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ALP Program Report

2019 Fall - Cycle 40

Robert O. Miller, PhD, Colorado State University. Fort Collins, CO
Christopher Czyryca, Collaborative Testing, Inc, Sterling, VA

ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference soil materials were highly uniform for Cycle 40.
- Sixty-two Laboratories provided soil pH (1:1) H_2O results and medians ranged from 4.59 - 8.13.
- Cycle 40 soil M3-P ICP ranged from 21.3 to 135 mg kg^{-1} with MAD values ranging 1.2 - 10.8 mg kg^{-1} across the five soils.
- NH4oAc-3 K values ranged from 77.3 - 515 mg kg^{-1} for the five ALP soils of PT Cycle 40.
- EC (1:1) values showed high consistency across 24 of 29 testing labs for PT Cycle 40.
- Botanical K, ranged from 0.86 - 4.4% with four of thirty-nine labs noted for inconsistency.
- Botanical Mn results showed high consistency across the thirty-four of thirty-nine labs for PT Cycle 40.
- Water Ca content showed very high consistency by thirteen of seventeen labs across all PT samples.

The Agriculture Laboratory Proficiency (ALP) Program fall 2019 Round Cycle 40 was completed November 25, 2019, with results from one-hundred eight labs enrolled from the US, Canada, South Africa, Honduras, 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 twelve 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 40 were: SRS-1911 is a Marvyn loamy sand collected near Auburn, AL; SRS-1912 Haverson clay loam collected near Hardin, MT; SRS-1913 a Shellabarger fine sandy loam collected near Danville, KS; SRS-1914 is a loam collected near St Lambert-de Lauzon, Quebec, Canada; and SRS-1915 a Canisteo clay loam collected near Badger, IA. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 4.59 - 8.13; NO_3-N 39.3 - 160 mg kg^{-1}; Bray P1 (1:10) 15.8 - 105 mg kg^{-1}; M3-K 82 - 526 mg kg^{-1}; SO_4-S 5.8 - 2560 mg kg^{-1}; DTPA-Zn 0.21 - 1.22 mg kg^{-1}; SOM-LOI 1.26 – 6.60%; CEC 3.1 - 34.2 cmol kg^{-1}; clay 6.1 - 47.0% and soil available H_2O 5.5 - 20.4 %.

Standard Reference Botanical (SRB) materials for Cycle 40 were: SRB-1909 an almond leaf composite from CA; SRB-1910 corn silage composite from WI; SRB-1911 parsley leaf composite from OR; and SRB-1912 spinach leaf composite from CA. SRB material median analytes ranged: NO_3-N 36 - 766 mg kg^{-1}; Dumas N 1.05 - 3.81%; total P 0.143 - 0.396%; total K 0.86 - 4.64%; total Mg 0.11 - 0.82%; total S 0.08 - 0.37 %, total Cu 6.9 - 12.7 mg kg^{-1}; and total Cd 0.04 - 1.02 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1907 a water sample collected from a canal near McCammon, ID ; SRW-1908 was collected from canal near Umatilla, OR; and SRW-1909 from a creek near Tinmath, CO. SRW median concentrations ranged: pH 7.41 - 8.25; EC 0.08 - 0.11 dSm^{-1}; SAR 0.35 - 0.97; Ca 0.314 - 3.10 mmolc L^{-1}; Na 0.21 - 0.93 mmolc L^{-1}; HCO_3 0.70 - 4.80 mmolc L^{-1} ; and NO_3 0.003 - 0.07 mmolc L^{-1}.

Soil Homogeneity Evaluation

SRS material homogeneity was evaluated based on soil test codes pH (1:1) H_2O, pH Adams Evans, EC (1:1), P Olsen, K Olsen, NO_3-N and SOM-WB on analysis of five jars, 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, EC and Olsen P analysis Stdev values for Cycle 40 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 40, 2019.

Sample	pH (1:1) H_2O		EC (1:1) (dSm^{-1})		Olsen P ($mg\ kg^{-1}$)		SOM (%)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-1911	5.38	*0.03*	0.40	*0.017*	26.5	*2.1*	1.37	*0.07*
SRS-1912	8.11	*0.01*	6.4	*0.03*	26.4	*1.2*	1.94	*0.09*
SRS-1913	4.48	*0.01*	0.97	*0.007*	13.8	*1.0*	1.01	*0.04*
SRS-1914	5.34	*0.01*	0.44	*0.013*	8.6	*0.9*	2.03	*0.05*
SRS-1915	7.37	*0.01*	1.34	*0.019*	16.8	*1.1*	6.36	*0.23*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 40.

2019 Cycle 40 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 40 averaged 0.07 pH units across the soils. Median within lab pH standard deviation was 0.061 pH units. Soil displacement CEC ranged 3.2 to 34.2 cmol kg^{-1} across the five soils. Sample SRS-1912 had a large discrepancy in soil CEC values: Displacement 24.4 cmol kg^{-1} and estimated CEC of 58.4 cmol kg^{-1}. SRS-1911 had an abnormally low Mehlich 3 Mg of 71.8 mg kg^{-1}, likely associated with Marvyn loamy sand soil series. Soil ammonium acetate K (Test code 140) MAD values ranged 4.4 - 22.4 mg kg^{-1} and ammonium acetate Mg MAD values ranged 8.9 to 240 mg kg^{-1} for the five soils. These results for K and Mg were consistent with past cycles in 2019 and are attributed to: (1) improved lab consistency; (2) soils generally higher in potassium; and (3) ICP operation.

Across the four botanical samples Dumas combustion N MAD values averaged 0.047% nitrogen with intra-lab *s* of 0.026%, 0.027%, 0.033% and 0.031%, respectively. Botanical sample SRB-1910 had median Zn levels 200 times typical with a concentration of 4673 ppm and with a MAD of 376 ppm. Generally the spinach leaf composite sample SRB-1912 had higher median concentrations of P, K, Ca, Mg, Al, Zn, Mo and Cd relative to the other three botanical samples. One observation on Cycle 40, intra-lab relative variability was lowest for N all other macro elements for all four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC Median values ranged from 0.090, 0.611 and 0.113 dSm^{-1}, respectively. Cl values ranged from 0.126 - 0.934 molc L^{-1} across the three water samples with MAD values ranging 0.028 to 0.057 molc L^{-1}. Sample SRW-1908 had and SAR of 0.57 with a MAD of 0.01.

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 4.59 - 8.13. Lab results were ranked low to high based on sample SRS-1911 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1914, and SRS-1915 showed good consistency across labs. Labs #2, #3, #8 and #59 were inconsistent across soils. Lab #1 showed low bias. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

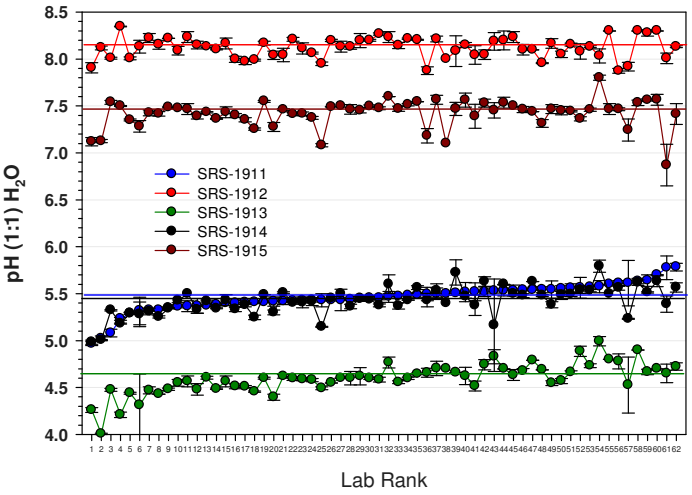

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2019 Cycle 40.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.048 to 0.079 pH units, the lowest noted for SRS-1912. For specific labs poor precision was noted for seven laboratories, exceeding by three times that noted for consensus median intra-lab *s*. Specifically *s* for labs #6, #43, #57, and #61 exceeded 0.10 pH units for two of five soils. Soil SRS-1911 was the least variable with respect to intra-lab variance for Cycle 40.

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 35 labs. Median soil Bray P1 values ranged from 15.8 - 105 mg kg^{-1} PO_4-P; Olsen P 7.7 to 30.6 mg kg^{-1} P and Bray P2 ranged from 56.2 to 130 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1914, median M3-P ICP concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1911 and SRS-1912 associated with the moderate P concentrations. Soil SRS-1914, lowest in concentration, showed low intra-lab variability. Lab #3 showed low bias on all five samples. Labs #1, #13, #19, #23, #32 and #35 were inconsistent. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

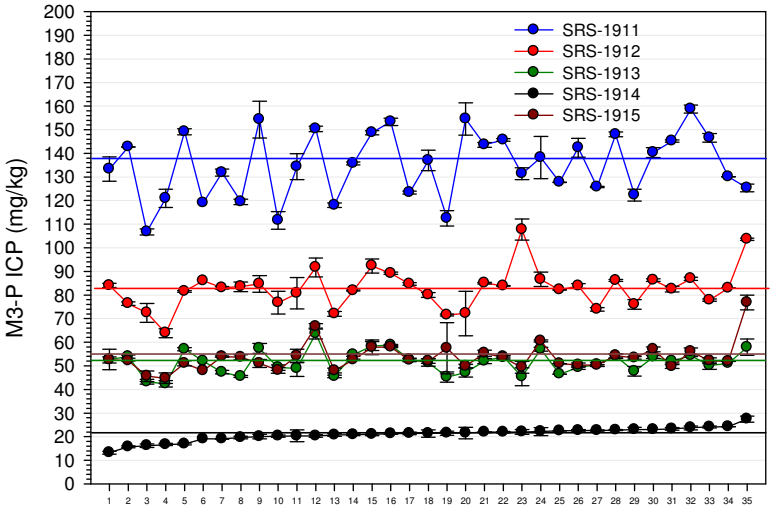

Figure 2. Olsen P distribution plots for SRS materials, ALP 2019 Cycle 40.

Four laboratories provided ALP results for Mehlich 1 P, with medians ranging from 32.7 to 168 mg kg^{-1} PO_4-P. M3-P Spec median concentrations were 20.3 - 104 mg kg^{-1} P reported by seven labs. Modified Kewolna was reported by two laboratories ranging from 9.9 - 70 mg kg^{-1} P and total P (US-EPA503 ranged 211 - 897 mg kg^{-1} P with the highest concentration noted for SRS-1912.

SRS - Potassium

Forty-nine laboratories provided ALP results for soil K (test code 141) results. Results were ranked low to high based on sample SRS-1911 (see Figure 3). Soils SRS-1913 and SRS-1915 were the most inconsistent across labs. Lab #48 had high bias on four of five soils. Labs #2, #6, #15, #44, and #47 were inconsistent across the five soils for K. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

Potassium intra-lab *s* values were lowest for soil SRS-1911, with a median intra-lab value of 7.3 mg kg^{-1} Kg and highest for SRS-1912 with a value of 30.8 mg kg^{-1} Kg. Potassium 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 labs #2, #12, #43, and #44 which exceeded 30 mg kg^{-1} K on SRS-1911; and labs #45, the value exceeded 10 mg kg^{-1} K for SRS-1915. Poor precision is attributed to extraction and/or analysis instrument operation.

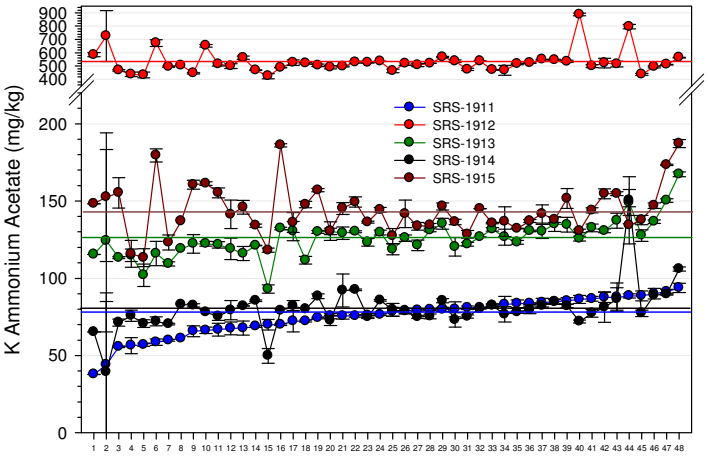

Figure 3. Extractable K distribution plots for SRS materials, ALP 2019 Cycle 40.

SRS - SOM-LOI

Forty-five laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.30 to 6.60%. Results were ranked based on sample SRS-1911 (see Figure 4). Labs #1, #2, #7, #23, and #41 had inconsistency three of five soils. Sample SRS-1908 shows high inconsistency likely associated with low SOM-LOI content. Bias was noted in three lab results. Source of bias is likely related to muffle furnace operation and/or method compliance.

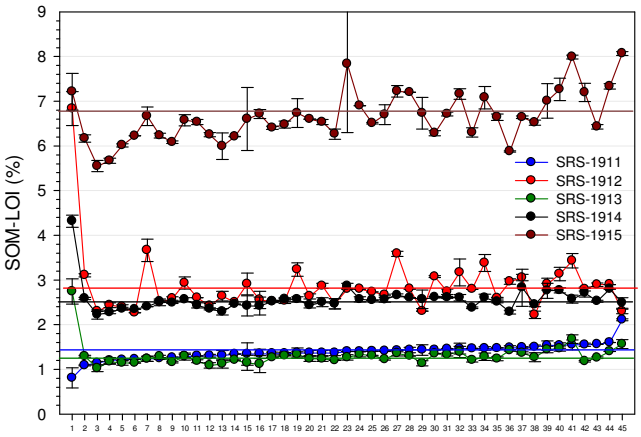

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2019 Cycle 40.

SOM-LOI precision across the five materials indicates high intra-lab precision, with median *s* values ranging from 0.07 to 0.29% SOM-LOI, the highest for SRS-1915. Across labs, *s* values for SRS-1912 ranged from 0.005 - 0.30 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #7, #15, #16, #19, #34 and #40, exceeded 0.15 % SOM for SRS-1912. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

SRS - EC (1:1)

Twenty-nine laboratories provided ALP results for EC (1:1) (test code 114). Results were ranked low to high based on sample SRS-1911 (see Figure 5). Soil SRS-1912 was the highest in concentration and was the most inconsistent across labs. Across soils, labs #2, #3, #14 and #27 were inconsistent across soils and #29 had high bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

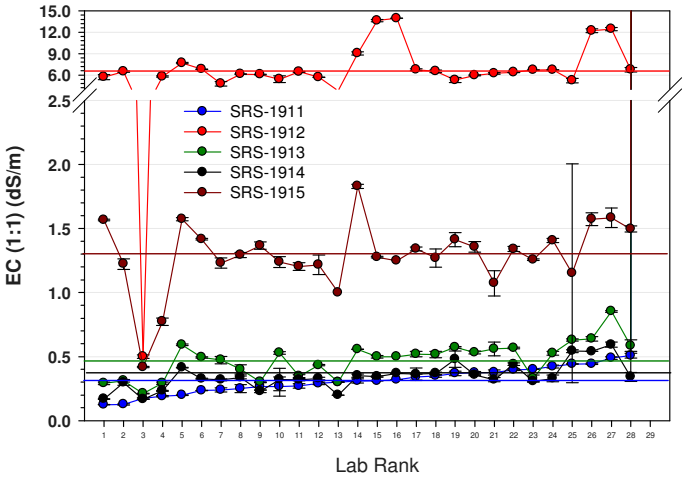

Figure 5. Soil EC (1:1) distribution plot, ALP 2019 Cycle 40.

EC (1:1) median intra-lab *s* values were lowest for ALP soil SRS-1911 and SRS-1914 with an intra-lab median value of 0.35 mg kg^{-1} and highest for SRS-1912 with a value of 2.8 mg kg^{-1} . Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1915 by five labs. Intra-lab precision was poor for labs #10, #21, and #25 on three of five soils. Poor precision maybe associated with extraction and/or ICP-OES instrument operation. Three labs were flagged for poor precision.

SRB - NO_3-N

Twenty-six laboratories provided ALP results for NO_3-N by cadmium reduction, ISE and other (test codes 202, 203 and 204). Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1909 (see Figure 6). The data plot shows lab #1 had low bias for labs #25 and #26. Labs #2, #18, #19 and #22 were inconsistent.

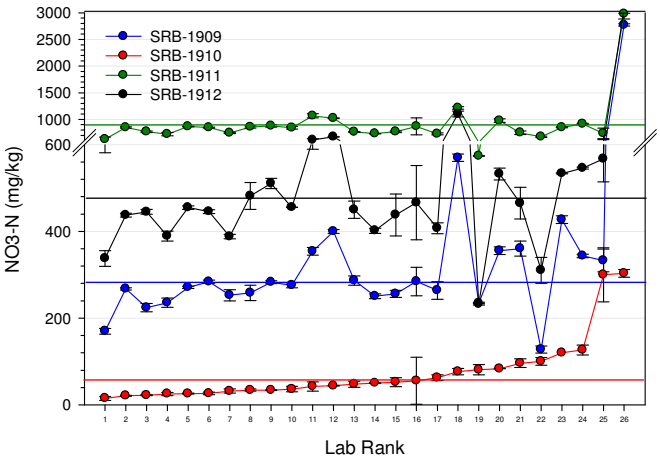

Figure 6. Nitrate distribution plots for SRB materials, ALP 2019, Cycle 40.

Botanical NO_3-N (test code 202) results for Cycle 40 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 11.8 to 23.8 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-1909 ranged from 2.5 – 26 mg kg^{-1}; SRB-1910 ranged from 0.3 - 62 mg kg^{-1}, SRB-1911 ranged from 2.5 – 97 mg kg^{-1} and SRB-1912 ranged from 0.5 - 53 mg kg^{-1} Lab #16 had consistently high standard deviations for three of four samples. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty-one laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and nine labs for TKN (Test code 209) for Cycle 39. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1909 (see Figure 7). It is note worthy that TKN was inconsistent and lower than Dumas for all four samples. Lab #2 showed inconsistency across the three of four botanical samples. Note labs #29 through #31 had in consistent high bias for Dumas-N.

Dumas N results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-1909, ranged 0.003 to 0.060% N, SRB-1910 ranged from 0.002 to 0.093 % N, SRB-1911 ranged from 0.010 to 0.081 % N, and SRB–1912 from 0.006 to 0.085 % N. Lab #11 had consistently high standard deviations on two samples. Lab TKN *s* values for SRB-1909 ranged from 0.004 to 0.068%, SRB-1910 ranged from 0.008 to 0.214% TKN, SRB-1911 ranged from 0.002 to 0.28% TKN nitrogen and SRB-1912 ranged from 0.006 to 0.375% TKN nitrogen. Lab #2 was inconsistent.

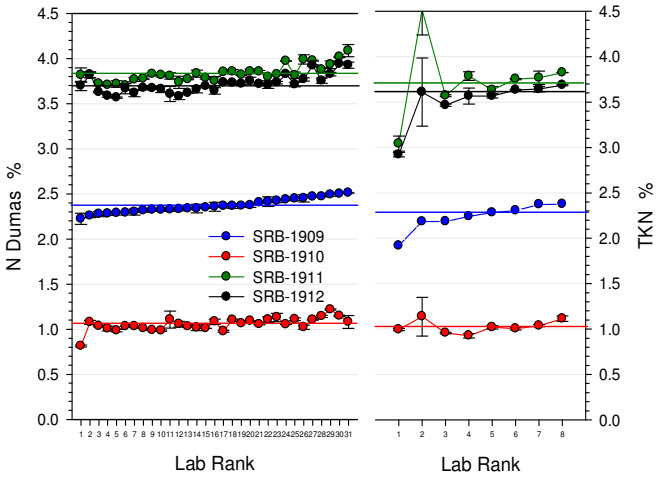

Figure 7. N distribution plots for SRB materials, ALP 2019 Cycle 40.

SRB - Potassium

Thirty-nine 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-1909 (see Figure 8). Laboratories #1 showed low bias on three of four samples. Labs #2, and #8 were inconsistent. Lab #26 swapped results for two 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 0.011 to 0.068 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1909, ranged from 0.037 to 0.112 % K; SRB-1910, 0.015 — 0.061 % K; SRB-1911, 0.045 - 0.15 % K; and SRS-1912, 0.07 to 0.40 % K. Eight labs had high standard deviations exceeding 0.20 %K for SRB-1912. Zero labs were flagged for poor K precision.

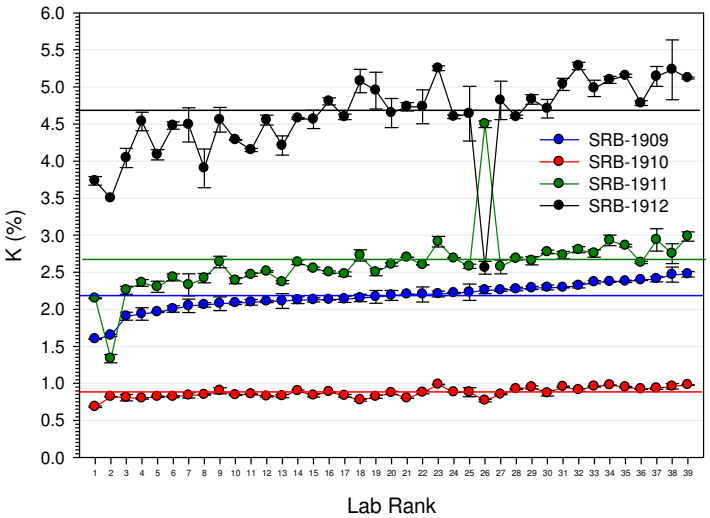

Figure 8. Potassium (code 213) plots for SRB materials, ALP 2019 Cycle 40.

SRB - Phosphorus

Thirty-nine laboratories provided ALP results for Cycle 40 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-1909 (see Figure 9). Consistent high bias was noted for labs #38 and #39. Labs #2, #7, #18, #26, and #34 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 0.004 to 0.007 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1909; ranged from 0.001 - 0.020 % P; SRB-1910 ranged from 0.001 – 0.90 % P and SRB-1911 0.001 - 0.082 % P; and SRB-1912 0.001 - 0.064 % P. Labs #18 and #27 had a high standard deviation exceeding 0.06 % P on two of four botanical samples. One lab was flagged for poor precision for botanical P.

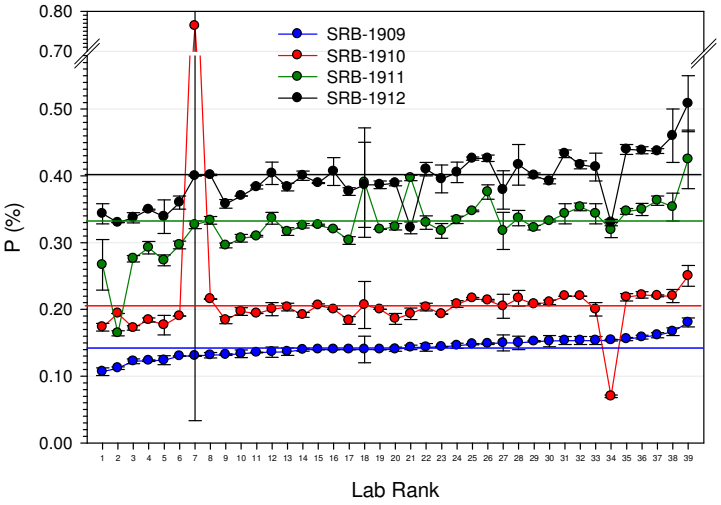

Figure 9. Phosphorus distribution plots for SRB materials, ALP 2019 Cycle 40.

SRB - Manganese

Thirty-nine laboratories provided ALP results for manganese (Mn) (test code 223). 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-1909 (see Figure 10). Across samples Labs #1 through #6, #13, and #39 were inconsistent and data suggests that samples may have switched during analysis. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Mn results indicate very high precision, with intra-lab standard deviation (*s*) values ranged from 0.88 to 11.5 mg kg^{-1} Mn for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1909; ranged from 0.2 - 7.6 mg kg^{-1} Mn; SRB-1910 ranged from 0.5 – 3.4 mg kg^{-1} Mn; SRB-1911 0.6 - 11.1 mg kg^{-1} Mn; and SRB-1912 0.2 - 13.4 mg kg^{-1} Mn. Lab #13 had consistently high standard deviations for two botanical samples.

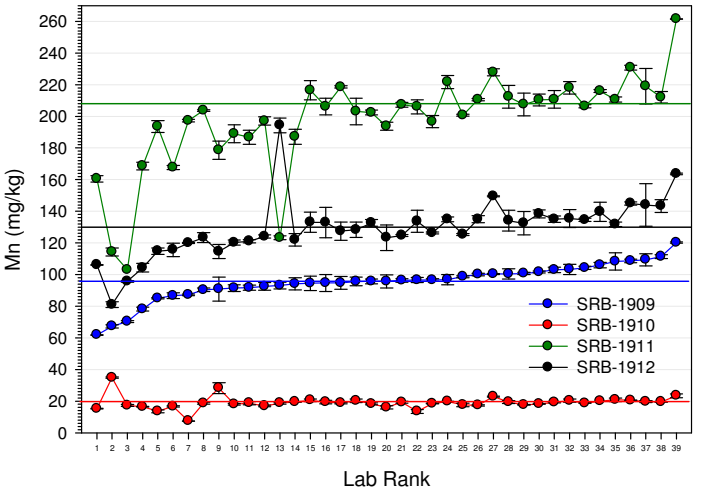

Figure 10. Manganese distribution plots for SRB materials, ALP 2019 Cycle 40.

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-1901 (see Figure 11). Sample SRW-1907 had the lowest EC in Cycle 40. Lab #14 indicated consistent high bias on all samples. Lab #16 showed inconsistently across the three samples. Source of bias is likely associated with EC probe performance and/or calibration.

EC precision across the three water materials indicates good high precision, with intra-lab median Std values of 0.001, 0.004 and 0.001 dSm^{-1}, respectively. Precision for sample SRW-1908 was the most consistent across the sixteen participating laboratories. Intra-lab s values for lab #14 exceeded 0.07 dSm^{-1} on SRW-1908. Highest precision was noted for lab #4 with intra-lab s values of < than 0.004 dSm^{-1} on all three samples.

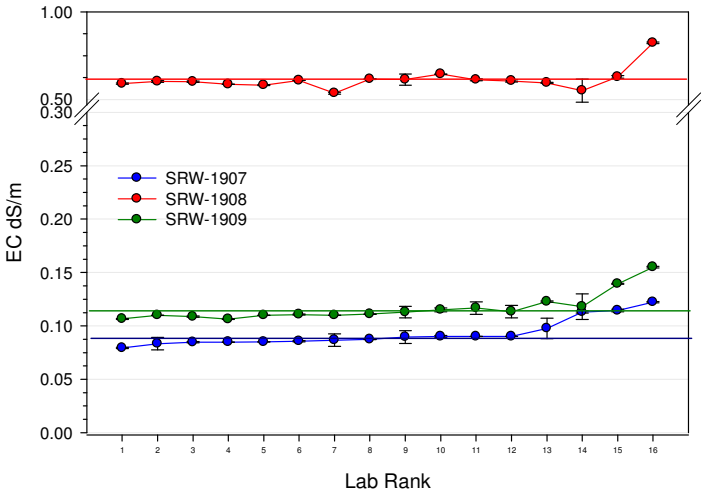

Figure 11 . Water EC distribution plots for SRW materials, ALP 2019 Cycle 40.

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-1907 (see Figure 12) lowest in Ca concentration. Median values are designated by horizontal lines. Labs #1, #2 and #3 had showed inconsistency across samples.

Ca precision across the three water solution matrices indicates excellent precision, with intra-lab s values of 0.032, 0.092, and 0.030 meq L^{-1} for SRW-1907, SRW-1908, and for SRW-1909, respectively. Water Ca precision was excellent for all individual labs with only lab #4 exceeding 0.10 meq L^{-1} on two of the three samples. Across samples intra-lab s was less than 0.02 meq L^{-1} for lab #6. Three labs were flagged for poor precision on ALP Cycle 40 for Ca content.

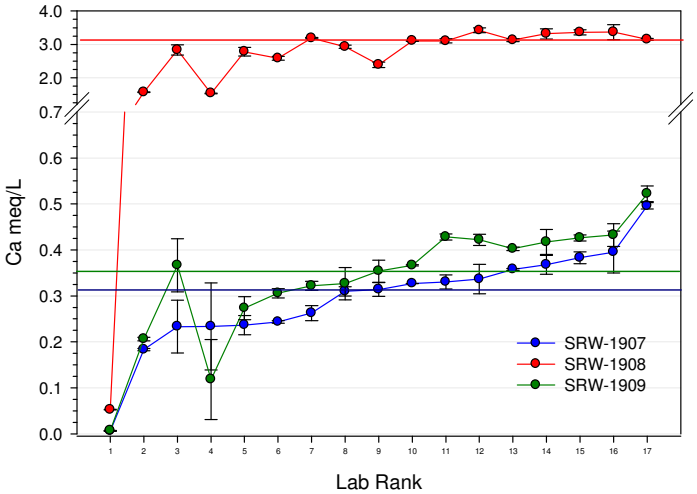

Figure 12. Water Ca distribution plots for SRW materials, ALP 2019 Cycle 40.

Announcements

- The Illinois Soil Testing Association (ISTA) has a winter, February 21, 2020, in Galena, Illinois. Topics include, Lab QC and lab management. For more information contact: ISTA Secretary, gfisher@unitedsoilsinc.com.

- The Soil and Plant Analysis Council (SPAC) and the Illinois Soil Testing Association (ISTA) have jointly developed a international certification program (PAC) for plant analyses: 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. The program initiates March 2020.

- ALP is collaborating with Dr. Russell Harmon of North Carolina State University to assess the use of Laser Induced Breakdown Spectroscopy (LIBS) for the analysis of soil organic carbon. One-hundred and forty-three ALP soils from the ALP archive were evaluated and results were presented at the November SSSA meeting in San Antonio, TX.

- ALP will be adding new test methods to the soil program in 2020. Methods include Soil pH (1:1) 1.0 N KCL, Sikora 2 buffer pH, soil protein, and soil POxC and H3A P and K.. For more information on these methods contact the ALP technical Director.

- A summer lab analysis workshop is being developed in conjunction with Soil Work Group meeting at Clemson University in June 2020. The workshop agenda will be announced in February.

Summary

ALP is celebrating twelve years of service with the completion of Cycle 40. Since 2006 ALP has completed the analysis of 200 soils, 124 plant samples and 113 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 40. 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 41 Ship

March 17, 2020

"We know more about the movement of celestial bodies than about the soil underfoot."

— Leonardo Da Vinci

ALP
Agricultural Laboratory Proficiency Program