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ALP Program Report

2018 Summer - Cycle 36

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ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 36.
- Sixty-two Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.33 - 7.80.
- Cycle 36 soil M3-P ICP ranged from 14.7 to 85.2 mg kg^{-1} with MAD values ranging 1.1 - 5.2 mg kg^{-1} across the five soils.
- Lab results for Amm. Acetate K were inconsistent on two of five proficiency soils for cycle 36.
- Botanical P, ranged from 0.070 - 0.335% with two of forty-two labs noted for high bias.
- Botanical Cu results showed high consistency across the four samples for thirty-five of forty labs for PT Cycle 36.
- Water Ca content showed very high consistency by thirteen of fifteen labs across all samples.

The Agriculture Laboratory Proficiency (ALP) Program spring 2018 Round Cycle 36 was completed August 24, 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:

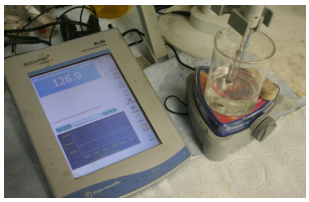
Proficiency Materials

Standard Reference Soils (SRS) materials utilized for cycle 36 were: SRS-1806 is a loam collected Oxford Cty, ON Canada; SRS-1807 a Madison sandy loam, from Jackson County, GA; SRS-1808 a Eldean loam collected Wayne Cty, IN; SRS-1809 a Doak loam collected San Juan Cty, NM; and SRS-1810 a Nicollet clay loam collected Jackson Cty, MN. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.33 - 7.80; NO_3-N 3.2 - 61.8 mg kg^{-1}; Bray P1 (1:10) 10.3 - 92.4 mg kg^{-1}; M3-K 76 - 344 mg kg^{-1}; SO_4-S 4.8 - 30.3 mg kg^{-1}; Mehlich 3 P (ICP) 14.7 - 85.2 mg kg^{-1}; DTPA-Zn 0.35 - 5.07 mg kg^{-1}; SOM-LOI 0.74 – 5.12%; CEC 5.7 - 26.0 cmol kg^{-1}; clay 7.2 - 34.0% and field capacity H_2O 9.8 - 34.4 %.

Standard Reference Botanical (SRB) materials for Cycle 36 were: SRB-1805 a eucalyptus leaf sample from CA; SRB-1806 senna leaf composite; SRB-1807 potato petiole composite from WA; and SRB-1808 alfalfa leaf composite from MI. SRB material median analytes ranged: NO_3-N 31 - 20,210 mg kg^{-1}; Dumas N 1.34 - 3.43%; total P 0.07 - 0.33%; total K 0.91 - 9.77%; total Mg 0.28 - 0.69%; total S 0.13 - 0.31 %, total Zn 10.7 - 38.0 mg kg^{-1}; and total Cd 0.059 - 1.37 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1804 a water sample collected from a Brush Creek, WV; SRW-1805 from an irrigation canal near Severance, CO; and SRW-1806 from a surface canal near Carr, CO. SRW median concentrations ranged: pH 7.70 - 8.61; EC 0.29 - 10.8 dSm^{-1}; SAR 0.25 - 395; Ca 0.17 - 2.28 mmolc L^{-1}; Na 0.39 - 131 mmolc L^{-1}; HCO_3 1.26 - 117.1 mmolc L^{-1}; and NO_3 0.013 - 0.14 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 36 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 36, 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-1806	5.27	*0.02*	0.28	*0.007*	19.1	*0.9*	29.5	*1.5*
SRS-1807	5.51	*0.01*	0.32	*0.01*	34.5	*0.9*	11.4	*0.5*
SRS-1808	6.59	*0.04*	0.58	*0.06*	18.1	*0.9*	64.8	*3.5*
SRS-1809	7.78	*0.03*	0.62	*0.03*	10.8	*0.6*	42.7	*1.6*
SRS-1810	6.55	*0.02*	0.21	*0.02*	8.7	*0.6*	3.5	*0.5*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 36.

2018 Cycle 36 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 36 averaged 0.07 pH units across the soils. Median within lab pH standard deviation was 0.043 pH units. Soil density (test code 188) results were provided by eight laboratories with median results ranging from 1.24 - 1.44 $g\ cm^{-3}$ with MAD values averaging > 0.02 $g\ cm^{-3}$ for two of five samples. Soil displacement CEC ranged 5.7 to 26.0 $cmol\ kg^{-1}$ across the five soils. Sample SRS-1810 had a large discrepancy in soil CEC values: Displacement 26.0 $cmol\ kg^{-1}$ and Estimated CEC of 22.7 $cmol\ kg^{-1}$. Soil ammonium acetate K (Test code 140) MAD values ranged 73.6 - 343 $mg\ kg^{-1}$ and ammonium acetate Mg MAD values ranged 5.8 to 41.6 $mg\ kg^{-1}$ 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 0.062% nitrogen with intra-lab *s* of 0.027%, 0.033%, 0.062% and 0.031%, 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 eucalyptus leaf composite sample SRB-1801 had lower median concentrations of PO_4-P, N, P, K, Mg, Na, S, Zn, Cu, and Ba relative to the other three botanical samples. One observation on Cycle 36, intra-lab relative variability was higher for Mg 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 0.008 to 0.72 dSm^{-1}. NO_3-N values ranged from 0.013 - 0.13 $molc\ L^{-1}$ across the three water samples with MAD values ranging 0.011 to 0.021 $molc\ L^{-1}$.

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 5.15 - 7.93. Lab results were ranked low to high based on sample SRS-1806 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1806, SRS-1807 and SRS-1809 showed good consistency across labs. Labs #21, #42, and #62 were inconsistent across soils. Labs #14 showed high bias on 2 of 5 soils. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

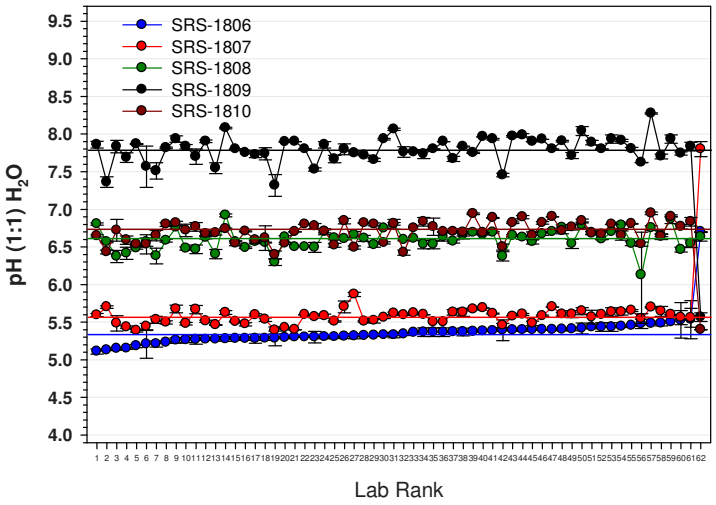


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2018 Cycle 36.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.041 to 0.083 pH units, the lowest noted for SRS-1807. For specific labs poor precision was noted for nine laboratories, exceeding by three times that noted for consensus median intra-lab *s*. Specifically *s* for lab #6 and #61 exceeded 0.10 pH units for two of five soils. Soil SRS-1807 was the least variable with respect to intra-lab variance for Cycle 36.

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 35 labs. Median soil Bray P1 values ranged from 10.1 - 92.4 mg kg^{-1} PO_4-P; Olsen P 7.0 to 39.4 mg kg^{-1} P and Bray P2 ranged from 20.7 to 132 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1806, median M3-P ICP concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1809, SRS-1806 and SRS-1807 had large dynamic ranges. Soil SRS-1810, lowest in concentration, had low intra-lab variability with a range of 0.1 - 52 mg kg^{-1}. Lab #35 showed high bias on four samples. Labs #1, #2, #14, #21, #24, and #32 were inconsistent, likely related to extraction, analysis instrument and/or method compliance.

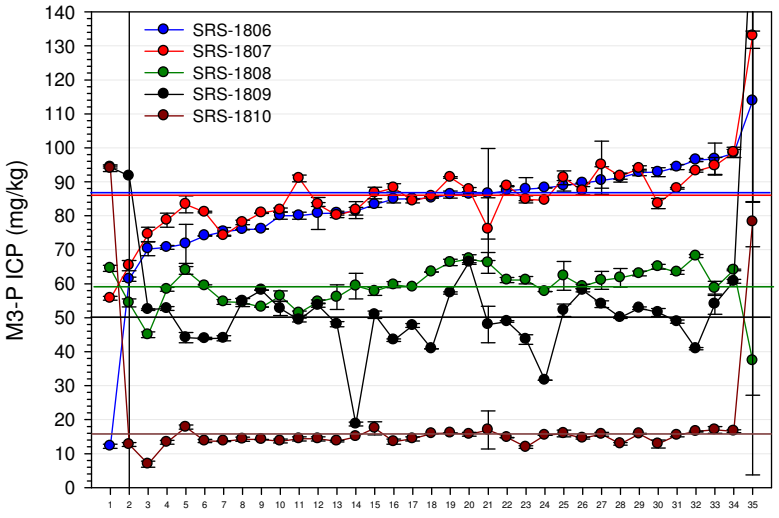


Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2018 Cycle 36.

Three laboratories provided ALP results for Mehlich 1 P, with medians ranging from 8.9 to 71.8 mg kg^{-1} PO_4-P. M3-P ICP median concentrations were 14.7 - 87.7 mg kg^{-1} P reported by thirty-five labs. Modified Morgan was reported by four laboratories ranging from 1.9 - 27.9 mg kg^{-1} P with the highest concentration noted for SRS-1809.

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-1806 (see Figure 3). Soils SRS-1802 and SRS-1803 were the most inconsistent across labs. Lab #1 showed low bias on four of five soils. Labs #2, #3, #20, #21, #29, and #45 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-1806, with a median intra-lab value of 3.8 mg kg^{-1} Kg and highest for SRS-1809 with a value of 81.7 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, #8, #13, #29 and #32 which exceeded 20 mg kg^{-1} K on SRS-1807; and labs #8, and #44 the value exceeded 10 mg kg^{-1} K for SRS-1808. Poor precision is attributed to extraction and/or analysis instrument operation.

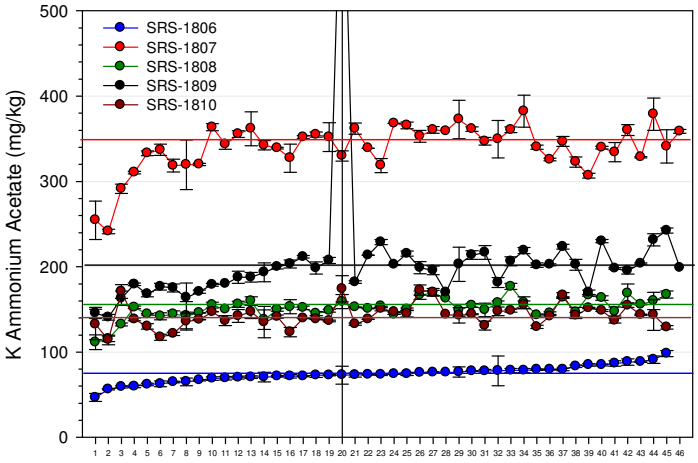


Figure 3. Amm. Extractable K distribution plots for SRS materials, ALP 2018 Cycle 36.

SRS SOM-LOI

Forty-nine laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 0.74 to 5.23%. Results were ranked based on sample SRS-1806 (see Figure 4). Labs #1, #15, #24, #40, #46 and #47 were noted having inconsistency three of five soils. Sample SRS-1807 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 0.06 to 0.20% SOM-LOI, the highest for SRS-1810. Across labs, *s* values for SRS-1806 ranged from 0.005 - 0.16 %. Across soil materials poor precision was noted for several laboratories. Specifically *s* for labs #4, #7, #9 and #24, exceeded 0.20 % SOM for SRS-1807. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

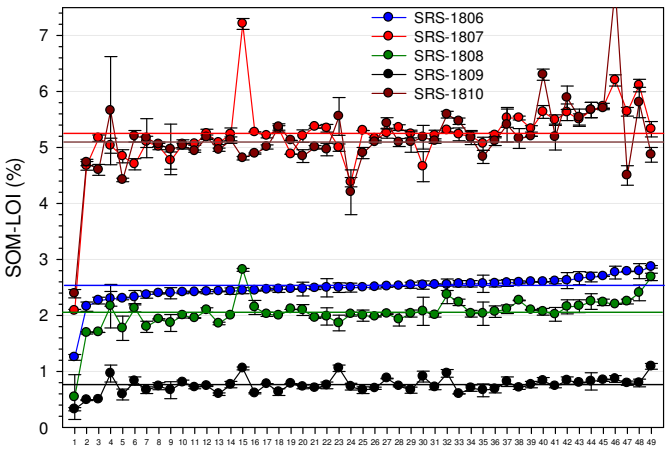


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2018 Cycle 36.

SRS - Extractable SO_4-S

Nineteen laboratories provided ALP results for extractable SO_4-S (test code 140). Results were ranked low to high based on sample SRS-1806 (see Figure 5). Soil SRS-1807 was the highest in concentration and the most inconsistent across labs. Across soils, labs #4 #7, #12, #15, and #19 were inconsistent across soils and #18 had high bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

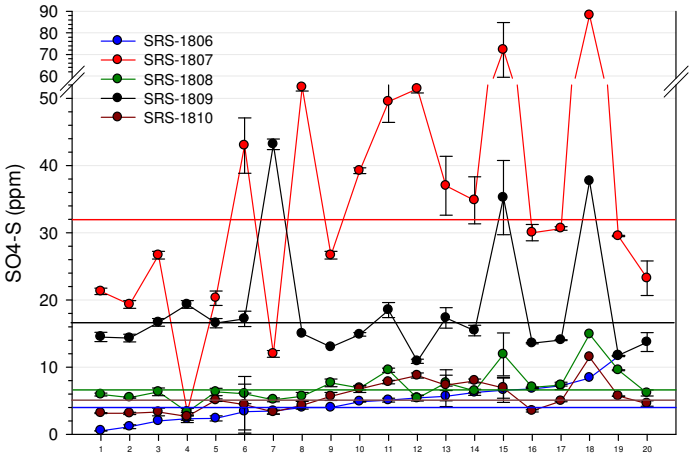


Figure 5. Soil extractable SO_4-S distribution plot, ALP 2018 Cycle 36.

Extractable SO_4-S median intra-lab *s* values were lowest for ALP soil SRS-1806 and SRS-1808 with an intra-lab median value of 0.9 mg kg^{-1} and highest for SRS-1807 with a value of 3.5 mg kg^{-1} . Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1807. Intra-lab precision was poor for labs #6, #13, and #15 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

Tenty-three laboratories provided ALP results for NO_3-N by cadmium reduction, ISE and other (test codes 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-1805 (see Figure 6). The data plot shows labs #21 and #22 had high bias for SRB-1802. Labs #9, #11, #18, and #20 were inconsistent.

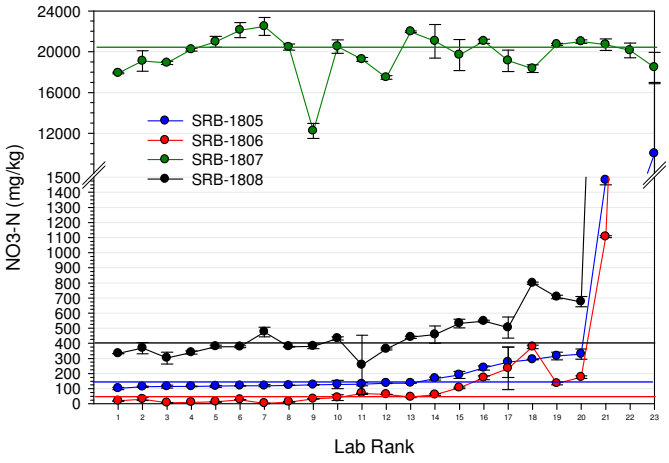


Figure 6. Nitrate distribution plots for SRB materials, ALP 2018, Cycle 36.

Botanical NO_3-N (test code 202) results for Cycle 36 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 27 to 714 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-1805 ranged from 0.8 – 6870 mg kg^{-1}; SRB-1806 ranged from 0.3 - 404 mg kg^{-1}, SRB-1807 ranged from 798 – 1640 mg kg^{-1} and SRB-1808 ranged from 0.8 - 300mg kg^{-1} Lab #17 had consistently high standard deviations for three of four samples. Three labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Twenty-nine laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and twelve labs for TKN (Test code 209) for Cycle 36. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1805 (see Figure 7). It is note worthy that TKN was lower than Dumas for three of four samples. Labs #1 showed low bias for Dumas N for three samples, whereas labs #3 and #29 showed inconsistency across the all four botanical samples.

Dumas N and TKN results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-1805, ranged 0.001 to 0.096 % N, SRB-1806 ranged from 0.001 to 0.127 % N, SRB-1807 ranged from 0.002 to 0.196 % N, and SRB–1808 from 0.002 to 0.093 % N. Lab #16 had consistently high standard deviations. Lab TKN *s* values for SRB-1805 ranged from 0.002 to 0.072 %TKN, SRB-1806 ranged from 0.006 to 0.223 % TKN, SRB-1807 ranged from 0.009 to 0.196 % TKN nitrogen and SRB-1808 ranged from 0.002 to 0.183% TKN nitrogen.

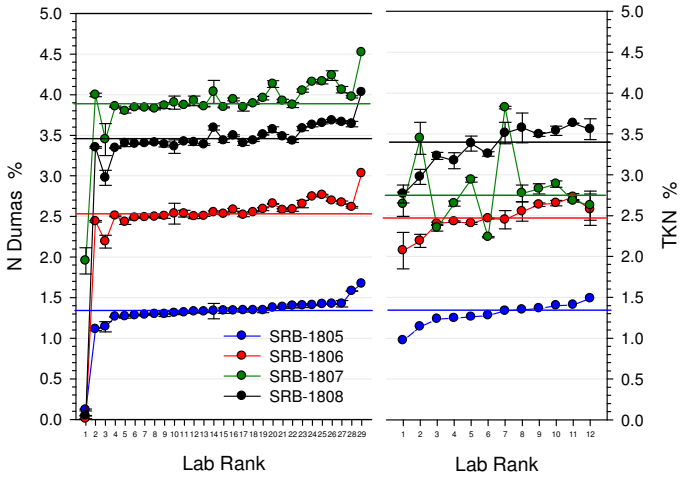


Figure 7. N distribution plots for SRB materials, ALP 2018 Cycle 36.

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-1805 (see Figure 8). Laboratory #1 showed low bias. Labs #10, #17, #19, #31 and #37 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 0.030 to 0.54 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1805, ranged from 0.002 to 0.11 % K; SRB-1806, 0.001 — 0.036 % K; SRB-1807, 0.001 - 1.06 % K; and SRS-1808, 0.002 to 0.80 % K. Six labs had high standard deviations exceeding 0.10 %K for SRB-1808. Five labs were flagged for poor K precision.

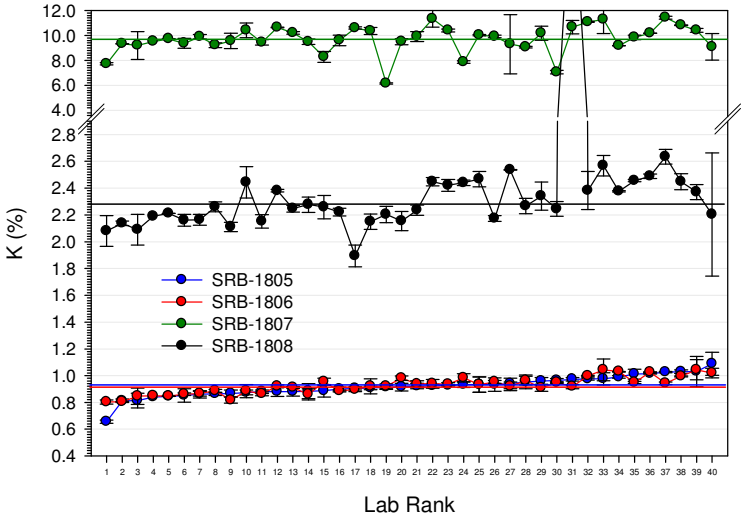


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2018 Cycle 36.

SRB - Phosphorus

Forty-two laboratories provided ALP results for Cycle 36 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-1805 (see Figure 9). Consistent low bias was noted for lab #1 and high bias for #41. Labs #3, #27, #31 and #42 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-1805; ranged from 0.001 - 0.320 % P; SRB-1806 ranged from 0.0006 – 0.021 % P and SRB-1807 0.0004 - 0.040 % P; and SRB-1808 0.001 - 0.052 % P. Labs #36 had a high standard deviation exceeding 0.025 % P on two of four botanical samples. Five labs were flagged for poor precision for botanical P.

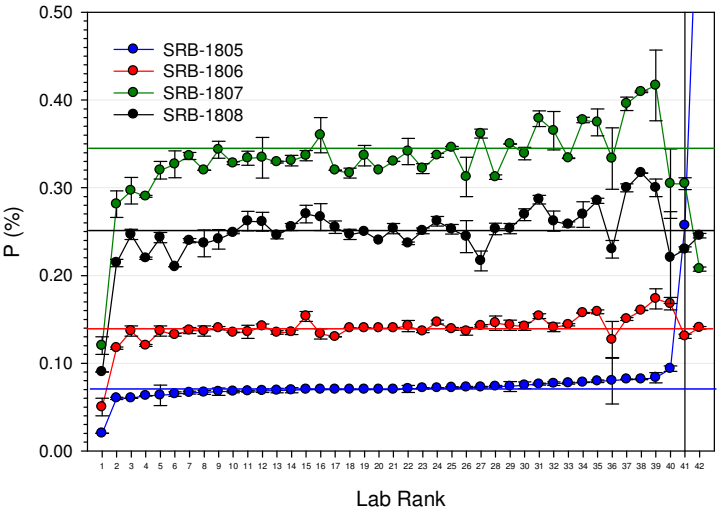


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2018 Cycle 36.

SRB - Copper

Forty laboratories provided ALP results for copper (Cu) (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-1805 (see Figure 10). Labs #1 showed low bias on 3 of 4 samples. Labs #5, #12, #26, #29 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 high precision, with median intra-lab standard deviation (*s*) values ranged from 0.41 to 3.04 mg kg^{-1} Cu for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1805; ranged from 0.002 - 1.4 mg kg^{-1} Cu; SRB-1806 from 0.004 – 2.12 % Cu; SRB-1807 0.08 - 2.82 mg kg^{-1} Cu; and SRB-1808 0.15 - 13.1 mg kg^{-1} Cu. Labs #5 and #37 had consistently high standard deviations for two of four botanical samples, and four labs were flagged for poor precision.

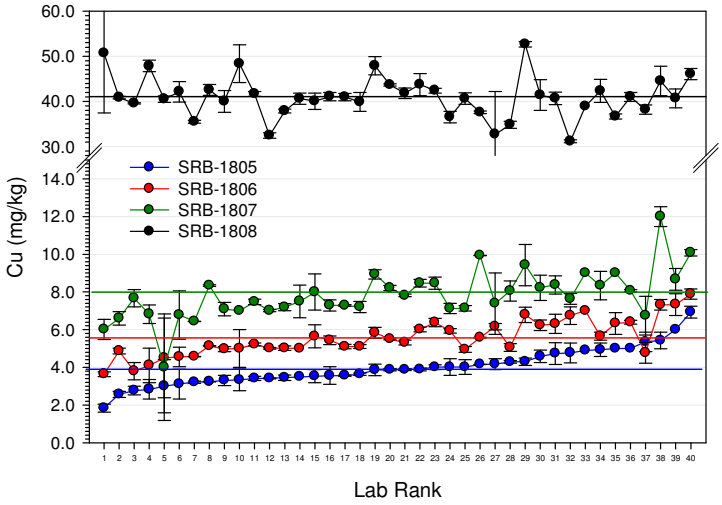
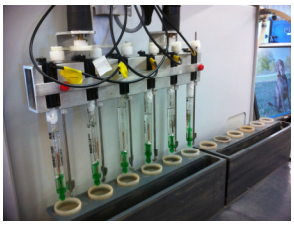


Figure 10. Copper distribution plots for SRB materials, ALP 2018 Cycle 36.

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-1804 (see Figure 11). Laboratories #1, #2, #3 and #4 had low pH bias on two of the three samples. Labs #4 and #8 showed inconsistently on SRW-1805. 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 0.074, 0.083 and 0.042, respectively. Precision for sample SRW-1806 was the most consistent across the fifteen participating laboratories. Intra-lab *s* values for lab #7 exceeded 0.20 pH units on SRW-1804 and SRW-1805. Precision for laboratory #14 exceeded 0.07 units for all three samples for ALP cycle 36. Highest precision was noted for lab #2 with intra-lab *s* values of < than 0.03 pH units.

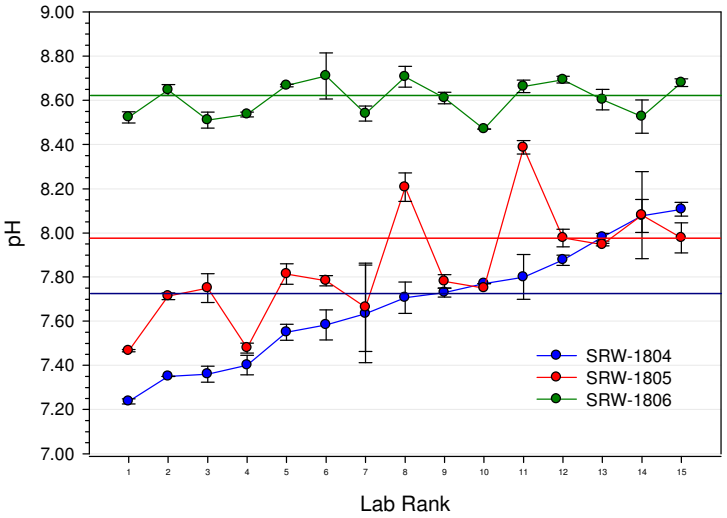


Figure 11 . Water pH distribution plots for SRW materials, ALP 2018 Cycle 36.

SRW - Ca Results

Fifteen laboratories provided ALP results for water Ca (test code 303). Lab results were ranked low to high based on sample SRW-1804 (see Figure 12). Median values are designated by horizontal lines. Lab #14 and #15 had high bias on SRW-1805 had high bias. Lab #8 showed inconsistency across samples.

Ca precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.061, 0.077, and 0.167 meq L^{-1} for SRW-1804, SRW-1805, and for SRW-1806, respectively. Water Ca precision was excellent for all 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 0.010 meq L^{-1} for lab #4. Three labs were flagged for poor precision for cycle 36.

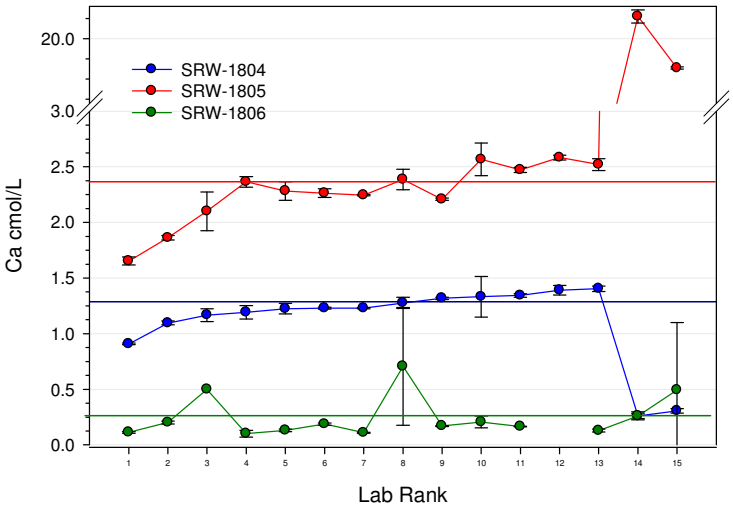


Figure 12. Water Ca distribution plots for SRW materials, ALP 2018 Cycle 36.

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.

- Two new ALP soils were collected in August from Oregon row crop fields. Another collection trip is planned for October 2018 in Michigan and Ontario.

- 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) 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@colostate.edu.

Summary

ALP is celebrating twelve years of service with the completion of Cycle 36. Since 2006 ALP has completed the analysis of 180 soils, 112 plant samples and 105 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 36. 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 37 Ship

September 17, 2018

"A new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it. " ***Max Planck*****, 1950**

ALP
Agricultural Laboratory Proficiency Program