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ALP Program Report

2015 Spring - Cycle 26

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ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 26.
- Fifty-six Laboratories provided soil pH (1:1) H_2O results and medians ranged from 4.94 - 7.55.
- Cycle 26 soil NH_4OAc K ranged from 37 to 340 mg kg^{-1} with MAD values ranging 4.3 - 24 mg kg^{-1} across the five soils.
- Mehlich 3 Mg was highly consistent on soil SRS-1503 at 28 ppm concentration.
- Botanical P, ranged from 0.20 - 0.43 mg kg^{-1}, with three of twenty-six labs noted for low bias.
- Botanical Cu values ranged from 5.8 to 38.1 ppm across the three samples.
- Water Mg concentration showed high consistency by seven of eleven labs across all three samples.

The Agriculture Laboratory Proficiency (ALP) Program spring 2015 Round cycle 26 was completed May 21, 2015, with ninety-five labs enrolled from the United States, Canada, and South Africa. Proficiency samples consisted of five soils, three botanical and three water samples. Analytical methods evaluated are base on those published by AOAC, four regional soil work groups, the Soil Plant Analysis Council and Forestry Canada.

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 lab standard deviation. Additional information on the ALP program testing methods and statistical protocols can be found at the program web site: http://www.collaborativetesting.com/reports/default.aspx?F_CategoryId=12,

Proficiency Materials

Standard Reference Soils (SRS), materials used for the soils and environmental programs were: SRS-1501 a loam collected from near Shubenacadie, Nova Scotia, Canada; SRS-1502 a Wymore silty clay loam collected from Brown Cty, KS; SRS-1503 a Darco loamy fine sand, collected from Nacogdoches Cty, TX; SRS-1504 a Purdam silt loam from Jerome Cty, ID; and SRS-1505 Webster-Nicollet complex clay loam Hardin Cty, IA. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 4.94 - 7.55; NO_3-N 4.3 - 116 mg kg^{-1}; Bray P1 (1:10) 10.9 - 138 mg kg^{-1}; K NH_4OAc 37 - 340 mg kg^{-1}; SO_4-S 4.2 - 32.1 mg kg^{-1}; Mehlich 3 P (ICP) 15.2 - 154 mg kg^{-1}; DTPA-Zn 0.75 - 2.45 mg kg^{-1}; SOM-WB 0.89 – 6.51 %; CEC 2.1 - 29.3 cmol kg^{-1}; clay 4.3 - 31.4% and Solvita CO_2 Respiration 6.3 - 96.4 mg kg^{-1}.

Standard Reference Botanical (SRB) materials were: SRB-1501 a spinach leaf leaf composite from Salinas California, SRB-1502 walnut leaf composite from the SJV of California and SRB-1503 composite potato petiole from Washington State. SRB material median analytes ranged: NO_3-N 203 - 18,300 mg kg^{-1}; Dumas N 3.15 - 5.32%; total P 0.19 - 0.47%; total K 1.93 - 9.22%; total Mg 0.33 - 1.42%; total S 0.19 - 0.47 %, total B 26.2 - 102 mg kg^{-1}; and total Cd 0.02 - 14.8 mg kg^{-1}.

Standard Reference Water samples represent an agriculture water sample collected: SRW-1501 a water sample collected from a well central OH; SRW-1502 from a drainage ditch near Badger, IA; and SRW-1503 Cache La Poudre River stream near Tinmath, CO, 2015. SRW median concentrations ranged: pH 7.02 - 8.06; EC 0.101 - 0.35 dSm^{-1}; SAR 0.31 - 1.73; Ca 0.17 - 1.49 mmolc L^{-1}; K 0.02 - 0.05 mmolc L^{-1}; Cl 0.05 - 0.50 mmolc L^{-1}; and NO_3–N 0.016 - 0.073 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), 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 EC (1:1). Homogeneity was also evaluated on SRB and SRW matrix samples.

"..soil pH, EC and Olsen P analysis Stdev values for cycle 26 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 26, 2015.

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-1501	5.59	*0.04*	0.58	*0.06*	56.0	*2.7*	62.0	*1.8*
SRS-1502	5.83	*0.03*	0.14	*0.03*	5.8	*1.1*	4.7	*0.5*
SRS-1503	4.63	*0.04*	0.16	*0.01*	25.8	*0.8*	12.9	*0.9*
SRS-1504	5.31	*0.02*	0.94	*0.13*	75.4	*3.6*	120	*4.3*
SRS-1505	7.36	*0.02*	0.44	*0.02*	27.6	*0.9*	24.3	*1.4*

[1] Statistics based on four soil replicates, each analyzed in triplicate ALP Cycle 26.

2015 Cycle 26 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 26 averaged 0.06 pH units. Within lab pH standard deviation was 0.082 pH units. Soil CEC ranged 2.1 to 29.3 cmol kg^{-1} across the five soils. Soil Solvtia CO_2 respiration (test code 191) results were provided by six laboratories with median results ranging from 6.3 - 96.4 mg kg^{-1} with an intra-lab precision, with s values averaging 1.2 for three of five samples. Sample SRS-1503 was the lowest in Saturate past B measured in the ALP Program at 0.048 mg L^{-1} with a MAD of 0.022 mg L^{-1}. Soil ammonium acetate K (Test code 140) MAD values ranged 3.9 - 23 mg kg^{-1} and ammonium acetate Ca MAD values 27 to 285 mg kg^{-1} for the five soils. These results lower than PT cycles in 2014 and represent a decrease in MAD values that are attributed to: (1) improved lab consistency; (2) soils generally higher in potassium; and (3) ICP operation.

Across the three botanical samples Dumas combustion N MAD values averaged 0.070% nitrogen with intra-lab *s* of 0.057%, 0.039% and 0.044%, respectively. There was a greater inter-lab variability (MAD) in total potassium values than combustion N, P, Ca, Mg or total S concentrations for SRB-1503. Generally the walnut leaf sample SRB-1502 had lower level median N, P, K, Mg, and Na relative to the other two botanical samples of cycle 26. Sample SRB-1501, spinach collect from near Salinas, California had a remarkable high level of Cd at 14.2 mg kg^{-1}.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.017 to 0.036 dSm^{-1}. NO_3-N values ranged from 0.016 - 0.072 mmolc L^{-1} across the three water samples.

SRS Results - pH

Fifty-six laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 4.94 to 7.55. Lab results were ranked low to high based on sample SRS-1501 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1501 and SRS-1504 were very similar in pH, and 83% of labs found only small differences between the two soils. Labs #3, #5, #20, #33, and #56 were inconsistent across soils. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

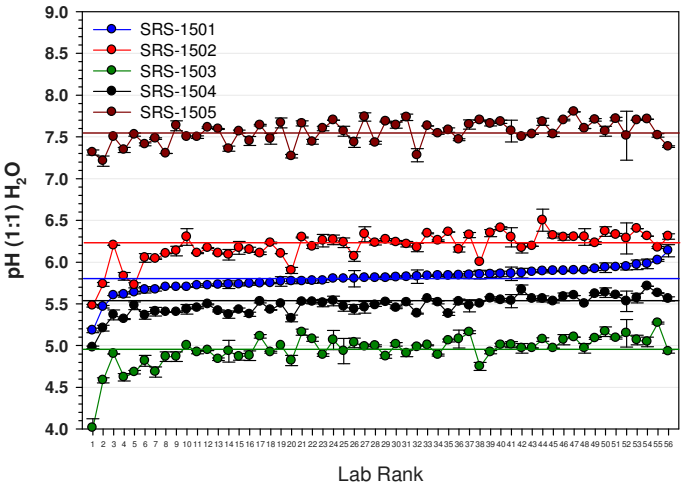

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2015 Cycle 26.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.034 to 0.054 pH units, the highest noted for SRS-1503. For specific labs poor precision was noted for two laboratories, exceeding by 1.5 times that noted for consensus intra-lab *s*. Specifically *s* for lab #52 exceeded 0.12 pH units for four of five soils. Soil SRS-1505 was the most variable with respect to intra-lab variance.

SRS - Phosphorus: Bray P1, Strong Bray, Olsen, Mehlich 1, and Mehlich 3

Bray P1 results were reported by twenty-four labs. Median soil Bray P1 values ranged from 10.9 to 138 mg kg^{-1} PO_4-P; Mehlich 1 P 8.1 to 212 mg kg^{-1} P and M-3-P ICP ranged from 15.2 to 154 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1501, median Bray P1 concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1504 associated with moderately high soil P concentrations. Soils SRS-1503 and SRS-1505 had near identical Bray P contents across all twenty-four labs. Lab #24 was inconsistent for samples SRS-1501 and SRS-1504. Inconsistency was also noted for labs #6 and #8 is likely related to extraction, analysis instrument and/or method compliance.

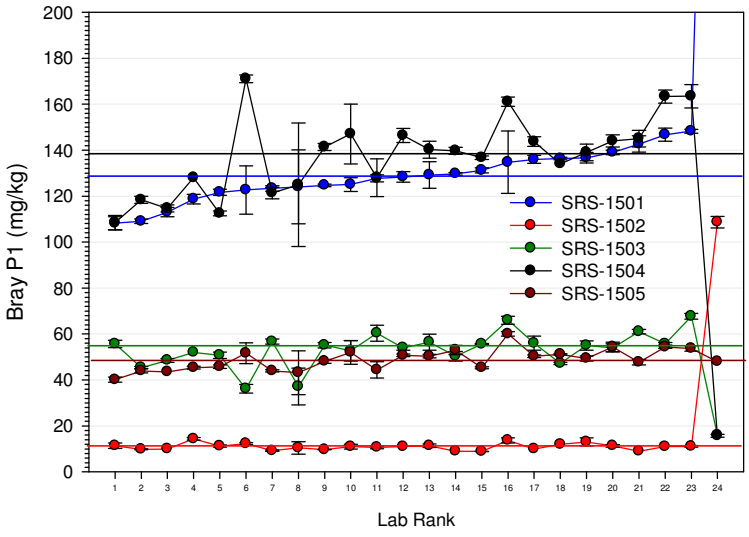

Figure 2. Bray P distribution plots for SRS materials, ALP 2015 Cycle 26.

Twenty-nine laboratories provided ALP results for Olsen P (test code 134), for the five soils with medians ranged from 10.3 to 119 PO_4-P mg kg^{-1}. Mehlich 3 P–SPEC median concentrations were 11.4 to 137 mg kg^{-1} PO_4-P reported by eight labs. Strong Bray (P2) was reported by seven laboratories ranging from 16.5 to 315 mg kg^{-1} PO_4-P with the highest P concentration noted for SRS-1504.

SRS - Potassium

Thirty-five laboratories provided ALP results for soil K (test code 140) results. These were ranked low to high based on sample SRS-1501 (see Figure 3). Soil SRS-1504 was the most inconsistent across labs. Lab #35 showed high bias on four of five soils. Labs #1, #2, #3, #9, #20, #34, and #34 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-1503, with a median intra-lab value of 2.9 mg kg^{-1} K and highest for SRS-1502 with a value of 10.9 mg kg^{-1} K. 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 #30 and #33 which exceeded 15 mg kg^{-1} K on three of five soils; and lab #2 the value exceeded 20 mg kg^{-1} K for SRS-1504. Poor precision is attributed to extraction and/or analysis instrument operation.

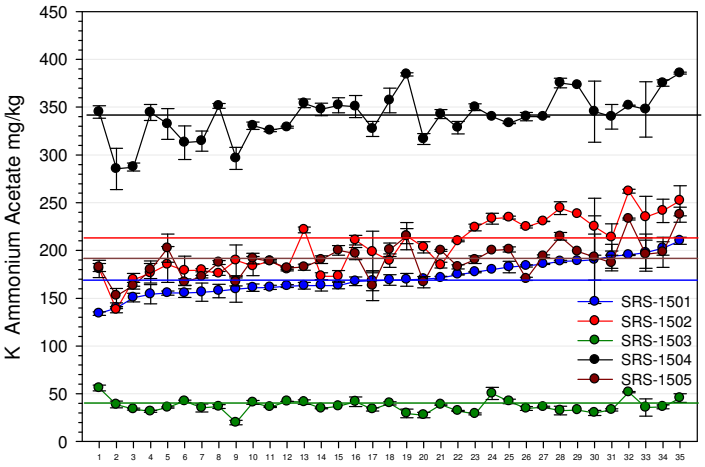

Figure 3. Extractable K distribution plots for SRS materials, ALP 2015 Cycle 26.

SRS SOM-LOI

Forty-six laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 0.89 to 6.52%. Results were ranked based on sample SRS-1501 (see Figure 4). Lab #46 was noted having consistent high bias. Labs #2, #3, #11, #40, #42, #45 and #46 were inconsistent across the five soils. 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 0.092 to 0.392% SOM-LOI, the highest for SRS-1504. Across labs *s* values for SRS-1501 ranged from 0.011 - 2.15 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #2, #11, #40, #46, exceeded 0.20 for two of five soils. Lab #2 exceeded 0.70 % SOM on soil SRS-1501 for ALP cycle 26. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

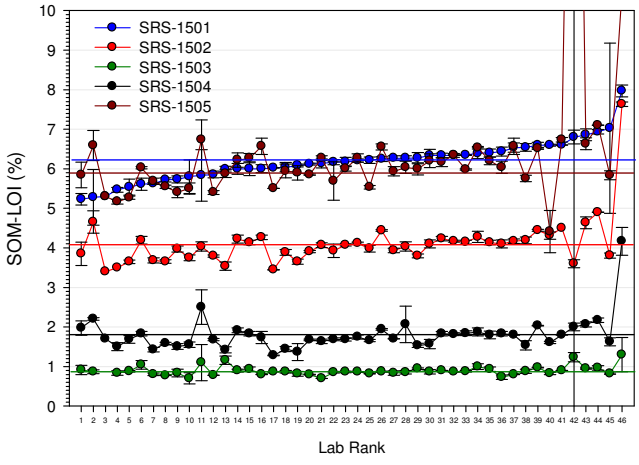

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2015 Cycle 26.

Mehlich 3 Mg

Twenty-eight laboratories provided ALP results for M3 Mg, (test code 160) results. These were ranked low to high based on sample SRS-1501 (see Figure 5). Soil SRS-1503 was the lowest in concentration and the most consistent across labs. Across soils, labs #1 had low bias on four of five soils, labs #28 high bias on four of five soils. Labs #8, #11 and #26, were inconsistent across a majority of soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

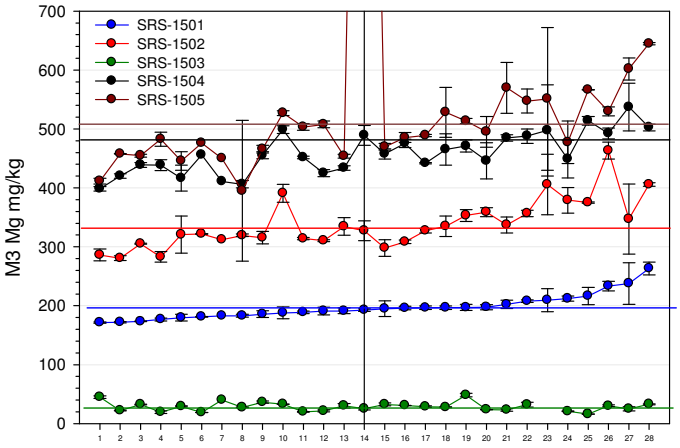

Figure 5. Soil M3 Mg distribution plot, ALP 2015 Cycle 26.

M3-Mg median intra-lab *s* values were lowest for ALP soil SRS-1503 with a consensus intra-lab value of 1.8 mg kg^{-1} and highest for SRS-1505 with a value of 42.5 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1505. Intra-lab precision was poor for labs #5, #8, #14, #23 and #27 on two of five soils. Poor precision maybe associated with ICP instrument operation.

SRB Nitrate-Nitrogen

Nineteen laboratories provided ALP results for NO_3-N (all test codes 202, 203, 204). Results were combined for all methods as medians were nearly identical. Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1501 (see Figure 6). Data plots show labs #1 and #2 have low bias for two of three botanical samples. Lab #18 showed high bias on SRB-1502. Labs #3, and #19 were inconsistent.

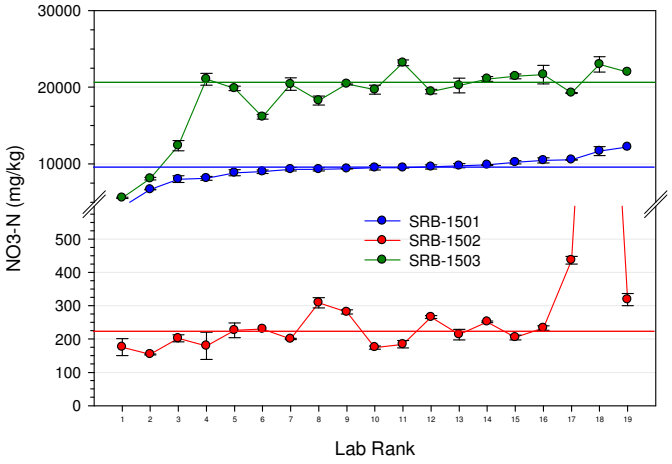

Figure 6. Nitrate distribution plots for SRB materials, ALP 2015, Cycle 26.

Botanical NO_3-N results for cycle 26 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 17 to 658 mg kg^{-1} for test code 202 for the three samples. Individual lab NO_3-N (test code 202) intra-lab *s* values for SRB-1501; ranged from 19.5 – 578 mg kg^{-1}; SRB-1502 ranged from 1.5 - 40 mg kg^{-1}, and SRB-1503 ranged from 62 – 1210 mg kg^{-1}. Lab #4 had consistently high standard deviation for botanical sample SRB-1502. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Twenty laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and seven for TKN (Test code 209). Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1501 (see Figure 7). It is note worthy that TKN was lower than Dumas for all samples. Labs #19 and #20 showed high bias for Dumas N SRS-1501 and SRB-1503, whereas lab #17 showed inconsistency across the three botanical samples.

Dumas N and TKN results indicate very high precision across all labs for all samples. Individual lab Dumas N *s* values for SRB-1501, ranged from 0.005 to 0.261 % N, SRB-1502 ranged from 0.006 to 0.118 % N and SRB-1503 ranged from 0.011 to 0.127 % N. Lab #14 had consistently high standard deviation for two of three botanical samples. Individual lab TKN *s* values for SRB-1501 ranged from 0.013 to 0.416 %, SRB-1502 ranged from 0.006 to 0.046 % and sample SRB-1503 ranged from 0.024 to 0.100 % TKN nitrogen.

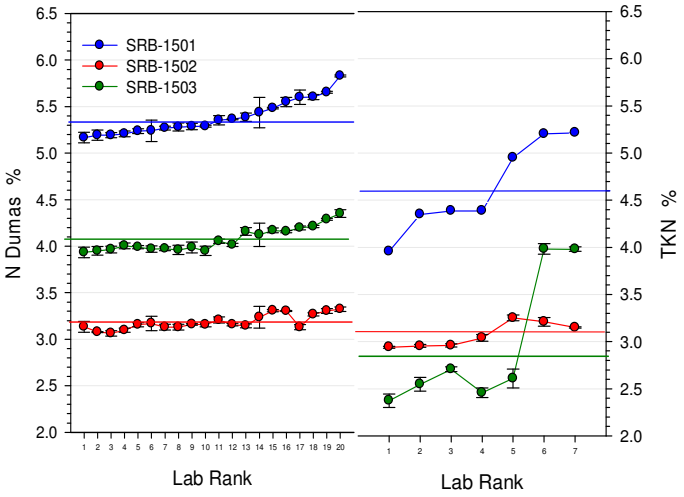

Figure 7. N distribution plots for SRB materials, ALP 2015 Cycle 26.

SRB - Potassium

Thirty-one laboratories provided ALP results for potassium (K) (test codes 213 and 226). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1501 for test code 213 (see Figure 8). Laboratories #1 and #3 showed low bias on two of three samples, whereas lab #31 indicate high bias. Labs #2, #5, #11 and #15 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 standard deviation (*s*) values ranging from 0.25 to 0.80 %K for test code 213 across the three samples. Individual lab intra-lab *s* values for SRB-1501; ranged from 0.014 to 0.81 % K; SRB-1502 and 0.005 — 0.69 % K; SRB-1503 0.007 - 3.2 %K. Lab #3 had consistently high standard deviations exceeding 3.0 %K for SRB-1502. Five labs were flagged for poor K precision.

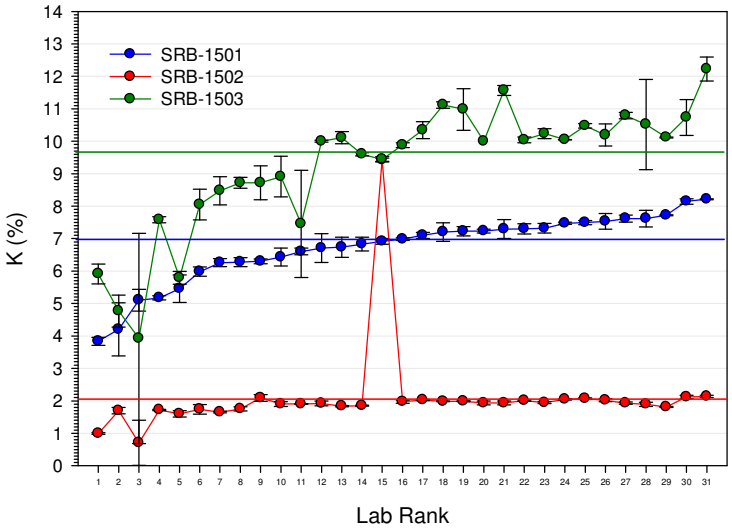

Figure 8. Potassium (code 213 and 223) plots for SRB materials, ALP 2015 Cycle 26.

SRB - Phosphorus

Thirty laboratories provided ALP results for cycle 26 phosphorus (P) combined (test codes 212 and 225). 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-1501 (see Figure 9). Consistent bias was noted for labs #1 and #2. Lab #32 showed high bias. Lab #27 was inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical P results indicate very high precision, with intra-lab standard deviation (*s*) values ranged 0.007 to 0.057 % P for test code 212 across the three botanical samples. Individual lab intra-lab *s* values for SRB-1501; ranged from 0.002 - 0.069 % P; SRB-1502 ranged from 0.001 – 0.003 % P and SRB-1503 0.001 - 0.16 % P. Labs #2 and #27 had a high standard deviations exceeding 0.10 % P for two of three botanical samples. Two labs were flagged for poor precision.

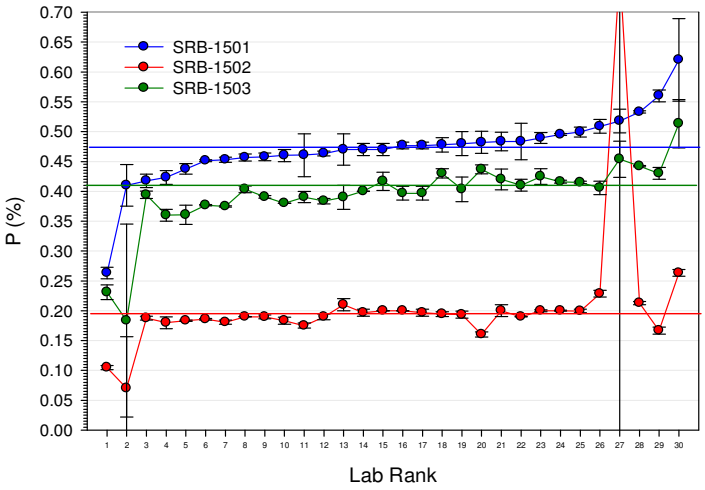

Figure 9. Phosphorus distribution plots for SRB materials, ALP 2015 Cycle 26.

SRB - Copper

Twenty-six laboratories provided ALP results for Copper (Cu) (test code 220). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1501 (see Figure 10). Laboratories #1, and #2 showed low bias on all three samples, whereas lab #26 indicated high bias on two of three samples. Lab #11 was inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Cu results indicate very high precision, with intra-lab standard deviation (*s*) values ranged from 0.09 to 2.0 mg kg^{-1} Cu for across the three botanical samples. Individual lab intra-lab *s* values for SRB-1501; ranged from 0.06 - 6.5 mg kg^{-1} Cu; SRB-1502 ranged from 0.25 – 19.8 mg kg^{-1} Cu and SRB-1503 0.01 - 2.4 mg kg^{-1} Cu. Lab #2 had consistently high standard deviations exceeding 10 mg kg^{-1} Cu for SRB-1502, the highest of all three or botanical samples.

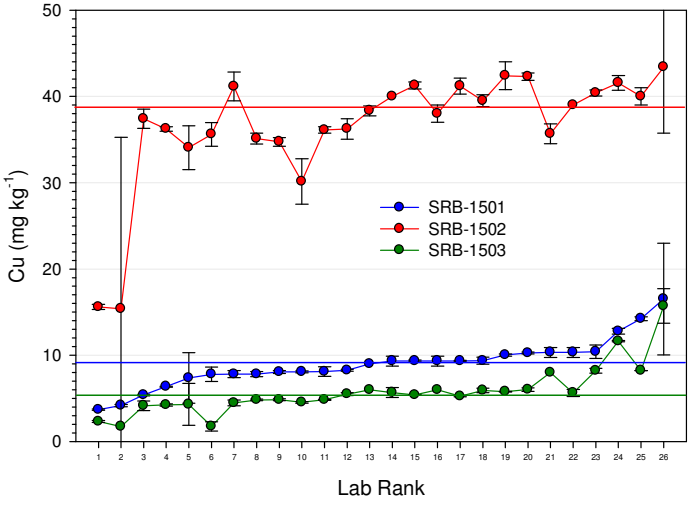

Figure 10. Copper distribution plots for SRB materials, ALP 2015 Cycle 26.

SRW - Water pH

Ten laboratories provided ALP results for water pH (test code 301). Ranking lab results low to high based on sample SRW-1501 (see Figure 11). Labs #1, and #2 indicated consistent low bias on all three samples. Labs #3, appeared inconsistent across the three samples. Source of bias is likely associated with pH electrode performance and/or calibration.

pH precision across the three water materials indicates good high precision, with intra-lab Std values of 0.031, 0.048 and 0.0503 pH units, respectively. Precision for sample SRW-1502 was the most consistent across the ten laboratories. Across water samples poor precision was noted for two laboratories. Specifically intra-lab the *s* values for lab #2 exceeded 0.10 pH on SRW-1408. Highest precision was noted for lab #7 with intra-lab *s* values of < than 0.02 pH units.

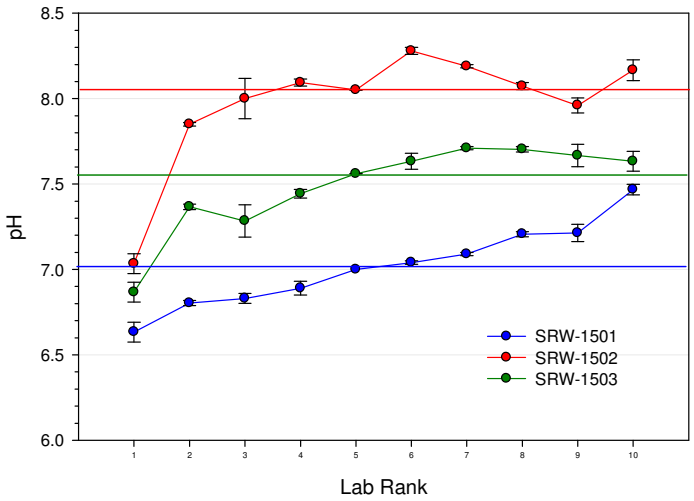

Figure 11 . Water pH distribution plots for SRW materials, ALP 2015 Cycle 26.

SRW - Mg Results

Eleven laboratories provided ALP results for water Mg (test code 304). Lab results were ranked low to high based on sample SRW-1501 (see Figure 12). Median values are designated by horizontal lines. Lab #11 had consistent high bias across all samples. Lab #10 showed inconsistency across samples.

Mg precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.020, 0.038, and 0.013 mmolc L^{-1} for SRW-1501, SRW-1502, and for SRW-1503, respectively. Water Mg precision was excellent for all individual labs with only lab #5 exceeding 0.07 mmolc L^{-1} Mg on sample SRW-1501. Across samples intra-lab *s* was less than 0.002 mmolc L^{-1} for lab #3. Two labs were flagged for poor precision.

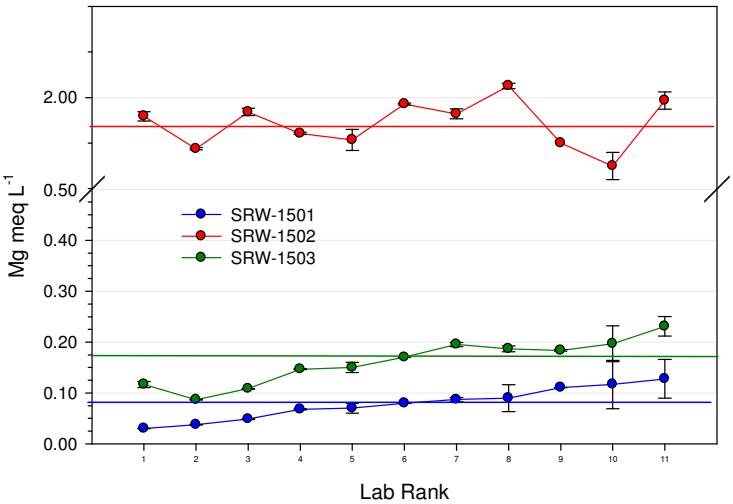

Figure 12. Water Mg distribution plots for SRW materials, ALP 2015 Cycle 26.

Announcements

- ALP is now an accredited proficiency provider for agricultural laboratory testing in North America under ISO 17043 by AClass, an accreditation board for Proficiency Providers (ANSI-ASQ National Accreditation Board). This is a major achievement and required an extensive audit of program standards, documentation and operation.

- ALP collected twelve proficiency soils in this spring from British Columbia, Washington and Oregon representing a diverse range of textures and chemical properties. Additional collections are planned for Alberta, Michigan, and Indiana in the summer of 2015.

- ALP was a sponsor at the Western Nutrient Management Meeting held in Reno, Nevada March 6-7, 2015.

- An evaluation study is underway to assess soil health methods for future inclusion in the ALP Program. These include: CO_2 burst; soluble C and; N and the H3A methods.

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

- A special remembrance of Dr. Yash Kalra of Forestry Canada who passed away in November. He co-authored the Western States methods manual and was an active supporter of laboratory proficiency testing.

Summary

ALP 2015 Cycle 26 round provided comprehensive data on inter and intra laboratory method performance. SRS, SRB and SRW materials were highly homogeneous and represented diverse analytical properties.

We thank all laboratories who participated in cycle 26. As the coordinators of the program we appreciate your consideration and participation in the proficiency program. We are seeking feedback from laboratory participants to improve the service and function of the program. Please forward all comments to info@cts-interlab.com.

Cycle 27 Ship

July 2, 2015

"There are no such things as applied sciences, only applications of science. "

- Louis Pasteur , 1854

ALP
Agricultural Laboratory Proficiency Program