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ALP Program Report

2015 Summer - Cycle 27

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ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 27.
- Fifty-nine Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.51 - 8.10.
- Cycle 27 soil NH_4OAc K ranged from 46 to 494 mg kg^{-1} with MAD values ranging 6.0 - 36 mg kg^{-1} across the five soils.
- Lab results for Hot Water B was highly consistent on soil SRS-1506 and SRS-1510 with concentrations < 0.4 ppm.
- Botanical P, ranged from 0.17 - 0.30 % with three of thirty labs noted for low bias.
- Botanical Zn values ranged from 53.5 to 260 ppm across the three samples.
- Water EC content showed high consistency by twelve of thirteen labs across all three samples.

The Agriculture Laboratory Proficiency (ALP) Program spring 2015 Round cycle 27 was completed August 18, 2015, with ninety-six labs enrolled from the United States, Canada, South Africa, Serbia and Guatamala. 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-1506 a Agawam fine sand loam collected from Tolland Cty CT; SRS-1507 a Blue Earth mucky silty clay loam collected Martin Cty, MN; SRS-1508 a Trix sandy clay loam, collected from Pinal Cty, AZ; SRS-1509 a Orthic Dark Brown Cherozem collected from Summerland, BC, Canada; and SRS-1510 Pacolet sandy loam collected Anderson Cty, SC. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.51 - 8.10; NO_3-N 4.0 - 110 mg kg^{-1}; Bray P1 (1:10) 7.0 - 204 mg kg^{-1}; K NH_4OAc 46 - 494 mg kg^{-1}; SO_4-S 4.2 - 113 mg kg^{-1}; Mehlich 3 P (ICP) 23 - 174 mg kg^{-1}; DTPA-Zn 0.47 - 13.5 mg kg^{-1}; SOM-LOI 1.70 – 8.05%; CEC 8.7 - 32.7 cmol kg^{-1}; clay 6.7 - 32.0% and Solvita CO_2 Burst Respiration 8.8 - 53.5 mg kg^{-1}.

Standard Reference Botanical (SRB) materials were: SRB-1504 a almond leaf composite from Tulare, California, SRB-1505 Gape Blades composite from the SJV of California and SRB-1506 composite pistachio leaf from California. SRB material median analytes ranged: NO_3-N 35 - 463 mg kg^{-1}; Dumas N 2.82 - 3.28%; total P 0.17 - 0.29%; total K 1.07 - 2.18%; total Mg 0.30 - 0.65%; total S 0.17 - 0.34 %, total B 47.7 - 143 mg kg^{-1}; and total Sr 89 - 194 mg kg^{-1}.

Standard Reference Water samples represent an agriculture water sample collected: SRW-1504 a water sample collected from a well central OH; SRW-1505 from a drainage ditch near Badger, IA; and SRW-1506 Cache La Poudre River stream near Tinmath, CO, 2015. SRW median concentrations ranged: pH 7.80 - 8.82; EC 0.24 - 1.30 dSm^{-1}; SAR 0.37 - 17.3; Ca 0.12 - 8.20 mmolc L^{-1}; Na 0.41 - 4.31 mmolc L^{-1}; Cl 0.16 - 0.84 mmolc L^{-1}; and NO_3–N 0.038 - 0.48 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 pH H_2O. Homogeneity was also evaluated on SRB and SRW matrix samples.

"..soil pH, EC and Olsen P analysis Stdev values for cycle 27 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 27, 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-1506	5.94	*0.04*	0.35	*0.03*	31.7	*1.2*	42.2	*1.3*
SRS-1507	7.58	*0.03*	1.05	*0.04*	36.7	*2.8*	127	*2.4*
SRS-1508	8.10	*0.02*	1.81	*0.11*	8.6	*0.6*	56.1	*1.6*
SRS-1509	6.75	*0.03*	0.14	*0.02*	24.3	*1.7*	3.9	*0.2*
SRS-1510	5.33	*0.01*	0.33	*0.03*	15.4	*0.7*	43.2	*1.0*

[1] Statistics based on four soil replicates, each analyzed in triplicate ALP Cycle 27.

2015 Cycle 27 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 27 averaged 0.07 pH units. Within lab pH standard deviation was 0.048 pH units. Soil CEC ranged 8.9 to 32.7 cmol kg^{-1} across the five soils. Soil Solvtia CO_2 respiration (test code 191) results were provided by seven laboratories with median results ranging from 8.8 - 53.5 mg kg^{-1} with an intra-lab precision, with s values averaging 4.2 for four of five samples. Sample SRS-1508 had a saturated paste SAR of 8.9 with a within lab standard deviation of 0.5 and a MAD of 0.7. Soil ammonium acetate K (Test code 140) MAD values ranged 6 - 36 mg kg^{-1} and ammonium acetate Ca MAD values 24 to 199 mg kg^{-1} for the five soils. These results for Ca were 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 0.079% nitrogen with intra-lab *s* of 0.055%, 0.113% and 0.069%, respectively. There was a greater inter-lab variability (MAD) in total potassium values than combustion N, Ca, Mg or total S concentrations for SRB-1506. Generally the pistachio sample SRB-1506 had lower level median P, Ca, S, Al, Zn and Mn relative to the other two botanical samples of cycle 27. Sample SRB-1504, Almond leaf collect from near Tulare, California had a remarkable high level of Sr at 203 mg kg^{-1}.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.004 to 0.013 dSm^{-1}. NO_3-N values ranged from 0.028 - 0.040 mmolc L^{-1} across the three water samples.

SRS Results - pH

Fifty-nine laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.51 to 8.10. Lab results were ranked low to high based on sample SRS-1506 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1508 and SRS-1510 showed god consistency across labs. Labs #9, #26, #46, #51, #52 and #59 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.

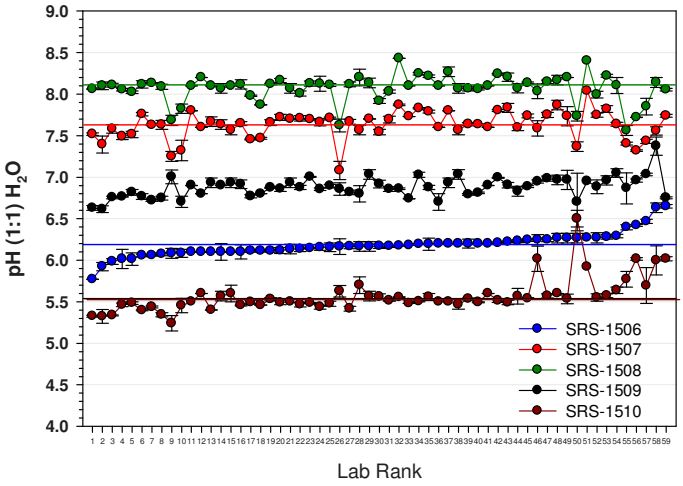

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2015 Cycle 27.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.023 to 0.030 pH units, the highest noted for SRS-1509. For specific labs poor precision was noted for SRS-1510 for three laboratories, exceeding by three times that noted for consensus intra-lab *s*. Specifically *s* for lab #46 exceeded 0.06 pH units for four of five soils. Soil SRS-1509 was the most variable with respect to intra-lab variance for cycle 27.

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 7 to 204 mg kg^{-1} PO_4-P; Mehlich 1 P 9.0 to 107 mg kg^{-1} P and M-3-P ICP ranged from 23 to 174 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1508, median Bray P1 concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1509 associated with moderately high soil P concentrations. Soils SRS-1507, lowest in concentration showed high variability with a range of 1 - 41 ppm. Lab #1 was showed low bias on the two samples lowest in concentration. Labs #12, #13 and #19 were inconsistent across the five samples. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

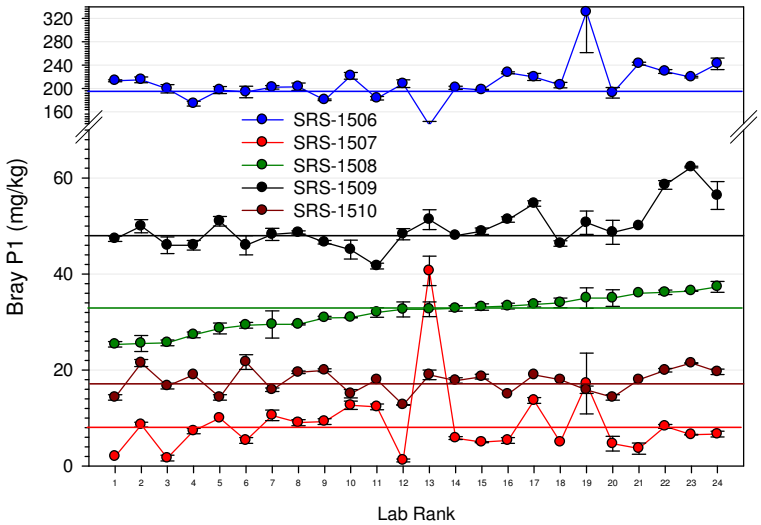

Figure 2. Bray P distribution plots for SRS materials, ALP 2015 Cycle 27.

Thirty-one laboratories provided ALP results for Olsen P (test code 134), for the five soils with medians ranged from 8.8 to 30.3 PO_4-P mg kg^{-1}. Mehlich 3 P–SPEC median concentrations were 21 to 158 mg kg^{-1} PO_4-P reported by eight labs. Strong Bray (P2) was reported by eight laboratories ranging from 40 to 263 mg kg^{-1} PO_4-P with the highest P concentration noted for SRS-1506.

SRS - Potassium

Thirty-eight laboratories provided ALP results for soil K (test code 140) results. These were ranked low to high based on sample SRS-1506 (see Figure 3). Soils SRS-1502 and SRS-1510 were the most inconsistent across labs. Lab #37 showed high bias on four of five soils. Labs #1, #2, #6, #14, #20, #24, and #33 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-1506, with a median intra-lab value of 2.0 mg kg^{-1} K and highest for SRS-1508 with a value of 6.1 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 #1 and #5 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-1507. Poor precision is attributed to extraction and/or analysis instrument operation.

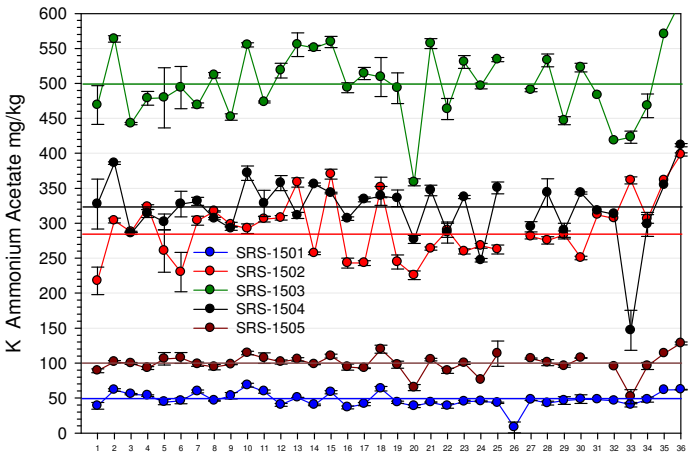

Figure 3. Extractable K distribution plots for SRS materials, ALP 2015 Cycle 27.

SRS SOM-LOI

Forty-six laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.70 to 8.05%. Results were ranked based on sample SRS-1508 (see Figure 4). Lab #46 was noted having high bias on three of five soils. Labs #11, #35, #43, #44, and #45 were inconsistent across the five soils. Source of bias is likely related to muffle furnace operation and/or method compliance.

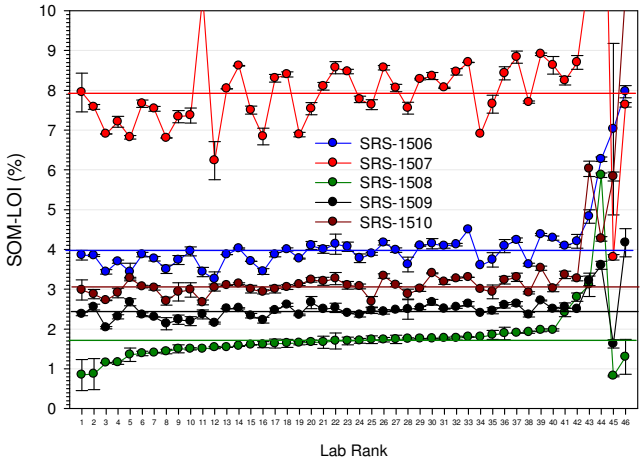

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2015 Cycle 27.

SOM-LOI precision across the five materials indicates high intra-lab precision, with median *s* values ranging from 0.056 to 0.093% SOM-LOI, the highest for SRS-1507. Across labs *s* values for SRS-1501 ranged from 0.01 - 0.25 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #5, #22, #28, #35, #36 #42 and #43, exceeded 0.15 for three of five soils. Lab #2 exceeded 0.30 % SOM on soil SRS-1508 for ALP cycle 26. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

Hot Water B

Twenty-one laboratories provided ALP results for Hot Water B, (test code 160) results. These were ranked low to high based on sample SRS-1506 (see Figure 5). Soil SRS-1506 and SRS-1510 were the lowest in concentration and the most consistent across labs. Soil SRS-1507 was highly erratic across labs. cross soils, labs #5 and #13 had low bias on three of five soils, labs #21 low bias on two of five soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

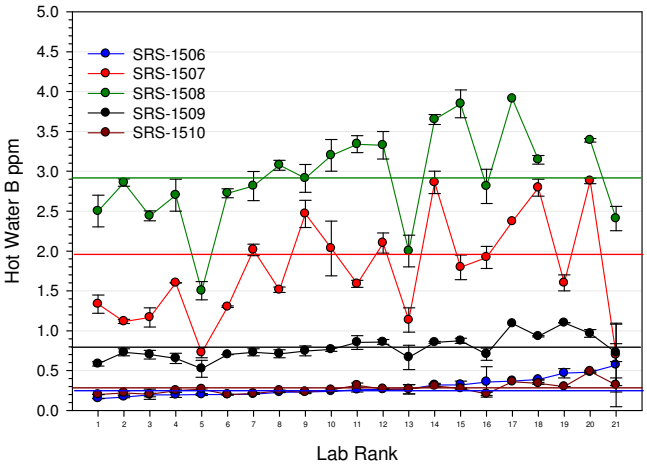

Figure 5. Soil Hot Water B distribution plot, ALP 2015 Cycle 27.

Hot-Water B median intra-lab *s* values were lowest for ALP soil SRS-1506 with an intra-lab median value of 0.012 mg kg^{-1} and highest for SRS-1508 with a value of 0.134 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1508. Intra-lab precision was poor for labs #7, #8, #13, #16 and #21 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-1504 (see Figure 6). Data plots show lab #1 has low bias for two of three botanical samples. Lab #21 showed high bias on all samples. Labs #4, and #8 were inconsistent.

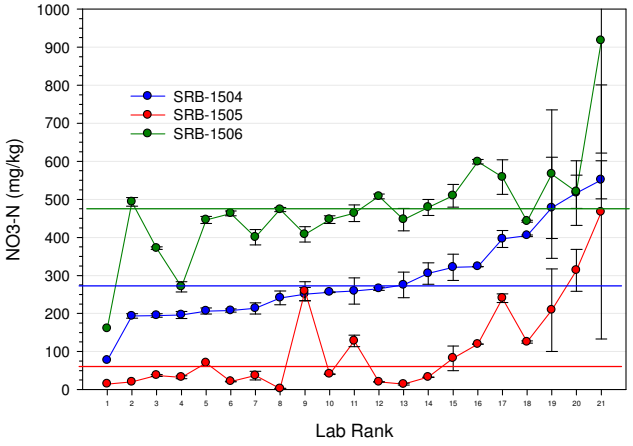

Figure 6. Nitrate distribution plots for SRB materials, ALP 2015, Cycle 27.

Botanical NO_3-N results for cycle 26 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 3 to 15 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-1504 ranged from 2 – 133 mg kg^{-1}; SRB-1505 ranged from 1 - 344 mg kg^{-1}, and SRB-1506 ranged from 2 – 296 mg kg^{-1}. Lab #19 had consistently high standard deviations for all samples , > 100 ppm. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Twenty-five laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and nine for TKN (Test code 209) for cycle 27. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1504 (see Figure 7). It is note worthy that TKN was lower than Dumas for all samples. Labs #22 - #25 showed high bias for Dumas N SRS-1504 and SRB-1505, whereas labs #1, #7, #12, and #16 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-1504, ranged from 0.006 to 0.153 % N, SRB-1505 ranged from 0.006 to 0.55 % N and SRB-1506 ranged from 0.002 to 0.208 % N. Lab #1 had consistently high standard deviations. Individual lab TKN *s* values for SRB-1504 ranged from 0.010 to 0.147 %, SRB-1505 ranged from 0.012 to 0.217 % and sample SRB-1506 ranged from 0.012 to 0.155 % TKN nitrogen.

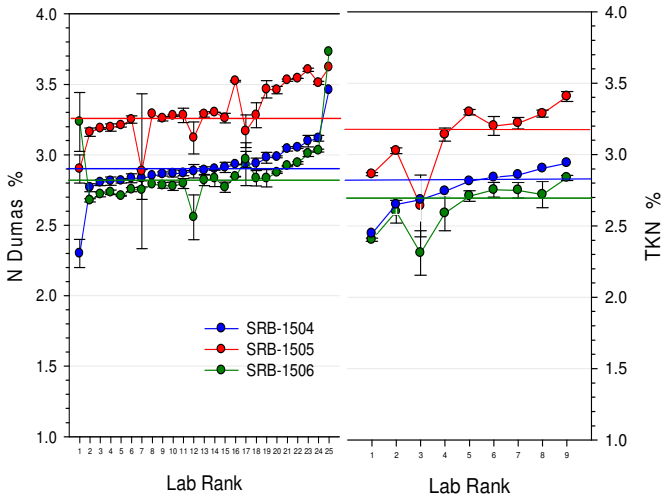

Figure 7. N distribution plots for SRB materials, ALP 2015 Cycle 27.

SRB - Potassium

Thirty-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-1504 (see Figure 8). Laboratories #2 and #3 showed low bias on all three samples, whereas labs #28, #29 #30 indicate high bias. Lab #1 was 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 0.021 to 0.046 %K for test code 213 across the three samples. Individual lab intra-lab *s* values for SRB-1504; ranged from 0.006 to 0.26 % K; SRB-1505 and 0.007 — 0.19 % K; SRB-1506 0.005 - 0.16 %K. Labs #2, #4, #9, #10 and #24 had consistently high standard deviations exceeding 0.10 %K for SRB-1504. Four labs were flagged for poor K precision.

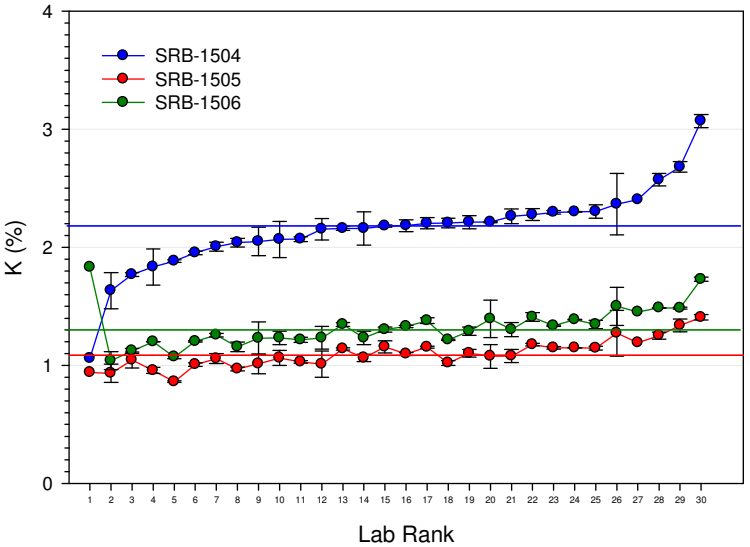

Figure 8. Potassium (code 213) plots for SRB materials, ALP 2015 Cycle 27.

SRB - Phosphorus

Thirty laboratories provided ALP results for cycle 27 phosphorus (P) combined (test code 212, wet digestion). 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-1504 (see Figure 9). Consistent high was noted for labs #28, #29 and #30. Lab #1 showed high bias. Lab #25 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 0.005 to 0.010 % P for test code 212 across the three botanical samples. Individual lab intra-lab *s* values for SRB-1504; ranged from 0.001 - 0.031 % P; SRB-1505 ranged from 0.001 – 0.047 % P and SRB-1506 0.001 - 0.025 % P. Labs #29 had a high standard deviations exceeding 0.03 % P for two of three botanical samples. Three labs were flagged for poor precision for botanical P.

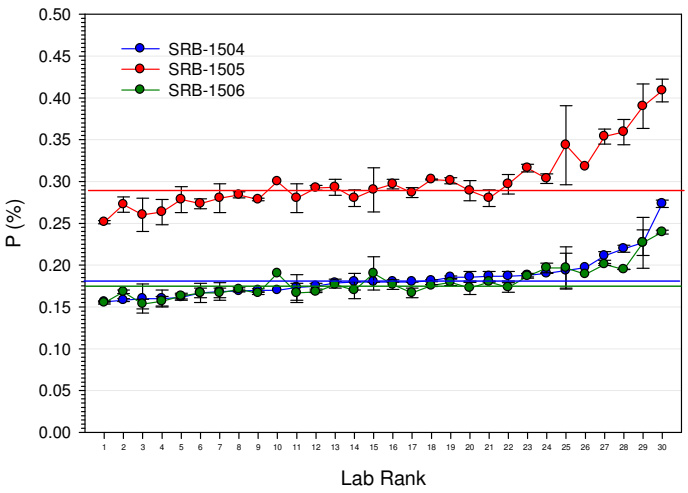

Figure 9. Phosphorus distribution plots for SRB materials, ALP 2015 Cycle 27.

SRB - Sulfur

Twenty-eight laboratories provided ALP results for Sulfur (S) (test code 216). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1504 (see Figure 10). Laboratories #1, and #2 showed low bias on all three samples, whereas labs #27 and #28 indicated high bias. Labs #2, #4 and #19 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical S results indicate very high precision, with intra-lab standard deviation (*s*) values ranged from 0.008 to 0.013 %S for across the three botanical samples. Individual lab intra-lab *s* values for SRB-1504; ranged from 0.006 - 0.020 %S; SRB-1505 ranged from 0.006 – 0.055 %S and SRB-1506 0.005 - 0.048 %S. Labs #15, #20, and #21 had consistently high standard deviations exceeding 0.04 %S for SRB-1505 the highest of all three or botanical samples. Three labs were flagged for poor S precision.

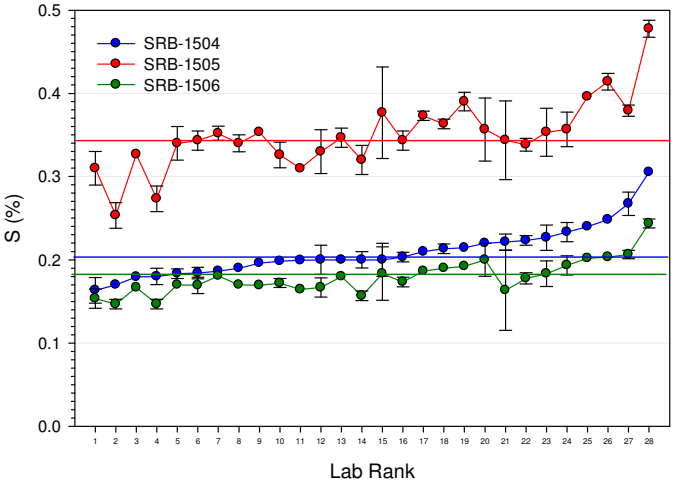

Figure 10. Sulfur distribution plots for SRB materials, ALP 2015 Cycle 27.

SRW - Water pH

Thirteen laboratories provided ALP results for water pH (test code 301). Ranking lab results low to high based on sample SRW-1504 (see Figure 11). Lab #1 indicated consistent low bias on all three samples. Labs #13, 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 median Std values of 0.032, 0.027 and 0.027 pH units, respectively. Precision for sample SRW-1506 was the most consistent across the thirteen laboratories. Across water samples poor precision was noted for one laboratory. Specifically intra-lab the *s* values for lab #2 exceeded 0.20 pH on SRW-1504 and SRS-1505. Highest precision was noted for lab #9 with intra-lab *s* values of < than 0.02 pH units.

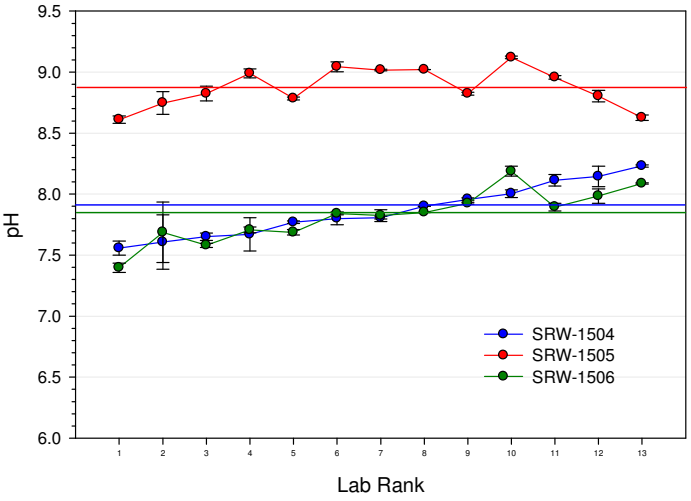

Figure 11 . Water pH distribution plots for SRW materials, ALP 2015 Cycle 27.

SRW - EC Results

Thirteen laboratories provided ALP results for water EC (test code 302). Lab results were ranked low to high based on sample SRW-1504 (see Figure 12). Median values are designated by horizontal lines. Lab #13 had consistent high bias on two of three samples. Lab #3 showed inconsistency across samples.

EC precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.010, 0.003, and 0.004 dS m^{-1} for SRW-1504, SRW-1505, and for SRW-1506, respectively. Water EC precision was excellent for all individual labs with only lab #5 exceeding 0.06 dS m^{-1} EC on sample SRW-1504. Across samples intra-lab *s* was less than 0.006 dS m^{-1} for lab #3. Three labs were flagged for poor precision for EC.

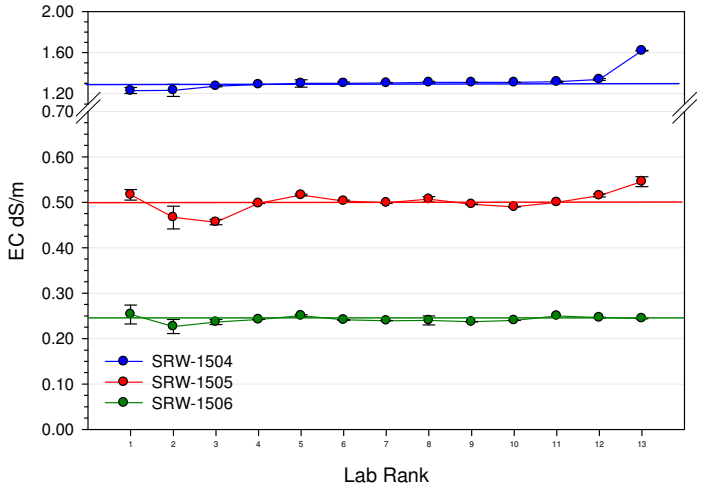

Figure 12. Water EC distribution plots for SRW materials, ALP 2015 Cycle 27.

Announcements

- ALP is now an accredited proficiency provider for agricultural laboratory testing in North America under ISO 17043 by ANAB (formerly 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 April from British Columbia, Washington and Oregon, and another ten soils from Ontario and Michigan in August representing a diverse range of textures and chemical properties. Additional collections are planned for Illinois and Minnesota in October 2015.

- ALP was a sponsor at the SERA-6 Regional Meeting held on Gainsville FL in June 9-10, 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.

- A survey of laboratories performing the Mehlich 3 method will be conducted in October.

- 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.

Summary

ALP 2015 Cycle 27 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 27. 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 28 Ship

September 24, 2015

"By denying scientific principles, one may maintain any paradox."

—Galileo Galilei

ALP
Agricultural Laboratory Proficiency Program