2021 Volume 2

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ALP Program Report

2021 Summer - Cycle 45

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ALP Overview

The Agriculture Laboratory Proficiency (ALP) Program fall 2021 Round Cycle 45 was completed August 18, 2021, with results from one-hundred seven labs enrolled from the US, Canada, South Africa, Italy, Ukraine, 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 45.
- Fifty-nine Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.30 - 7.11.
- Soil M3-P ICP for Cycle 45 ranged from 5.6 to 107 mg kg^{-1} with MAD values ranging 0.8 - 8.6 mg kg^{-1} across the five soils.
- Soil M3-K values ranged from 42 - 558 mg kg^{-1} for the five ALP soils of PT Cycle 45.
- Botanical N by combustion was reported by 38 labs, with four labs showing high bias values on all four botanical materials for Cycle 45.
- Botanical Total P, ranged from 0.220 - 0.365% with four of forty labs noted for inconsistency across the four samples.

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Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 45 were: SRS-2106 a Shano silt loam, collected Benton Cty, WA; SRS-2107 Miami silt loam collected Champaign Cty OH; SRS-2108 a Embden fine sandy loam collected Dickey Cty, ND; SRS-2109 is a Enon fine sandy loam collected in Rowan Cty NC; and SRS-2110 a loam, collected near Summerland, BC, Canada. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.30 - 7.11; SMP Buf 6.72 - 7.35 mg kg^{-1}; Bray P1 (1:10) 4.0 - 87.2 mg kg^{-1}; M3-K 42 - 558 mg kg^{-1}; M3-Ca 1397 - 2843 mg kg^{-1}; DTPA-Zn 0.80 - 68.9 mg kg^{-1}; SOM-LOI 1.59 – 3.63%; CEC 9.8 - 15.0 cmol kg^{-1}; sand 25.2 - 73.6% and total P 274 - 855 mg kg^{-1}.

Standard Reference Botanical (SRB) materials for Cycle 45 were: SRB-2105 cilantro leaf composite from CA; SRB-2106 alfalfa plant composite from KS; SRB-2107 potato petiole composite from CA; and SRB-2108 corn plant GS-V5 leaf composite from IA. SRB median analytes ranged: NO_3-N 53 - 8970 mg kg^{-1}; Dumas N 2.75 - 4.58%; wet digestion total P 0.220 - 0.365%; K 1.78 - 6.43%; Ca 0.80 - 1.61%; S 0.173 - 0.74 %, total B 13.6 - 45.0 mg kg^{-1}; and total Cd 0.080 - 0.751 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2104 a water sample collected from a James River, South Dakota: SRW-2105 was collected from a domestic well Sioux Center, IA; and SRW-2106 from a domestic water supply Ault, CO. SRW median concentrations: pH 8.11 - 8.34; EC 0.57 - 0.85 dSm^{-1}; SAR 0.29 - 2.53; Ca 2.82 - 5.56 mmolc L^{-1}; Na 0.59 - 4.00 mmolc L^{-1}; SO_4 0.61 - 5.79 mmolc L^{-1}; and Cl 0.051 - 0.46 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 five 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 sam-

"..soil pH, Buf pH A&E, Olsen P and SOM-WB analysis Stdev values for Cycle 45 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation 2021, Cycle 45.

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-2106	7.08	*0.02*	0.62	*0.010*	35.5	*1.8*	1.03	*0.02*
SRS-2107	7.12	*0.01*	2.10	*0.022*	12.5	*1.4*	2.63	*0.07*
SRS-2108	6.74	*0.02*	0.42	*0.010*	44.3	*2.6*	3.14	*0.09*
SRS-2109	5.62	*0.01*	0.11	*0.008*	5.1	*0.8*	1.10	*0.03*
SRS-2110	5.21	*0.02*	1.56	*0.019*	43.5	*1.9*	2.80	*0.14*

[1] Statistics based on six randomly selected soil replicates, each analyzed in triplicate ALP Cycle 45.

2021 Cycle 45 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis inter-lab MAD values for Cycle 45 averaged 0.05 pH units across the five soils. Median within lab pH standard deviation was 0.04 pH units. SRS-2102 had an abnormally low extractable M3-Mg of 658 mg kg^{-1}, likely associated with Miami silt loam soil series. Soil organic C values for the cycle 45 ranged form 0.55 to 1.68% SOC. Soil ammonium acetate Ca (Test code 140) MAD values ranged 61 - 107 mg kg^{-1} and ammonium acetate Mg MAD values ranged 11.9 to 35 mg kg^{-1} for the five soils. Across soils M3-P colorimetric within lab standard deviations were ranged from 0.79 - 2.2 mg kg^{-1}. Soil SRS-2110 had abnormally high M3-Zn and DTPA-Zn, 93.6 and 68.9 mg kg^{-1}, respectively. The soil site collection meta shows the loam soil was collected from an apple orchard site near Summerland, BC, Canada.

Across the four botanical samples Dumas combustion N MAD values averaged 0.084% nitrogen with intra-lab median *s* of 0.050%, 0.054%, 0.062% and 0.049, respectively. Botanical sample SRB-2105 had a high median S with a concentration of 0.74 % and with a MAD of 0.052 %. Botanical sample SRB-2107, the potato sample composite had elevated extractable Cl 1.56%. It also had higher median concentrations of NO_3-N, PO_4-P, K, Ba, Cd, and Pb and relative to the other three botanical samples. Consistent with past ALP cycles for 2021, cycle 45 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 0.57, 0.78 and 0.85 dSm^{-1}, respectively. Na mean concentrations ranged from 29 - 4.00 molc L^{-1} across the three ALP water samples with MAD values ranging 0.014 to 0.028 molc L^{-1}. Sample SRW-2106 had SO_4 of 5.79 with a MAD of 0.13.

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 5.23 - 7.10. Lab results were ranked low to high based on sample SRS-2106 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-2107 and SRS-2108 showed good consistency across labs. Labs #1 and #2 showed consistent low bias on four of five samples. Labs #7, #9, #26, #33 and #59 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.

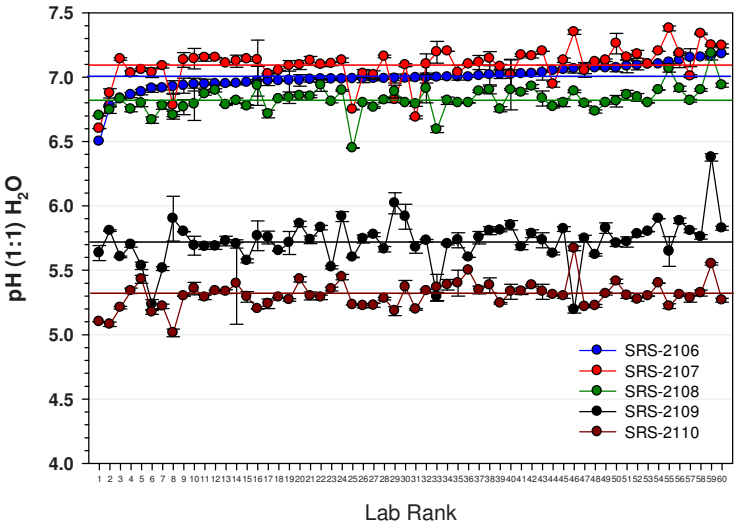

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2021 Cycle 45.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.040 to 0.053 pH units, the lowest noted for SRS-2106. Twelve labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #8, #16, #30, and #55 exceeded 0.10 pH units for SRS-2105. Soil SRS-2106 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-seven labs. M3-P ICP was reported by 39 labs. Median soil Bray P1 values ranged from 4.0 - 87.2 mg kg^{-1} PO_4-P; Olsen P 6.3 to 42.3 mg kg^{-1} P; Bray P2 ranged from 10.6 to 181 mg kg^{-1} P; and M1-P from 13.5 to 177 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-2106, median Bray P1 concentrations are shown in indicated in Figure 2. Soil SRS-2108, high in PO_4-P concentrations was highly variable between labs. Soils SRS-2106 and SRS-2110 had near identical concentrations of 62.0 mg kg^{-1} and 68.3 mg kg^{-1} PO_4-P. Lab #1 had consistently low bias across all five soils. Labs #4 and #18 were inconsistent for SRS-2108 relative to SRS-2106.

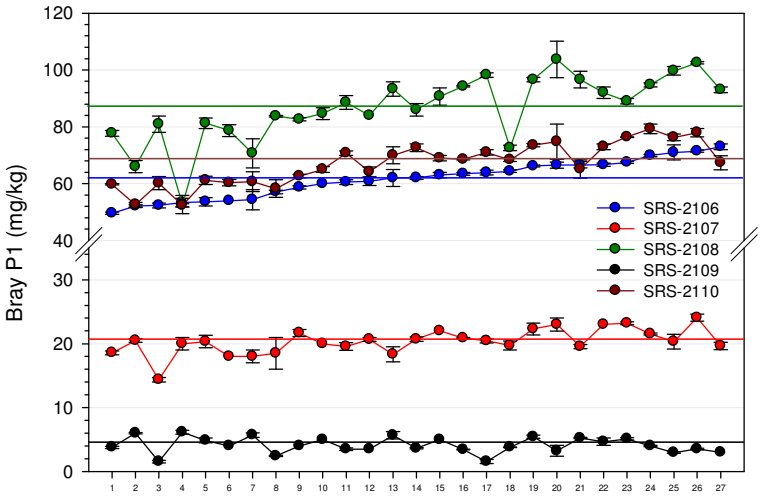

Figure 2. Bray P1 distribution plots for SRS materials, ALP 2021 Cycle 45.

Seven labs reported M3-P spec median concentrations ranging 5.6 - 92.3 mg kg^{-1} P. Thirty-nine laboratories reported M3-P ICP with medians ranging 5.6 –107.4 mg kg^{-1} P and two results for Modified Morgan P, with medians ranging from 1.6 - 23 mg kg^{-1} PO_4-P. Modified Kewlona was reported by two laboratories ranging from 1.2 - 31.2 mg kg^{-1} P and total P (US-EPA 503) ranged 274 - 855 mg kg^{-1} P with the highest concentration noted for SRS-2110.

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-2106 (see Figure 3). Soil SRS-2110 was the most inconsistent across all-labs. The source of the variability is unknown. Labs #1, #4 and #34 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-2108, with a median intra-lab value of 2.6 mg kg^{-1} for SRS-2109 and highest for SRS-2110 with a value of 16.6 mg kg^{-1}. M3-K within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 400 mg kg^{-1} K. Precision was poor (based on intra-lab *s*) for four labs which exceeded 10 mg kg^{-1} K on SRS-2107. Labs #4, #15, #23 and #35 had poor precision on two of four soils for cycle 45. Poor precision is attributed to extraction and/or analysis instrument operation.

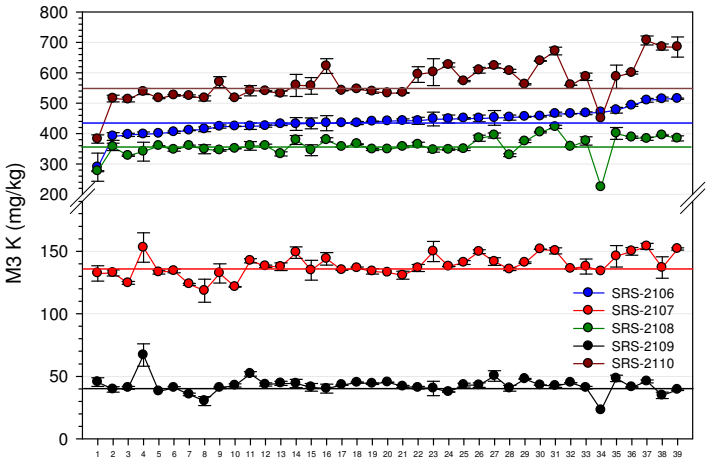

Figure 3. Extractable K distribution plots for SRS materials, ALP 2021 Cycle 45.

SRS - SOM-LOI

Forty-seven laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 1.58 to 3.36%. Results were ranked based on sample SRS-2107 (see Figure 4). Sample SRS-2106 had high consistency. Labs #19 through #45 had inconsistency all five soils. Labs #1 and #2 had low bias all 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 0.07 to 0.23% SOM-LOI, highest for SRS-2107. Across labs, *s* values for SRS-2109 ranged from 0.005 - 0.24%. Across soils low precision was noted for several laboratories. Specifically *s* for labs #11, #21, #43, #45 and #46, exceeded 0.15% SOM-LOI for SRS-2107. Lab #47 had poor precision on four of five soils. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

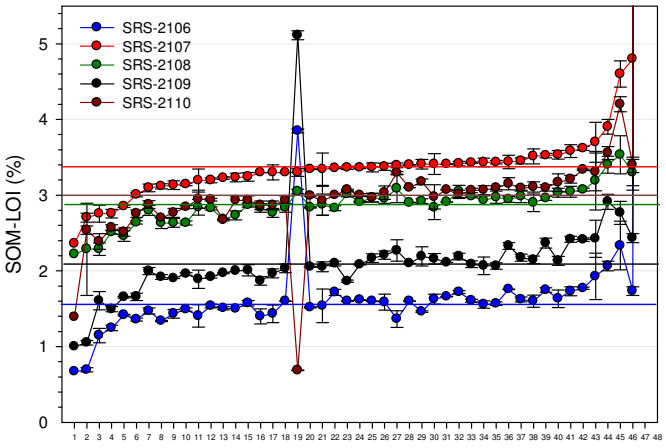

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2021 Cycle 45.

SRS - EC 1:1

Twenty-seven laboratories provided ALP results for soil EC 1:1 (test code 114). Results were ranked low to high based on sample SRS-2107 (see Figure 5). Soil SRS-2109 was the most consistent across labs. A general trend was noted for soils SRS-2107 and SRS-2110 with EC increasing for all labs, which was not evident on the three remaining soils from with EC concentrations < 0.7 dS/m. Lab #1 had consistent low bias on two of five soils. Across soils, labs #8 and #24 were inconsistent across soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

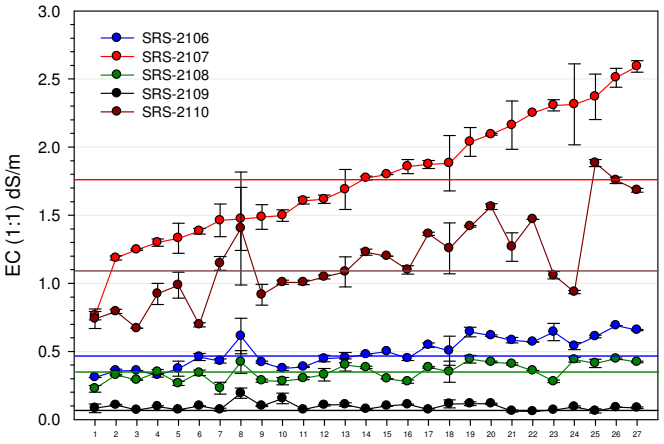

Figure 5. Comparison of soil EC 1:1 distributions, Cycle 45.

Soil EC median intra-lab *s* values were lowest for ALP soil SRS-2109, averaging 0.015 dS/m and highest for SRS-2107 with a value of 0.11 dS/m. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception labs #5, #13 #18 for EC values > 0.5 dS/m. Eight labs were flagged for poor precision over the five soils.

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 used and labs results are ranked low to high for twenty-four labs (codes 202-203) based on sample SRB-2108 (see Figure 6). The data plot shows labs #18- #21 were bias high on three of four samples.

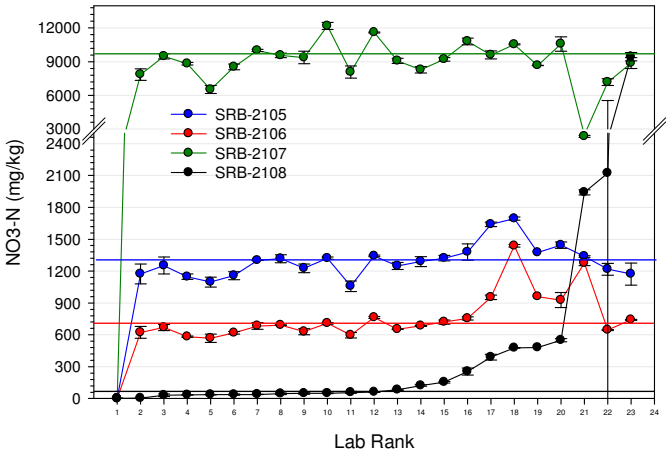

Figure 6. Nitrate distribution plots for SRB materials, ALP 2021, Cycle 45.

Botanical NO_3-N (test code 202) results for cycle 45 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 28 to 345 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-2105 ranged from 2.2 – 103 mg kg^{-1}; SRB-2106 ranged from 2.2 - 71 mg kg^{-1}, SRB-2107 ranged from 9.8 – 638 mg kg^{-1} and SRB-2108 ranged from 0.6 - 3414 mg kg^{-1}. Lab #22 had consistently high standard deviations for three of four samples. Two labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty-eight laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and nine labs for TKN (Test code 209) for Cycle 45. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2105 (see Figure 7). Labs #1, #6 and #31 were inconsistent for SRB-2107 relative to SRB-2105. It is note worthy that TKN was inconsistent and lower than Dumas for SRB-2105. Lab #1 had low bias for TKN.

Dumas N results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-2105, ranged 0.004 to 0.206% N, SRB-2106 ranged from 0.002 to 0.244% N, SRB-2107 ranged from 0.010 to 0.221 % N, and SRB–2108 from 0.006 to 0.240 % N. Lab #6 and #31 had consistently high standard deviations on all samples. Lab TKN *s* values for SRB-2105 ranged from 0.009 to 0.233%, SRB-2106 ranged from 0.012 to 0.165% TKN, SRB-2107 ranged from 0.011 to 0.206% TKN nitrogen and SRB-2108 ranged from 0.010 to 0.196% TKN nitrogen.

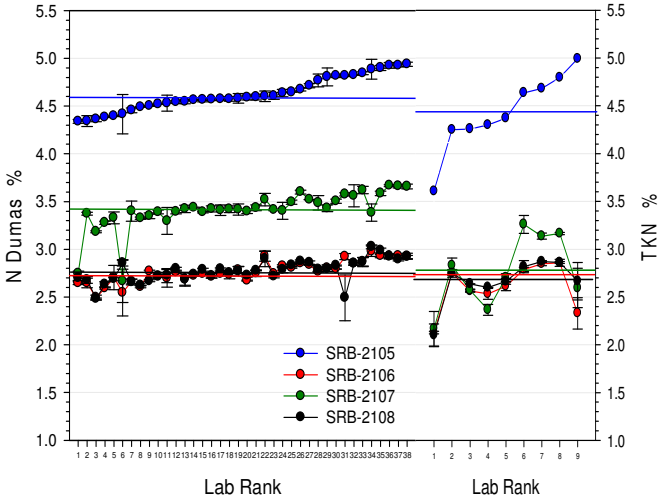

Figure 7. N distribution lab plots for SRB materials, ALP 2021 Cycle 45.

SRB - Phosphorus

Forty-eight laboratories provided ALP results for Cycle 45 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-2108 (see Figure 8). Consistent high bias was noted for lab #45. Labs #12, #37, #38, and #39 showed inconsistency. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

Botanical P results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged 0.002% to 0.010% P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-2105; ranged from 0.001 - 0.206% P; SRB-2106 ranged from 0.002 – 0.240 % P and SRB-2107 0.006 - 0.231 % P; and SRB-2108 0.001 - 0.240 % P. Lab #4 had a high standard deviation exceeding 0.20 % P on SRB-2108 PT sample. Eight labs were flagged for poor precision for botanical P for Cycle 45.

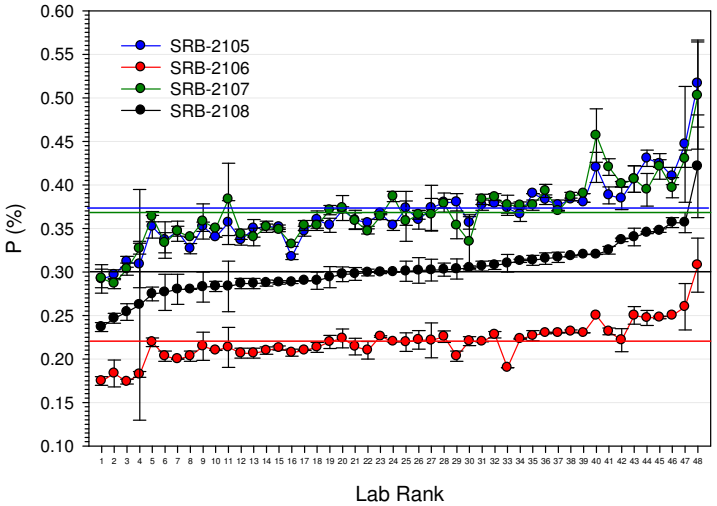

Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2021 Cycle 45.

SRB - Potassium

Forty-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-2108 (see Figure 9). Labs #1 and #2 had low bias and #21, #23 and #48 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 0.029 to 0.102 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2105, ranged from 0.006 - 0.276 % K; SRB-2106, 0.009 - 0.208 % K; SRB-2107, 0.006 - 0.90 % K; and SRS-2108, 0.005 - 1.03 % K. Lab #20 had high standard deviations exceeding 0.2 %K on two of four samples. Four labs were flagged for poor K precision for Cycle 45.

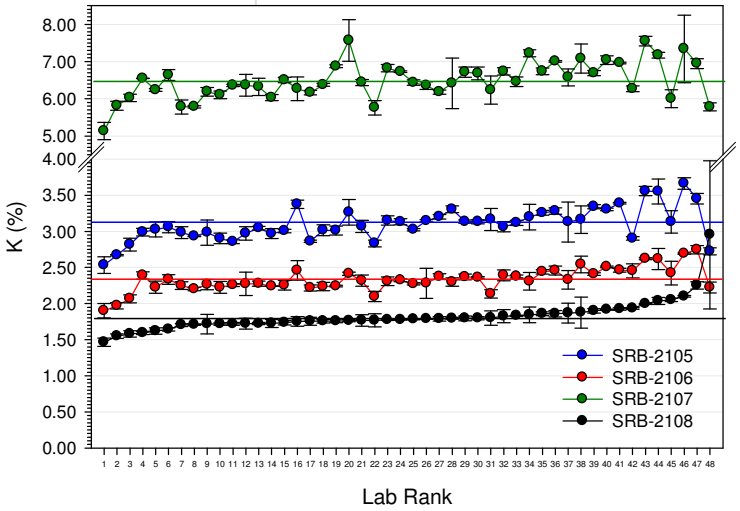

Figure 9. Potassium lab plot for SRB materials, ALP 2021 Cycle 45.

SRB - Manganese

Forty-five 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-2105 (see Figure 10). Across samples labs #1 and #2 exhibited low bias. Labs #7, #29, #39 and #40 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 0.45 to 2.0 mg kg^{-1} Mn for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2105; ranged from 0.45 - 7.0 mg kg^{-1} Mn; SRB-2106 ranged from 0.05 – 2.6 mg kg^{-1} Mn; SRB-2107 0.26 - 9.5 mg kg^{-1} Mn; and SRB-2108 0.11 - 25.7 mg kg^{-1} Mn. Lab #2 and #11 had consistently high standard deviations for two samples. Eight labs were flagged for poor Mn precision for Cycle 45.

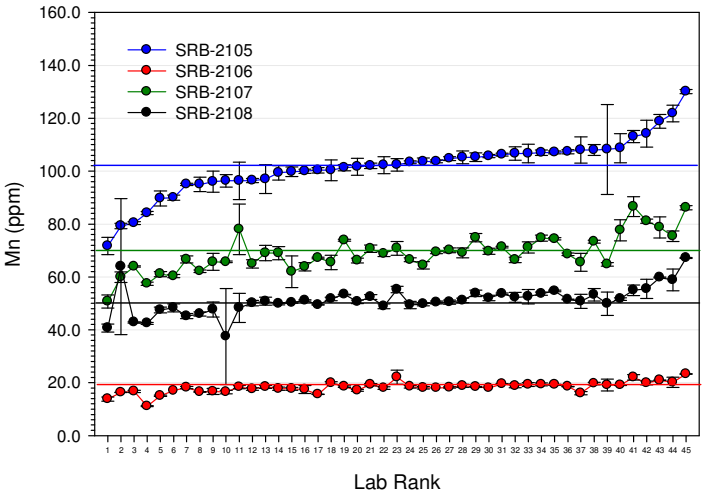

Figure 10. Manganese lab plots for SRB materials, ALP 2021 Cycle 45.

SRW - Water EC

Sixteen laboratories provided ALP results for water EC (test code 302). Lab result were ranked low to high based on sample SRW-2104 (see Figure 11). Sample SRW-2106 had the highest EC in Cycle 45. Labs #1 and #2 indicated consistency low bias on all samples. Lab #15 had high bias on SRW-2103. 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 0.008, 0.010 and 0.009 dSm^{-1}, respectively. Precision for sample SRW-2106 was the most consistent across the sixteen participating laboratories. Intra-lab *s* values for lab #2 exceeded 0.025 dSm^{-1} on SRW-2105. Highest precision was noted for lab #14 with intra-lab *s* values of < than 0.001 dSm^{-1} for all three samples.

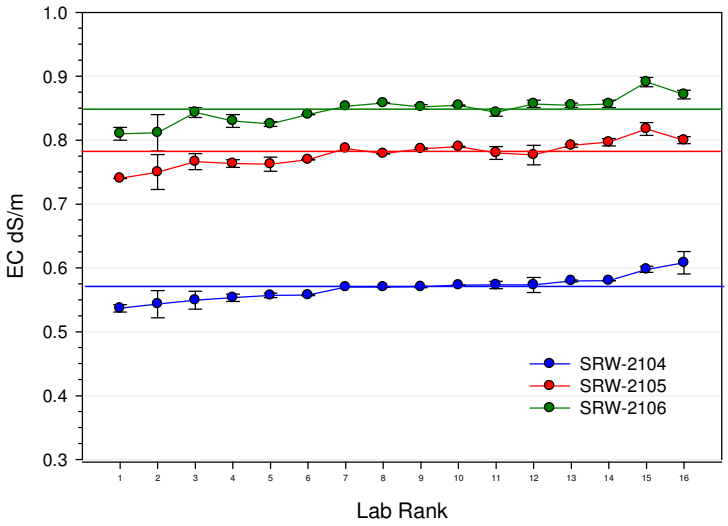

Figure 11 . Water EC distribution plots for SRW materials, ALP 2021 Cycle 45.

SRW - SO4 Results

Eleven laboratories provided ALP results for water SO4 (test code 315). Lab results were ranked low to high based on sample SRW-2104 (see Figure 12) lowest in SO4 concentration. Median values are designated by horizontal lines. Labs #1 showed consistent high bias on two of thee samples, and is likely a result of a calibration error.

SO4 precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.071, 0.063, and 0.213 meq L^{-1} for SRW-2104, SRW-2105, and for SRW-2108, respectively. Water SO4 precision was excellent for all individual labs with only lab #7 exceeding 0.60 meq L^{-1} on water sample SRW-2106. Three labs were flagged for poor precision on ALP Cycle 45 for SO4 content.

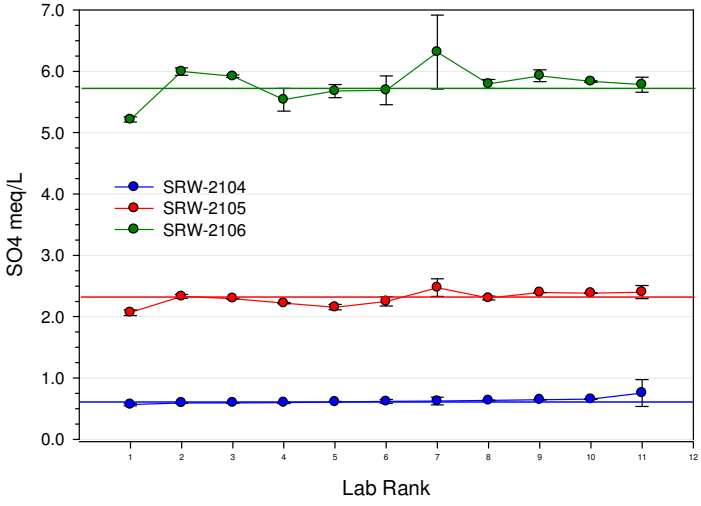

Figure 12. Water SO4 distribution plots for SRW materials, ALP 2021 Cycle 45.

Announcements

- The Soil and Plant Analysis Council (SPAC) and Agricultural Laboratory Testing Association (ALTA) have developed an international plant analysis certification program (PAC) for laboratories. Analyses include: N, P, K, S, Ca, Mg, Zn, B, Mn, Fe, and Cu. The PAC program will be based exclusively on ALP proficiency testing data evaluated on a yearly basis. For more information can be found at ALTA.Ag.

- The Agricultural Laboratory Testing Association (ALTA) and SPAC presented a webinar "*Soil Scooping Assumptions and Issues*", August 24, 2021. For more information contact the ALTA secretary, gfisher@unitedsoilsinc.com.

- ALTA will have their 2021 summer meeting August 30, 2021 in Decatur, Illinois. Topics include presentations on lab quality management; soil health; and ALTA-SAC certification.

- The Soil and Plant Analysis Council has launched a new web site, www.sp-council.org. The site includes information on the SPAC board, current projects and sales of soil scoops.

- ALP has standard reference soils and plant tissue samples available for purchase in quantities of 0.2—20 kg. For more information on these methods contact the ALP Technical Director, Robert.Miller@cts-interlab.com.

Summary

ALP is has provided sixteen years of service with the completion of Cycle 45. Since 2005 ALP has completed the analysis of 225 soils, 144 plant samples and 128 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 45. 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 46 Ship

September 12, 2021

"Thinking something does not make it true.
Wanting something does not make it real."

– Michelle Hodkin, 2011

ALP
Agricultural Laboratory Proficiency Program