2019 Volume 1

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ALP Program Report

2019 Spring - Cycle 38

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ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 38.
- Sixty-two Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.35 - 8.07.
- Cycle 38 soil Bray P1 ranged from 16.5 to 45.2 mg kg^{-1} with MAD values ranging 1.9 - 4.0 mg kg^{-1} across the five soils.
- Mehlich-3 K values ranged from 69.2 - 271 mg kg^{-1} for the five ALP soils of Cycle 38.
- Botanical P, ranged from 0.13 - 0.60% with two of thirty-eight labs noted for high bias.
- Botanical Zn results showed high consistency across the four samples for thirty-two of thirty-eight labs for PT Cycle 38.
- Water Ca content showed very high consistency by twelve of fourteen labs across all samples.

Inside this issue:

The Agriculture Laboratory Proficiency (ALP) Program spring 2019 Round Cycle 38 was completed May 27, 2019, with one-hundred eight labs enrolled from the United States, Canada, South Africa, Honduras, Serbia, Ukraine, Philippines and Guatemala. 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.

Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 38 were: SRS-1901 is a Cropley clay collected San Louis Obispo Cty, CA; SRS-1902 a loam, from Middlesex, Ontario, Canada; SRS-1903 a Busti silt loam collected Chautauqua Cty, NY; SRS-1904 a Crosby Silt loam Madison Cty, IL; and SRS-1905 a Deerford silt loam collected East Baton Rouge Cty, LA. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.13 - 7.94; NO_3-N 2.4 - 96.3 mg kg^{-1}; Bray P1 (1:10) 3.3 - 47.3 mg kg^{-1}; K NH_4OAc 71 - 280 mg kg^{-1}; SO_4-S 8.6 - 63.4 mg kg^{-1}; Mehlich 3 P (ICP) 20.0 - 88.9 mg kg^{-1}; DTPA-Zn 0.71 - 3.63 mg kg^{-1}; SOM-LOI 2.41 – 5.98%; CEC 9.7 - 44.4 cmol kg^{-1}; clay 8.5 - 49.4% and soil available H_2O 11.1 - 19.4 %.

Standard Reference Botanical (SRB) materials for Cycle 38 were: SRB-1901 a pistachio leaf composite from CA; SRB-1902 spinach leaf composite from CA; SRB-1903 corn leaf composite from IA; and SRB-1904 citrus leaf composite from CA. SRB material median analytes ranged: NO_3-N 39 - 19400 mg kg^{-1}; Dumas N 2.53 - 6.36%; total P 0.13 - 0.60%; total K 1.01 - 7.31%; total Mg 0.35 - 1.46%; total S 0.17 - 0.41 %, total Zn 20.4 - 127.4 mg kg^{-1}; and total Cd 0.02 - 1.80 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1901 a water sample collected from a well near Wellington, CO SRW-1902 was collected from canal near Ault, CO; ; and SRW-1903 from a surface canal near Sterling, CO. SRW median concentrations ranged: pH 7.49 - 8.17; EC 0.15 - 3.49 dSm^{-1}; SAR 0.34 - 23.7; Ca 0.11 - 2.73 mmolc L^{-1}; Na 0.29 - 31.6 mmolc L^{-1}; HCO_3 1.12 - 3.04 mmolc L^{-1} ; and NO_3 0.005 - 0.07 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 38 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 38, 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-1901	7.94	*0.02*	0.61	*0.036*	26.0	*1.3*	4.18	*0.9*
SRS-1902	7.56	*0.01*	0.83	*0.026*	13.9	*0.9*	6.71	*0.17*
SRS-1903	5.28	*0.03*	1.90	*0.038*	19.3	*0.8*	4.71	*0.14*
SRS-1904	6.07	*0.04*	0.85	*0.025*	23.8	*1.6*	3.53	*0.08*
SRS-1905	7.45	*0.03*	0.91	*0.019*	11.1	*0.6*	2.20	*0.13*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 38.

2019 Cycle 38 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 38 averaged 0.07 pH units across the soils. Median within lab pH standard deviation was 0.042 pH units. Soil displacement CEC ranged 9.7 to 44.4 cmol kg^{-1} across the five soils. Sample SRS-1903 had a large discrepancy in soil CEC values: Displacement 13.4 cmol kg^{-1} and estimated CEC of 10.8 cmol kg^{-1}. SRS-1901 had an abnormally high Mehlich 3 Mg of 3660 mg kg^{-1}, likely associated with Cropley clay soil series. Soil ammonium acetate K (Test code 140) MAD values ranged 5.9 - 16.2 mg kg^{-1} and ammonium acetate Mg MAD values ranged 9.6 to 269 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 0.052% nitrogen with intra-lab *s* of 0.027%, 0.058%, 0.041% and 0.035%, respectively. As with cycle 37 there was a generally greater inter-lab relative variability (MAD) in total boron values than for combustion N, P, K, Ca, Mg, Zn, or Mn concentrations across all samples. Generally the corn leaf composite sample SRB-1903 had lower median concentrations of Ca, B, Cu, Zn and NO_3-N relative to the other three botanical samples. One observation on Cycle 38, 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 0.083, 0.013 and 0.003 dSm^{-1}, respectively. Cl values ranged from 0.059 - 2.16 molc L^{-1} across the three water samples with MAD values ranging 0.035 to 0.46 molc L^{-1}. Sample SRW-1901 had and SAR of 23.1 with a MAD of 0.9.

SRS Results - pH

Sixty-two laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.38 - 8.08. Lab results were ranked low to high based on sample SRS-1901 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1902, SRS-1904 and SRS-1905 showed good consistency across labs. Labs #2, #9, and #25 were inconsistent across soils. Labs #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.

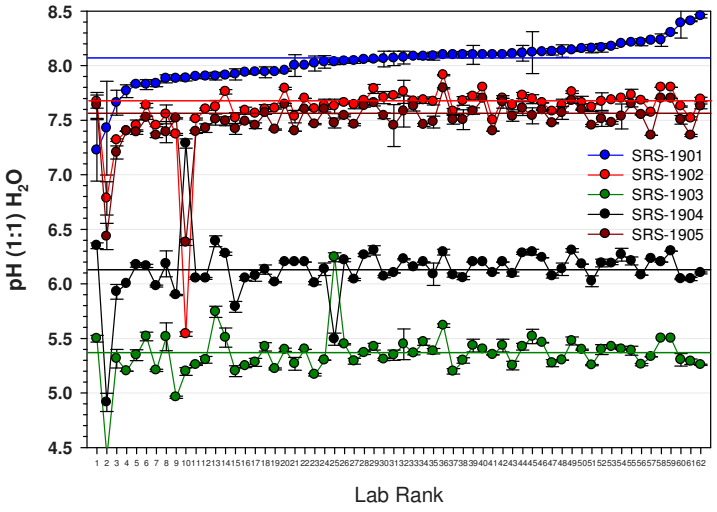


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2019 Cycle 38.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.015 to 0.025 pH units, the lowest noted for SRS-1904. For specific labs poor precision was noted for four laboratories, exceeding by three times that noted for consensus median intra-lab *s*. Specifically *s* for lab #2, #8 and #32 exceeded 0.10 pH units for two of five soils. Soil SRS-1904 was the least variable with respect to intra-lab variance for Cycle 38.

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

Bray P1 results were reported by thirty-two labs. M3-P ICP was reported by 32 labs. Median soil Bray P1 values ranged from 16.5 - 49.6 mg kg^{-1} PO_4-P; Olsen P 11.0 to 26.2 mg kg^{-1} P and Bray P2 ranged from 32.6 to 369 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1901, median Olsen P concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1902 and SRS-1904 associated with the moderate P concentrations. Soil SRS-1905, lowest in concentration, showed low intra-lab variability with a range of 0.09 - 2.5 mg kg^{-1}. Lab #1 showed low bias on three samples. Labs #1, #6, #15, #21 #33 and #35 were inconsistent. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

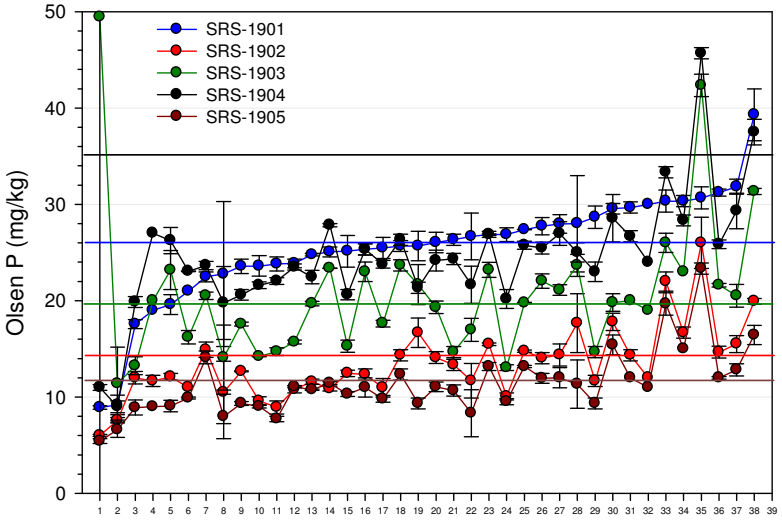


Figure 2. Bray P1 distribution plots for SRS materials, ALP 2019 Cycle 38.

Four laboratories provided ALP results for Mehlich 1 P, with medians ranging from 8.5 to 140 mg kg^{-1} PO_4-P . M3-P ICP median concentrations were 19.9 - 88.9 mg kg^{-1} P reported by thirty-two labs. Modified Morgan was reported by two laboratories ranging from 2.5 - 70.1 mg kg^{-1} P with the highest concentration noted for SRS-1901.

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-1905 (see Figure 3). Soils SRS-1901 and SRS-1904 were the most inconsistent across labs. Labs #1 and #2 had low bias on all five soils. Labs #10, #20, #28, #35, and #40 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-1903, with a median intra-lab value of 3.1 mg kg^{-1} Kg and highest for SRS-1901 with a value of 11.8 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, #3, #10, and #20 which exceeded 10 mg kg^{-1} K on SRS-1901; and labs #18, and #30 the value exceeded 8 mg kg^{-1} K for SRS-1905. Poor precision is attributed to extraction and/or analysis instrument operation.

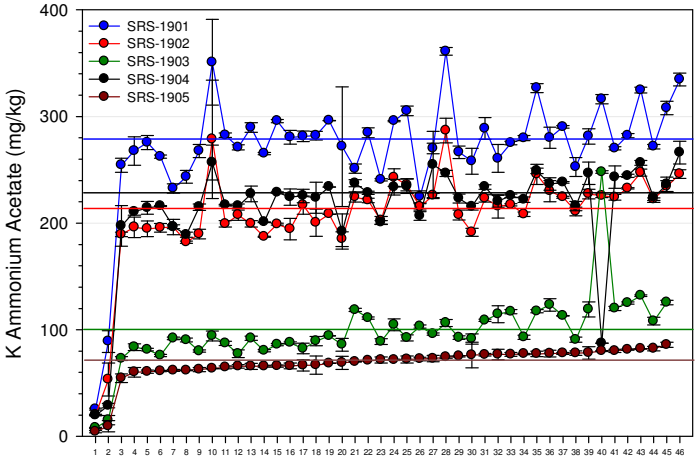


Figure 3. Extractable K distribution plots for SRS materials, ALP 2019 Cycle 38.

SRS SOM-LOI

Forty-four laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 2.41 to 5.98%. Results were ranked based on sample SRS-1901 (see Figure 4). Labs #2, #9, #30, #39, and #44 were noted having inconsistency three of five soils. Sample SRS-1902 shows high inconsistency likely associated with 5.0 % SOM content. Bias was noted in three lab results. Source of bias is likely related to muffle furnace operation and/or method compliance.

SOM-LOI precision across the five materials indicates high intra-lab precision, with median *s* values ranging from 0.08 to 0.17% SOM-LOI, the highest for SRS-1902. Across labs, *s* values for SRS-1901 ranged from 0.005 - 0.59 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #8, #18, #26, #32, and #42, exceeded 0.15 % SOM for SRS-1902. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

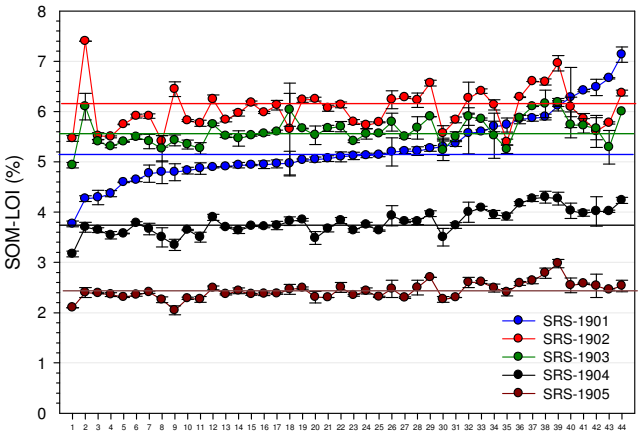


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2019 Cycle 38.

SRS M3-Mg

Thirty-one laboratories provided ALP results for M3-Mg (test code 161). Results were ranked low to high based on sample SRS-1905 (see Figure 5). Soil SRS-1901 was the highest in concentration and the most in consistent across labs. Across soils, labs #1 #12, #29, and #30 were inconsistent across soils and #1 had high bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

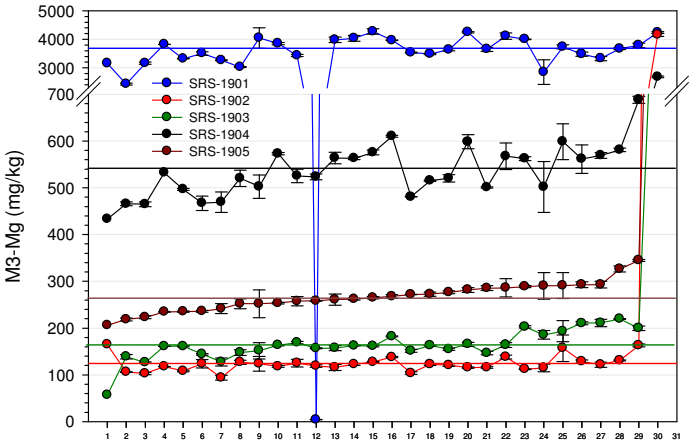


Figure 5. Soil NO3-N distribution plot, ALP 2019 Cycle 38.

M3-Mg median intra-lab *s* values were lowest for ALP soil SRS-1902 and SRS-1905 with an intra-lab median value of 11 mg kg^{-1} and highest for SRS-1901 with a value of 119 mg kg^{-1} . Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1901. Intra-lab precision was poor for labs #9, #22, #24, and #25 on three of five soils. Poor precision maybe associated with extraction and/or ICP-OES instrument operation. Five labs were flagged for poor precision.

SRB Nitrate-Nitrogen

Twenty-two laboratories provided ALP results for NO_3-N by cadmium reduction and ISE (test code 202 and 203). Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1902 (see Figure 6). The data plot shows labs #1, and #2 had low bias for SRB-1902. Labs #2, #5 and #9 were inconsistent.

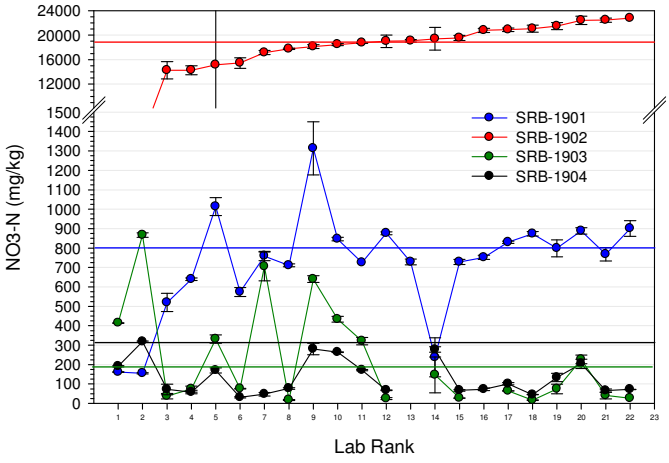


Figure 6. Nitrate distribution plots for SRB materials, ALP 2019, Cycle 38.

Botanical NO_3-N (test code 202) results for Cycle 38 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 10.9 to 808 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-1901 ranged from 2.0 – 136 mg kg^{-1}; SRB-1902 ranged from 10.2 - 11141 mg kg^{-1}, SRB-1903 ranged from 1.8 – 92 mg kg^{-1} and SRB-1904 ranged from 1.0 - 30 mg kg^{-1} Lab #14 had consistently high standard deviations for two of four samples. Three 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 eight labs for TKN (Test code 209) for Cycle 38. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1901 (see Figure 7). It is note worthy that TKN was lower than Dumas for all four samples. Labs #1 and #2 showed low bias for Dumas N for three samples, whereas lab #29 showed inconsistency across the all four botanical samples.

Dumas N and TKN results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-1901, ranged 0.005 to 0.065% N, SRB-1902 ranged from 0.001 to 0.231% N, SRB-1903 ranged from 0.006 to 0.155 % N, and SRB–1904 from 0.002 to 0.136 % N. Lab #16 had consistently high standard deviations. Lab TKN *s* values for SRB-1901 ranged from 0.002 to 0.205%, SRB-1902 ranged from 0.015 to 0.351% TKN, SRB-1903 ranged from 0.011 to 0.206% TKN nitrogen and SRB-1904 ranged from 0.010 to 0.265% TKN nitrogen.

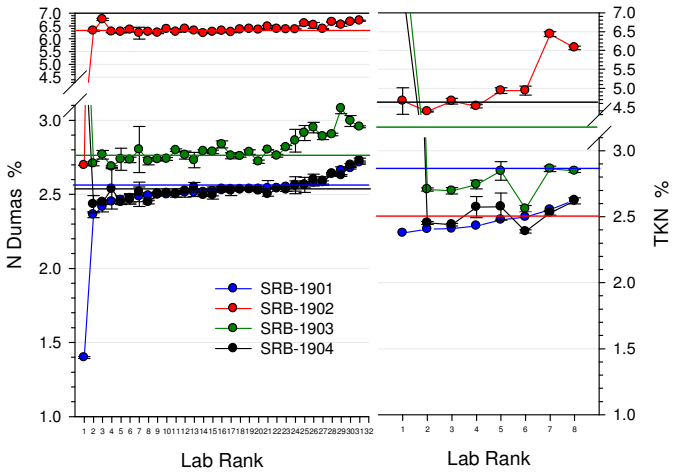


Figure 7. N distribution plots for SRB materials, ALP 2019 Cycle 38.

SRB - Potassium

Thirty-eight 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-1901 (see Figure 8). Laboratories #1 and #2 showed low bias. Labs #3, #36, #37, #38 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 0.042 to 0.292 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1901, ranged from 0.001 to 0.202 % K; SRB-1902, 0.003 — 0.874 % K; SRB-1903, 0.002 - 0.189 % K; and SRS-1904, 0.002 to 0.112 % K. Four labs had high standard deviations exceeding 0.20 %K for SRB-1903. Six labs were flagged for poor K precision.

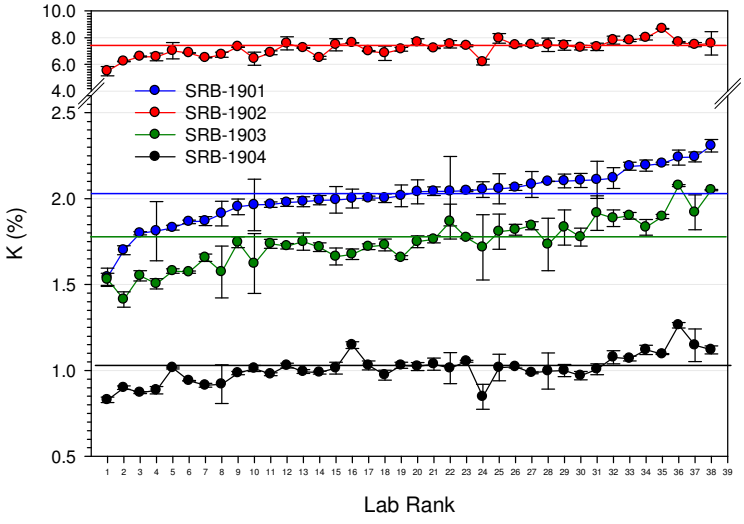


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2019 Cycle 38.

SRB - Phosphorus

Thirty-eight laboratories provided ALP results for Cycle 38 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-1901 (see Figure 9). Consistent high bias was noted for lab #38. Labs #1, #2, #4, $24, #27 and #37 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 0.006 to 0.019 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1901; ranged from 0.001 - 0.025 % P; SRB-1902 ranged from 0.002 – 0.051 % P and SRB-1903 0.001 - 0.030 % P; and SRB-1904 0.001 - 0.017 % P. Labs #42 had a high standard deviation exceeding 0.02 % P on two of four botanical samples. Six labs were flagged for poor precision for botanical P.

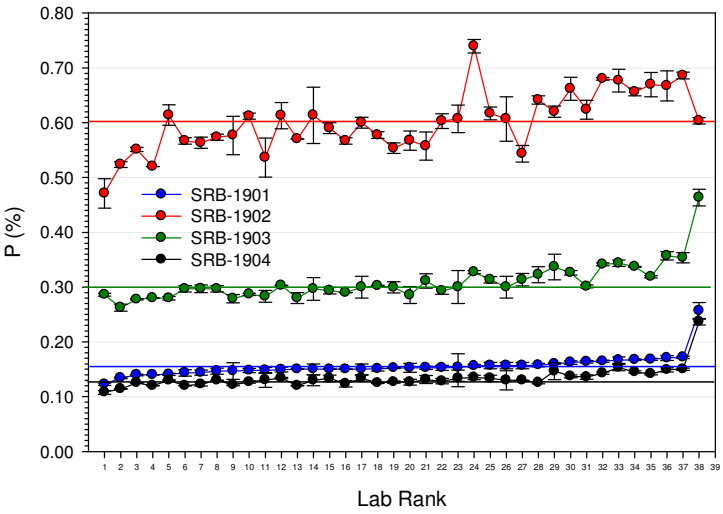


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2019 Cycle 38.

SRB - Zinc

Thirty-seven laboratories provided ALP results for boron (Zn) (test code 220). 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-1901 (see Figure 10). Labs #1 showed low bias on all samples. Labs #8, #14, #22, #31 and #33 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 Zn results indicate very high precision, with intra-lab standard deviation (*s*) values ranged from 1.37 to 2.51 mg kg^{-1} Zn for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1901; ranged from 0.32 - 12.5 mg kg^{-1} Zn; SRB-1902 ranged from 0.30 – 6.5 % Zn; SRB-1903 0.05 - 7.1 mg kg^{-1} Zn; and SRB-1904 0.30 - 8.1 mg kg^{-1} Zn. Lab #8 had consistently high standard deviations for three botanical samples. Five labs were flagged for poor precision for botanical Zn.

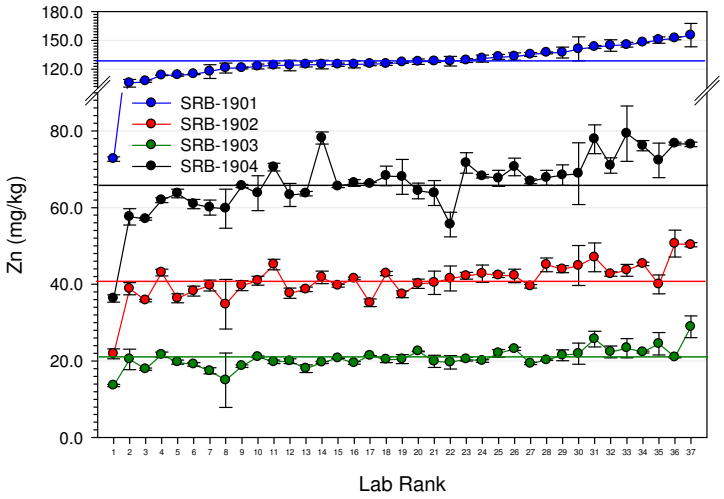
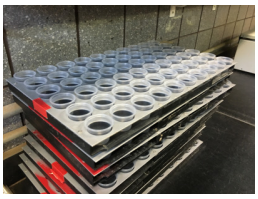


Figure 10. Zinc distribution plots for SRB materials, ALP 2019 Cycle 38.

SRW - Water EC



Fifteen laboratories provided ALP results for water EC (test code 302). Lab result were ranked low to high based on sample SRW-1901 (see Figure 11). Sample SRW-1902 had the lowest EC in Cycle 38. Lab #1 indicated consistent low bias on SRS-1901 and SRS-1902. Labs #2 and #3 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 0.025, 0.005 and 0.004 dSm^{-1}, respectively. Precision for sample SRW-1903 was the most consistent across the fifteen participating laboratories. Intra-lab *s* values for lab #12 exceeded 0.05 dSm^{-1} on SRW-1901. Highest precision was noted for lab #7 with intra-lab *s* values of < than 0.001 dSm^{-1} on all three samples.

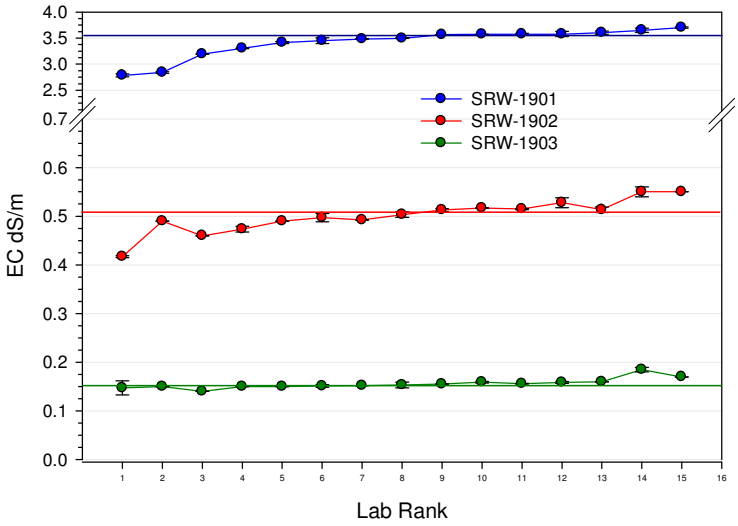


Figure 11 . Water EC distribution plots for SRW materials, ALP 2019 Cycle 38.

SRW - SO4 Results

Twelve laboratories provided ALP results for water SO4 (test code 303). Lab results were ranked low to high based on sample SRW-1901 (see Figure 12). Median values are designated by horizontal lines. Lab #16 had high bias. Labs #1 and #15 showed inconsistency across samples.

SO4 precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 1.79, 0.07, and 0.11 meq L^{-1} for SRW-1901, SRW-1902, and for SRW-1903, respectively. Water SO4 precision was excellent for all individual labs with only lab #2 exceeding 2.0 meq L^{-1} on two of the three samples. Across samples intra-lab *s* was less than 0.20 meq L^{-1} for lab #8. Four labs were flagged for poor precision on ALP Cycle 38 for SO4 content.

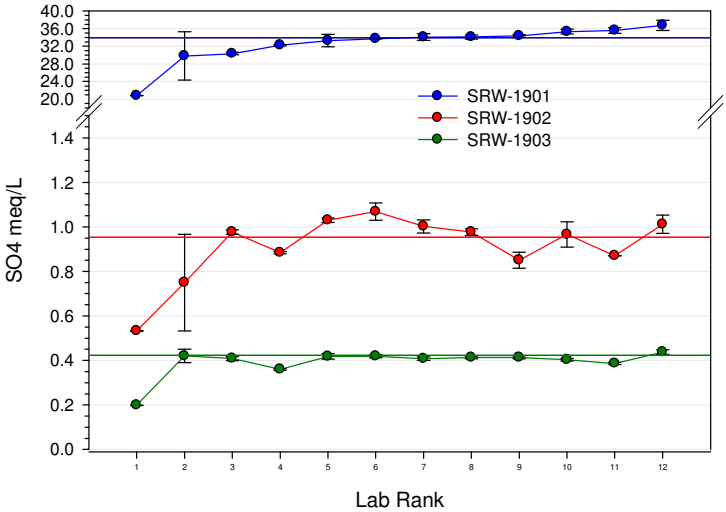


Figure 12. Water SO4 distribution plots for SRW materials, ALP 2019 Cycle 38.

Announcements

- International exchange of proficiency soils. ALP cycle 38 soils SRS-1903 and SRS-1905 exchanged with the Australasian Soil and Plant Analysis Council (ASPAC) for use in the soil proficiency program, managed by Global Proficiency.

- Five new ALP water samples were collected in early 2019 from: Oregon, Washington, Idaho, Wyoming and Minnesota. A soil collection trip is planned for July in Canada.

- The 16th International Soil and Plant Analysis Symposium was held June 17,-20, 2019, in Wageningein, The Netherlands. Symposium topics included: use of NIR for soil analysis, laboratory quality control and new analytical techniques. A tour of the Eurofinn testing laboratory was included. Symposium info can be found at: https://www.isspa2019.com/100119

- The Soil and Plant Analysis Council (SPAC) and the Illinois Soil Testing Association (ISTA) is developing a national certification program for botanical analysis. The program will be based on proficiency testing data evaluate on a yearly basis.

- A laboratory analysis workshop, in conjunction with SPAC, is scheduled for September, 17, 2019, in Bloomington, Illinois. Topics include, Soil pH, lab instrumentation and soil health. For more information contact: ALP Technical Director, rmiller@colostate.edu.

Summary

ALP is celebrating twelve years of service with the completion of Cycle 38. 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 38. 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 39 Ship

June 24, 2019

"Tell me and I forget, teach me and I may remember, involve me and I learn "

— Benjamin Franklin, 1785

ALP
Agricultural Laboratory Proficiency Program