118, and 0.097 meq L^{-1} for SRW-2204, SRW-2205, and for SRW-2206, respectively. Water Na precision was excellent for all individual labs with only labs #9 and #16 exceeding 0.07 meq L^{-1} Na on two of the three samples. Five labs were flagged for poor precision across all three samples for cycle 48.

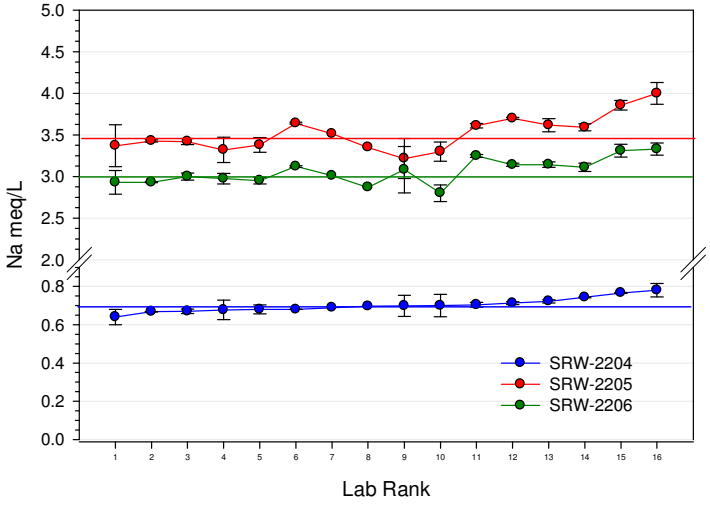

Figure 12. Water Na distribution plots for SRW materials, ALP 2022 Cycle 48.

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/.

- ALTA had their summer meeting August 29, 2022, in Des Moines, Iowa. 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/

- The Agricultural Laboratory Testing Association (ALTA) is planning their winter laboratory meeting scheduled for March 1, 2023 at Purdue University For more information contact the ALTA secretary, gfisher@unitedsoilsinc.com.

- 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 48. Since 2005 ALP has completed the analysis of 240 soils, 156 plant samples and 137 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 48. 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 49 Ship

September 19, 2022

"Be passionate about solving the problem, not proving your solution."

- *Nathan Furr*, 2001

ALP
Agricultural Laboratory Proficiency Program