2019 Volume 2

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ALP Program Report

2019 Summer - Cycle 39

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ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference soil materials were highly uniform for Cycle 39.
- Sixty-two Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.78 - 8.34.
- Cycle 39 soil Olsen P ranged from 9 to 113 mg kg^{-1} with MAD values ranging 1.3 - 13.4 mg kg^{-1} across the five soils.
- NH4oAc-3 K values ranged from 129 - 358 mg kg^{-1} for the five ALP soils of PT Cycle 39.
- Mehlich 3 Zn values showed high consistency across 25 of 30 testing labs for PT Cycle 39.
- Botanical K, ranged from 0.69 - 10.0% with four of forty-one labs noted for inconsistency.
- Botanical Cu results showed high consistency across the thirty-four of thirty-nine labs for PT Cycle 39.
- Water Mg content showed very high consistency by thirteen of sixteen labs across all PT samples.

The Agriculture Laboratory Proficiency (ALP) Program summer 2019 Round Cycle 39 was completed August 23, 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 39 were: SRS-1906 is a Mainly Orthic sandy loam collected near Arcola, SK, Canada; SRS-1907 Loring silt loam, from Haywood Cty, TN; SRS-1908 a Casa Grande sandy loam collected Pinal, Cty, AZ; SRS-1909 a Broadbrook silt loam, Hartford Cty, CT; and SRS-1910 a Monona-Ida silt loam collected Sarpy Cty, NE. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.78 - 8.34; NO_3-N 30.7 - 93.4 mg kg^{-1}; Bray P1 (1:10) 18.2 - 660 mg kg^{-1}; M3-K 130 - 275 mg kg^{-1}; SO_4-S 4.3 - 23.8 mg kg^{-1}; Mehlich 3 P (ICP) 21.1 - 737 mg kg^{-1}; DTPA-Zn 0.22 - 3.30 mg kg^{-1}; SOM-LOI 1.27 – 3.39%; CEC 8.1 - 19.1 cmol kg^{-1}; clay 5.6 - 27.4% and soil available H_2O 3.3 - 10.3 %.

Standard Reference Botanical (SRB) materials for Cycle 39 were: SRB-1905 a soybean leaf composite from AR; SRB-1906 potato leaf composite from WA; SRB-1907 grape petiole composite from CA; and SRB-1908 arugula leaf composite from CA. SRB material median analytes ranged: NO_3-N 51 - 18840 mg kg^{-1}; Dumas N 2.69 - 5.05%; total P 0.29 - 0.55%; total K 0.69 - 10.0%; total Mg 0.44 - 0.86%; total S 0.21 - 1.19 %, total Zn 39 - 171 mg kg^{-1}; and total Cd 0.05 - 1.68 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1904 a water sample collected from a field tile drain near Geneva, MN; SRW-1905 was collected from canal near Cokeville, WY; and SRW-1906 from a creek near Goldendale, WA. SRW median concentrations ranged: pH 7.65 - 8.19; EC 0.12 - 0.66 dSm^{-1}; SAR 0.24 - 0.47; Ca 0.53 - 4.3 mmolc L^{-1}; Na 0.33 - 0.44 mmolc L^{-1}; HCO_3 0.92 - 5.23 mmolc L^{-1}; and NO_3 0.015 - 0.64 mmolc L^{-1}.

Homogeneity Evaluation Soil

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 39 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 39, 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-1906	7.65	*0.07*	0.89	*0.02*	11.9	*0.9*	1.32	*0.12*
SRS-1907	7.50	*0.02*	0.55	*0.01*	18.1	*0.8*	2.03	*0.10*
SRS-1908	8.16	*0.02*	0.71	*0.03*	4.8	*0.7*	0.78	*0.08*
SRS-1909	5.70	*0.03*	0.70	*0.01*	100	*5.3*	3.54	*0.14*
SRS-1910	5.63	*0.01*	0.59	*0.02*	8.7	*0.6*	2.94	*0.19*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 39.

2019 Cycle 39 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 39 averaged 0.07 pH units across the soils. Median intra-lab lab pH standard deviation was 0.046 pH units. Soil displacement CEC ranged 8.1 to 19.1 cmol kg^{-1} across the five soils. Sample SRS-1906 had a large discrepancy in soil CEC values: Displacement 8.1 cmol kg^{-1} and estimated CEC of 16.5 cmol kg^{-1}. SRS-1908 had an abnormally high Mehlich 3 P of 737 mg kg^{-1}, associated with Broadbrook silt loam, Hartford Cty, CT. Soil ammonium acetate K (Test code 140) MAD values ranged 8.1 - 23.7 mg kg^{-1} and ammonium acetate Mg MAD values ranged 3.7 to 17.4 mg kg^{-1} for the five soils. These results for K and Mg were consistent with past cycles in 2018 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 0.18% nitrogen with intra-lab *s* of 0.040%, 0.054%, 0.038% and 0.044%, respectively. As with cycle 38 there was a generally greater inter-lab relative variability (MAD) for total boron values than for combustion N, P, K, Ca, Mg, Zn, or Mn concentrations across all samples. Generally the soybean leaf composite sample SRB-1905 had lower median concentrations of Cl, K, NO3-N and Cu relative to the other three botanical samples. One observation on Cycle 39, intra-lab relative variability was lowest for N and P than all other macro elements for all four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.021, 0.003 and 0.010 dSm^{-1}, respectively. Median Cl values ranged from 0.013 - 0.47 molc L^{-1} across the three water samples with MAD values ranging 0.030 to 0.051 molc L^{-1}. Sample SRW-1904 had a median HCO_3 of 5.23 molc L^{-1} with a MAD of 0.33.

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 5.39 - 8.08. Lab results were ranked low to high based on sample SRS-1910 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1909, and SRS-1910 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.

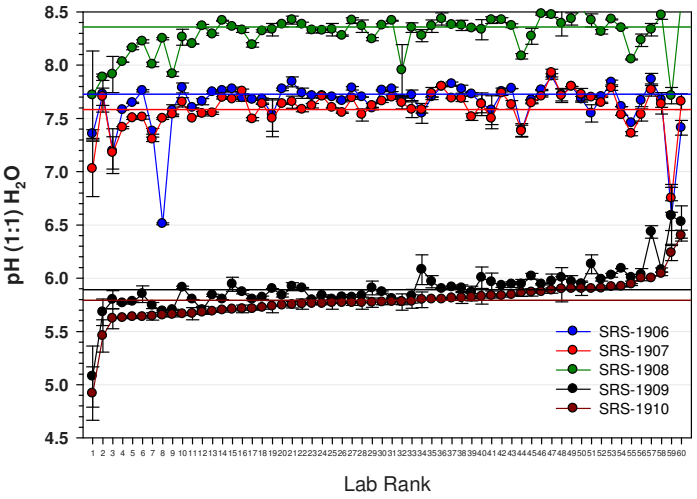


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2019 Cycle 39.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.038 to 0.056 pH units, the lowest noted for SRS-1910. 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 #1, #2, #3, #19, #40, #48 and #59 exceeded 0.10 pH units for two of five soils. Soil SRS-1910 was the least variable with respect to intra-lab variance for Cycle 39.

SRS - Phosphorus: Bray P1, Bray P2, Olsen, Modified Morgan, M1, and M3

Bray P1 results were reported by thirty-one labs. M3-P ICP was reported by 35 labs. Median soil Bray P1 values ranged from 18.1 - 660 mg kg^{-1} PO_4-P; Olsen P 9.0 to 113 mg kg^{-1} P and Bray P2 ranged from 45.6 to 1068 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1908, median Olsen P concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1906 and SRS-1907 associated with the moderate P concentrations. Soil SRS-1908, lowest in concentration, showed low intra-lab variability with a range of 0.62 - 5.0 mg kg^{-1}. Lab #1 showed low bias on all five samples. Labs #2, #4, #6, #12 #33 and #35 were inconsistent. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

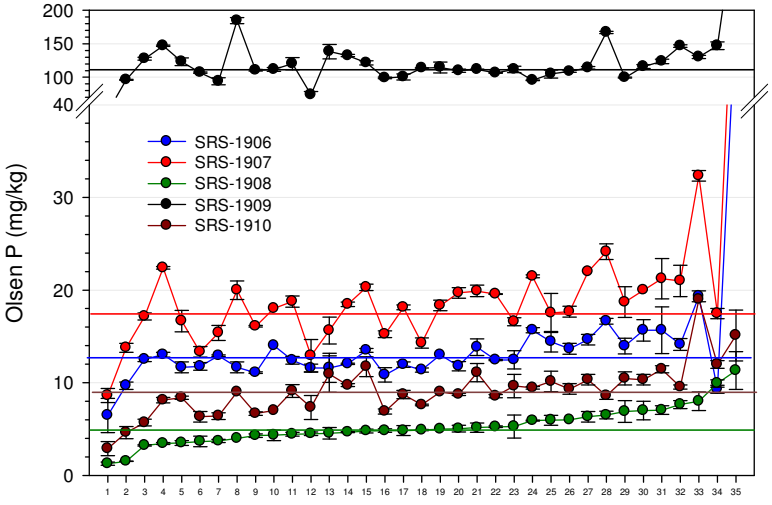


Figure 2. Olsen P distribution plots for SRS materials, ALP 2019 Cycle 39.

Four laboratories provided ALP results for Mehlich 1 P, with medians ranging from 7.1 to 335 mg kg^{-1} PO_4-P . M3-P ICP median concentrations were 21.1 - 737 mg kg^{-1} P reported by thirty-five labs. Modified Morgan was reported by two laboratories ranging from 1.7 - 43.5 mg kg^{-1} P with the highest concentration noted for SRS-1909.

SRS - Potassium

Forty-six laboratories provided ALP results for soil K (test code 141) results. Results were ranked low to high based on sample SRS-1909 (see Figure 3). Soils SRS-1908 and SRS-1910 were the most inconsistent across labs. Labs #1 and #2 had low bias on all five soils. Labs #7, #19, #31, #43, and #44 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-1907, with a median intra-lab value of 5.0 mg kg^{-1} Kg and highest for SRS-1910 with a value of 9.3 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 #4, #5, #26, and #31 which exceeded 15 mg kg^{-1} K on SRS-1907; and labs #36, the value exceeded 20 mg kg^{-1} K for SRS-1909. Poor precision is attributed to extraction and/or analysis instrument operation.

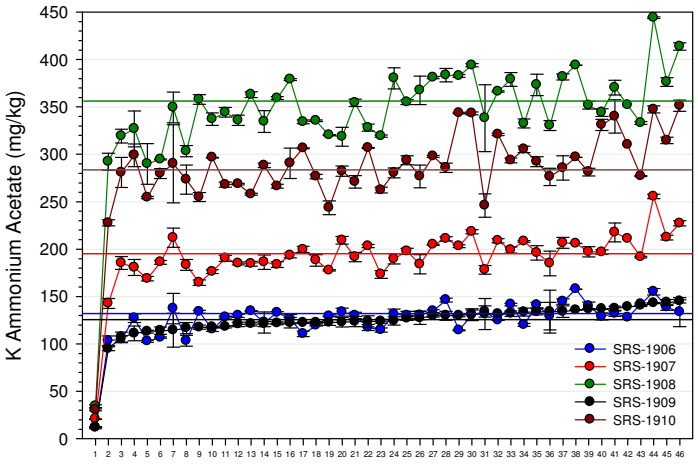


Figure 3. Extractable K distribution plots for SRS materials, ALP 2019 Cycle 39.

SRS - SOM-LOI

Forty-six laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.27 to 3.39%. Results were ranked based on sample SRS-1906 (see Figure 4). Labs #31, #33, #43, #45, and #46 were noted having 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.

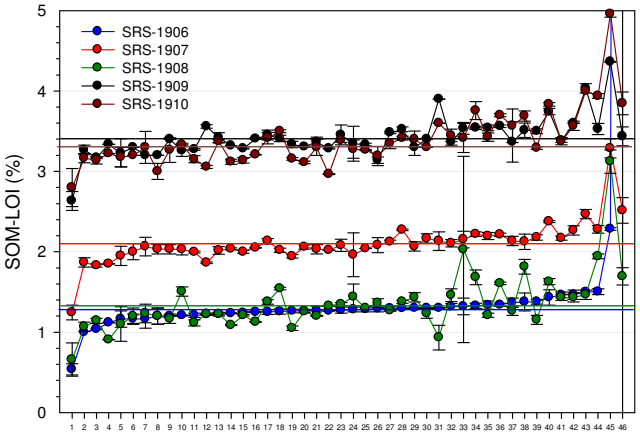


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2019 Cycle 39.

SOM-LOI precision across the five materials indicates high intra-lab precision, with median *s* values ranging from 0.03 to 0.05% SOM-LOI, the highest for SRS-1908. Across labs, *s* values for SRS-1906 ranged from 0.005 - 0.27 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #1, #5, #24, #31, #33 and #45, exceeded 0.15 % SOM for SRS-1908. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

SRS - M3-Zn

Thirty laboratories provided ALP results for Mehlich 3 (M3-Zn) Zn (test code 165). Results were ranked low to high based on sample SRS-1906 (see Figure 5). Soil SRS-1909 was the highest in concentration. Soil ID SRS-1907 was the most inconsistent across labs. Across soils, labs #26 through #30 were inconsistent across soils and #1 had low bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

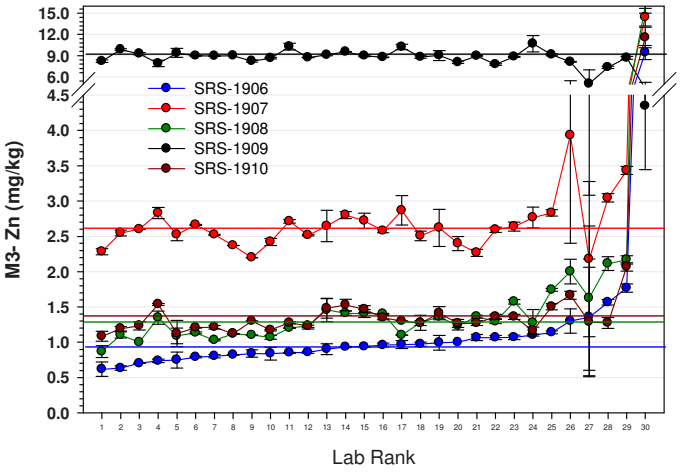


Figure 5. Soil M3-Zn distribution plot, ALP 2019 Cycle 39.

M3-Zn Mg median intra-lab *s* values were lowest for ALP soil SRS-1906 and SRS-1908 with an intra-lab median value of 0.25 mg kg^{-1} and highest for SRS-1909 with a value of 0.50 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1907 by nine labs. Intra-lab precision was poor for labs #26, #27, and #30 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-four 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-1905 (see Figure 6). The data plot shows lab #1 had low bias for SRB-1906 and SRB-1908. Labs #3, #16, #23 and #24 were inconsistent.

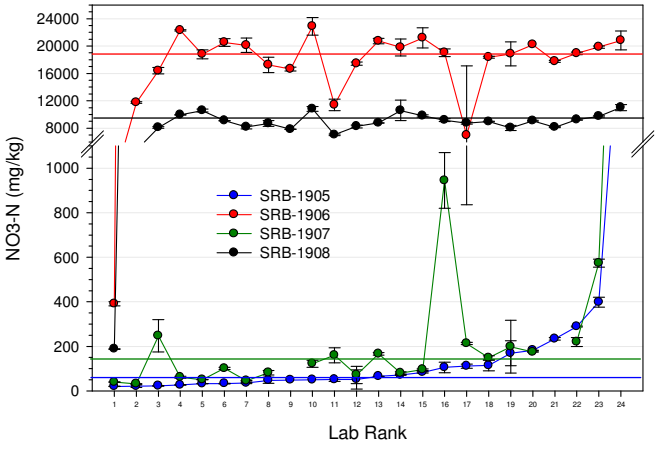


Figure 6. Nitrate distribution plots for SRB materials, ALP 2019, Cycle 39.

Botanical NO_3-N (test code 202) results for Cycle 39 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 19.4 to 824 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-1905 ranged from 1.0 – 56 mg kg^{-1}; SRB-1906 ranged from 90 - 1750 mg kg^{-1}, SRB-1907 ranged from 1.1 – 125 mg kg^{-1} and SRB-1908 ranged from 21 - 1450 mg kg^{-1} Lab #17 had consistently high standard deviations for sample SRB-1906. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty 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-1907 (see Figure 7). It is note worthy that TKN was inconsistent and lower than Dumas for all four samples. Labs #1 and #5 showed inconsistency across the three of four botanical samples. It was worth noting labs #24 through #30 had consistent high bias.

Dumas N results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-1905, ranged 0.004 to 0.115% N, SRB-1906 ranged from 0.002 to 0.199 % N, SRB-1907 ranged from 0.005 to 0.123 % N, and SRB–1908 from 0.006 to 0.150 % N. Lab #16 had consistently high standard deviations. Lab TKN *s* values for SRB-1905 ranged from 0.005 to 0.39%, SRB-1906 ranged from 0.015 to 0.48% TKN, SRB-1907 ranged from 0.009 to 0.43% TKN nitrogen and SRB-1908 ranged from 0.015 to 0.48% TKN nitrogen. Lab #6 had consistently high standard deviations.

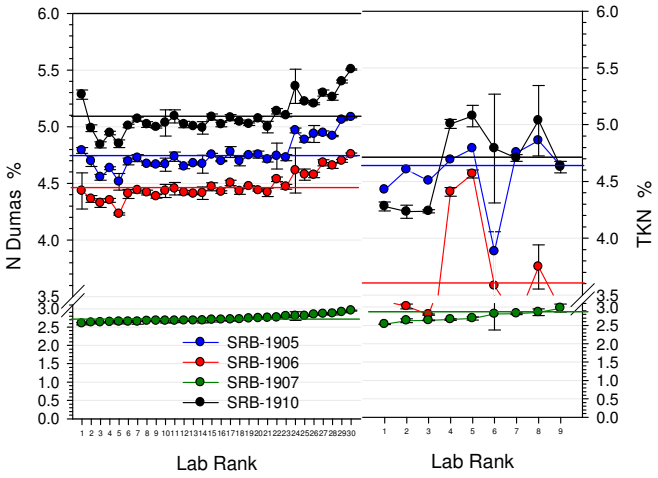


Figure 7. N distribution plots for SRB materials, ALP 2019 Cycle 39.

SRB - Potassium

Forty-one laboratories provided ALP results for potassium (K) (test code 213). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1905 (see Figure 8). Laboratories #1 showed low bias on two of four samples. Labs #3, #14, #33, #37 were inconsistent. Source of bias is likely 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 0.030 to 0.590 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1905, ranged from 0.003 to 0.124 % K; SRB-1906, 0.05 — 2.7 % K; SRB-1907, 0.002 - 0.07 % K; and SRS-1908, 0.01 to 0.58 % K. Four labs had high standard deviations exceeding 0.25 %K for SRB-1908. Six labs were flagged for poor K precision.

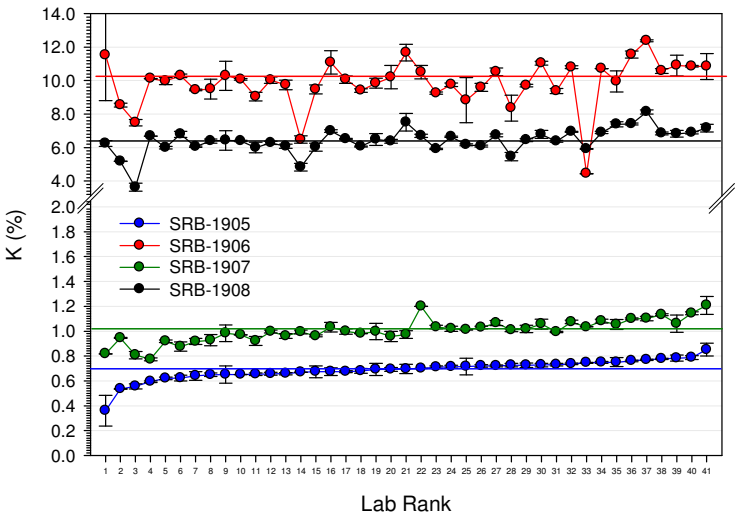


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2019 Cycle 39.

SRB - Phosphorus

Forty-one laboratories provided ALP results for Cycle 39 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-1907 (see Figure 9). Consistent high bias was noted for labs #39 - #41. Labs #1, #2, #3, #8, and #29 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 0.005 to 0.010 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1905; ranged from 0.001 - 0.066 % P; SRB-1906 ranged from 0.007 – 0.117 % P and SRB-1907 0.002 - 0.025 % P; and SRB-1908 0.001 - 0.090 % P. Labs #8 and #9 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.

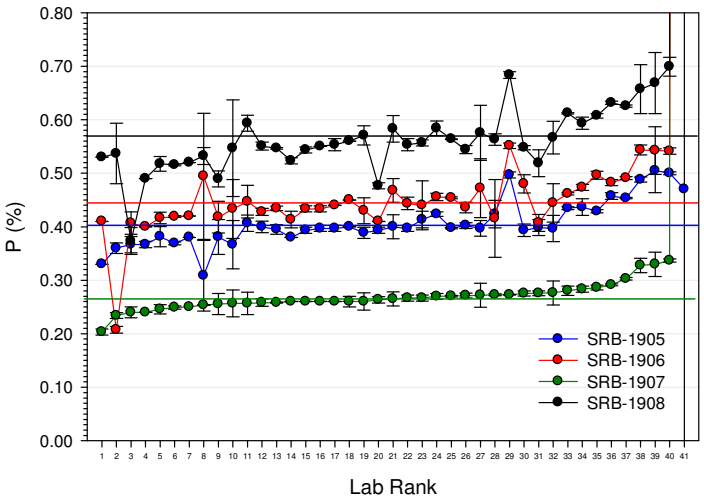


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2019 Cycle 39.

SRB - Copper

Thirty-nine laboratories provided ALP results for copper (Cu) (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-1905 (see Figure 10). Across samples Labs #1, #10, #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 Cu results indicate very high precision, with intra-lab standard deviation (*s*) values ranged from 0.81 to 1.9 mg kg^{-1} Cu for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1905; ranged from 0.01 - 2.3 mg kg^{-1} Cu; SRB-1906 ranged from 0.12 – 7.1 mg kg^{-1} Cu; SRB-1907 0.06 - 4.3 mg kg^{-1} Cu; and SRB-1908 0.08 - 2.5 mg kg^{-1} Cu. Lab #13 had consistently high standard deviations for two botanical samples. Six labs were flagged for poor precision for botanical Cu.

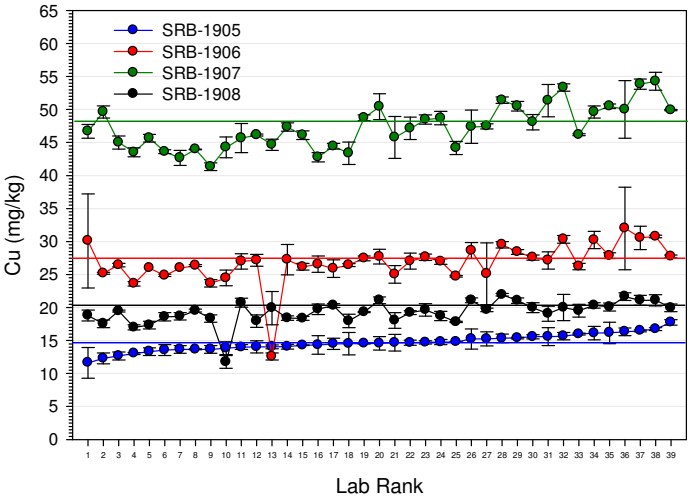
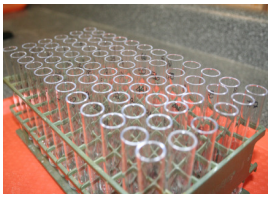


Figure 10. Zinc distribution plots for SRB materials, ALP 2019 Cycle 39.

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-1905 had the lowest EC in Cycle 39. Lab #14 indicated consistent high bias on all samples. Lab #15 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 0.005, 0.002 and 0.002 dSm^{-1}, respectively. Precision for sample SRW-1905 was the most consistent across the sixteen participating laboratories. Intra-lab *s* values for lab #4 exceeded 0.06 dSm^{-1} on SRW-1904. Highest precision was noted for lab #11 with intra-lab *s* values of < than 0.002 dSm^{-1} on all three samples.

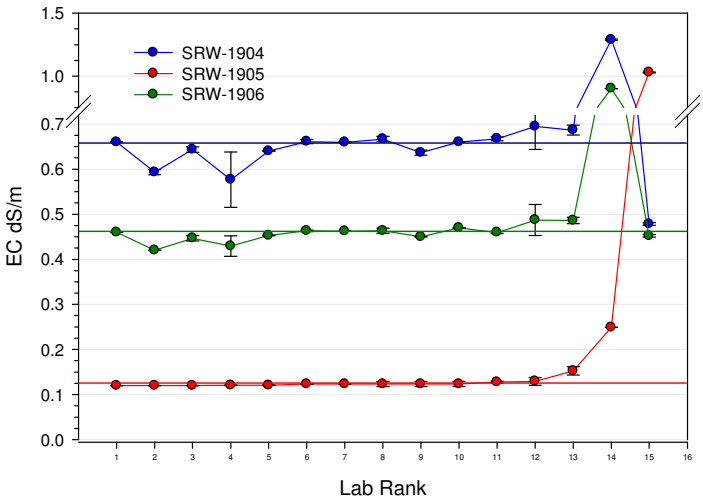


Figure 11 . Water EC distribution plots for SRW materials, ALP 2019 Cycle 39.

SRW - Mg Results

Sixteen laboratories provided ALP results for water Mg (test code 304). Lab results were ranked low to high based on sample SRW-1905 (see Figure 12) lowest in Mg concentration. Median values are designated by horizontal lines. Labs #1, #2 and #3 had showed inconsistency across samples.

Mg precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.067, 0.019, and 0.030 meq L^{-1} for SRW-1904, SRW-1905, and for SRW-1906, respectively. Water Mg precision was excellent for all individual labs with only lab #5 exceeding 0.08 meq L^{-1} on two of the three samples. Across samples intra-lab *s* was less than 0.02 meq L^{-1} for lab #14. Four labs were flagged for poor precision on ALP Cycle 39 for Mg content.

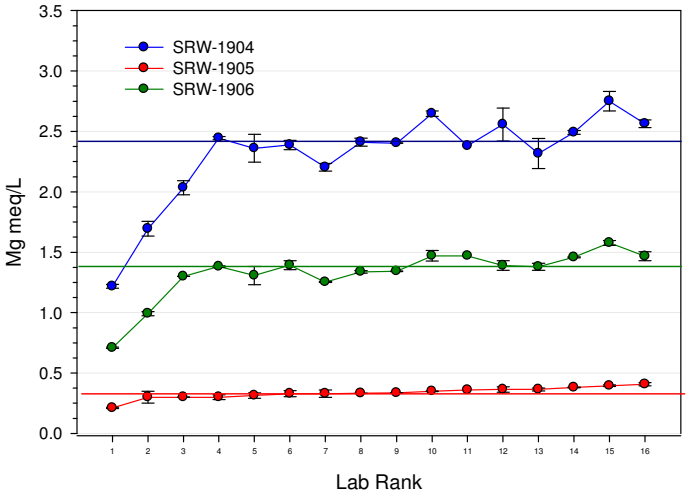


Figure 12. Water Mg distribution plots for SRW materials, ALP 2019 Cycle 39.

Announcements

- The Illinois Soil Testing Association (ISTA) has a laboratory analysis workshop, for September, 17, 2019, in Bloomington, Illinois. Topics include, soil pH, lab quality, potassium analysis by ICP and new instrumentation. For more information contact: ISTA Secretary, gfisher@unitedsoilsinc.com.

- International exchange of proficiency botanical sample. ALP cycle 38 botanical SRB-1901 (pistachio leaves) was exchanged with Wageningen Evaluating programs for Analytical Laboratories (WEPAL) for use in their 2019 plant proficiency program, managed by Wageningen University.

- The Soil and Plant Analysis Council (SPAC) and the Illinois Soil Testing Association (ISTA) have jointly developed a international certification program for plant analyses: N, P, K, S, Ca, Mg Zn, B, Mn, Fe, and Cu. The program will be based exclusively on ALP proficiency testing data evaluated on a yearly basis. The program initiates in January 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 are being evaluated and results will be presented at the November SSSA meeting in San Antonio, TX.

- A winter 2020 lab analysis workshop is being developed for the soil and plant analysis labs in the Pacific North West. A specific date and location will be announced in October 2019.

Summary

ALP is celebrating twelve years of service with the completion of Cycle 39. Since 2006 ALP has completed the analysis of 190 soils, 120 plant samples and 111 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 39. 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 40 Ship

September 18, 2019

"We can't have positive knowledge of the existence of the unknowable."

— Andrei Kolmogorov , 1965

ALP
Agricultural Laboratory Proficiency Program