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ALP Program Report

2018 Fall - Cycle 37

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ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 37.
- Sixty-two Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.36 - 7.25.
- Cycle 37 soil M3-P ICP ranged from 2.9 to 91.3 mg kg^{-1} with MAD values ranging 1.0 - 4.6 mg kg^{-1} across the five soils.
- Lab results for Amm. Acetate K were inconsistent on three of five proficiency soils for cycle 37.
- Botanical K, ranged from 01.88 - 3.77% with two of forty-two labs noted for high bias on SRB-1810.
- Botanical B results showed high consistency across the three samples for thirty-six of thirty-eight labs for PT Cycle 37.
- Water Na content showed very high consistency by thirteen of fifteen labs across all samples.

The Agriculture Laboratory Proficiency (ALP) Program spring 2018 Round Cycle 37 was completed November 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.

Inside this issue:

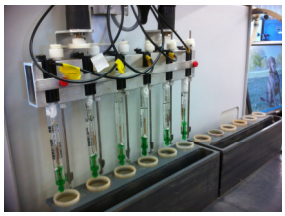
Proficiency Materials

Standard Reference Soils (SRS) materials utilized for cycle 37 were: SRS-1811 is a Cookport-Nallen complex silt loam collected Raleigh, WV; SRS-1812 a clay, from Division #2, near Lethbridge, AB, Canada; SRS-1813 a Cecil clay loam collected Anderson Cty, SC; SRS-1814 a Brownton silty clay loam collected Wright Cty, IA; and SRS-1815 a Stayton silt loam collected Marion Cty, OR. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.36 - 7.25; NO_3-N 4.3 - 132.5 mg kg^{-1}; Bray P1 (1:10) 2.9 - 87.7 mg kg^{-1}; M3-K 79.7 - 419 mg kg^{-1}; SO_4-S 6.1 - 52.3 mg kg^{-1}; Mehlich 3 P (ICP) 2.9 - 91.3 mg kg^{-1}; DTPA-Zn 0.54 - 1.9 mg kg^{-1}; SOM-LOI 4.1 – 10.4%; CEC 7.1 - 32.3 cmol kg^{-1}; clay 24.0 - 46.8% and field capacity H_2O 15.4 - 19.1 %.

Standard Reference Botanical (SRB) materials for cycle 37 were: SRB-1809 a hay silage sample from MN; SRB-1810 box elder leaf composite; SRB-1811 tall fescue leaf composite from ID; and SRB-1812 Grape leaf composite from CA. SRB material median analytes ranged: NO_3-N 30.1 - 4800 mg kg^{-1}; Dumas N 1.70 - 2.91%; Total P 0.19 - 0.42%; total K 1.88 - 3.77%; total Mg 0.26 - 0.45%; total S 0.13 - 0.36 %, total Zn 13.2 - 36.5 mg kg^{-1}; and total Cd 0.026 - 0.54 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1807 a water sample collected from Umatilla, OR; SRW-1808 from an irrigation canal near Tinmath, CO; and SRW-1809 from a well near Johnstown, CO. SRW median concentrations ranged: pH 7.64 - 8.91; EC 0.15 - 0.84 dSm^{-1}; SAR 0.30 - 21.1; Ca 0.09 - 3.89 mmolc L^{-1}; Na 0.25 - 4.37 mmolc L^{-1}; HCO_3 0.80 - 2.72 mmolc L^{-1} ; and NO_3 0.010 - 0.031 mmolc L^{-1}.

Homogeneity Evaluation Soil



SRS material homogeneity was evaluated based on soil test codes pH (1:1) H_2O, Buffer pH, 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 37 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 37, 2018.

Sample	pH (1:1) H_2O		EC (1:1) (dSm^{-1})		Olsen P ($mg\ kg^{-1}$)		NO3-N ($mg\ kg^{-1}$)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-1811	6.00	*0.01*	0.23	*0.012*	9.86	*0.7*	15.1	*1.0*
SRS-1812	7.17	*0.03*	0.65	*0.042*	12.9	*0.8*	20.3	*1.7*
SRS-1813	5.29	*0.02*	0.23	*0.005*	14.7	*0.3*	19.8	*0.6*
SRS-1814	5.84	*0.02*	1.15	*0.20*	42.3	*1.8*	133.7	*7.8*
SRS-1815	5.62	*0.01*	0.10	*0.003*	8.03	*0.6*	4.6	*0.2*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 37.

2018 Cycle 37 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 37 averaged 0.06 pH units across the five soils. Median within lab pH standard deviation was 0.072 pH units. Soil density (test code 188) results were provided by eight laboratories with median results ranging from 0.96 - 1.35 g cm^{-3} with MAD values averaging > 0.06 g cm^{-3} for two of five samples. Soil displacement CEC ranged 7.1 to 32.2 cmol kg^{-1} across the five soils. Sample SRS-1815 had a large discrepancy in soil CEC values: displacement 23.3 cmol kg^{-1} and estimated CEC of 14.3 cmol kg^{-1}. Soil Mehlich 3 K (Test code 159) MAD values ranged 5.7 - 19.8 mg kg^{-1} and Mehlich 3 (Test code 162) Mg MAD values ranged 9.2 to 40.1 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 0.037% nitrogen with intra-lab *s* of 0.049%, 0.061%, 0.034% and 0.037%, 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 box elder leaf composite sample SRB-1810 had lower median concentrations of NO3-N, PO_4-P, Cl, N, P, K, Na, S, Zn, Cu, Mo, Cd, and Pb relative to the other three botanical samples. One observation on Cycle 37, intra-lab relative variability was higher for Na than all other macro elements for the four botanical samples.

Water Na results showed high consistency across samples. Across the three water samples Na MAD values ranged from 0.026 to 0.153 mmolc L^{-1}. HCO_3 values ranged from 0.80 - 2.72 mmolc L^{-1} across the three water samples with MAD values ranging 0.11 to 0.14 molc L^{-1}.

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 5.36 - 7.25. Lab results were ranked low to high based on sample SRS-1813 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1813 and SRS-1814 showed good consistency across labs. Labs #1, #6, #26 and #55 were inconsistent across soils. Labs #62 showed high bias on 3 of 5 soils. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

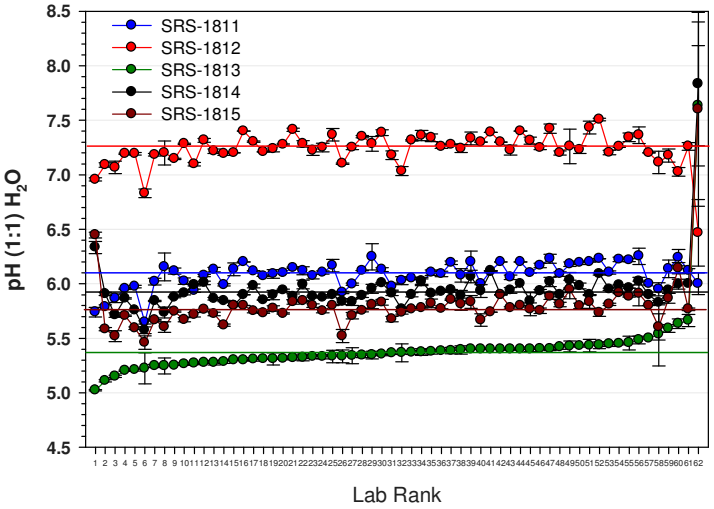


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2018 Cycle 37.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.016 to 0.020 pH units, the lowest noted for SRS-1814. For specific labs poor precision was noted for eight laboratories, exceeding by three times that noted for consensus median intra-lab *s*. Specifically *s* for lab #58 and #62 exceeded 0.10 pH units for two of five soils. Soil SRS-1814 was the least variable with respect to intra-lab variance for Cycle 37.

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

Bray P1 results were reported by thirty labs. M3-P ICP was reported by 38 labs. Median soil Bray P1 values ranged from 2.9 - 87.7 mg kg^{-1} PO_4-P; Olsen P 6.8 to 42.1 mg kg^{-1} P, Bray P2 ranged from 4.5 to 146 mg kg^{-1} P, and Bray P 1:7 1.8 - 63.7 mg kg^{-1} Pacross the five soils. Ranking lab results based on sample SRS-1811, median Bray P1 concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1813, and SRS-1814 associated with higher concentrations. Soil SRS-1815, lowest in concentration, had low intra-lab variability with a range of 1.0 - 6.0 mg kg^{-1}. Lab #5 showed high bias on three samples. Labs #7, #11, #15, #20, #24, and #27 were inconsistent, likely related to extraction, analysis instrument and/or method compliance.

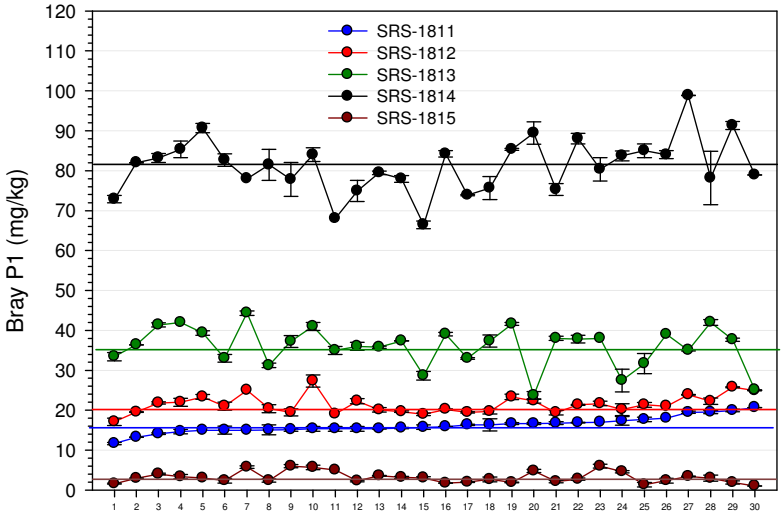


Figure 2. Bray P1 distribution plots for SRS materials, ALP 2018 Cycle 37.

Three laboratories provided ALP results for Mehlich 1 P, with medians ranging from 2.5 to 69.1 mg kg^{-1} PO_4-P. M3-P ICP median concentrations were 2.9 - 91.7 mg kg^{-1} P reported by thirty-four labs. Modified Morgan was reported by four laboratories ranging from 0.8 - 30.5 mg kg^{-1} P with the highest concentration noted for SRS-1814.

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-1811 (see Figure 3). Soils SRS-1812 and SRS-1813 were the most inconsistent across labs. Lab #49 showed high bias on four of five soils. Labs #4, #8, #30, #31, #35, #41 and #42 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-1811, with a median intra-lab value of 9.2 mg kg^{-1} Kg and highest for SRS-1812 with a value of 30.2 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 #3, #4, #5, #9, #35, #40 and #49 which exceeded 20 mg kg^{-1} K on SRS-1814; and labs #40 and #49 the value exceeded 20 mg kg^{-1} K for SRS-1815. Poor precision is attributed to extraction and/or analysis instrument operation.

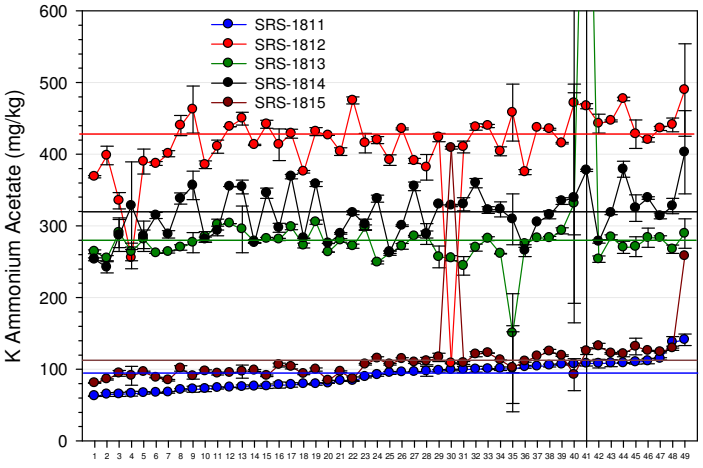


Figure 3. Amm. Extractable K distribution plots for SRS materials, ALP 2018 Cycle 37.

SRS SOM-LOI

Forty-eight laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 4.15 to 10.40%. Results were ranked from low to high based on sample SRS-1811 (see Figure 4). Labs #1, #2, #3, #4, and #48 were noted having inconsistency on three of five soils. Sample SRS-1815 shows high inconsistency likely associated with 10.0 % SOM content. Bias was noted for 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 0.11 to 0.21% SOM-LOI, the highest for SRS-1815. Across labs, *s* values for SRS-1812 ranged from 0.010 - 0.38 %. Across soil materials poor precision was noted for several laboratories. Specifically *s* for labs #2, #3, #14, #18 and #24, exceeded 0.20 % SOM for SRS-1812. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

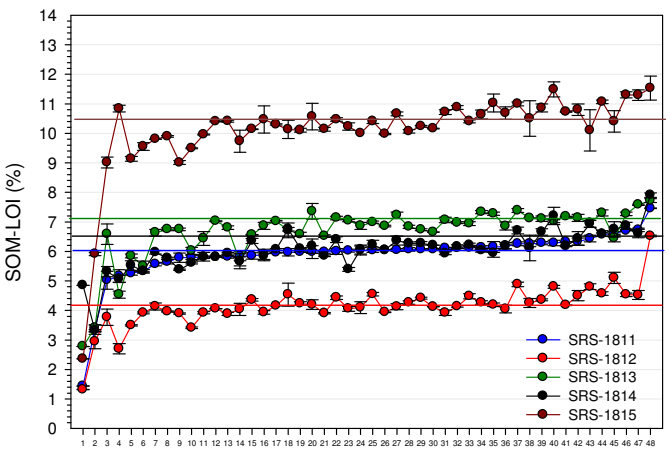


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2018 Cycle 37.

SRS - Extractable NO_3-N

Forty-six laboratories provided ALP results for extractable NO_3-N (test code 140). Results were ranked low to high based on sample SRS-1815 (see Figure 5). Soil SRS-1814 was the highest in concentration and the most inconsistent across labs. Across soils, labs #1 #8, #18, #36, #39 and #46 were inconsistent across the five soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

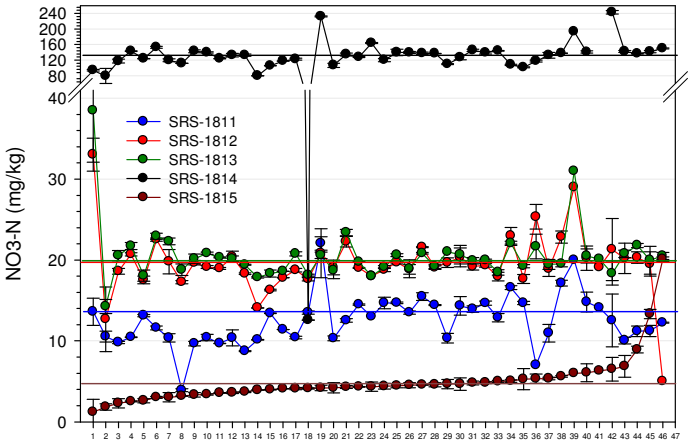


Figure 5. Soil extractable NO_3–N distribution plot, ALP 2018 Cycle 37.

Extractable NO_3-N median intra-lab *s* values were lowest for ALP soil SRS-1815 with an intra-lab median value of 0.56 mg kg^{-1} and highest for SRS-1814 with a value of 4.5 mg kg^{-1} . Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1812. Intra-lab precision was poor for labs #18, #36, 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 - Dumas Nitrogen and TKN

Thirty-three laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and nine labs for TKN (Test code 209) for Cycle 37. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1810 (see Figure 6). It Labs #32 showed high bias for Dumas N for all samples, whereas labs #2, #8, #33 showed inconsistency across the all four botanical samples.

Dumas N results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-1809, ranged 0.001 to 0.226 % N, SRB-1810 ranged from 0.002 to 0.32 % N, SRB-1811 ranged from 0.003 to 0.14 % N, and SRB–1812 from 0.003 to 0.11 % N. Lab #3 had consistently high standard deviations. Median within lab TKN *s* values for the four botanical materials were 0.093, 0.068, 0.126 and 0.115 % N, respectively. TKN *s* values ranged from 0.015 - 0.322 % N.

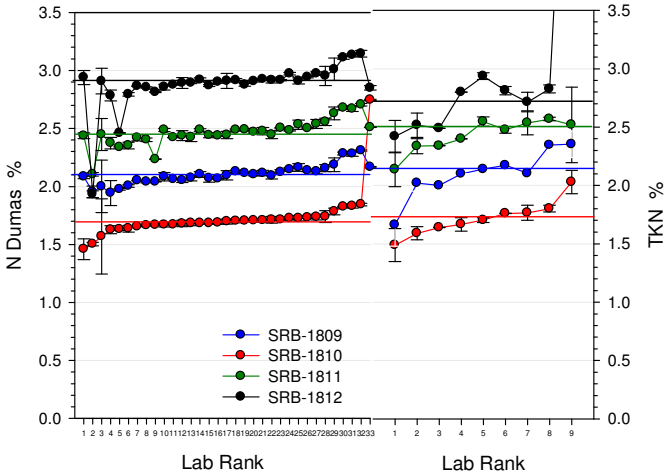


Figure 6. N distribution plots for SRB materials, ALP 2018 Cycle 37.

SRB - Phosphorus

Forty laboratories provided ALP results for Cycle 37 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-1809 (see Figure 7). Consistent high bias was noted for lab #39 and #40. Labs #4, #12, #21 and #32 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 0.051 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1809; ranged from 0.001 - 0.02 % P; SRB-1810 ranged from 0.0005 – 0.05 % P and SRB-1811 0.001 - 0.080 % P; and SRB-1812 0.0006 - 0.04 % P. Labs #36 had a high standard deviation exceeding 0.025 % P on two of four botanical samples.

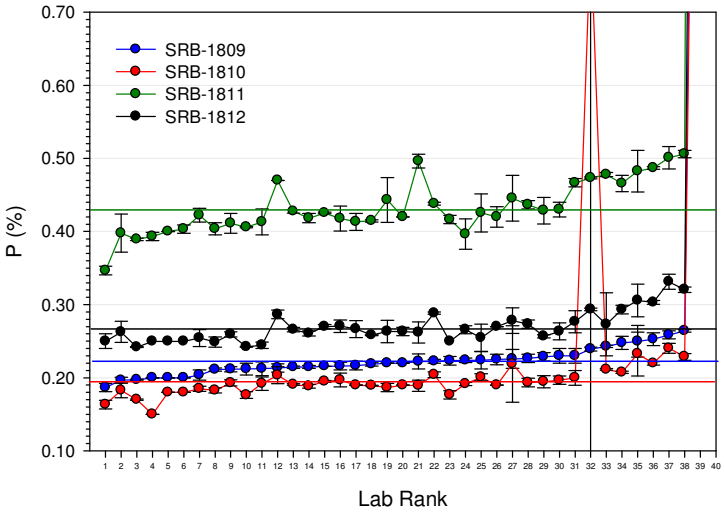


Figure 7. Phosphorus distribution plots for SRB materials, ALP 2018 Cycle 37.

SRB - Potassium

Forty 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-1810 (see Figure 8). Laboratory #1 showed low bias. Labs #2, #17, #19, #38 and #39 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 0.048 to 0.063 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1809, ranged from 0.006 to 0.20 % K; SRB-1810, 0.004 — 0.55 % K; SRB-1811, 0.002 - 0.79 % K; and SRS-1812, 0.004 to 1.4 % K. Seven labs had high standard deviations exceeding 0.20 %K for SRB-1812. Two labs were flagged for poor K precision.

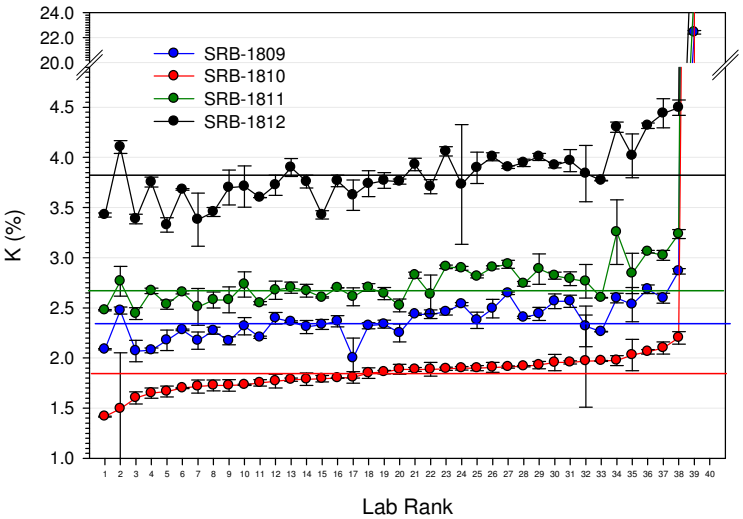


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2018 Cycle 37.

SRB - Magnesium

Forty laboratories provided ALP results for magnesium (Mg) (test code 215). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1809 (see Figure 9). Laboratory #1 showed low bias. Labs #4, #6, #10, #33 and #39 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Mg results indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 0.062 to 0.101 %Mg for test code 215 across the four samples. Individual lab intra-lab *s* values were: SRB-1809, ranged from 0.001 to 0.03 % Mg; SRB-1810, 0.002 — 0.12 % Mg; SRB-1811, 0.001 - 0.09 % Mg; and SRS-1812, 0.001 to 0.07 % Mg. Two labs had high standard deviations exceeding 0.05 % Mg for SRB-1810. Five labs were flagged for poor Mg precision.

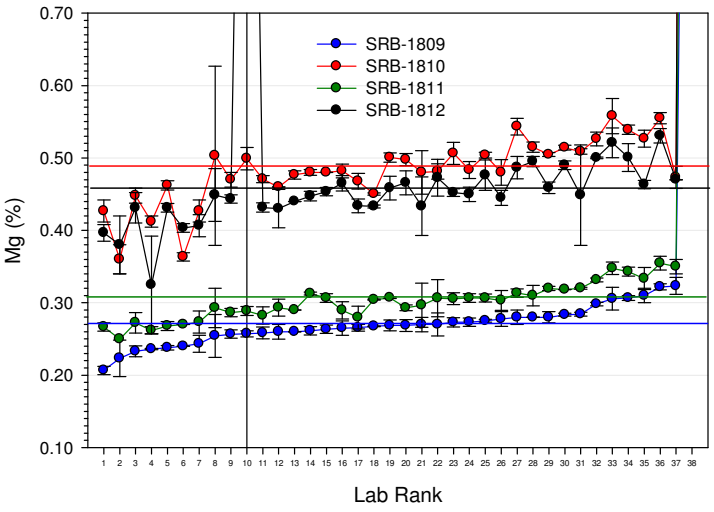


Figure 9. Magnesium distribution plots for SRB materials, ALP 2018 Cycle 37.

SRB - Boron

Thirty–eight 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-1809 (see Figure 10). Lab #1 showed low bias on 3 of 4 samples. Labs #12, #35, #37 and #38 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 high precision, with median intra-lab standard deviation (*s*) values ranged from 1.43 to 2.83 mg kg^{-1} B for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1809; ranged from 0.06 - 7.0 mg kg^{-1} B; SRB-1810 from 0.15 – 12.1 % B; SRB-1811 0.005 - 8.4 mg kg^{-1} B; and SRB-1812 0.07 - 3.4 mg kg^{-1} B. Labs #12 and #28 had consistently high standard deviations for two of four botanical samples, and nine labs were flagged for poor precision.

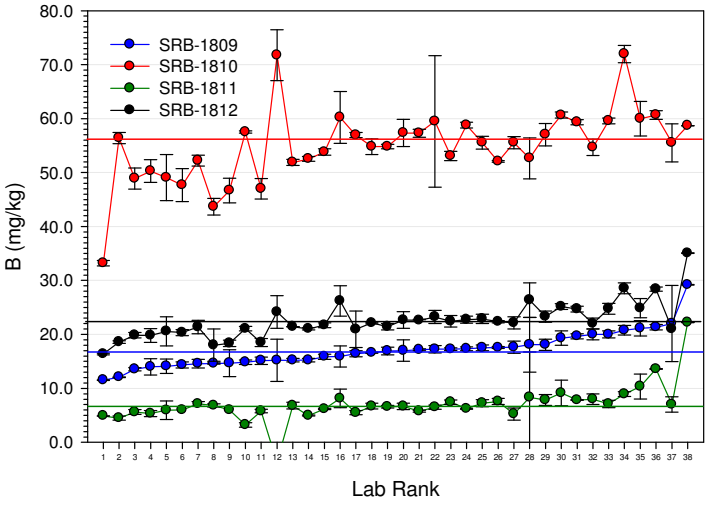
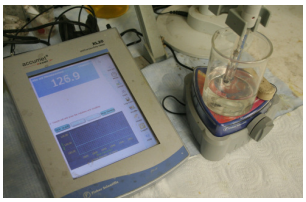


Figure 10. Boron distribution plots for SRB materials, ALP 2018 Cycle 37.

SRW - Water pH



Fifteen laboratories provided ALP results for water pH (test code 301). Lab result were ranked low to high based on sample SRW-1807 (see Figure 11). Laboratory #2 had low pH bias on two of the three samples. Labs #1, #3, #7 and #11 showed inconsistently on SRW-1809. Source of bias is likely associated with EC probe performance and/or calibration.

pH precision across the three water materials indicates good high precision, with intra-lab median Std values of 0.010, 0.151 and 0.099, respectively. Precision for sample SRW-1807 was the most consistent across the fifteen participating laboratories. Intra-lab *s* values for lab #6 exceeded 0.20 pH units on SRW-1807 and SRW-1809. Precision for laboratory #14 exceeded 0.07 units for all three samples for ALP cycle 37. Highest precision was noted for lab #2 with intra-lab *s* values of < than 0.03 pH units.

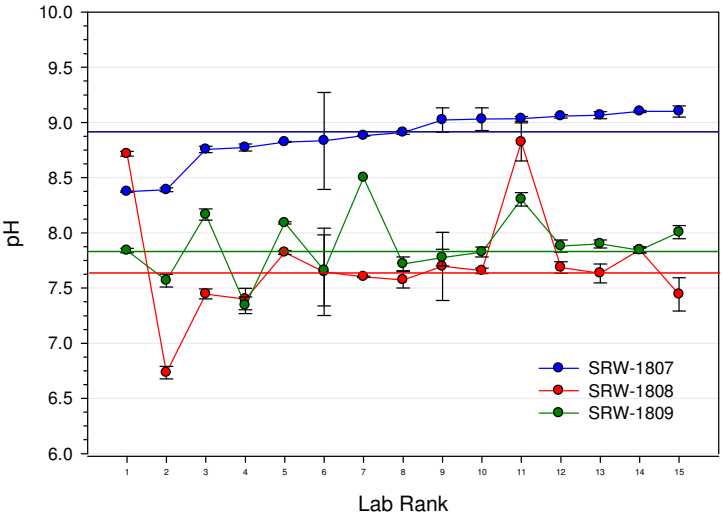


Figure 11 . Water pH distribution plots for SRW materials, ALP 2018 Cycle 37.

SRW - Na Results

Fifteen laboratories provided ALP results for water Naa (test code 303). Lab results were ranked low to high based on sample SRW-1807 (see Figure 12). Median values are designated by horizontal lines. Lab #14 and #15 had high bias on SRW-1807 had high bias. Lab #1 showed inconsistency across samples.

Na precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.14, 0.014, and 0.060 meq L^{-1} for SRW-1807, SRW-1808, and for SRW-1809, respectively. Water Na precision was excellent for individual labs with only lab #15 exceeding 0.14 meq L^{-1} on two of the three samples. Across samples intra-lab *s* was less than 0.020 meq L^{-1} for lab #5. Four labs were flagged for poor precision for cycle 37.

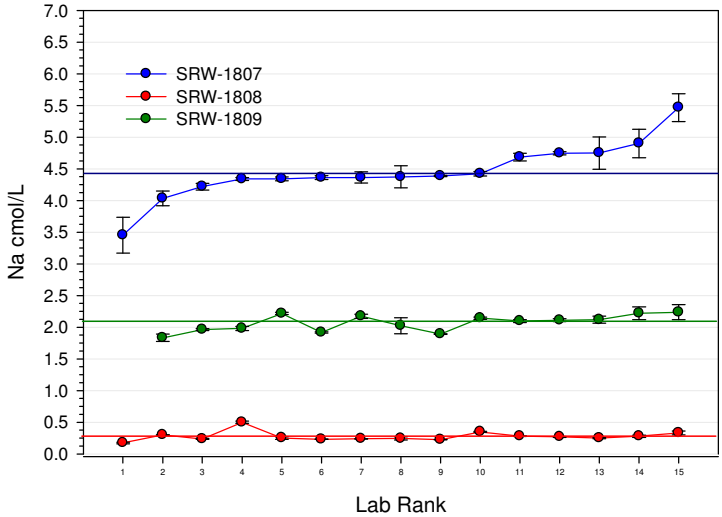


Figure 12. Water Na distribution plots for SRW materials, ALP 2018 Cycle 37.

Announcements

- A scientific paper comparing eight soil extractable phosphorus methods, based on data of 180 ALP soils, has been developed and submitted to a scientific Journal. Results indicate regression models of Bray P1 and Olsen P are significantly impacted by soil texture. Results to be published in early 2019.

- An additional new ALP soils was collected in November 2018 from St James, Minnesota 2019 collection trips are planned for March in the Pacific Northwest.

- The 16th International Soil and Plant Analysis Symposium is set for June 17,-20, 2019, in Wageningein, The Netherlands. Symposium topics include: use of NIR for soil analysis, laboratory quality control and new analytical techniques. A tour of the Eurofinn testing laboratory will be included in a mid week tour. 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 March 5, 2019 in Turlock, California. Topics include, Soil CEC, 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 37. Since 2006 ALP has completed the analysis of 185 soils, 116 plant samples and 108 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 37. 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 38 Ship

March 16, 2019

"Common sense is the most widely shared commodity in the world, for every man is convinced that he is well supplied with it. "

— René Descartes (1596-1650)