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ALP Program Report

2015 Fall - Cycle 28

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ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 28.
- Fifty-nine Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.31 - 7.15.
- Cycle 28 soil M3-P ICP ranged from 18.3 to 79.3 mg kg^{-1} with MAD values ranging 1.5 - 6.3 mg kg^{-1} across the five soils.
- Lab results for M3-Mg was highly consistent on soil SRS-1511 and SRS-1513 with concentrations < 120 ppm.
- Botanical P, ranged from 0.15 - 0.61 % with two of thirty-two labs noted for low bias.
- Botanical Mn values ranged from 33.2 to 242 ppm across the three samples.
- Water EC content showed high consistency by twelve of fourteen labs across all samples.

The Agriculture Laboratory Proficiency (ALP) Program spring 2015 Round cycle 28 was completed December 1, 2015, with ninety-nine labs enrolled from the United States, Canada, South Africa, Italy, 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-1511 a silt loam collected from Les Chures-de-la-Chaudiere, Quebec, Canada; SRS-1512 a Cozad silt loam collected Buffalo Cty, NE; SRS-1513 a Millhopper-Urban complex loamy sand collected Archula Cty, FL; SRS-1514 a Tama silt loam collected Iowa Cty, WI; and SRS-1515 Danvers-Shaak clay loam collected Yellowstone Cty, MT. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.30 - 7.15; NO_3-N 4.0 - 110 mg kg^{-1}; Bray P1 (1:10) 13.7 - 68.5 mg kg^{-1}; K NH_4OAc 31 - 406 mg kg^{-1}; SO_4-S 3.8 - 7.6 mg kg^{-1}; Mehlich 3 P (ICP) 18.3 - 79.3 mg kg^{-1}; DTPA-Zn 0.37 - 8.8 mg kg^{-1}; SOM-LOI 0.96 – 4.31%; CEC 3.5 - 18.9 cmol kg^{-1}; clay 4.1 - 29.1% and Solvita CO_2 Burst Respiration 5.1 - 43.4 mg kg^{-1}.

Standard Reference Botanical (SRB) materials were: SRB-1507 a spinach leaf composite from Salinas, California; SRB-1508 grape blades composite from SJV of California; and SRB-1509 composite citrus leaf from California. SRB material median analytes ranged: NO_3-N 80 - 16610 mg kg^{-1}; Dumas N 2.30 - 623%; total P 0.15 - 0.61%; total K 1.24 - 7.36%; total Ca 1.17 - 3.89%; total S 0.22 - 0.41%, total B 28 - 78 mg kg^{-1}; and total Cd 0.01 - 1.74 mg kg^{-1}.

Standard Reference Water samples represent an agriculture water sample collected: SRW-1507 a water sample collected from a well in eastern SD; SRW-1508 from a well near Kearney, NE; and SRW-1509 a well near Hensall, Ontario, Canada, 2015. SRW median concentrations ranged: pH 7.67 - 8.04; EC 0.59 - 1.32 dSm^{-1}; SAR 1.05 - 2.49; Ca 2.4 - 3.27 mmolc L^{-1}; Na 1.65 - 4.28 mmolc L^{-1}; SO4 0.72 - 6.5 mmolc L^{-1}; and NO_3–N 0.02 - 1.37 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 28 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 28, 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-1511	5.64	*0.01*	0.23	*0.006*	12.6	*0.6*	19.7	*0.9*
SRS-1512	6.62	*0.02*	0.30	*0.01*	6.9	*0.4*	24.7	*1.0*
SRS-1513	6.34	*0.01*	0.22	*0.006*	15.6	*0.8*	17.1	*0.8*
SRS-1514	7.15	*0.02*	0.46	*0.01*	33.5	*1.3*	50.1	*1.3*
SRS-1515	5.46	*0.04*	0.65	*0.02*	27.3	*0.8*	67.6	*2.4*

[1] Statistics based on four soil replicates, each analyzed in triplicate ALP Cycle 28.

2015 Cycle 28 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 28 averaged 0.06 pH units. Within lab pH standard deviation was 0.056 pH units. Soil CEC ranged 2.7 to 21.6 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 5.1 - 43.4 mg kg^{-1} with an intra-lab precision, with s values averaging 6.8 for four of five samples. Sample SRS-1511 had a saturated paste SAR of 0.7 with a within lab standard deviation of 0.3 and a MAD of 0.9. Soil ammonium acetate K (Test code 140) MAD values ranged 5 - 24 mg kg^{-1} and ammonium acetate Ca MAD values 41 to 232 mg kg^{-1} for the five soils. These results for Ca were similar to cycles 27 results in 2015 and 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 0.233%, 0.083% and 0.042%, respectively. There was a greater inter-lab variability (MAD) in total potassium values than combustion N, Ca, Mg, Na or total S concentrations for SRB-1507. Generally the citrus sample SRB-1509 had lower level median P, Ca, S, Al, Zn and Mn relative to the other two botanical samples of cycle 28. Sample SRB-1507, spinach leaf collect from near Salinas, California had a significant level of Cd at 1.72 mg kg^{-1}.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.008 to 0.027 dSm^{-1}. NO_3-N values ranged from 0.022 - 1.37 molc L^{-1} across the three water samples with MAD values ranging 0.001 to 0.039 molc L^{-1}.

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 5.32 to 7.15. Lab results were ranked low to high based on sample SRS-1511 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1513 and SRS-1515 showed good consistency across labs. Labs #1, #8, #27, #55, 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.

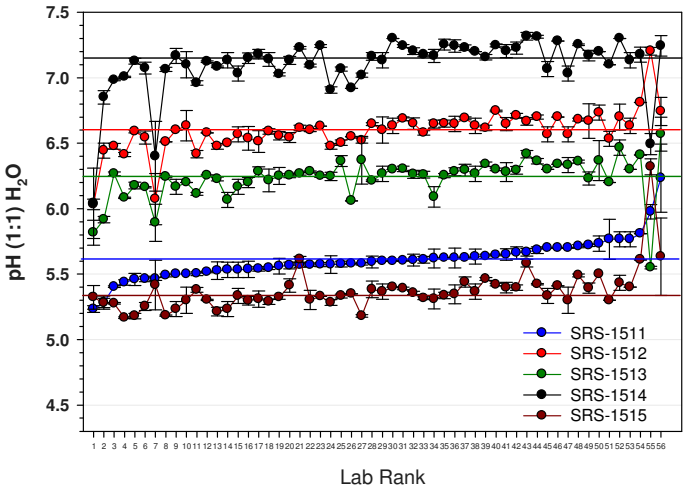


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2015 Cycle 28.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.021 to 0.026 pH units, the highest noted for SRS-1512. For specific labs poor precision was noted for SRS-1512 for five laboratories, exceeding by three times that noted for consensus intra-lab *s*. Specifically *s* for lab #56 exceeded 0.10 pH units for four of five soils. Soil SRS-1511 was the least variable with respect to intra-lab variance for cycle 28.

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 34.4 to 68.8 mg kg^{-1} PO_4-P; Mehlich 1 P 28.1 to 102 mg kg^{-1} P and M-3-P ICP ranged from 19.1 to 123 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1511, median M3-P ICP concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1513 associated with high soil P concentrations. Soils SRS-1512, lowest in concentration showed high variability with a range of 13.2 - 33.4 ppm. Lab #1 was showed low bias on three samples. Labs #6, #18 #29, #30 and #31 were inconsistent across the five samples. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

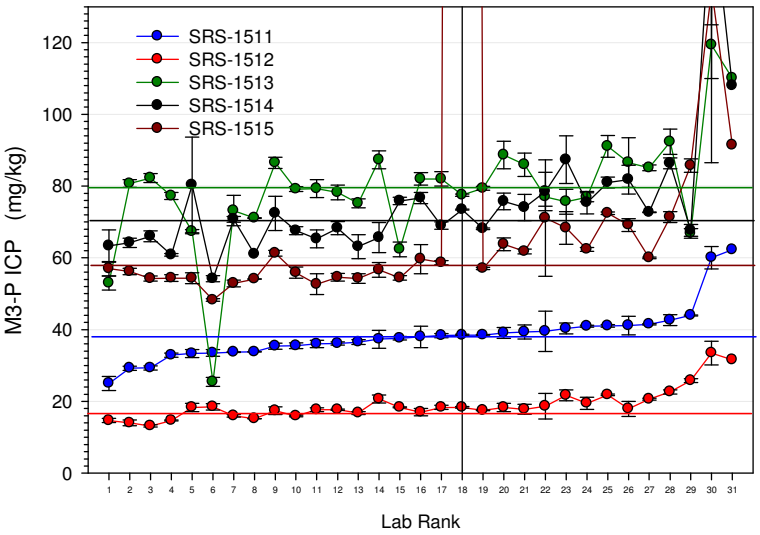


Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2015 Cycle 28.

Thirty-one laboratories provided ALP results for Olsen P (test code 134), for the five soils with medians ranged from 8.9 to 39.0 PO_4-P mg kg^{-1}. Mehlich 3 P–SPEC median concentrations were 13.7 to 61.2 mg kg^{-1} PO_4-P reported by seven labs. Strong Bray (P2) was reported by five laboratories ranging from 51.6 to 155 mg kg^{-1} PO_4-P with the highest P concentration noted for SRS-1515.

SRS - Potassium

Forty-one laboratories provided ALP results for soil K (test code 140) results. These were ranked low to high based on sample SRS-1511 (see Figure 3). Soils SRS-1512, SRS-1514 and SRS-1515 were the most inconsistent across labs. Lab #41 showed high bias on four of five soils. Labs #4, #7, #6, #18, and #36 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-1511, with a median intra-lab value of 3.6 mg kg^{-1} K and highest for SRS-1515 with a value of 34 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 #4 and #13 which exceeded 20 mg kg^{-1} K on three of five soils; and lab #29 the value exceeded 10 mg kg^{-1} K for SRS-1512. Poor precision is attributed to extraction and/or analysis instrument operation.

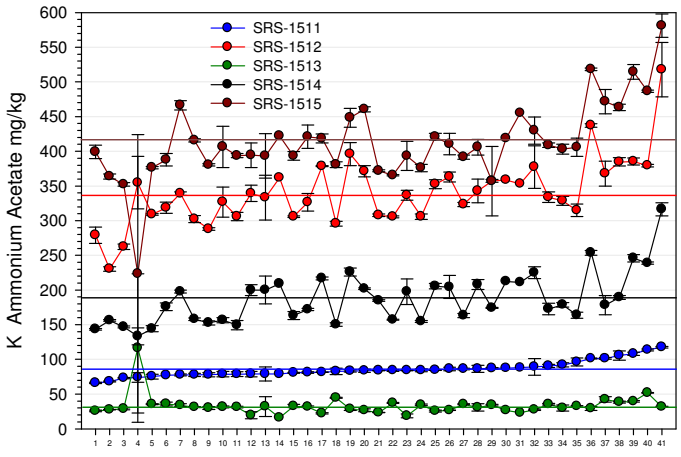


Figure 3. Extractable K distribution plots for SRS materials, ALP 2015 Cycle 28.

SRS SOM-LOI

Forty-three laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 0.96 to 4.36%. Results were ranked based on sample SRS-1511 (see Figure 4). Lab #43 was noted having high bias on four of five soils. Labs #3, #11, #15, #30, and #36 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 0.12 to 0.35% SOM-LOI, the highest for SRS-1515. Across labs *s* values for SRS-1511 ranged from 0.01 - 0.17 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #3, #11, #30, #39, and #42, exceeded 0.15 for three of five soils. Lab #30 exceeded 0.40 % SOM on soil SRS-1515 for ALP cycle 28. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

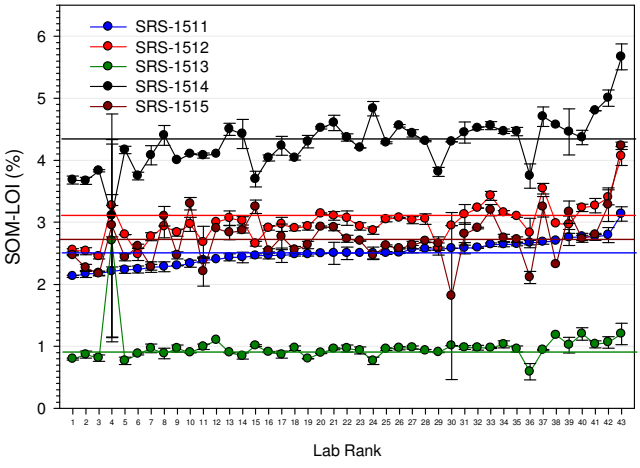


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2015 Cycle 28.

M3-Mg

Thirty-three laboratories provided ALP results for M3-Mg, (test code 160) results. These were ranked low to high based on sample SRS-1511 (see Figure 5). Soil SRS-1511 and SRS-1513 were the lowest in concentration and the most consistent across labs. Soil SRS-1515 was highly erratic across labs. Across soils, labs #4 #15, #12 and #30 were inconsistent across soils and #33 had high bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

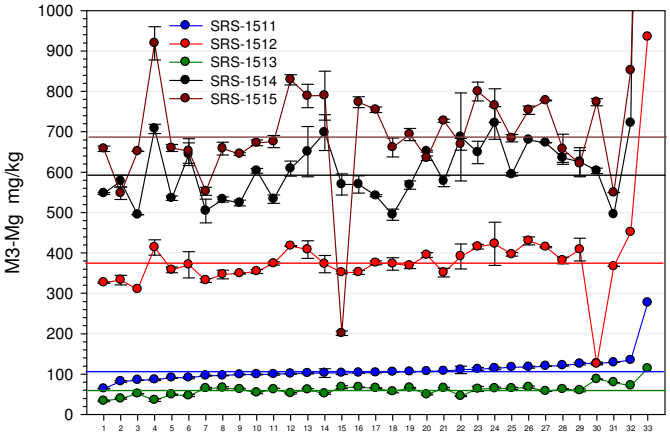


Figure 5. Soil Hot Water B distribution plot, ALP 2015 Cycle 28.

M3-Mg median intra-lab *s* values were lowest for ALP soil SRS-1513 with an intra-lab median value of 2.4 mg kg^{-1} and highest for SRS-1514 with a value of 27 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1514. Intra-lab precision was poor for labs #4, #15, #22, and #24 on two of five soils. Poor precision maybe associated with M3 extraction and/or ICP instrument operation.

SRB Nitrate-Nitrogen

Twenty-five 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-1507 (see Figure 6). Data plots show lab #1 has low bias on all three botanical samples. Lab #26 showed high bias on all samples. Labs #2, #15, #16, and #20 were inconsistent.

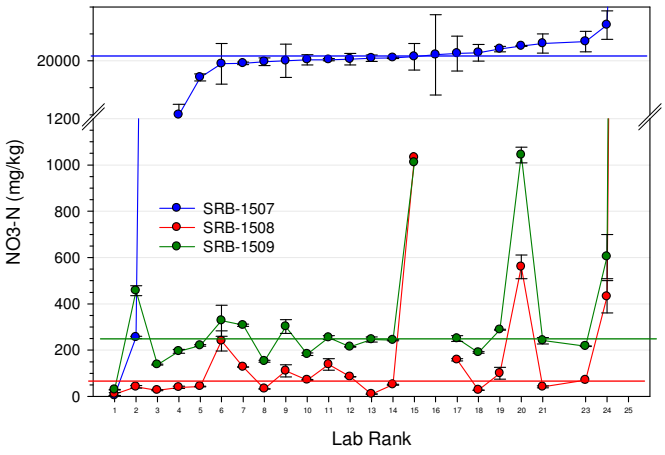


Figure 6. Nitrate distribution plots for SRB materials, ALP 2015, Cycle 28.

Botanical NO_3-N (test code 202) results for cycle 28 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 26 to 710 mg kg^{-1} for the three samples. Individual lab NO_3-N (test code 202) intra-lab *s* values for SRB-1507 ranged from 5 – 1600 mg kg^{-1}; SRB-1508 ranged from 1 - 70 mg kg^{-1}, and SRB-1509 ranged from 1 – 95 mg kg^{-1}. Lab #12 had consistently high standard deviations for all samples , > 70 ppm. Four 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 28. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1507 (see Figure 7). It is note worthy that TKN was lower than Dumas for sample SRB-1507. Labs #1 - #2 showed low bias for Dumas N SRB-1507, whereas labs #7, #18, and #24 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 lab *s* values for SRB-1507, ranged 0.006 to 0.573% N, SRB-1508 ranged from 0.002 to 0.111% N and SRB-1509 ranged from 0.006 to 0.170 % N. Lab #1 had consistently high standard deviations. Lab TKN *s* values for SRB-1507 ranged from 0.006 to 1.6% TKN, SRB-1508 ranged from 0.006 to 0.175% TKN and sample SRB-1509 ranged from 0.006 to 0.425% TKN nitrogen.

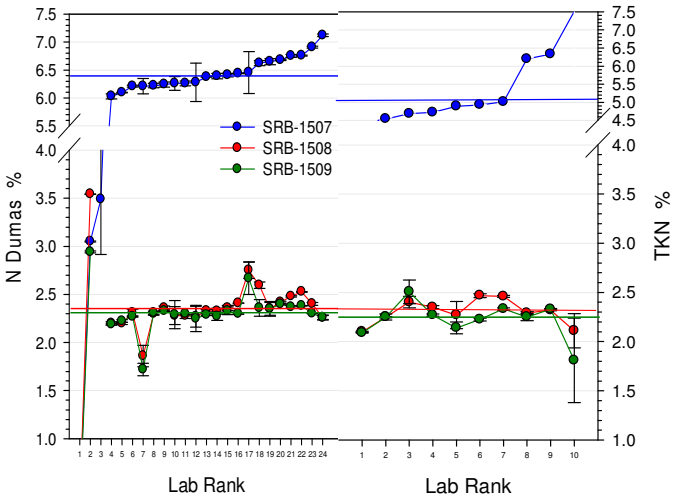


Figure 7. N distribution plots for SRB materials, ALP 2015 Cycle 28.

SRB - Potassium

Thirty-two 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-1507 (see Figure 8). Laboratories #2 showed low bias on two of three samples. Lab #1, #4, and #5 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 0.06 to 0.44 %K for test code 213 across the three samples. Individual lab intra-lab *s* values for SRB-1507; ranged from 0.032 to 1.8 % K; SRB-1508 and 0.004 — 0.223 % K; SRB-1509 0.001 - 0.239 %K. Labs #6, #16, #28 had consistently high standard deviations exceeding 0.08 %K for SRB-1508. Four labs were flagged for poor K precision.

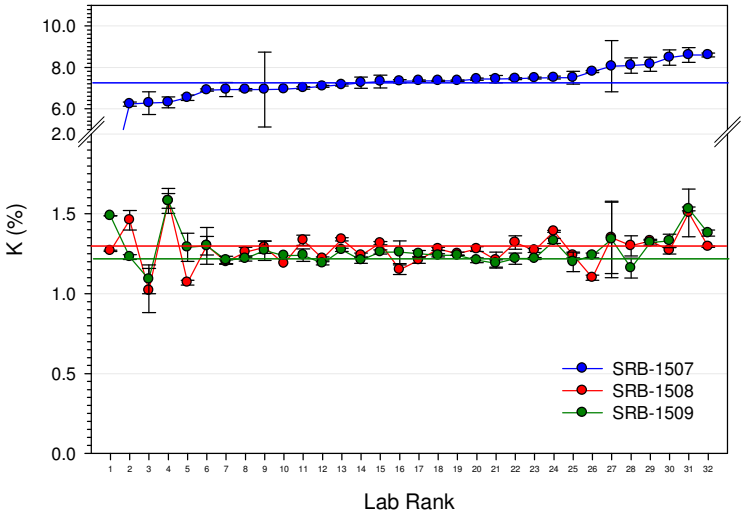


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2015 Cycle 28.

SRB - Phosphorus

Thirty-two laboratories provided ALP results for cycle 28 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-1507 (see Figure 9). Inconsistent high was noted for labs #1, #10 and #27. Lab #2 and #3 showed overall low bias. 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 0.011 to 0.019 % P for test code 212 across the three botanical samples. Individual lab intra-lab *s* values for SRB-1507; ranged from 0.001 - 0.044 % P; SRB-1508 ranged from 0.001 – 0.030 % P and SRB-1509 0.001 - 0.020 % P. Labs #31 had a high standard deviations exceeding 0.020 % P for all three botanical samples. Three labs were flagged for poor precision for botanical P.

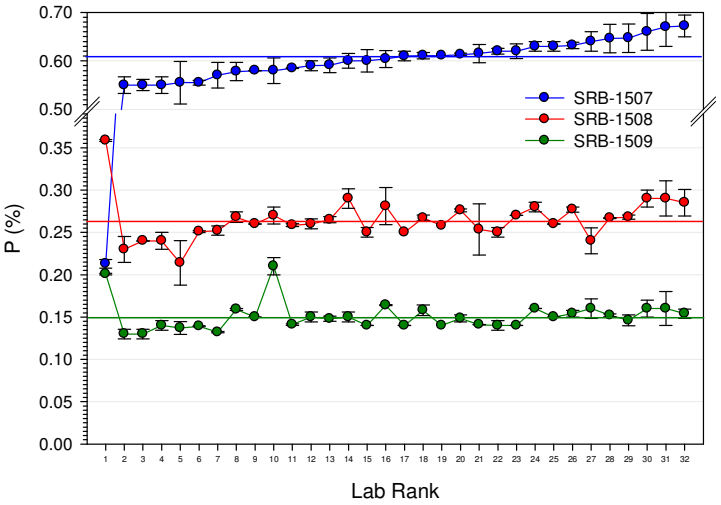


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2015 Cycle 28.

SRB - Manganese

Thirty-one laboratories provided ALP results for manganese (Mn) (test code 221). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1507 (see Figure 10). Laboratory #1 showed low bias on all three samples, whereas lab #31 indicated high bias. Labs #2, #5 and #30 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Mn results indicate very high precision, with intra-lab standard deviation (*s*) values ranged from 17.4 to 32.8 mg kg^{-1} Mn for across the three botanical samples. Individual lab intra-lab *s* values for SRB-1507; ranged from 0.3 - 95 mg kg^{-1} Mn; SRB-1508 ranged from 0.4 – 142 mg kg^{-1} Mn and SRB-1509 0.1 - 97 mg kg^{-1} Mn. Labs #18 and #31 had consistently high standard deviations exceeding 10.0 mg kg^{-1} Mn for SRB-1507 the highest of all three or botanical samples. Two labs were flagged for poor Mn precision.

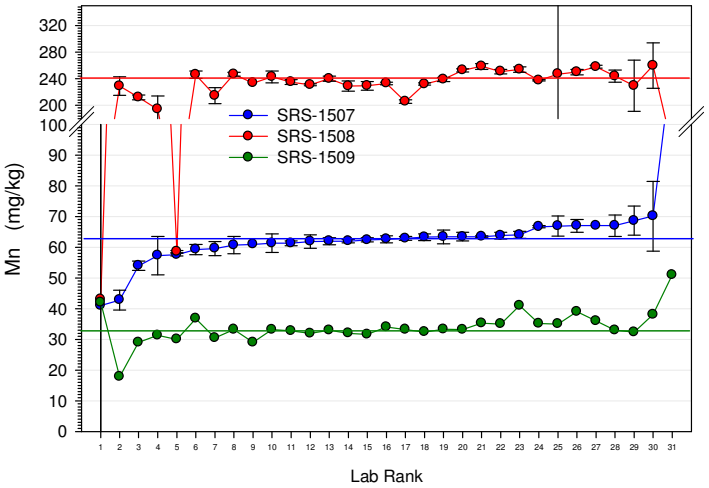
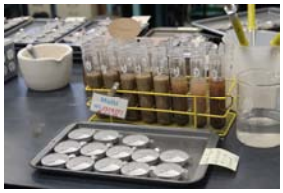


Figure 10. Sulfur distribution plots for SRB materials, ALP 2015 Cycle 28.

SRW - Water pH



Fourteen laboratories provided ALP results for water pH (test code 301). Ranking lab results low to high based on sample SRW-1507 (see Figure 11). Labs #1 and #2 indicated consistent low bias on all three samples. Labs #14, had high bias 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 0.087, 0.12 and 0.065 pH units, respectively. Precision for sample SRW-1509 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 #3 exceeded 0.08 pH on SRW-1508 and SRS-1509. Highest precision was noted for lab #7 with intra-lab *s* values of < than 0.02 pH units.

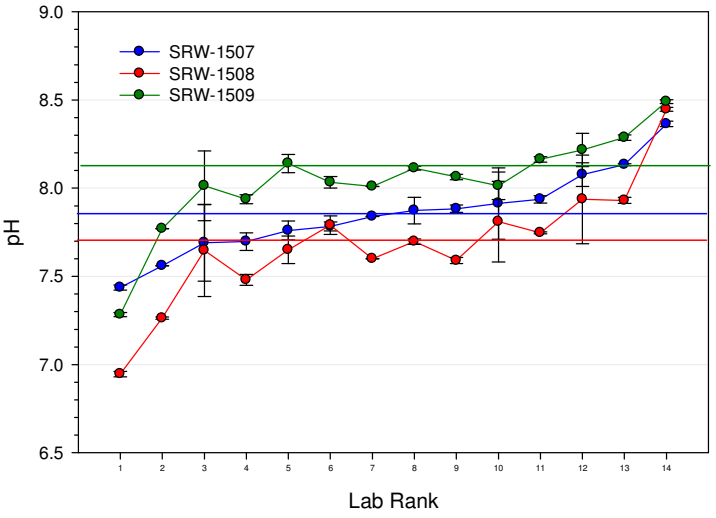


Figure 11 . Water pH distribution plots for SRW materials, ALP 2015 Cycle 28.

SRW - EC Results

Fourteen laboratories provided ALP results for water EC (test code 302). Lab results were ranked low to high based on sample SRW-1507 (see Figure 12). Median values are designated by horizontal lines. Lab #14 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 0.024, 0.027, and 0.013 dS m^{-1} for SRW-1507, SRW-1508, and for SRW-1509, respectively. Water EC precision was excellent for all individual labs with only lab #3 exceeding 0.10 dS m^{-1} EC on sample SRW-1508. Across samples intra-lab *s* was less than 0.006 dS m^{-1} for lab #6. Four labs were flagged for poor precision on ALP Cycle 28 for EC.

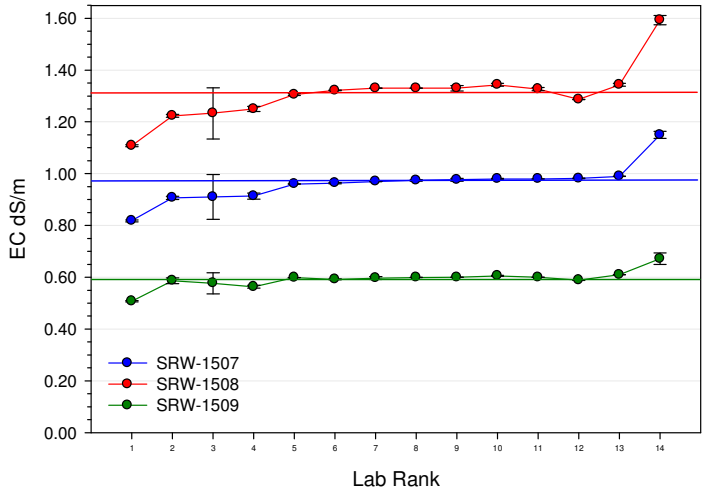


Figure 12. Water EC distribution plots for SRW materials, ALP 2015 Cycle 28.

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 a total of twenty-seven proficiency soils in 2015 from the states and provinces of British Columbia, Ontario, Wisconsin, Iowa, Michigan, South Dakota, Washington and Oregon representing a diverse range of textures and chemical properties.

- A preliminary evaluation study is nearing completion 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. These methods will be introduced in 2016 as provisional; status in ALP.

- The Soil and Plant Analysis Council (SPAC) is developing a national certification program for botanical analysis. The program will be based on proficiency testing program data. Details on the program will be available March 1, 2016.

- 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 28 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 28. 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

March 16, 2016

"More than ever, the creation of the ridiculous is almost impossible because of the competition it receives from reality.

— Robert A. Baker (1971)