2018 Volume 1

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ALP Program Report

2018 Spring - Cycle 35

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

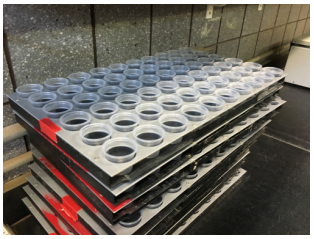
ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 35.
- Fifty-eight Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.13 - 7.94.
- Cycle 35 soil Bray P1 ranged from 3.3 to 47.3 mg kg^{-1} with MAD values ranging 0.6 - 5.3 mg kg^{-1} across the five soils.
- Lab results for Mehlich-3 K were inconsistent on two of five proficiency soils for cycle 35.
- Botanical P, ranged from 0.12 - 0.43% with one of thirty-eight labs noted for high bias.
- Botanical B results showed high consistency across the four samples for thirty-three of thirty-eight labs for PT Cycle 35.
- Water Ca content showed very high consistency by fifteen of sixteen labs across all samples.

Inside this issue:

The Agriculture Laboratory Proficiency (ALP) Program spring 2018 Round Cycle 35 was completed May 21, 2018, with one-hundred eight labs enrolled from the United States, Canada, South Africa, Italy, Honduras, Serbia, Ukraine, Philippines and Guatemala. Proficiency samples consisted of five soils, four botanical and three water samples. Analytical methods evaluated are base on those published by AOAC, regional soil work groups, the Soil Plant Analysis Council and Forestry Canada. ALP has completed ten 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.

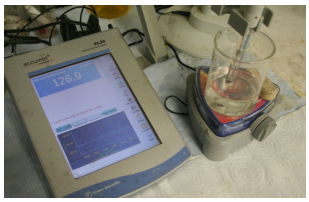
Proficiency Materials

Standard Reference Soils (SRS) materials utilized for cycle 35 were: SRS-1801 is a loam collected Cascade Cty, MT; SRS-1802 a loam, from Colchester, Nova Scotia, Canada; SRS-1803 a Cecil sandy loam collected Anderson Cty, SC; SRS-1804 a Bluford silt loam collected Clay Cty, IL; and SRS-1805 a silt loam collected Broome Cty, NY. 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 70 - 642 mg kg^{-1}; SO_4-S 3.5 - 57.7 mg kg^{-1}; Mehlich 3 P (ICP) 15.7 - 64.8 mg kg^{-1}; DTPA-Zn 0.49 - 2.89 mg kg^{-1}; SOM-LOI 2.36 – 5.00%; CEC 9.2 - 17.8 cmol kg^{-1}; clay 17.7 - 27.5% and soil available H_2O 13.3 - 20.7 %.

Standard Reference Botanical (SRB) materials for Cycle 35 were: SRB-1801 a oat grass sample composite from CA; SRB-1802 neem leaf composite; SRB-1803 corn plant composite from IA; and SRB-1804 walnut leaf composite from CA. SRB material median analytes ranged: NO_3-N 110 - 3725 mg kg^{-1}; Dumas N 1.08 - 3.07%; total P 0.12 - 0.43%; total K 1.46 - 5.27%; total Mg 0.10 - 0.50%; total S 0.11 - 0.36 %, total Zn 13.3 - 79.6 mg kg^{-1}; and total Pb 0.03 - 0.68 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1801 a water sample collected from a canal near Ault, CO; SRW-1802 from a well near Wellington, CO; and SRW-1803 from a surface canal near Sterling, CO. SRW median concentrations ranged: pH 7.56 - 8.42; EC 0.09 - 17.93 dSm^{-1}; SAR 0.16 - 341; Ca 0.38 - 1.24 mmolc L^{-1}; Na 0.19 - 224 mmolc L^{-1}; HCO_3 0.67 - 218 mmolc L^{-1}; and NO_3 0.017 - 0.04 mmolc L^{-1}.

Homogeneity Evaluation Soil



SRS material homogeneity was evaluated based on soil test codes pH (1:1) H_2O, 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 35 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 35, 2018.

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-1801	7.79	*0.04*	0.44	*0.080*	58.5	*2.1*	2.42	*0.9*
SRS-1802	7.37	*0.03*	0.51	*0.036*	48.6	*1.9*	5.07	*0.17*
SRS-1803	6.23	*0.13*	0.25	*0.066*	26.8	*0.9*	4.85	*0.14*
SRS-1804	6.96	*0.03*	0.88	*0.115*	25.5	*0.9*	2.80	*0.08*
SRS-1805	5.15	*0.05*	0.24	*0.011*	4.9	*0.6*	1.67	*0.13*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 35.

2018 Cycle 35 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 35 averaged 0.07 pH units across the soils. Median within lab pH standard deviation was 0.028 pH units. Soil displacement CEC ranged 9.2 to 17.8 cmol kg^{-1} across the five soils. Soil Solvtia CO_2 respiration (test code 191) results were provided by three laboratories with median results ranging from 23 - 223 mg kg^{-1} with MAD values averaging >20 mg kg^{-1} for two of five samples. Sample SRS-1801 had a large discrepancy in soil CEC values: Displacement 17.8 cmol kg^{-1} and Estimated CEC of 29.7 cmol kg^{-1}. Soil ammonium acetate K (Test code 140) MAD values ranged 12.7 - 45 mg kg^{-1} and ammonium acetate Mg MAD values ranged 5.7 to 35 mg kg^{-1} for the five soils. These results for K and Mg were consistent with past cycles in 2017 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 0.078% nitrogen with intra-lab *s* of 0.044%, 0.034%, 0.051% and 0.048%, respectively. 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 neem leaf composite sample SRB-1801 had lower median concentrations of N, Ca, Mg, S, Al, Cu, Cd and Pb relative to the other four botanical samples. One observation on Cycle 35, intra-lab relative variability was higher for S 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 0.003 to 0.66 dSm^{-1}. NO_3-N values ranged from 0.006 - 0.013 molc L^{-1} across the three water samples with MAD values ranging 0.006 to 0.013 molc L^{-1}.

SRS Results - pH

Fifty-eight laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.15 - 7.93. Lab results were ranked low to high based on sample SRS-1801 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1802, SRS-1803 and SRS-1804 showed good consistency across labs. Labs #53, #55, and #56 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.

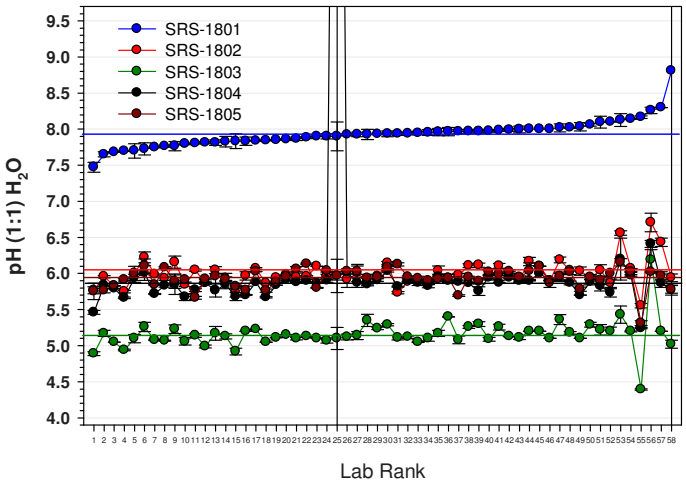


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2018 Cycle 35.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.020 to 0.029 pH units, the lowest noted for SRS-1804. 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 #41 and #55 exceeded 0.10 pH units for two of five soils. Soil SRS-1803 was the least variable with respect to intra-lab variance for Cycle 35.

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

Bray P1 results were reported by twenty-nine labs. M3-P ICP was reported by 35 labs. Median soil Bray P1 values ranged from 3.3 - 47.3 mg kg^{-1} PO_4-P; Olsen P 5.8 to 33.9 mg kg^{-1} P and Bray P2 ranged from 19.2 to 119 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1801, median Bray P1 ICP concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1802 and SRS-1803 associated with the moderate P concentrations. Soil SRS-1801, lowest in concentration, showed low intra-lab variability with a range of 0.9 - 30.6 mg kg^{-1}. Lab #1 showed low bias on three samples. Labs #4, #6, #11, #25 and #27 were inconsistent. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

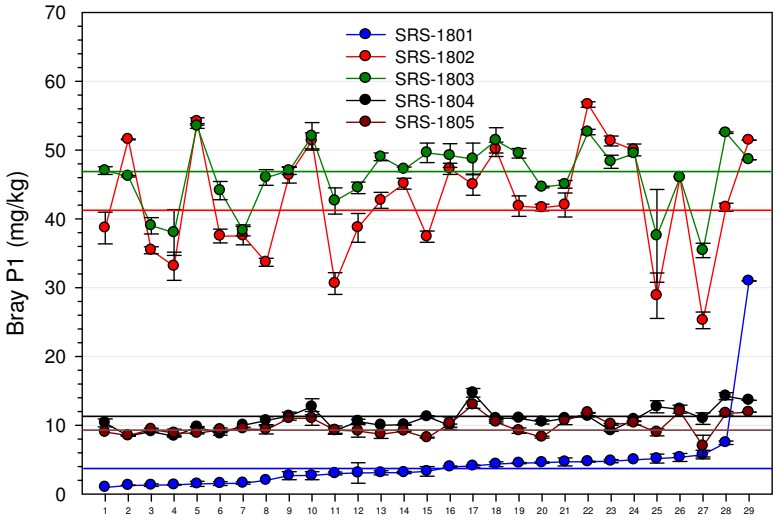


Figure 2. Bray P1 distribution plots for SRS materials, ALP 2018 Cycle 35.

Three laboratories provided ALP results for Mehlich 1 P, with medians ranging from 9.2 to 24.2 mg kg^{-1} PO_4-P . M3-P ICP median concentrations were 15.6 - 64.6 mg kg^{-1} P reported by thirty-five labs. Modified Morgan was reported by four laboratories ranging from 1.1 - 17.9 mg kg^{-1} P with the highest concentration noted for SRS-1801.

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-1804 (see Figure 3). Soils SRS-1802 and SRS-1803 were the most inconsistent across labs. Lab #1 showed low bias on 4 of 5 five soils. Labs #2, #13, #22, #25, #26, #30, #35 and #41 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-1804, with a median intra-lab value of 1.5 mg kg^{-1} Kg and highest for SRS-1801 with a value of 12.2 mg kg^{-1} Kg. Potassium within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 150 mg kg^{-1} K. Precision was poor (based on intra-lab *s*) for labs #1, #22, #30, and #45 which exceeded 12 mg kg^{-1} K on SRS-1802; and labs #1, and #46 the value exceeded 20 mg kg^{-1} K for SRS-1803. Poor precision is attributed to extraction and/or analysis instrument operation.

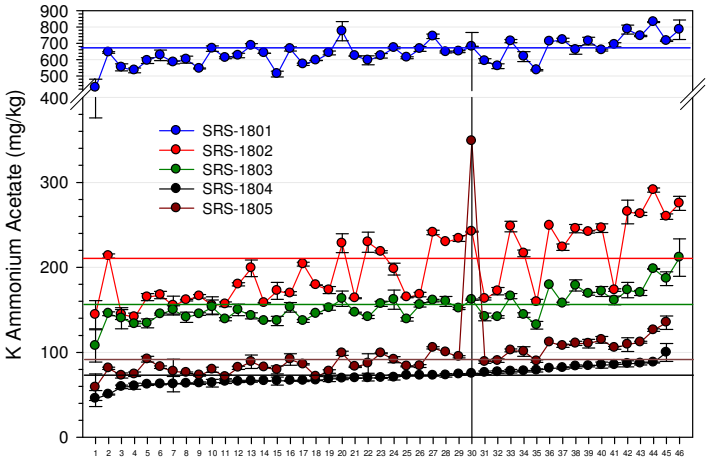


Figure 3. Extractable K distribution plots for SRS materials, ALP 2018 Cycle 35.

SRS SOM-LOI

Forty-seven laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 2.43 to 5.00%. Results were ranked based on sample SRS-1801 (see Figure 4). Labs #1, #18, #45, #46, and #47 were noted having inconsistency three of five soils. Sample SRS-1802 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 0.04 to 0.06% SOM-LOI, the highest for SRS-1802. Across labs, *s* values for SRS-1801 ranged from 0.005 - 0.39 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #13, #35, and #47, exceeded 0.20 % SOM for SRS-1802. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

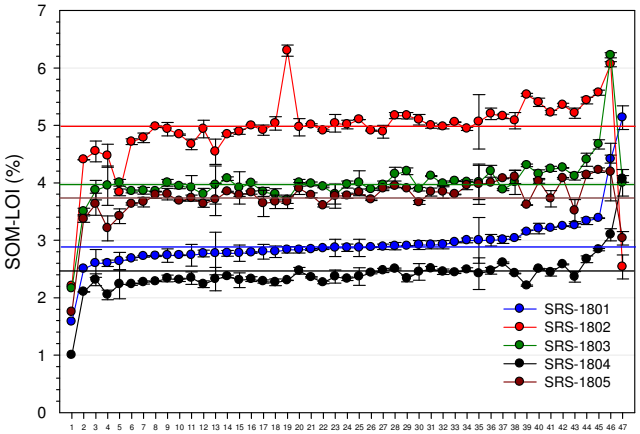


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2018 Cycle 35.

SRS - NO3-N

Forty-two laboratories provided ALP results for NO3-N (test code 127). Results were ranked low to high based on sample SRS-1805 (see Figure 5). Soil SRS-1803 was the highest in concentration and the most in consistent across labs. Across soils, labs #4 #19, #24, #36, #39 and #40 were inconsistent across soils and #1 had high bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

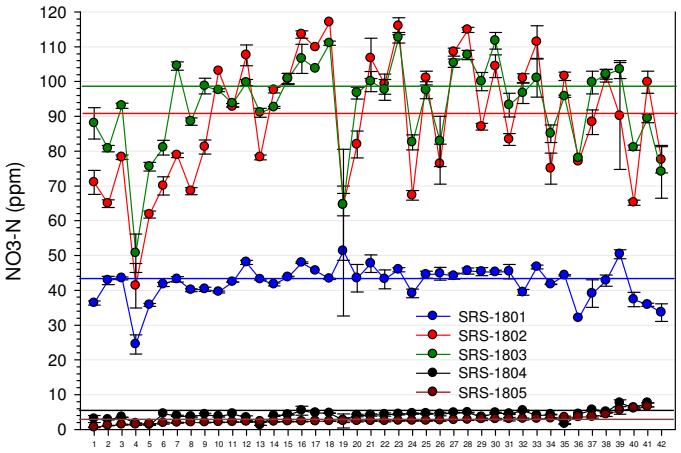


Figure 5. Soil NO3-N distribution plot, ALP 2018 Cycle 35.

NO3-N median intra-lab *s* values were lowest for ALP soil SRS-1804 and SRS-1805 with an intra-lab median value of 0.1 mg kg^{-1} and highest for SRS-1801 with a value of 0.6 mg kg^{-1} . Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1801. Intra-lab precision was poor for labs #4, #19, #37, and #42 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

Nineteen 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-1801 (see Figure 6). The data plot shows labs #21, and #22 had high bias for SRB-1802. Labs #1, #2, #11, and #18 were inconsistent.

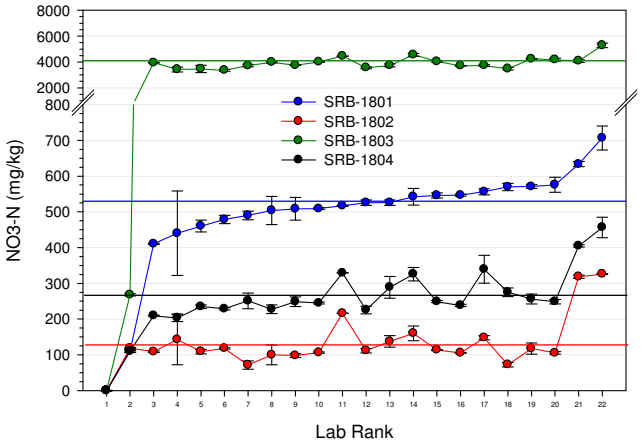


Figure 6. Nitrate distribution plots for SRB materials, ALP 2018, Cycle 35.

Botanical NO_3-N (test code 202) results for Cycle 35 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 5.1 to 74.6 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-1801 ranged from 1.2– 118 mg kg^{-1}; SRB-1802 ranged from 0.8 - 71 mg kg^{-1}, SRB-1803 ranged from 3.0 – 286 mg kg^{-1} and SRB-1804 ranged from 1.5 - 39 mg kg^{-1} Lab #4 had consistently high standard deviations for two of four samples. Three labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Twenty-eight laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and twelve labs for TKN (Test code 209) for Cycle 35. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1801 (see Figure 7). It is note worthy that TKN was lower than Dumas for two of four samples. Labs #1 and #2 showed low bias for Dumas N for three samples, whereas lab #25 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-1801, ranged 0.004 to 0.0173% N, SRB-1802 ranged from 0.001 to 0.101% N, SRB-1803 ranged from 0.001 to 0.140 % N, and SRB–1804 from 0.004 to 0.117 % N. Lab #16 had consistently high standard deviations. Lab TKN *s* values for SRB-1801 ranged from 0.003 to 0.186%, SRB-1802 ranged from 0.003 to 0.190% TKN, SRB-1803 ranged from 0.002 to 0.115% TKN nitrogen and SRB-1804 ranged from 0.018 to 0.156% TKN nitrogen.

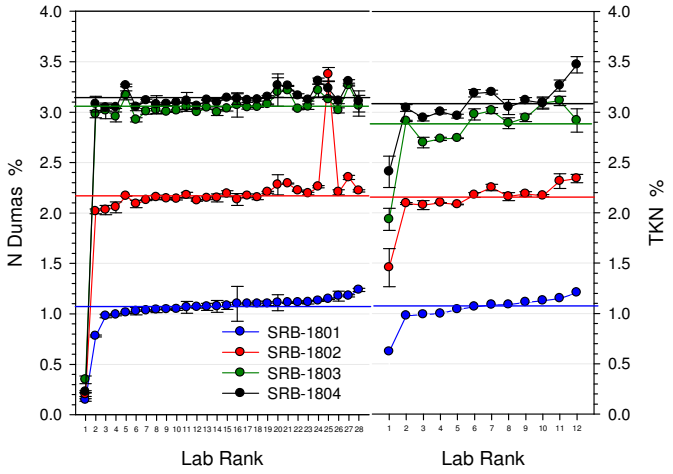


Figure 7. N distribution plots for SRB materials, ALP 2018 Cycle 35.

SRB - Potassium

Forty-two 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-1801 (see Figure 8). Laboratories #1 and #2 showed low bias. Labs #8, #7, #21, #26 and #33 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 0.022 to 0.080 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1801, ranged from 0.005 to 0.57 % K; SRB-1802, 0.001 — 0.24 % K; SRB-1803, 0.015 - 0.29 % K; and SRS-1804, 0.010 to 0.39 % K. Four labs had high standard deviations exceeding 0.20 %K for SRB-1803. Seven labs were flagged for poor K precision.

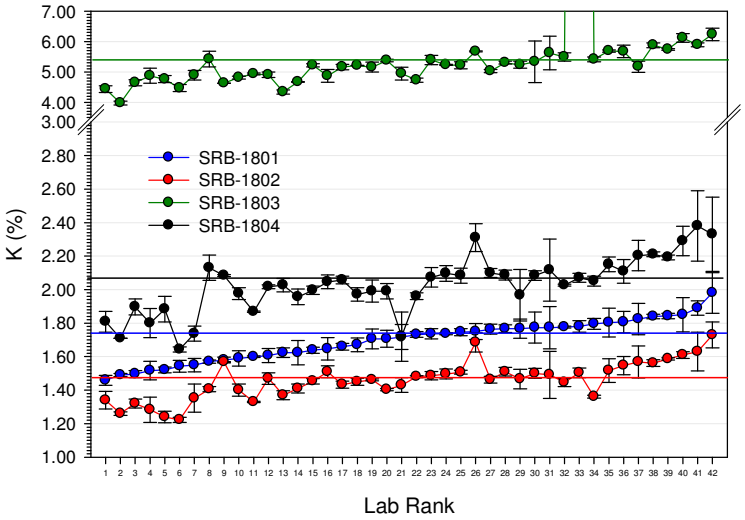


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2018 Cycle 35.

SRB - Phosphorus

Forty-two laboratories provided ALP results for Cycle 35 phosphorus (P) combined (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-1801 (see Figure 9). Consistent high bias was noted for labs #42 and #38. Labs #3, #14, #29 and #40 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-1801; ranged from 0.001 - 0.015 % P; SRB-1802 ranged from 0.002 – 0.082 % P and SRB-1803 0.002 - 0.087 % P; and SRB-1804 0.001 - 0.103 % P. Labs #42 had a high standard deviation exceeding 0.08 % P on two of four botanical samples. Five labs were flagged for poor precision for botanical P.

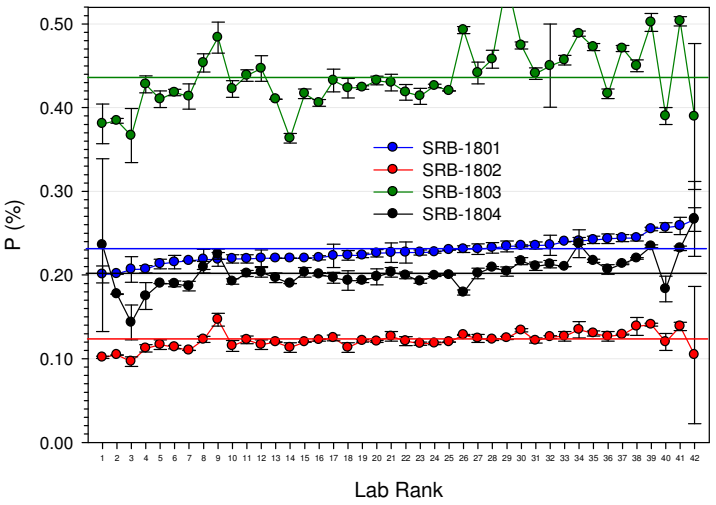


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2018 Cycle 35.

SRB - Boron

Thirty-six 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-1803 (see Figure 10). Labs #1 showed low bias on all samples. Labs #2, #10, #19, #34 and #36 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 B results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.88 to 4.4 mg kg^{-1} B for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1801; ranged from 0.01 - 1.2 mg kg^{-1} B; SRB-1802 ranged from 0.26 – 11.1 % B; SRB-1803 0.04 - 3.9 mg kg^{-1} B; and SRB-1804 0.18 - 6.0 mg kg^{-1} B. Labs #25 and #36 had consistently high standard deviations for two of four botanical samples.

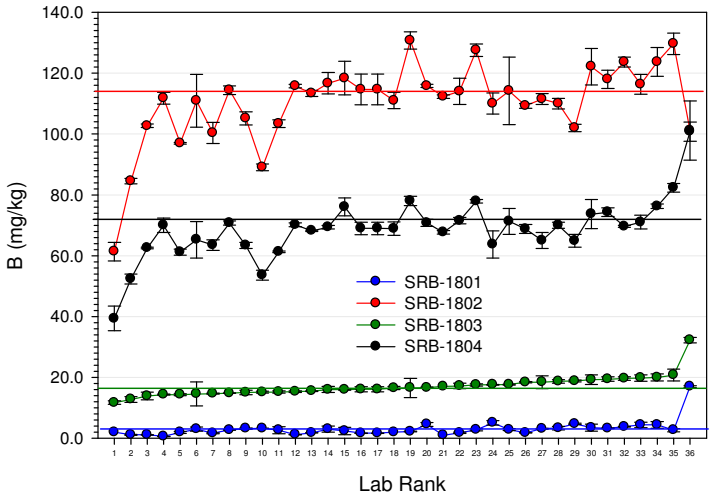


Figure 10. Boron distribution plots for SRB materials, ALP 2018 Cycle 35.

SRW - Water Ca

Fifteen laboratories provided ALP results for water Ca (test code 302). Lab result were ranked low to high based on sample SRW-1801 (see Figure 11). Sample SRW-1802 had the lowest Ca ever recorded in the ALP Program. Lab #1 indicated consistent low bias on SRS-1802. Labs #3 and #11 showed inconsistently across the three samples. Source of bias is likely associated with EC probe performance and/or calibration.

Ca precision across the three water materials indicates good high precision, with intra-lab median Std values of 0.013, 0.019 and 0.024 dSm^{-1}, respectively. Precision for sample SRW-1801 was the most consistent across the fifteen participating laboratories. Intra-lab *s* values for lab #13 exceeded 0.11 dSm^{-1} on SRW-1803. Highest precision was noted for lab #4 with intra-lab *s* values of < than 0.001 dSm^{-1}.

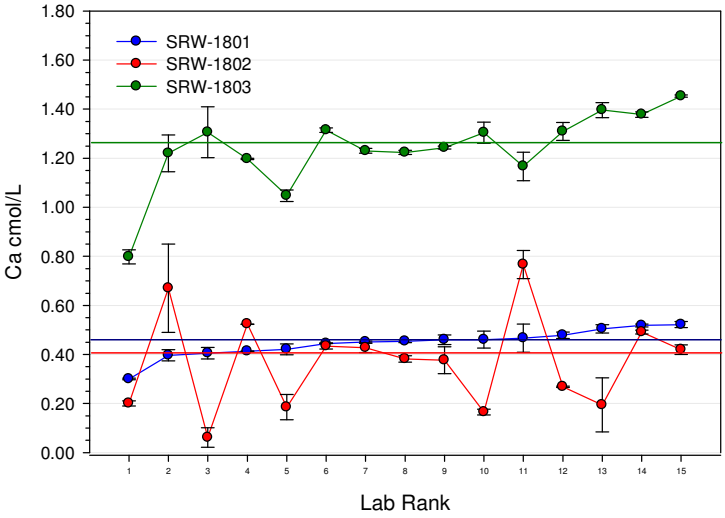


Figure 11 . Water Ca distribution plots for SRW materials, ALP 2018 Cycle 35.

SRW - Cl Results

Sixteen laboratories provided ALP results for water Cl (test code 303). Lab results were ranked low to high based on sample SRW-1801 (see Figure 12). Median values are designated by horizontal lines. Lab #16 had high bias. Labs #1 and #15 showed inconsistency across samples.

Cl precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.011, 0.200, and 0.015 meq L^{-1} for SRW-1801, SRW-1802, and for SRW-1803, respectively. Water Cl precision was excellent for all individual labs with only lab #15 exceeding 0.20 meq L^{-1} on two of the three samples. Across samples intra-lab *s* was less than 0.010 meq L^{-1} for lab #4. Four labs were flagged for poor precision on ALP Cycle 35 for Cl content.

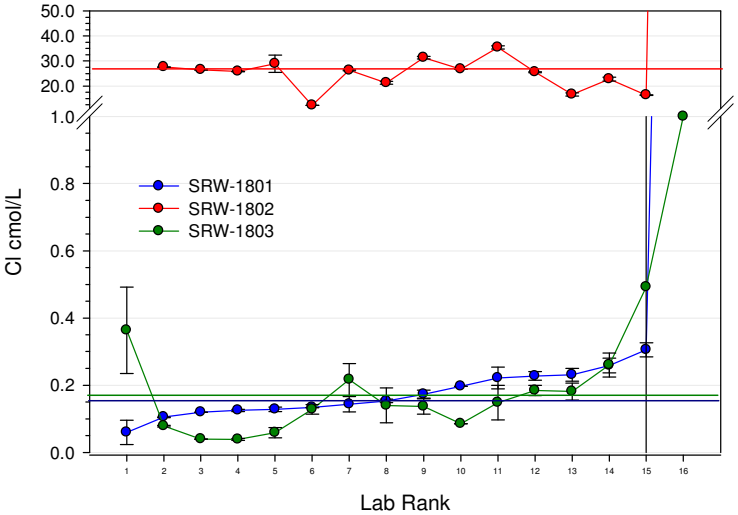


Figure 12. Water Cl distribution plots for SRW materials, ALP 2018 Cycle 35.

Announcements

- Improved soil homogeneity. Soils for the ALP program are processed to achieve 100% 0.7 mm minus. Specific soils with SOM > 1.0% are now double sieved to 0.7 mm minus to removed fine root fragments and improve SOM homogeneity. Soils are blended in two successive operations to assure optimum uniformity.

- Nine new ALP soils were collected in April from: West Virginia, North Carolina, South Carolina, Georgia and Kentucky from pastures and row crop fields. Another colelctuion trip is planned for October in the upper Midwest.

- A laboratory tour is scheduled of soil/plant testing labs in the Pacific Northwest the week of August 28th 2018. The tour will include four testing labs and an Ag industry facility. Tour is space is limited. Email rmiller@colostate.edu for more information.

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

- If there is a specific soil type, soil properties or botanical sample materials that you believe should be considered for the proficiency program please contact the ALP Program Technical Director, rmiller@lamar.colostate.edu.

Summary

ALP is celebrating twelve years of service with the completion of Cycle 35. Since 2006 ALP has completed the analysis of 175 soils, 108 plant samples and 102 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 35. 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 33 Ship

June 22, 2018

"The more often a stupidity is repeated, the more it gets the appearance of wisdom. Skepticism "

— Voltaire, 1758

ALP
Agricultural Laboratory Proficiency Program