2017 Volume 3

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ALP Program Report

2017 Fall - Cycle 34

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ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials had good uniformity for Cycle 34.
- Sixty-one Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.23 - 7.87.
- Cycle 34 soil M3-P ICP ranged from 2.3 to 137 mg kg^{-1} with MAD values ranging 0.6 - 16.2 mg kg^{-1} across the five soils.
- Lab results for EC 1:1 were consistent on four of five proficiency soils for cycle 34.
- Botanical P, ranged from 0.067 - 0.41% with low bias for two of forty labs.
- Botanical Mn results showed high consistency across the four samples for thirty-nine of forty-four labs for PT Cycle 34.
- Water EC content showed very high consistency by fourteen of fifteen of labs across all samples.

The Agriculture Laboratory Proficiency (ALP) Program spring 2017 Round Cycle 34 was completed November 30, 2017, with one-hundred twelve 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 eleven 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

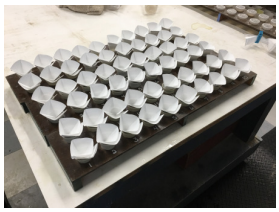
Standard Reference Soils (SRS) materials utilized for cycle 34 were: SRS-1711 is a Sac silty clay loam collected O'Brien Cty, IA; SRS-1712 a Linneus silt loam, from Aroostok Cty, ME; SRS-1713 a Spreckels loam collected Sonoma Cty, CA; SRS-1714 Typic Haploxeroll collected near Summerland, BC Canada; and SRS-1715 a Nacogdoches gravelly fine sandy loam collected Nacogdoches Cty, TX. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.23 - 7.87; NO_3-N 17.5 - 101 mg kg^{-1}; Bray P1 (1:10) 7.6 - 106 mg kg^{-1}; K NH_4oAc 85 - 488 mg kg^{-1}; SO_4-S 5.2 - 9.1 mg kg^{-1}; DTPA-Zn 0.55 - 11.1 mg kg^{-1}; SOM-LOI 1.44 – 6.53%; CEC 4.3 - 18.9 cmol kg^{-1}; clay 9.0 - 29.2% and soil available Solvita 16.0 - 93.7 ppm.

Standard Reference Botanical (SRB) materials for Cycle 34 were: SRB-1709 a soybean leaf composite from Arkansas; SRB-1710 eucalyptus leaf composite from CA; SRB-1711 citrus leaves from CA; and SRB-1712 potato petiole from WA. SRB material median analytes ranged: NO_3-N 22 - 19300 mg kg^{-1}; Dumas N 1.28 - 4.58%; total P 0.067 - 0.41%; total K 0.71 - 9.86%; total Ca 1.48 - 3.64%; total S 0.12 - 0.23 %, total Zn 11 - 56 mg kg^{-1}; total B 29.5 - 156 mg kg^{-1} and Sr 57 - 202 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1707 a water sample collected from a well in Madera, CA; SRW-1708 from Severance, CO; and SRW-1709 from a lake Garfield Cty, NE. SRW median concentrations ranged: pH 7.86 - 8.23; EC 0.12 - 0.97 dSm^{-1}; SAR 0.8 - 1.23; Ca 0.42 - 5.57 mmolc L^{-1}; Mg 0.13 - 2.9 mmolc L^{-1}; SO_4 0.16 - 4.4 mmolc L^{-1} ; and NO_3 0.008 - 0.32 mmolc L^{-1}.

Inside this issue:

Homogeneity Evaluation Soil



SRS material homogeneity was evaluated based on soil test codes pH (1:1) H_2O, EC (1:1), Olsen P, Olsen K, 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 exception of NO_3-N on SRS-1713. Homogeneity was also evaluated on SRB and SRW matrix samples.

"..soil pH, EC ,Olsen P and SOM analysis Stdev values for Cycle 34 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 34 of 2017.

Sample	pH (1:1) H_2O		EC (1:1) (dSm^{-1})		Olsen P ($mg\ kg^{-1}$)		SOM—WB (%)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-1711	7.79	*0.04*	0.44	*0.08*	58.4	*2.1*	2.42	*0.09*
SRS-1712	7.37	*0.03*	0.51	*0.04*	48.6	*1.9*	5.07	*0.17*
SRS-1713	6.23	*0.03*	0.25	*0.06*	26.8	*0.9*	4.85	*0.14*
SRS-1714	6.96	*0.03*	0.88	*0.11*	25.5	*0.9*	2.80	*0.08*
SRS-1715	5.15	*0.05*	0.24	*0.01*	4.9	*0.6*	1.67	*0.13*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 34.

2017 Cycle 34 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 34 averaged 0.067 pH units across four of the five the soils. Median within lab pH standard deviation was 0.045 pH units. Soil displacement CEC ranged 4.3 to 18.9 cmol kg^{-1} across the five soils. Soil Solvtia CO_2 respiration (test code 191) results were provided by four laboratories with median results ranging from 16 - 94 mg kg^{-1}. Sample SRS-1710 had a large discrepancy in soil CEC values: Displacement 18.9 cmol kg^{-1} and Estimated CEC of 28.9 cmol kg^{-1}. Soil ammonium acetate K (Test code 140) MAD values ranged 3.7 - 94 mg kg^{-1} and ammonium acetate Mg MAD values ranged 11 to 115 mg kg^{-1} for the five soils. These results for K and Mg were improved relative to cycle 32 results 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 0.044% nitrogen with intra-lab *s* of 0.075%, 0.028%, 0.055% and 0.051%, respectively. There was a greater inter-lab variability (MAD) in total Na values than for combustion N, P, K, Ca, Mg, Zn, or Mn concentrations across all samples. Generally the eucalyptus leaf composite sample SRB-1710 had lower median concentrations of NO_3-N, SO_4-S, N, P, Mg, Cu and Ba relative to the other three botanical samples. One observation on Cycle 34, MAD intra-lab variability was lower for total S than total P for two of four four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.002 to 0.021 dSm^{-1}. NO_3-N values ranged from 0.008 - 0.32 molc L^{-1} across the three water samples with MAD values ranging 0.007 to 0.023 molc L^{-1}.

SRS Results - pH

Sixty-one laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.20 - 7.90. Lab results were ranked low to high based on sample SRS-1711 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally all soils except SRS-1713 showed good consistency across labs. Labs #1, and #3 were inconsistent across soils. Labs #2 showed low bias. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

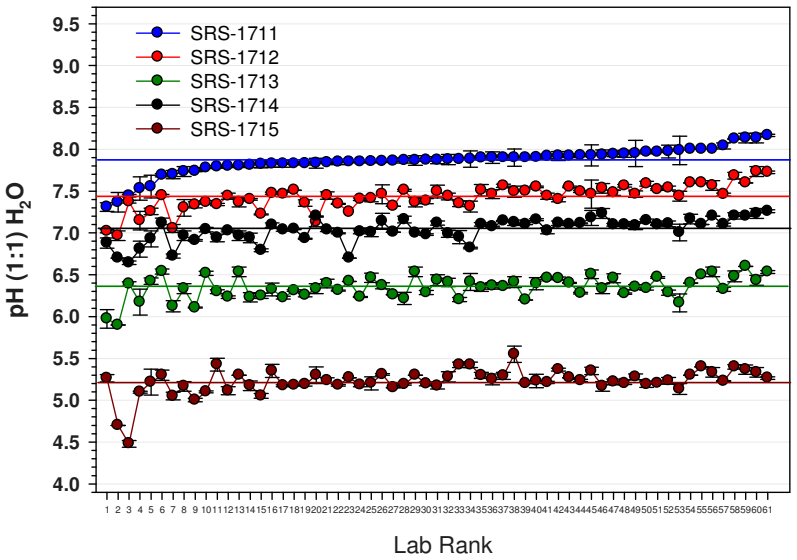


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2017 Cycle 34.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.041 to 0.058 pH units, the lowest noted for SRS-1713. 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 #5, #45 and #58 exceeded 0.10 pH units for three of five soils. Soil SRS-1713 was the least variable with respect to intra-lab variance for Cycle 34.

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

M3-P ICP results were reported by thirty-three labs. Bray P1 was reported by 28 labs. Median soil M3-P ICP values ranged from 10 - 141 mg kg^{-1} P; Olsen P 4 to 68 mg kg^{-1} P and Bray P2 ranged from 11 to 267 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1711, median Olsen P concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1712 and associated with the higher P concentrations. Soil SRS-1715, lowest in concentration, showed low intra-lab variability with a range of 0.1 - 1.3 mg kg^{-1}. Lab #1 showed low bias on all five samples. Labs #5, #9, #19, #31, #33 and #34 were inconsistent. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

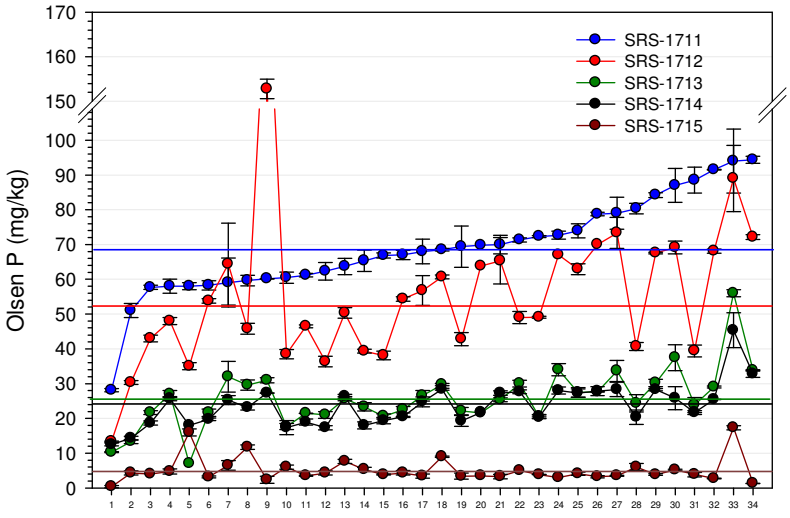


Figure 2. Olsen P distribution plots for SRS materials, ALP 2017 Cycle 34.

Four laboratories provided ALP results for Mehlich 1 P, with medians ranging from 4.2 to 35.3 mg kg^{-1} P. Bray P1 (1:7) median concentrations were 9.0 to 80 mg kg^{-1} PO_4-P reported by four labs. Modified Morgan was reported by three laboratories ranging from 4.6 - 116 mg kg^{-1} PO_4-P with the highest concentration noted for SRS-1715.

SRS - Potassium

Forty-seven laboratories provided ALP results for soil K (test code 141) results. Results were ranked low to high based on sample SRS-1715 (see Figure 3). Soils SRS-1713 and SRS-1714 were the most inconsistent across labs. Lab #47 showed high bias on 3 of 5 five soils. Labs #2, #5, #27, #45, and #46 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-1715, with a median intra-lab value of 3.3 mg kg^{-1} Kg and highest for SRS-1714 with a value of 13.3 mg kg^{-1} Kg. Potassium within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 250 mg kg^{-1} K. Precision was poor (based on intra-lab *s*) for labs #17 and #37 which exceeded 15 mg kg^{-1} K on two of five soils; and labs #28, the value exceeded 50 mg kg^{-1} K for on of five soils. Poor precision is attributed to extraction and/or analysis instrument operation.

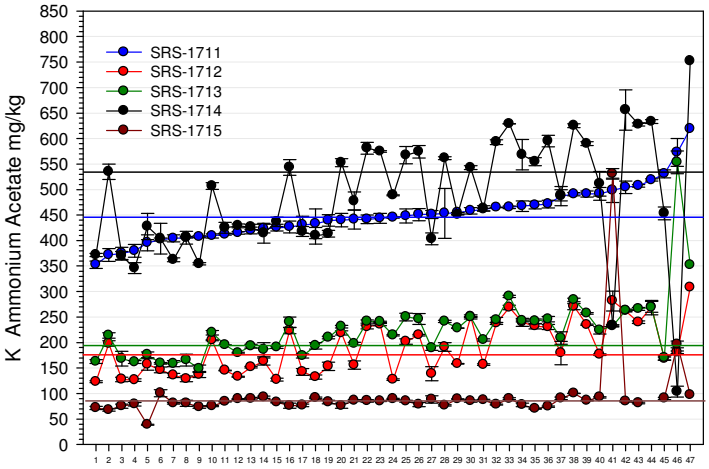


Figure 3. Extractable K distribution plots for SRS materials, ALP 2017 Cycle 34.

SRS SOM-LOI

Forty-three laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.43 to 6.53%. Results were ranked based on sample SRS-1711 (see Figure 4). Labs #43 had consistent high, and labs #9, #25, and #42 were noted having inconsistency the five soils. Sample SRS-1712 was the most inconsistency of the five soils of cycle 34. Bias was noted in eight 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 0.07 to 0.20% SOM-LOI, the highest for SRS-1712. Across labs, *s* values for SRS-1711 ranged from 0.006 - 0.44 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #9, #20, #31, #37 and #43, exceeded 0.15 % SOM for SRS-1713. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

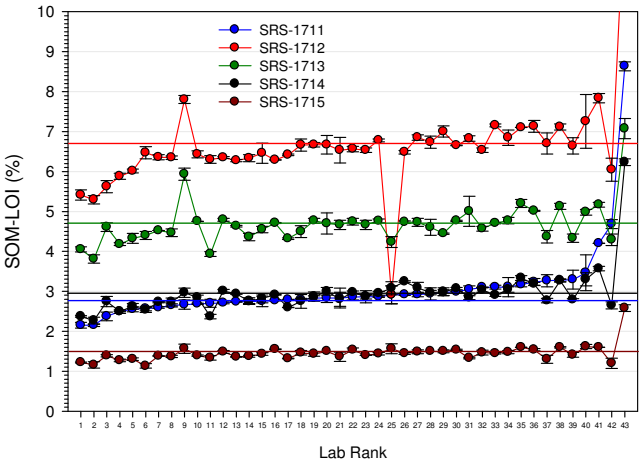


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2017 Cycle 34.

SRS - EC 1:1

Twenty-nine laboratories provided ALP results for Electrical Conductivity 1:1 (test code 105). Results were ranked low to high based on sample SRS-1711 (see Figure 5). Soil SRS-1714 was the highest in concentration and SRS-1715 the most in consistent across labs. Across soils, labs #3, and #7 were inconsistent across soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

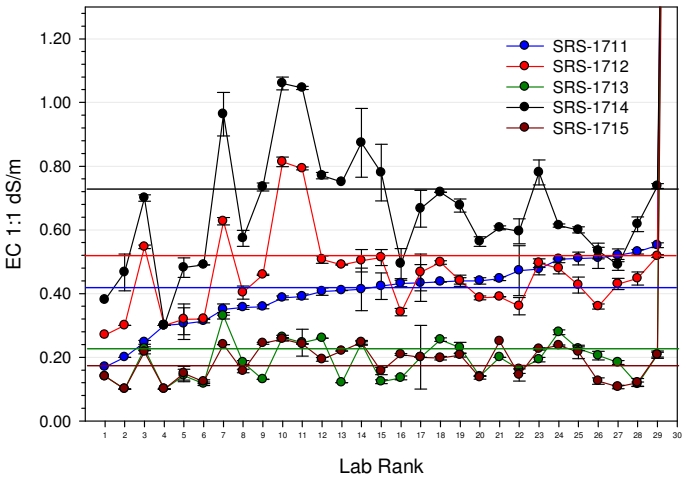


Figure 5. Soil EC 1:1 distribution plot, ALP 2017 Cycle 34.

Electrical Conductivity 1:1 median intra-lab *s* values were lowest for ALP soil SRS-1713 with an intra-lab median value of 0.005 dSm^{-1} and highest for SRS-1714 with a value of 0.01 dSm^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1714. Intra-lab precision was poor for labs #5, #14, and #17 on two of five soils. Poor precision maybe associated with extraction and/or instrument operation. Four labs were flagged for poor precision for cycle 34.

SRB Nitrate-Nitrogen

Twenty-five laboratories provided ALP results for NO_3-N by cadmium reduction (test code 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-1709 (see Figure 6). The data plot shows labs #23, #24 and #25 had high bias for SRB-1709 and SRB-1711. Labs #1, #20, and #22 were inconsistent.

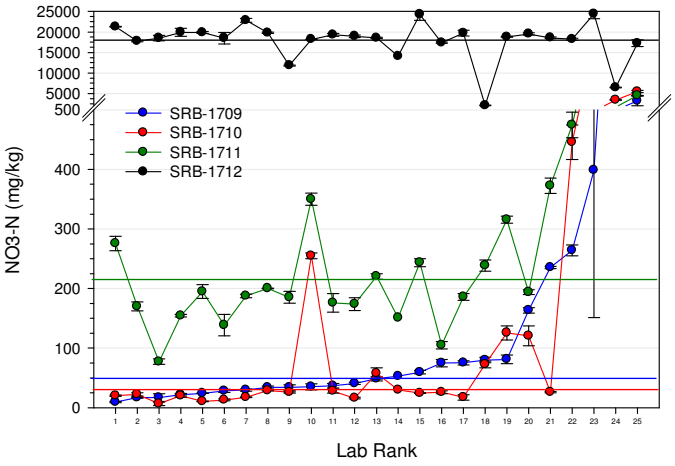


Figure 6. Nitrate distribution plots for SRB materials, ALP 2017, Cycle 34.

Botanical NO_3-N (test code 202) results for Cycle 34 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 9.0 to 646 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-1709 ranged from 0.5 – 247 mg kg^{-1}; SRB-1710 ranged from 0.4 - 268 mg kg^{-1}, SRB-1711 ranged from 0.6 – 79 mg kg^{-1} and SRB-1712 ranged from 28 - 1422 mg kg^{-1}. Lab #16 had consistently high standard deviations for two of four samples. Seven 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 34. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1709 (see Figure 7). It is note worthy that TKN for SRB-1712 showed poor reproducibility between labs. Labs #29 and #30 showed high bias for Dumas N for three samples, whereas labs #11 and #24 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-1709, ranged 0.005 to 0.35% N, SRB-1710 ranged from 0.003 to 0.095% N, SRB-1711 ranged from 0.006 to 0.23 % N, and SRB–1712 from 0.004 to 0.16 % N. Lab #1 had consistently high standard deviations. Lab TKN *s* values for SRB-1709 ranged from 0.014 to 0.35%, SRB-1710 ranged from 0.005 to 0.18% TKN, SRB-1711 ranged from 0.006 to 0.17% TKN nitrogen and SRB-1712 ranged from 0.005 to 0.35% TKN nitrogen.

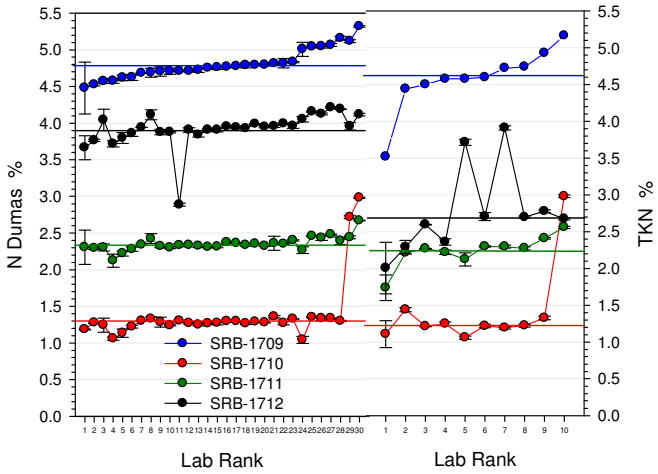


Figure 7. N distribution plots for SRB materials, ALP 2017 Cycle 34.

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-1709 (see Figure 8). Laboratories #40 and #41 showed high bias. Labs #1, #12 and #34 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 0.034 to 0.44 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1709, ranged from 0.003 to 0.15 % K; SRB-1710, 0.003 — 0.23 % K; SRB-1711, 0.001 - 0.31 % K; and SRS-1712, 0.025 to 1.19 % K. Four labs had high standard deviations exceeding 0.10 %K for SRB-1710. Eight labs were flagged for poor K precision.

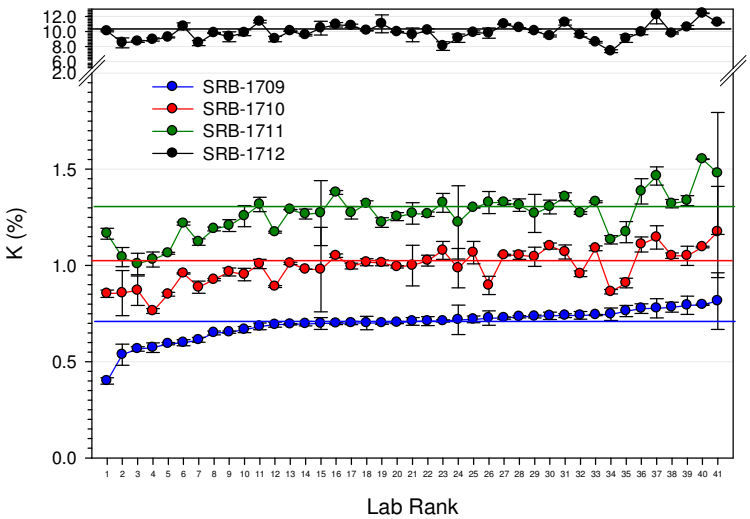


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2017 Cycle 34.

SRB - Phosphorus

Forty laboratories provided ALP results for Cycle 34 phosphorus (P) combined (test codes 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-1709 (see Figure 9). Consistent low bias was noted for lab #1 and high bias for lab #40. Labs #3, #7 and #28 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 0.017 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1709; ranged from 0.001 - 0.043 % P; SRB-1710 ranged from 0.001 – 0.022 % P and SRB-1711 0.001 - 0.030 % P; and SRB-1712 0.001 - 0.044 % P. Labs #40 had a high standard deviation exceeding 0.020 % P on three of four botanical samples. Six labs were flagged for poor precision for botanical P.

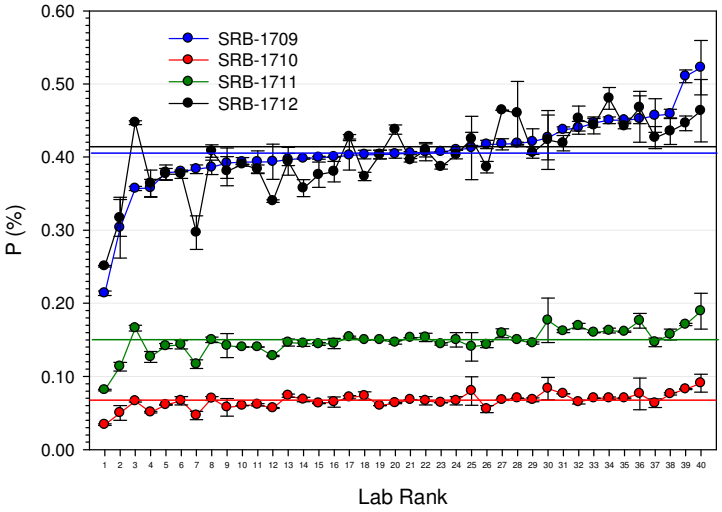


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2017 Cycle 34.

SRB - Manganese

Forty-four laboratories provided ALP results for manganese (Mn) (test codes 221 and 233). 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-1709 (see Figure 10). Labs #1 showed low bias on two of four samples. Labs #3, #17, #29, and #42 were inconsistent and data suggests that samples may have switched during analysis. Source of bias is likely related to sample digestion or method compliance.

Botanical Mn results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 1.3 to 6.2 mg kg^{-1} Mn for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1709; ranged from 0.09 - 12.2 mg kg^{-1} Mn; SRB-1710 ranged from 0.04 – 12.1 mg kg^{-1} Mn; SRB-1711 0.005 - 2.4 mg kg^{-1} Mn; and SRB-1712 0.05 - 8.4 mg kg^{-1} Mn. Labs #1, #17, #39 and #40 had consistently high standard deviations for three of four botanical samples.

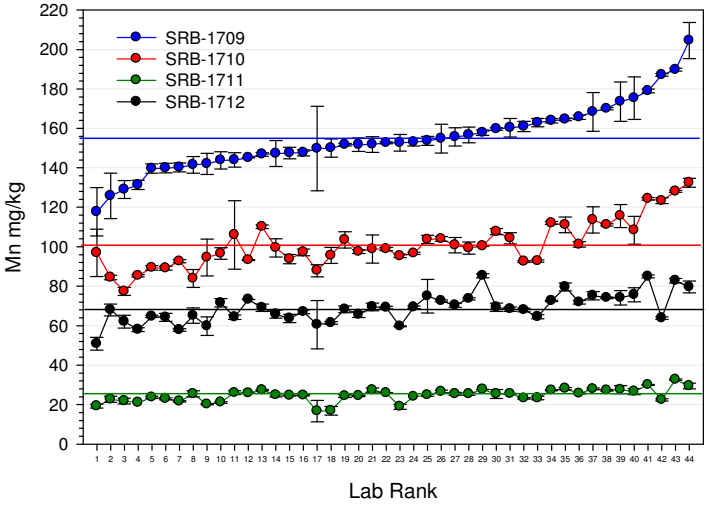


Figure 10. Manganese distribution plots for SRB materials, ALP 2017 Cycle 34.

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-1707 (see Figure 11). Lab #1 and #2 indicated consistent low bias on SRS-1706 and SRW-1708. Lab #15 showed high bias pn SRW-1707. 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 0.018, 0.0094 and 0.0032 dSm^{-1}, respectively. Precision for sample SRW-1709 was the most consistent across the sixteen participating laboratories. Intra-lab *s* values for lab #5 exceeded 0.006 dSm^{-1} on SRW-1708. Highest precision was noted for lab #4 with intra-lab *s* values of < than 0.0001 dSm^{-1}. Four labs were flagged for poor precision across the three samples.

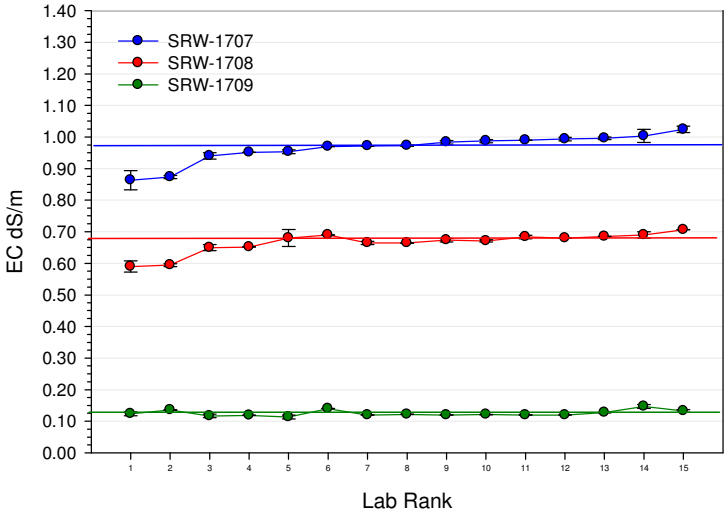


Figure 11 . Water EC distribution plots for SRW materials, ALP 2017 Cycle 34.

SRW - Cl Results

Fifteen laboratories provided ALP results for water Cl (test code 313). Lab results were ranked low to high based on sample SRW-1707 (see Figure 12). Median values are designated by horizontal lines. Lab #15 had high bias. Labs #1 and #14 showed inconsistency across samples.

Cl precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.050, 0.016, and 0.015 meq L^{-1} for SRW-1707, SRW-1708, and for SRW-1709, respectively. Water Cl precision was excellent for all individual labs with only lab #9 exceeding 0.025 meq L^{-1} on two of the three samples. Across samples intra-lab *s* was less than 0.005 meq L^{-1} for lab #13. Two labs were flagged for poor precision on ALP Cycle 34 for Cl content.

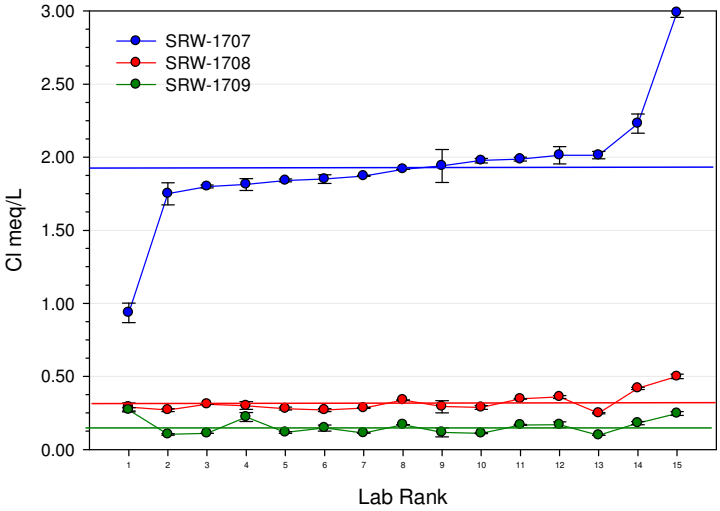


Figure 12. Water Cl distribution plots for SRW materials, ALP 2017 Cycle 34.

Announcements

- New ALP soils were collected in September in Cropsey, Illinois, Louisville, Illinois and Rost, Minnesota.
- 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.
- 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.
- CTS will be initiating a greenhouse media and nutrient solution PT program in January 2018. The program will cover pH, EC and nutrients in soil less media and fertilizer solutions. It will be based on 3 exchange cycles per year of with three PT materials per cycle.
- 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@colostate.edu.

Summary

ALP is celebrating twelve years of service with the completion of cycle 34. Since 2006 ALP has completed the analysis of 170 soils, 108 plant samples and 103 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 34. 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 35 Ship

March 21, 2017

"Two things are infinite: the universe and human stupidity; and I'm not sure about the universe. "

— Albert Einstein, 1944

ALP
Agricultural Laboratory Proficiency Program