2021 Volume 1

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ALP Program Report

2021 Spring - Cycle 44

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

ALP Overview

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 44.
- Fifty-nine Laboratories provided soil pH (1:1) H_2O results and medians ranged from 4.23 - 7.40.
- Soil M3-P ICP for Cycle 44 ranged from 11.2 to 135 mg kg^{-1} with MAD values ranging 0.8 - 7.9 mg kg^{-1} across the five soils.
- Soil M3-K values ranged from 86 - 252 mg kg^{-1} for the five ALP soils of PT Cycle 44.
- Botanical N by combustion was reported by 36 labs, with eight labs showing high bias values on the two materials with > 2.5% N for Cycle 44.
- Botanical Total P, ranged from 0.070 - 0.424% with four of forty labs noted for inconsistency across the four samples.

Inside this issue:

The Agriculture Laboratory Proficiency (ALP) Program fall 2021 Round Cycle 44 was completed May 17, 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.

Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 44 were: SRS-2101 a Del Rey silt loam, collected Iroquois Cty, IL; SRS-2102 Kaski loam collected Kingman Cty KS; SRS-2103 a silt loam collected near Kippen, ON, Canada; SRS-2104 is a Chino fine sandy loam collected in Madera CA; and SRS-2105 a Chagrin-Grigsby complex, loam, collected in Breadthitt Cty, KY. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 4.23 - 7.40; SMP Buf 6.17 - 7.39 mg kg^{-1}; Bray P1 (1:10) 8.3 - 55.3 mg kg^{-1}; M3-K 86 - 252 mg kg^{-1}; M3-Ca 373 - 3216 mg kg^{-1}; DTPA-Zn 0.48 - 2.19 mg kg^{-1}; SOM-LOI 1.19 – 5.20%; CEC 6.5 - 16.3 cmol kg^{-1}; sand 18.6 - 66.1% and total P 298 - 508 mg kg^{-1}.

Standard Reference Botanical (SRB) materials for Cycle 44 were: SRB-2101 almond leaf composite from CA; SRB-2102 grass leaf composite from KS; SRB-2103 mint leaf composite from CA; and SRB-2104 eucalyptus leaf composite from IA. SRB median analytes ranged: NO_3-N 35 - 7840 mg kg^{-1}; Dumas N 1.30 - 2.59%; wet digestion total P 0.070 - 0.424%; total K 0.98 - 4.35%; total Ca 0.48 - 4.00%; total S 0.127 - 0.308 %, total B 4.7 - 156.3 mg kg^{-1}; and total Mo 0.099 - 5.50 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2101 a water sample collected from a domestic well near McCook, NE: SRW-2102 was collected from a domestic well Wellington, CO; and SRW-2103 from a domestic water supply Tinmath, CO. SRW median concentrations: pH 7.61 - 7.98; EC 0.10 - 3.54 dSm^{-1}; SAR 0.66 - 23.7; Ca 0.50 - 5.2 mmolc L^{-1}; Na 0.38 - 31.4 mmolc L^{-1}; HCO_3 0.75 - 5.5 mmolc L^{-1}; and NO_3 0.008 - 0.91 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 44 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation 2021, Cycle 44.

Sample	pH (1:1) H_2O		pH A&E Buffer		Olsen P (mg kg^{-1})		SOM-WB (%)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-2101	5.06	*0.010*	7.14	*0.03*	9.7	*0.7*	5.02	*0.14*
SRS-2102	4.19	*0.015*	7.39	*0.02*	47.6	*3.2*	1.18	*0.08*
SRS-2103	7.42	*0.013*	7.69	*0.01*	11.3	*0.7*	2.98	*0.08*
SRS-2104	6.82	*0.009*	7.80	*0.01*	22.7	*1.3*	1.56	*0.14*
SRS-2105	6.10	*0.013*	7.57	*0.02*	4.7	*1.0*	3.59	*0.23*

[1] Statistics based on six randomly selected soil replicates, each analyzed in triplicate ALP Cycle 44.

2021 Cycle 44 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis inter-lab MAD values for Cycle 44 averaged 0.07 pH units across the five soils. Median within lab pH standard deviation was 0.05 pH units. SRS-2102 had an abnormally low extractable M3-Ca of 373 mg kg^{-1}, likely associated with Kaski loam soil series and low CEC. Soil Organic C values for the cycle 44 ranged form 0.63 to 2.79% SOC. Soil ammonium acetate Ca (Test code 140) MAD values ranged 47 - 335 mg kg^{-1} and ammonium acetate Mg MAD values ranged 5.3 to 42 mg kg^{-1} for the five soils. For soils SRS-2101 through SRS-2104 M3-P colorimetric within lab standard deviations were consistently 30 - 60% lower than values for the M3-ICP method. Results for SRS-2105 were near identical. The higher M3-P colorimetric within lab standard deviation for SRSR-2105 maybe related to the higher clay content and/or cropping history of the collection site, a corn field in in Breadthitt County, KY.

Across the four botanical samples Dumas combustion N MAD values averaged 0.056% nitrogen with intra-lab median *s* of 0.026%, 0.036%, 0.054% and 0.029%, respectively. Botanical sample SRB-2102 had a very low median B with a concentration of 4.7 ppm and with a MAD of 0.63 ppm. The mint leaf composite composite sample SRB-2103 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 2021, cycle 44 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 0.88, 3.54 and 0.106 dSm^{-1}, respectively. Na values ranged from 0.38 - 31.4 molc L^{-1} across the three ALP water samples with MAD values ranging 0.017 to 1.56 molc L^{-1}. Sample SRW-2102 had and SAR of 23.7 with a MAD of 0.97.

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 4.23 - 7.41. Lab results were ranked low to high based on sample SRS-2102 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-2101 and SRS-2102 showed good consistency across labs. Labs #59 #60 and #61 showed consistent high bias on SRS-2102. Labs #5, #12, #25, #35 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.

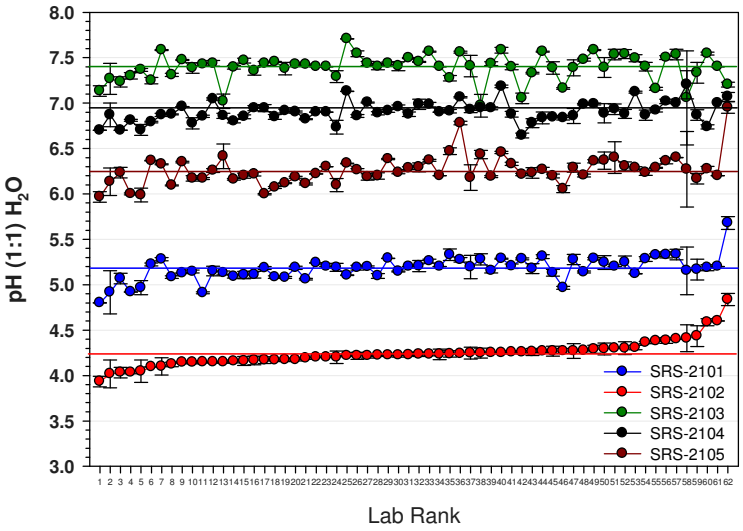

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2021 Cycle 44.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.017 to 0.024 pH units, the lowest noted for SRS-2105. Five labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #11, #34, #47, #54, #56, and #58 exceeded 0.10 pH units for SRS-2105. Soil SRS-2012 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 thirty labs. M3-P ICP was reported by 40 labs. Median soil Bray P1 values ranged from 20.1 - 137 mg kg^{-1} PO_4-P; Olsen P 6.3 to 67.7 mg kg^{-1} P; Bray P2 ranged from 18.3 to 363 mg kg^{-1} P; and M1-P from 16.9 to 93.3 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-2101, median Bray P1 concentrations are shown in indicated in Figure 2. Soil SRS-2104, moderately high in concentrations was highly variable between labs. Soils SRS-2101 and SRS-2103 had near identical concentrations of 18 mg kg^{-1} P; soils SRS-2101 and SRS-2013 had ear identical concentrations of 39 mg kg^{-1} P. Lab #1 had consistently low bias across all five soils. Labs #3 and #29 were inconsistent across soils three of five soils.

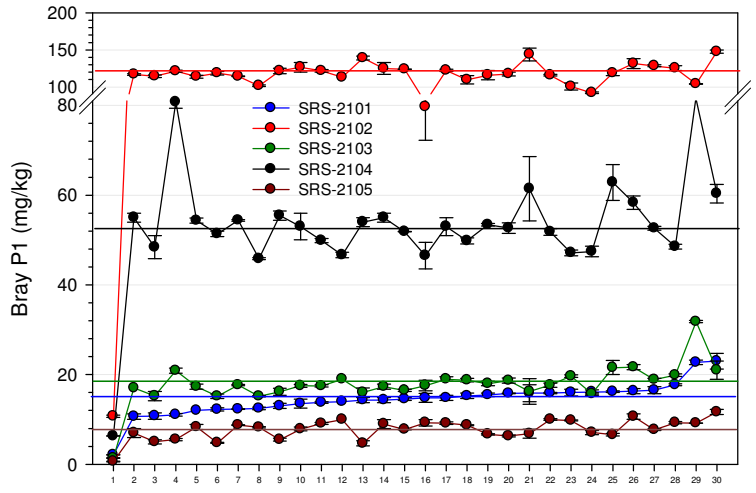

Figure 2. Bray P1 distribution plots for SRS materials, ALP 2021 Cycle 44.

Eight labs reported M3-P spec median concentrations ranging 10 - 123 mg kg^{-1} P. Nine laboratories reported Bray P2 with medians ranging 17 –147 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 4.5 - 88 mg kg^{-1} P and total P (US-EPA 503) ranged 298 - 508 mg kg^{-1} P with the highest concentration noted for SRS-2103.

SRS - Potassium

Forty-one laboratories provided ALP results for soil M-3 K (test code 159) results. Results were ranked low to high based on sample SRS-2101 (see Figure 3). Soil SRS-2103 and SRS-2105 were the most inconsistent across labs #39 - #40. The source of the variability is unknown. Labs #3, #9 and #17 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-2103, with a median intra-lab value of 1.8 mg kg^{-1} Kg and highest for SRS-2102 with a value of 4.5 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 four labs which exceeded 5 mg kg^{-1} K on SRS-2103. Labs #7 and # 11 had poor precision on three of four soil for cycle 44. Poor precision is attributed to extraction and/or analysis instrument operation.

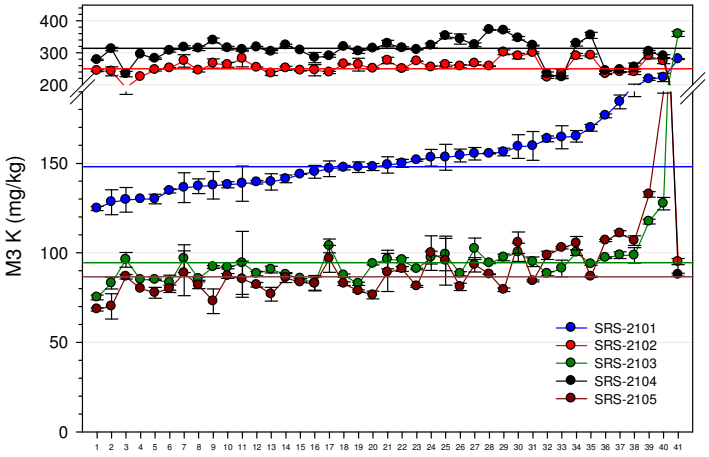

Figure 3. Extractable K distribution plots for SRS materials, ALP 2021 Cycle 44.

SRS - SOM-LOI

Forty-eight 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-2102 (see Figure 4). Sample SRS-2101 had high consistency. Labs #46 through #48 had inconsistency all five soils. Lab #1 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 0.04 to 0.06% SOM-LOI, highest for SRS-2105. Across labs, *s* values for SRS-2104 ranged from 0.005 - 0.22%. Across soils low precision was noted for several laboratories. Specifically *s* for labs #7, #16, #32, #34 and #37, exceeded 0.15% SOM-LOI for SRS-2104. Lab #34 had poor precision on four of five soils. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

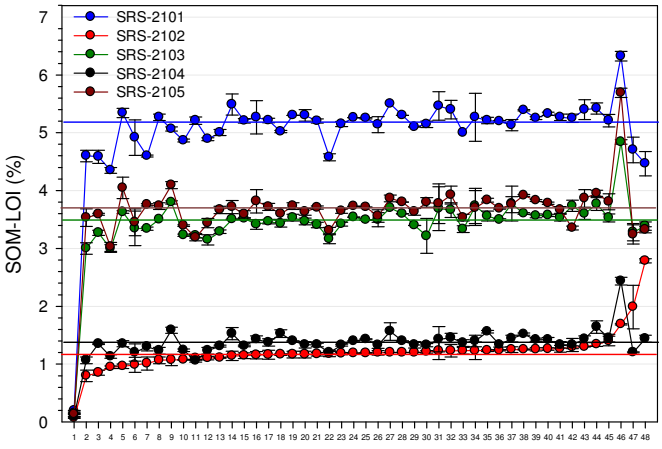

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2021 Cycle 44.

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 44 (see Figure 5). Sixty-two labs reported results for the pH 1:1 H_2O and seventeen for pH 1:1 0.01 M $CaCl_2$. pH method medians differences range from 0.23 to 0.46 pH units, with the pH 1:1 0.01 M $CaCl_2$ consistently lower. For soil SRS-2105, pH 1:1 H_2O had higher intra-lab variability resulting in a MAD of 0.07 pH units, whereas the value for pH 1:1 0.01 M $CaCl_2$ was 0.02 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 pH 1:1 0.01 M $CaCl_2$ method.

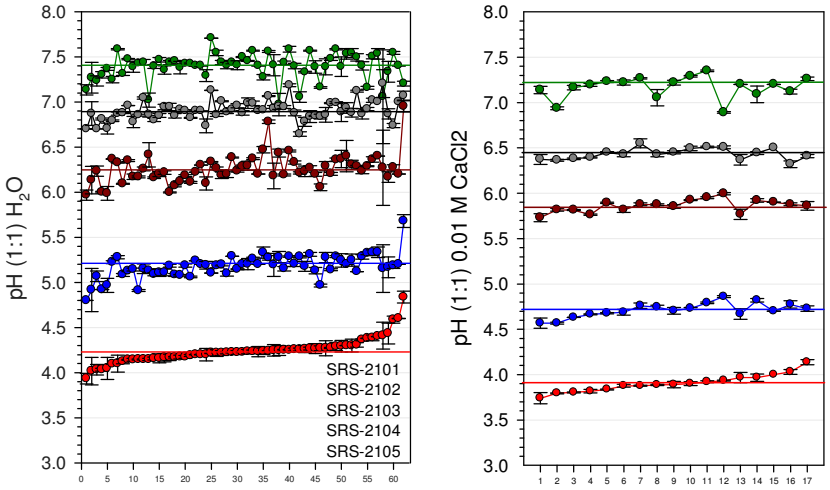

Figure 5. Comparison of two soil pH methods, Cycle 44.

SRB - NO_3-N

Twenty-four 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-2101 (see Figure 6). The data plot shows labs #20-#24 were bias high on three of four samples.

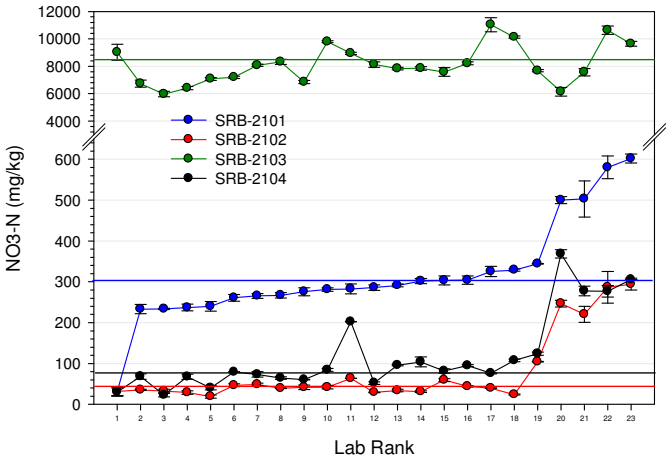

Figure 6. Nitrate distribution plots for SRB materials, ALP 2021, Cycle 44.

Botanical NO_3-N (test code 202) results for cycle 44 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 3.9 to 242 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-2101 ranged from 1.0 – 44 mg kg^{-1}; SRB-2102 ranged from 0.6 - 38 mg kg^{-1}, SRB-2103 ranged from 70 – 578 mg kg^{-1} and SRB-2104 ranged from 0.8 - 14 mg kg^{-1} Lab #22 had consistently high standard deviations for three of four samples. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty-six laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and eight labs for TKN (Test code 209) for Cycle 44. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2101 (see Figure 7). Labs #30, #31 and #32 were inconsistent for SRB-2104 relative to SRB-2101. It is note worthy that TKN was inconsistent and lower than Dumas for SRB-2103. Samples SRB-2102 and SRB-2103 were inconsistent for TKN.

Dumas N results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-2101, ranged 0.005 to 0.077% N, SRB-2102 ranged from 0.004 to 0.168% N, SRB-2103 ranged from 0.008 to 0.288 % N, and SRB–2104 from 0.001 to 0.093 % N. Lab #31 and #32 had consistently high standard deviations on all samples. Lab TKN *s* values for SRB-2101 ranged from 0.007 to 0.115%, SRB-2102 ranged from 0.006 to 0.173% TKN, SRB-2103 ranged from 0.008 to 0.118% TKN nitrogen and SRB-2104 ranged from 0.002 to 0.039% TKN nitrogen.

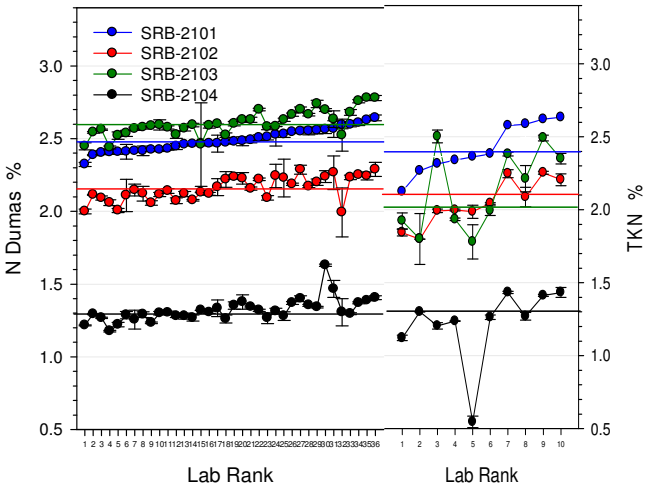

Figure 7. N distribution lab plots for SRB materials, ALP 2021 Cycle 44.

SRB - Phosphorus

Forty-four laboratories provided ALP results for Cycle 44 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-2101 (see Figure 8). Consistent high bias was noted for lab #44. 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-2101; ranged from 0.001 - 0.076% P; SRB-2102 ranged from 0.001 – 0.050 % P and SRB-2103 0.001 - 0.044 % P; and SRB-2104 0.001 - 0.010 % P. Lab #12 had a high standard deviation exceeding 0.12 % P on SRB-2101 PT sample. Five labs were flagged for poor precision for botanical P for Cycle 44.

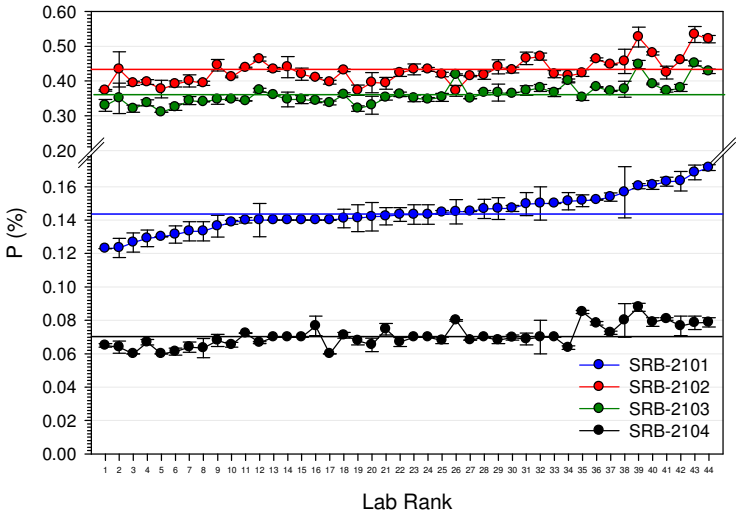

Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2021 Cycle

SRB - Potassium

Forty-four 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-2101 (see Figure 9). Labs #1, #4, #21, #and #31 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 0.039 to 0.076 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2101, ranged from 0.002 - 0.210 % K; SRB-2102, 0.004 - 0.44 % K; SRB-2103, 0.010 - 0.38 % K; and SRS-2104, 0.001 - 0.130 % K. Lab #1 had high standard deviations exceeding 0.3 %K on two of four samples. Five labs were flagged for poor K precision for Cycle 44.

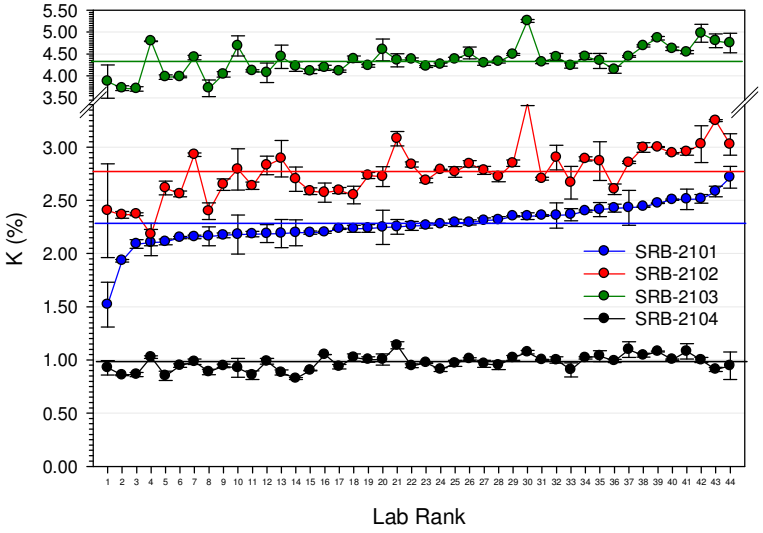

Figure 9. Potassium lab plot for SRB materials, ALP 2021 Cycle 44.

SRB - Boron

Forty laboratories provided ALP results for boron (B) (test code 219). 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-2101 (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 B results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.84 to 4.7 mg kg^{-1} B for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2101; ranged from 0.06 - 3.8 mg kg^{-1} B; SRB-2102 ranged from 0.03 – 1.3 mg kg^{-1} B; SRB-2103 0.08 - 2.0 mg kg^{-1} B; and SRB-2104 0.1 - 13.6 mg kg^{-1} B. Lab #38 had consistently high standard deviations for two samples. Five labs were flagged for poor B precision for Cycle 44.

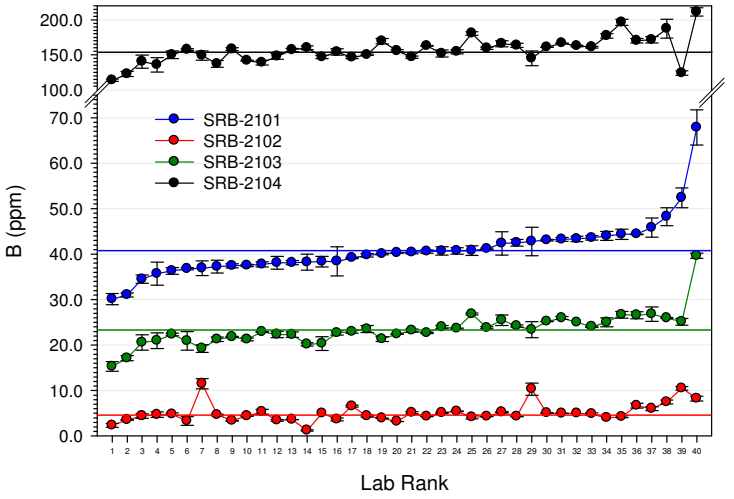

Figure 10. Boron (code 219) lab plots for SRB materials, ALP 2021 Cycle 44.

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-2101 (see Figure 11). Sample SRW-2102 had the highest EC in Cycle 44. Labs #3 and #12 indicated consistency sample SRW-2102 all samples. Lab #16 had high bias on SRW-2012. 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 0.007, 0.034 and 0.008 dSm^{-1}, respectively. Precision for sample SRW-2101 was the most consistent across the thirteen participating laboratories. Intra-lab *s* values for lab #2 exceeded 0.080 dSm^{-1} on SRW-2102. Highest precision was noted for lab #10 with intra-lab *s* values of < than 0.001 dSm^{-1} for all three samples.

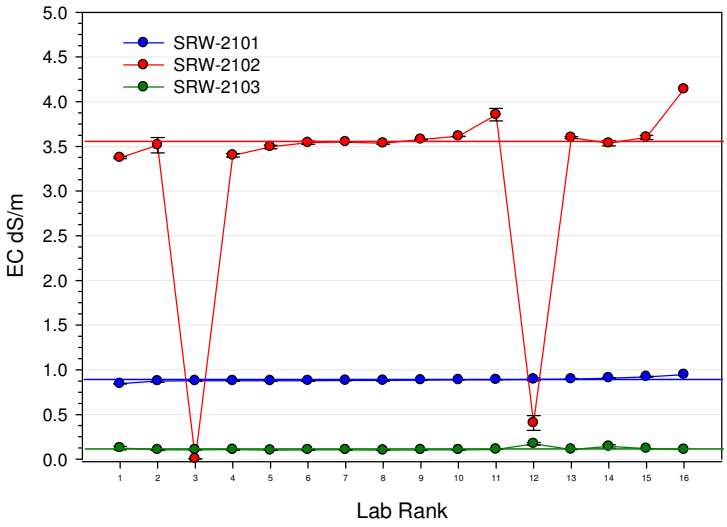

Figure 11 . Water EC distribution plots for SRW materials, ALP 2021 Cycle 44.

SRW - Na Results

Fifteen laboratories provided ALP results for water Na (test code 304). Lab results were ranked low to high based on sample SRW-2101 (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 0.036, 1.31, and 0.035 meq L^{-1} for SRW-2101, SRW-2102, and for SRW-2103, respectively. Water Na precision was excellent for all individual labs with only labs #11 and #12 exceeding 0.20 meq L^{-1} on two of the three samples. Four labs were flagged for poor precision on ALP Cycle 44 for Na content.

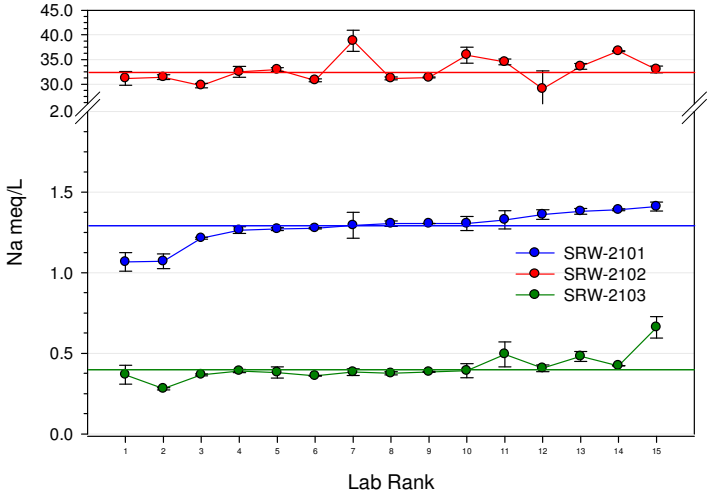

Figure 12. Water Mg distribution plots for SRW materials, ALP 2021 Cycle 44.

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) is planning a webinar on determining the Method Detection Limit (MDL) July 27, 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 will be launching a new web site the week of June 28th, 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 0.5—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 44. Since 2005 ALP has completed the analysis of 220 soils, 140 plant samples and 125 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 44. 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 45 Ship

June 22, 2021

"Somewhere something incredible is waiting to be known?"

– Carl Sagan, 1977

ALP
Agricultural Laboratory Proficiency Program