2017 Volume 2

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ALP Program Report

2017 Summer - Cycle 33

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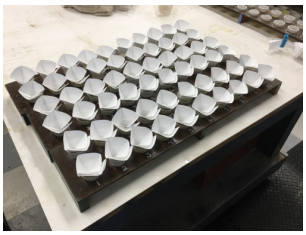
ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 33.
- Sixty-three Laboratories provided soil pH (1:1) H_2O results and medians ranged from 4.20 - 7.65.
- Cycle 33 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 saturated paste K were consistent on four of five proficiency soils for cycle 33.
- Botanical P, ranged from 0.247 - 0.676% with two of forty-one labs noted for low bias.
- Botanical Cu results showed high consistency across the four samples for thirty-six of thirty-nine labs for PT Cycle 33.
- Water EC content showed very high consistency by fifteen of sixteen of labs across all samples.

The Agriculture Laboratory Proficiency (ALP) Program spring 2017 Round Cycle 33 was completed August 25, 2017, 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 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.

Inside this issue:

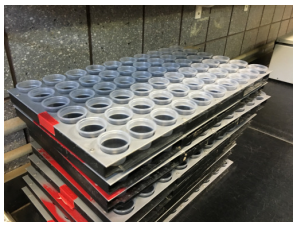
Proficiency Materials

Standard Reference Soils (SRS) materials utilized for cycle 33 were: SRS-1706 is a Fuquay loamy sand collected Crisp Cty, GA; SRS-1707 a Colton loamy fine sand, from Cheshire cty, VT; SRS-1708 a clay loam collected Arcola, SK, Canada; SRS-1709 a Goulding-Toomes sandy loam collected Sonoma Cty, CA; and SRS-1710 a Thurman sandy loam collected Nobles cty, MN. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 4.20 - 7.65; NO_3-N 2.6 - 292 mg kg^{-1}; Bray P1 (1:10) 2.6 - 107 mg kg^{-1}; K NH_4OAc 36 - 1262 mg kg^{-1}; SO_4-S 6.7 - 33.9 mg kg^{-1}; Mehlich 3 P (ICP) 2.3 - 136 mg kg^{-1}; DTPA-Zn 0.29 - 2.72 mg kg^{-1}; SOM-LOI 1.23 – 6.93%; CEC 2.7 - 28.4 cmol kg^{-1}; clay 6.2 - 45.5% and soil available Solvita 8.3 - 90.1 %.

Standard Reference Botanical (SRB) materials for Cycle 33 were: SRB-1705 a asparagus composite from Mexico; SRB-1706 Basil leaf composite from CO; SRB-1707 corn leaves from IA; and SRB-1708 potato petiole from WA. SRB material median analytes ranged: NO_3-N 53 - 19470 mg kg^{-1}; Dumas N 2.50 - 4.75%; total P 0.25 - 0.67%; total K 1.91 - 9.09%; total Ca 0.32 - 1.78%; total S 0.16 - 0.57 %, total Zn 23.1 - 70.1 mg kg^{-1}; and total Ba 4.3 - 59.0 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1704 a water sample collected from a canal near Walnut Creek, CA; SRW-1705 from Evanston, WY; and SRW-1706 from Tinmath, CO. SRW median concentrations ranged: pH 7.81 - 8.22; EC 0.14 - 0.54 dSm^{-1}; SAR 0.38 - 1.12; Ca 0.58 - 2.95 mmolc L^{-1}; Mg 0.24 - 3.0 mmolc L^{-1}; SO_4 0.18 - 0.58 mmolc L^{-1} ; and NO_3 0.01 - 0.021 mmolc L^{-1}.

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 lowest noted for pH H_2O. Homogeneity was also evaluated on SRB and SRW matrix samples.

"..soil pH, EC ,Olsen P and SOM analysis Stdev values for Cycle 33 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 33 of 2017.

Sample	pH (1:1) H_2O		EC (1:1) (dSm^{-1})		Olsen P ($mg\ kg^{-1}$)		NO_3-N ($mg\ kg^{-1}$)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-1706	5.28	*0.02*	0.56	*0.03*	28.3	*3.3*	61.2	*4.4*
SRS-1707	4.19	*0.02*	0.45	*0.03*	7.4	*1.1*	65.6	*2.6*
SRS-1708	7.59	*0.02*	3.67	*0.07*	43.5	*1.9*	331.7	*9.3*
SRS-1709	5.53	*0.01*	0.08	*0.01*	2.4	*1.5*	1.4	*0.27*
SRS-1710	6.76	*0.03*	0.57	*0.02*	17.0	*0.8*	54.4	*4.5*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 33.

2017 Cycle 33 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 33 averaged 0.07 pH units across four of the five the soils. Median within lab pH standard deviation was 0.021 pH units. Soil displacement CEC ranged 2.7 to 28.4 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 9 - 90 mg kg^{-1}. Sample SRS-1707 had a large discrepancy in soil CEC values: Displacement 10.1 cmol kg^{-1} and Estimated CEC of 4.0 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 0.060% nitrogen with intra-lab *s* of 0.069%, 0.128%, 0.065% and 0.048%, 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 corn leaf composite sample SRB-1707 had lower median concentrations of SO4-S, N, P, S, B, Zn, Ni, Cd and Sr relative to the other three botanical samples. One observation on Cycle 33, MAD intra-lab variability was lower for total S than total P for all four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.005 to 0.010 dSm^{-1}. NO_3-N values ranged from 0.010 - 0.021 molc L^{-1} across the three water samples with MAD values ranging 0.006 to 0.010 molc L^{-1}.

SRS Results - pH

Sixty-three laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 4.20 - 7.65. Lab results were ranked low to high based on sample SRS-1706 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally all soils except SRS-1709 showed good consistency across labs. Labs #7, #25, #50, and #59 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.

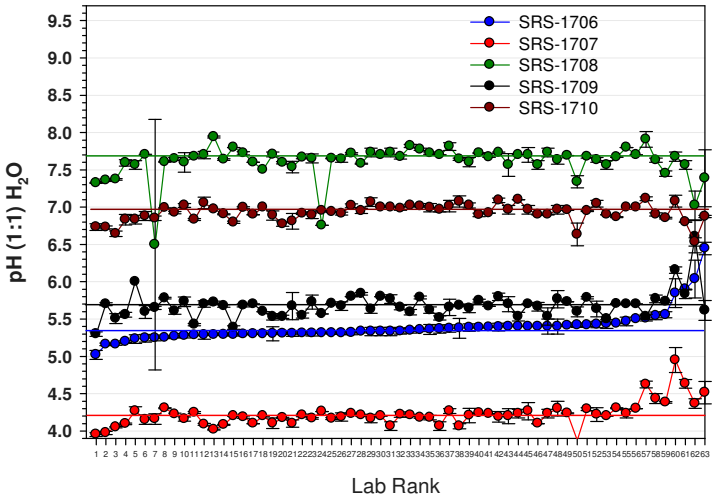


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2017 Cycle 33.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.021 to 0.031 pH units, the lowest noted for SRS-1707. 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 #58 and #62 exceeded 0.10 pH units for three of five soils. Soil SRS-1706 was the least variable with respect to intra-lab variance for Cycle 33.

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

M3-P ICP results were reported by thirty-five labs. Bray P1 was reported by 33 labs. Median soil M3-P ICP values ranged from 2.3 - 137 mg kg^{-1} P; Olsen P 2.1 to 42.5 mg kg^{-1} P and Bray P2 ranged from 4.1 to 151 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1710, median M3 P ICP concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1706 and SRS-1708 associated with the higher P concentrations. Soil SRS-1709, lowest in concentration, showed low intra-lab variability with a range of 1.0 - 6.0 mg kg^{-1}. Lab #1 showed low bias on three samples. Labs #7, #13, #27, and #32 were inconsistent. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

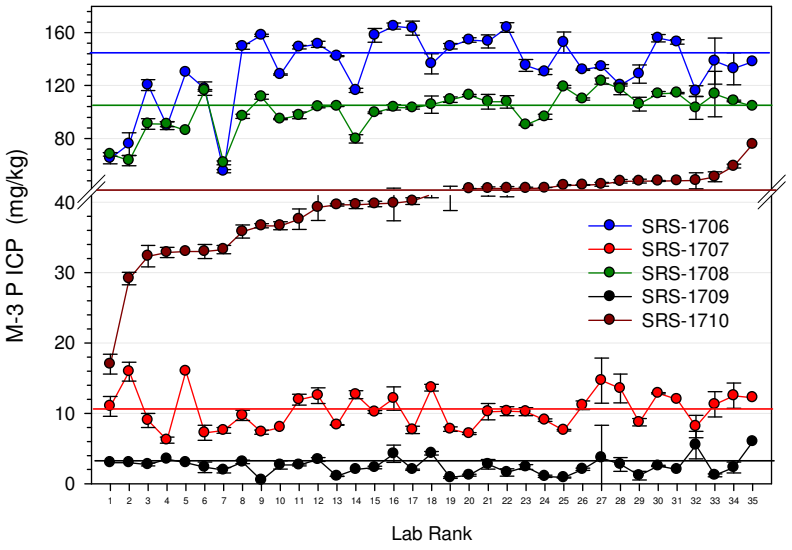


Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2017 Cycle 33.

Four laboratories provided ALP results for Mehlich 1 P, with medians ranging from 1.1 to 70 mg kg^{-1} P. Bray P1 (1:7) median concentrations were 1.6 to 92 mg kg^{-1} PO_4-P reported by five labs. Modified Morgan was reported by four laboratories ranging from 0.6 - 76 mg kg^{-1} PO_4-P with the highest concentration noted for SRS-1708.

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-1706 (see Figure 3). Soils SRS-1709 and SRS-1710 were the most inconsistent across labs. Lab #1 showed low bias on 3 of 5 five soils. Labs #4, #8, #12, #39, 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-1707, with a median intra-lab value of 1.6 mg kg^{-1} Kg and highest for SRS-1708 with a value of 21 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 #5, and #13 which exceeded 10 mg kg^{-1} K on four of five soils; and labs #47, the value exceeded 30 mg kg^{-1} K for three of five soils. Poor precision is attributed to extraction and/or analysis instrument operation.

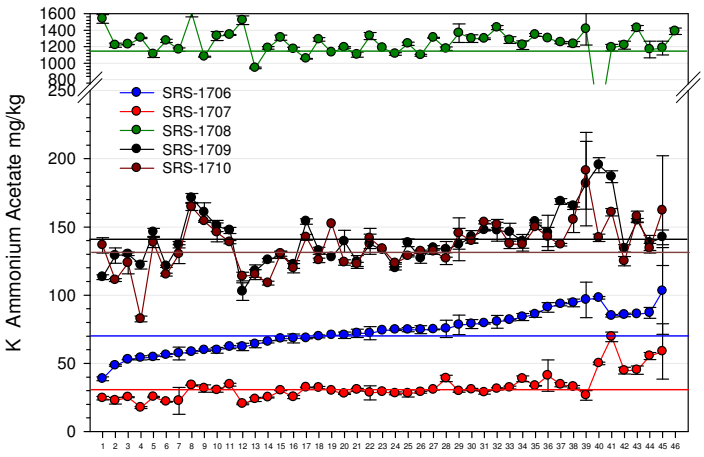


Figure 3. Extractable K distribution plots for SRS materials, ALP 2017 Cycle 33.

SRS SOM-LOI

Forty-five laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.23 to 7.93%. Results were ranked based on sample SRS-1706 (see Figure 4). Labs #1 had consistent low bias, and labs #5, #11, #18, #36, and #42 were noted having inconsistency four of five soils. Sample SRS-1709 ws the most inconsistency acof the five soils of cycle 33. 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 0.03 to 0.10% SOM-LOI, the highest for SRS-1707. Across labs, *s* values for SRS-1710 ranged from 0.005 - 0.26 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #2, #3, #4, #11, #22, #34 and #37, exceeded 0.30 % SOM for SRS-1707. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

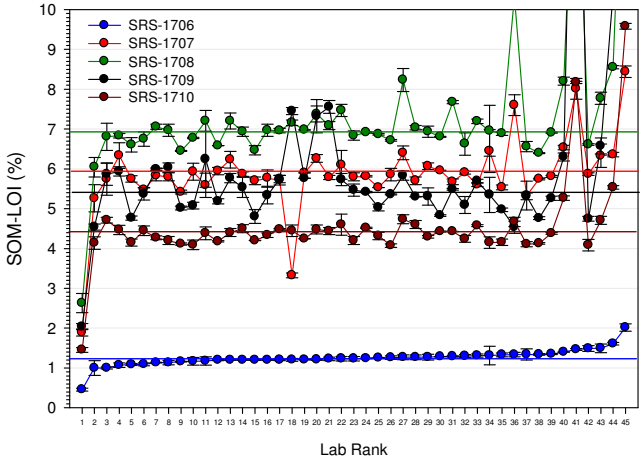


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2017 Cycle 33.

SRS - Sat Paste K

Seventeen laboratories provided ALP results for Saturated Paste K (test code 105). Results were ranked low to high based on sample SRS-1709 (see Figure 5). Soil SRS-1708 was the highest in concentration and SRS-1710 the most in consistent across labs. Across soils, labs #13, #14 and #17 were inconsistent across soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

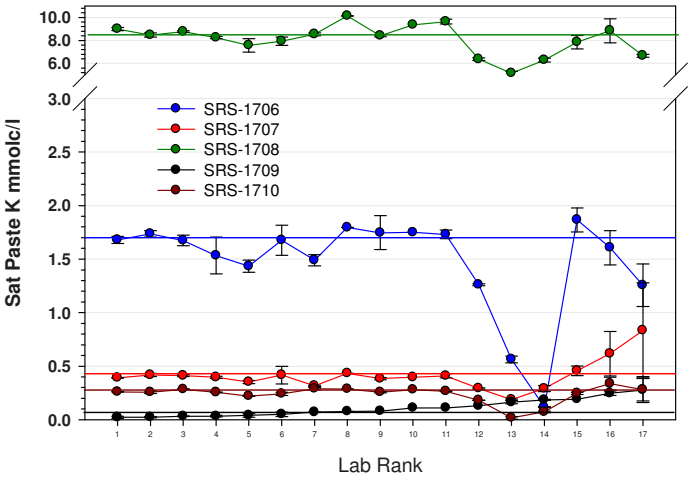


Figure 5. Soil M3-Mg distribution plot, ALP 2017 Cycle 33.

Sat Paste K median intra-lab *s* values were lowest for ALP soil SRS-1710 with an intra-lab median value of 0.01 mmolc l^{-1} and highest for SRS-1708 with a value of 0.14 mg kg^{-1} . Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1706. Intra-lab precision was poor for labs #6, #16, and #17 on two of five soils. Poor precision maybe associated with saturated paste extraction and/or ICP-OES instrument operation. Three labs were flagged for poor precision for cycle 33.

SRB Nitrate-Nitrogen

Twenty-two 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-1705 (see Figure 6). The data plot shows labs #20, #21 and #22 had high bias for SRB-1705 and SRB-1706. Labs #3, #9, and #18 were inconsistent.

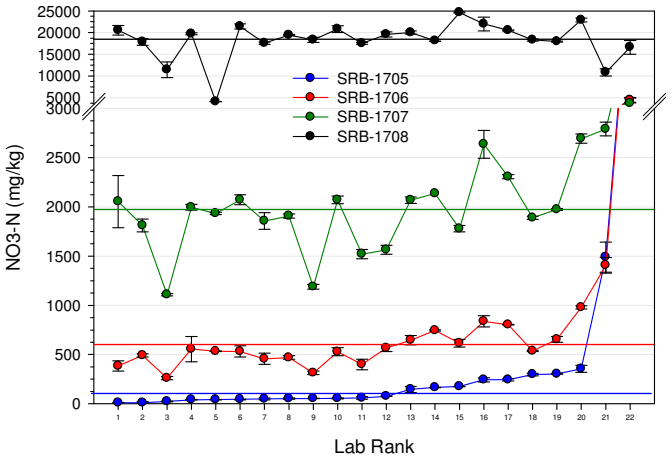


Figure 6. Nitrate distribution plots for SRB materials, ALP 2017, Cycle 33.

Botanical NO_3-N (test code 202) results for Cycle 33 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 4.0 to 369 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-1705 ranged from 0.4 – 35 mg kg^{-1}; SRB-1706 ranged from 4 - 127 mg kg^{-1}, SRB-1707 ranged from 10 – 263 mg kg^{-1} and SRB-1708 ranged from 23 - 1780 mg kg^{-1}. Lab #16 had consistently high standard deviations for two of four samples. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and nine labs for TKN (Test code 209) for Cycle 33. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1705 (see Figure 7). It is note worthy that TKN was lower than Dumas N for all four samples. Labs #29 and #30 showed high bias for Dumas N for three samples, whereas labs #1 and #27 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-1705, ranged 0.012 to 0.21% N, SRB-1706 ranged from 0.001 to 0.48% N, SRB-1707 ranged from 0.003 to 0.11 % N, and SRB–1708 from 0.004 to 0.13 % N. Lab #24 had consistently high standard deviations. Lab TKN *s* values for SRB-1705 ranged from 0.02 to 0.30%, SRB-1706 ranged from 0.01 to 0.49% TKN, SRB-1707 ranged from 0.02 to 0.11% TKN nitrogen and SRB-1708 ranged from 0.02 to 0.15% TKN nitrogen.

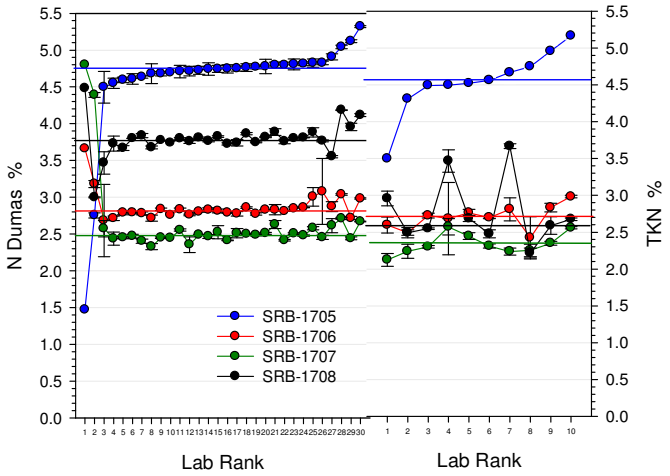


Figure 7. N distribution plots for SRB materials, ALP 2017 Cycle 33.

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-1705 (see Figure 8). Laboratories #1 and #2 showed low bias. Labs #19, #38 and #41 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-1705, ranged from 0.007 to 0.25 % K; SRB-1706, 0.006 — 0.21 % K; SRB-1707, 0.005 - 0.63 % K; and SRS-1708, 0.02 to 1.52 % K. Four labs had high standard deviations exceeding 0.20 %K for SRB-1707. Seven labs were flagged for poor K precision.

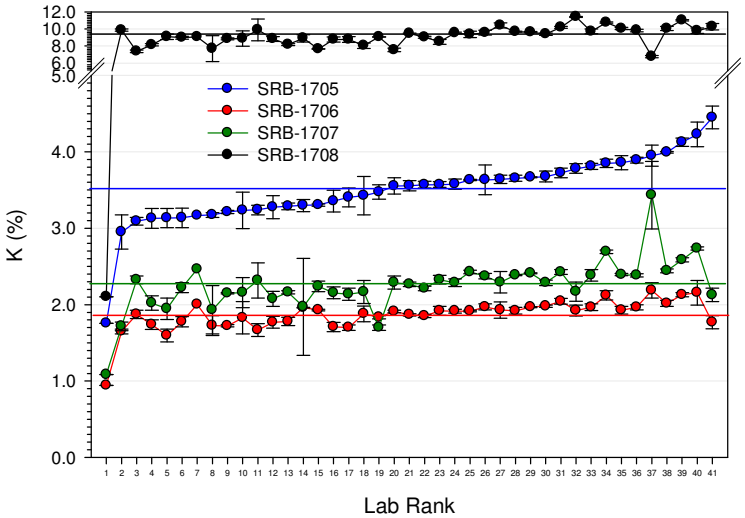


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2017 Cycle 33.

SRB - Phosphorus

Forty-one laboratories provided ALP results for Cycle 33 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-1705 (see Figure 9). Consistent low bias was noted for labs #1 and #2. Labs #3 #14 and #27 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 0.014 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1705; ranged from 0.002 - 0.085 % P; SRB-1706 ranged from 0.001 – 0.023 % P and SRB-1707 0.001 - 0.038 % P; and SRB-1708 0.001 - 0.044 % P. Labs #30 had a high standard deviation exceeding 0.020 % P on three of four botanical samples. Seven labs were flagged for poor precision for botanical P.

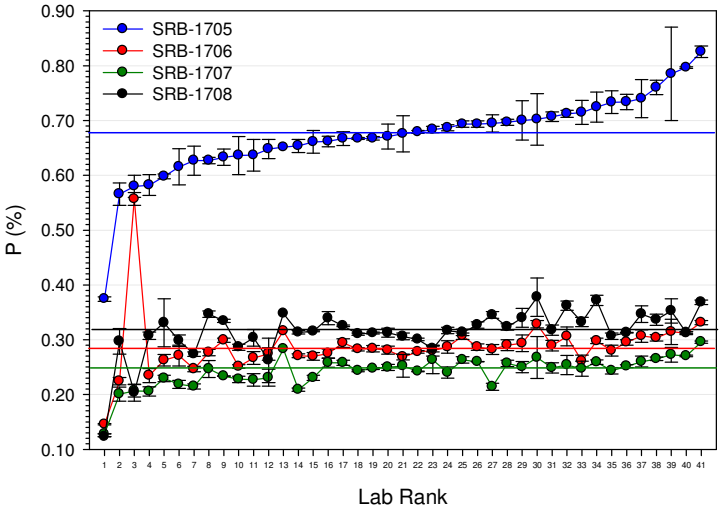


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2017 Cycle 33.

SRB - Copper

Thirty-nine laboratories provided ALP results for zinc (Cu) (test code 235). 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-1705 (see Figure 10). Labs #1 showed low bias on all three of four samples. Labs #2, #10, #37, and #39 were inconsistent and data suggests that samples may have switched during analysis. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Cu results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.29 to 0.80 mg kg^{-1} Cu for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1705; ranged from 0.03 - 3.1 mg kg^{-1} Cu; SRB-1706 ranged from 0.11 – 2.8 % Cu; SRB-1707 0.07 - 7.9 mg kg^{-1} Cu; and SRB-1708 0.02 - 3.9 mg kg^{-1} Cu. Labs #4, #29 and #34 had consistently high standard deviations for three of four botanical samples.

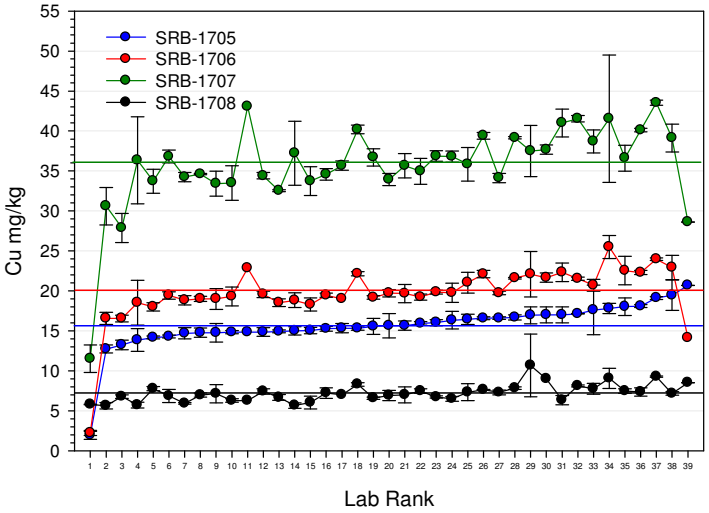
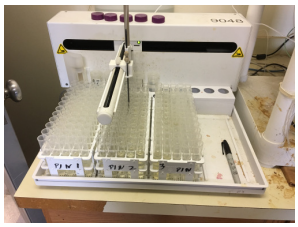


Figure 10. Copper distribution plots for SRB materials, ALP 2017 Cycle 33.

SRW - Water EC



Sixteen laboratories provided ALP results for water EC (test code 302). Lab result were ranked low to high based on sample SRW-1704 (see Figure 11). Lab #16 indicated consistent high bias on SRS-1704 and SRW-1705. Lab #6 showed inconsistently across two of 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 0.004, 0.0004 and 0.0002 dSm^{-1}, respectively. Precision for sample SRW-1704 was the most consistent across the sixteen participating laboratories. Intra-lab *s* values for lab #5 exceeded 0.05 dSm^{-1} on SRW-1704 and SRW-1705. Highest precision was noted for lab #7 with intra-lab *s* values of < than 0.0001 dSm^{-1}.

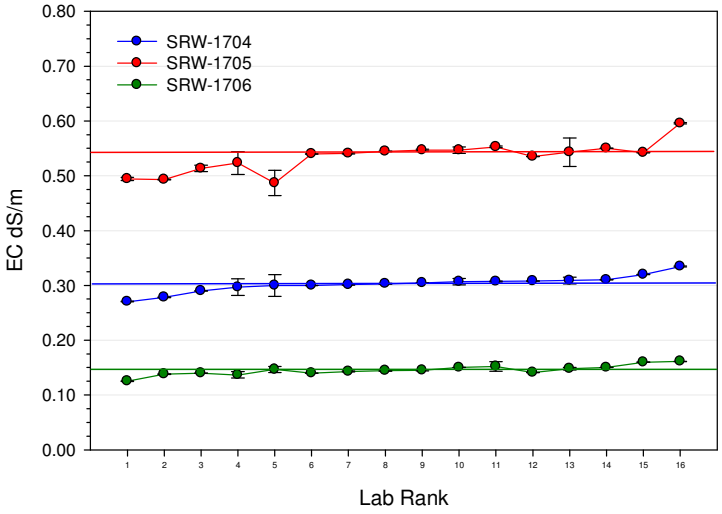


Figure 11 . Water EC distribution plots for SRW materials, ALP 2017 Cycle 33.

SRW - Mg Results

Fourteen laboratories provided ALP results for water Mg (test code 303). Lab results were ranked low to high based on sample SRW-1704 (see Figure 12). Median values are designated by horizontal lines. Lab #14 had high bias. Labs #1 and #13 showed inconsistency across samples.

Mg precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.019, 0.022, and 0.004 meq L^{-1} for SRW-1704, SRW-1705, and for SRW-1706, respectively. Water Mg precision was excellent for all individual labs with only lab #6 exceeding 0.30 meq L^{-1} on two of the three samples. Across samples intra-lab *s* was less than 0.002 meq L^{-1} for lab #7. Four labs were flagged for poor precision on ALP Cycle 33 for Mg content.

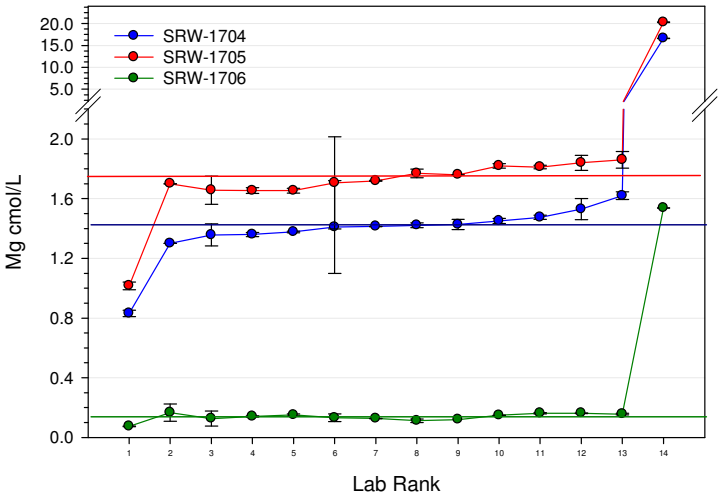


Figure 12. Water Mg distribution plots for SRW materials, ALP 2017 Cycle 33.

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.

- New ALP soils were collected in June, from Ellsworth Minnesota. Additional collections are scheduled in September for Indiana, Illinois and Kentucky.

- 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 three exchange cycles per year of with three PT materials per cycle. Details to follow in November 2017.

- 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 ten years of service with the completion of cycle 33. Since 2006 ALP has completed the analysis of 165 soils, 104 plant samples and 100 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 33. 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 34 Ship

September 21, 2017

"The value of a college education is not the learning of many facts but the training of the mind to think. "

— Albert Einstein, 1921