2016 Volume 1

18, May 2016

ALP Program Report

2016 Spring - Cycle 29

Robert O. Miller, PhD, Colorado State University. Fort Collins, CO
Christopher Czyryca, Collaborative Testing, Inc, Sterling, VA

ALP Overview

The Agriculture Laboratory Proficiency (ALP) Program spring 2016 Round cycle 29 was completed May 16, 2016, with one-hundred six labs enrolled from the United States, Canada, South Africa, Italy, Serbia, Philippines and Guatamala. 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. New for cycle 29 was the addition of 4th botanical sample.

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 methods and statistical protocols can be found at the program web site: http://www.collaborativetesting.com/reports/default.aspx?F_CategoryId=12,

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 29.
- Sixty-two Laboratories provided soil pH (1:1) H_2O results and medians ranged from 4.60 - 7.98.
- Cycle 29 soil M3-P ICP ranged from 25.37 to 207 mg kg^{-1} with MAD values ranging 1.75 - 10 mg kg^{-1} across the five soils.
- Lab results for M3-Mg was highly consistent on soil SRS-1603 and SRS-1605 with concentrations < 120 ppm.
- Botanical P, ranged from 0.113 - 0.388 % with two of thirty-four labs noted for low bias.
- Botanical K results showed high intra-lab variability across all four PT cycle 29 samples.
- Water Ca content showed high consistency by twelve of fourteen labs across all samples.

Inside this issue:

Soil Homogeneity Evaluation	2
2016 Cycle 29 Observations	2
SRS Results: pH, P, K, SOM	3
M3-Mg	5
SRB Results	5
SRB: N, P, K and Cu	6
SRW Results	8
Announcements	9

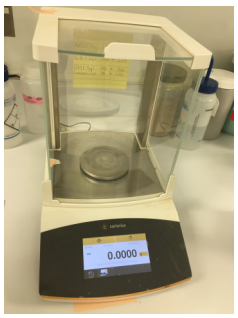
Proficiency Materials

Standard Reference Soils (SRS), materials used for the soils and environmental programs were: SRS-1601 a Clarno-Davison loam collected from McCook Cty, SD; SRS-1602 a sandy clay loam collected Huron Cty, ON; SRS-1603 a Woodbridge fine sandy loam collected Kennebec Cty, ME; SRS-1604 a Sebastopol sandy loam collected Sonoma Cty, CA; and SRS-1605 Marvyn loamy sand collected Lee Cty, AL. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 4.60 - 7.98; NO_3-N 6.3 - 101 mg kg^{-1}; Bray P1 (1:10) 17.6 - 236 mg kg^{-1}; K NH_4oAc 22 - 145 mg kg^{-1}; SO_4-S 2.6 - 24.8 mg kg^{-1}; Mehlich 3 P (ICP) 25.7 - 207 mg kg^{-1}; DTPA-Zn 0.48 - 5.48 mg kg^{-1}; SOM-LOI 0.74 – 5.00%; CEC 2.1 - 23.2 cmol kg^{-1}; clay 5.4 - 31.2% and Solvita CO_2 Burst Respiration 2.3 - 36.4 mg kg^{-1}.

Standard Reference Botanical (SRB) materials were: SRB-1601 a corn stalk leaf composite from Connecticut; SRB-1602 almond leaves composite from SJV of California; SRB-1603 corn leaves V5 from Colorado and SRB-1604 sorghum leaves. SRB material median analytes ranged: NO_3-N 216 - 3014 mg kg^{-1}; Dumas N 0.72 - 3.16%; total P 0.113 - 0.375%; total K 1.79 - 2.88%; total Ca 0.14 - 3.17%; total S 0.05 - 0.25 %, total B 3.4 - 42.7 mg kg^{-1}; and total Pb 0.20 - 18.1 mg kg^{-1}.

Standard Reference Water samples represent an agriculture water sample collected: SRW-1601 a water sample collected from a water source in Conneticut; SRW-1602 from a well near Ogden, IA; and SRW-1603 is irrigation water, Tinmath, CO. SRW median concentrations ranged: pH 7.48 - 8.48; EC 0.11 - 0.22 dSm^{-1}; SAR 0.47 - 2.14; Ca 0.35 - 0.53 mmolc L^{-1}; Mg 0.16 - 0.67 mmolc L^{-1}; SO_4 0.09 - 0.27 mmolc L^{-1} ; and NO_3–N 0.008 - 0.059 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 29 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 29, 2016.

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-1601	7.99	*0.02*	0.21	*0.01*	11.6	*0.5*	6.7	*0.8*
SRS-1602	7.60	*0.03*	0.32	*0.02*	15.1	*0.8*	22.2	*0.6*
SRS-1603	5.69	*0.06*	0.75	*0.01*	31.8	*2.9*	93.6	*3.6*
SRS-1604	5.56	*0.05*	0.90	*0.02*	11.1	*0.5*	108	*2.5*
SRS-1605	4.65	*0.07*	0.38	*0.008*	18.6	*1.4*	43.3	*1.4*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 29.

2016 Cycle 29 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 29 averaged 0.09 pH units. Within lab pH standard deviation was 0.058 pH units. Soil CEC ranged 2.1 to 23.2 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 2.3 - 36.4 mg kg^{-1} with an intra-lab precision, with s values averaging < 4 for three of five samples. Sample SRS-1511 had a saturated paste NO_3-N of 16.3 with a within lab standard deviation of 0.4 cmol L^{-1} and a MAD of 1.3. Soil ammonium acetate K (Test code 140) MAD values ranged 22 - 155 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 2016 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 0.066% nitrogen with intra-lab *s* of 0.029%, 0.036%. 0.046 and 0.052%, respectively. There was a greater inter-lab variability (MAD) in total potassium values than combustion N, P, Ca, Mg, Na, S or total Cl concentrations for SRB-1601. Generally the sorghum leaf sample SRB-1604 had higher level median N, P, Mo, Cd and Pb relative to the other three botanical samples. One observation on Cycle 29, intra-lab variability was higher for K than all other elements for all four botanical samples. Variability was attributed to ICP instrumentation operation/calibration.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.005 to 0.006 dSm^{-1}. NO_3-N values ranged from 0.008 - 0.059 molc L^{-1} across the three water samples with MAD values ranging 0.008 to 0.027 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 4.60 to 7.98. Lab results were ranked low to high based on sample SRS-1601 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1602 and SRS-1604 showed good consistency across labs. Labs #1, #9, #49, #54 and #62 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.

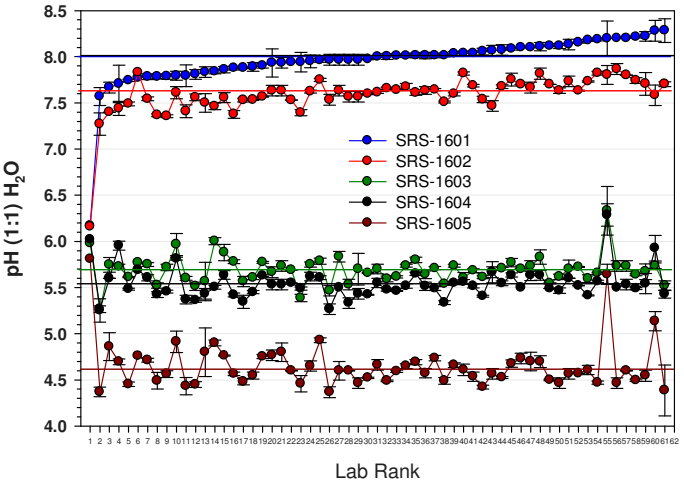


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2016 Cycle 29.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.042 to 0.071 pH units, the highest noted for SRS-1605. For specific labs poor precision was noted for SRS-1605 for six 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-1601 was the least variable with respect to intra-lab variance for cycle 29.

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

Bray P1 results were reported by twenty-seven labs. Median soil Bray P1 values ranged from 17.6 to 236 mg kg^{-1} PO_4-P; Mehlich 1 P 8.2 to 79.5 mg kg^{-1} P and M-3-P ICP ranged from 25.7 to 207 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1601, median Bray P1 1:10 concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1602 and SRS-1604 associated with medium soil P concentrations. Soils SRS-1601, lowest in concentration showed high variability with a range of 12 - 27 ppm. Lab #4 was showed low bias on three samples. Labs #1, #2 #14, #25 and #26 were inconsistent across the five samples. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

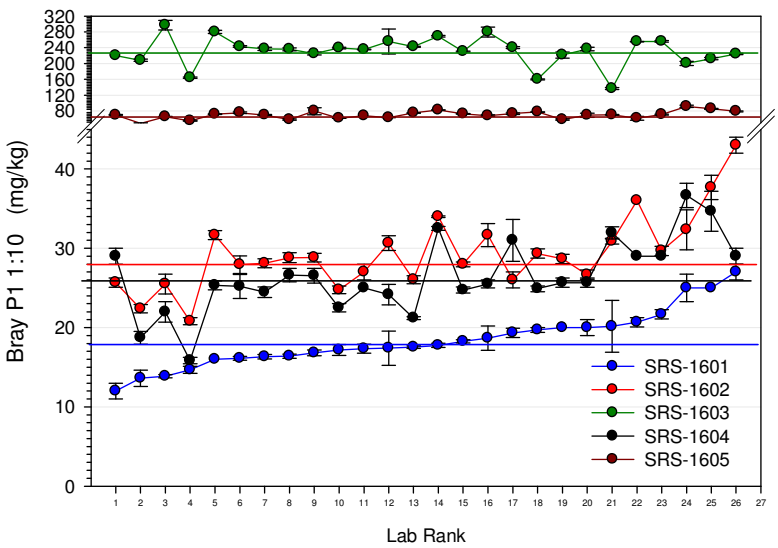


Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2016 Cycle 29.

Thirty-four 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 1 median concentrations were 8.27 to 79.5 mg kg^{-1} PO_4-P reported by four labs. Strong Bray (P2) was reported by eight laboratories ranging from 43.8 to 450 mg kg^{-1} PO_4-P with the highest P concentration noted for SRS-1603.

SRS - Magnesium

Forty-seven laboratories provided ALP results for soil Mg (test code 143) results. These were ranked low to high based on sample SRS-1601 (see Figure 3). Soils SRS-1601, SRS-1602 and SRS-1604 were the most inconsistent across labs. Labs #1 - #3 showed low bias on all five soils. Labs #12, #44, #45, and #46 were inconsistent across the five soils for Mg. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

Magnesium intra-lab *s* values were lowest for soil SRS-1603, with a median intra-lab value of 5.5 mg kg^{-1} Mg and highest for SRS-1601 with a value of 24 mg kg^{-1} Mg. Magnesium within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 200 mg kg^{-1} Mg. Precision was poor (based on intra-lab *s*) for labs #10, #12, #24, and #42 which exceeded 20 mg kg^{-1} Mg on three of five soils; and lab #46 the value exceeded 40 mg kg^{-1} Mg for SRS-1601. Poor precision is attributed to extraction and/or analysis instrument operation.

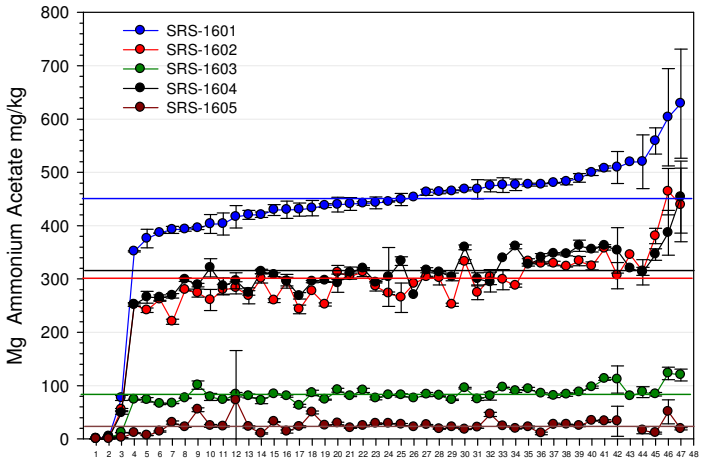


Figure 3. Extractable Mg distribution plots for SRS materials, ALP 2016 Cycle 29.

SRS SOM-LOI

Twenty-two laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 0.75 to 4.98%. Results were ranked based on sample SRS-1601 (see Figure 4). Labs #21 and #22 were noted having high bias on four of five soils. Labs #1, #10, #18, and #19 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 0.11 to 0.15% SOM-LOI, the highest for SRS-1605. Across labs *s* values for SRS-1601 ranged from 0.01 - 0.30 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #3, #8, #15, and #19, exceeded 0.10 for three of five soils. Lab #19 exceeded 0.50 % SOM on soil SRS-1605 for ALP cycle 29. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

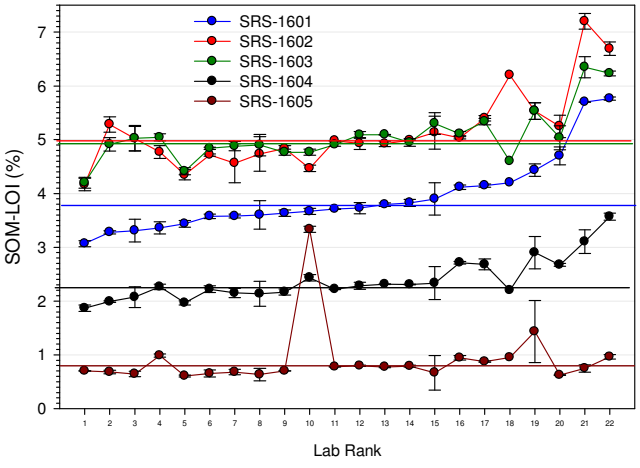


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2016 Cycle 29.

SRS - Zn DTPA

Forty-four laboratories provided ALP results for - Zn-DTPA (test code 170) results. These were ranked low to high based on sample SRS-1601 (see Figure 5). Soil SRS-1601 and SRS-1605 were the lowest in concentration and the most consistent across labs. Soil SRS-1602 was highly erratic across labs. Across soils, labs #2 #13, #25 and #42 were inconsistent across soils and #44 had high bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

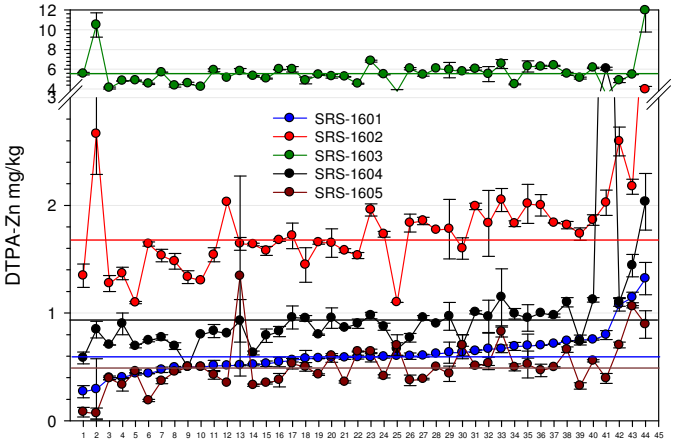


Figure 5. Soil Zn -DTPA distribution plot, ALP 2016 Cycle 29.

Zn-DTPA median intra-lab *s* values were lowest for ALP soil SRS-1601 with an intra-lab median value of 0.06 mg kg^{-1} and highest for SRS-1603 with a value of 0.44 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1603. Intra-lab precision was poor for labs #13, #33, and #44 on three of five soils. Poor precision maybe associated with Zn-DTPA extraction and/or ICP instrument operation.

SRB Nitrate-Nitrogen

Sixteen laboratories provided ALP results for NO_3-N by cadmium Reduction (test code 202). New for Cycle 29 is the inclusion of a 4th botanical sample material. Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1601 (see Figure 6). The data plot shows lab #1 has low bias on two of four botanical samples whereas, lab #16 had high bias on all four materials. Labs #7, #12, #13, and #15 were inconsistent.

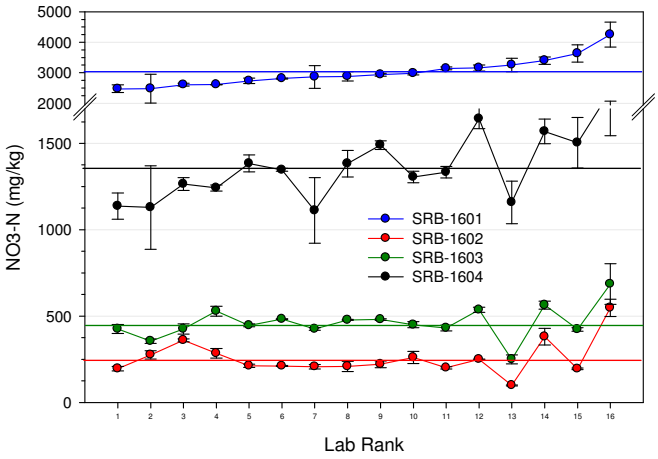


Figure 6. Nitrate distribution plots for SRB materials, ALP 2016, Cycle 29.

Botanical NO_3-N (test code 202) results for cycle 29 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 24 to 302 mg kg^{-1} for the four samples. Individual lab NO_3-N by Cadmium Reduction (test code 202) intra-lab *s* values for SRB-1601 ranged from 7 – 471 mg kg^{-1}; SRB-1602 ranged from 2 - 50 mg kg^{-1}, and SRB-1603 ranged from 2 – 116 mg kg^{-1}. Lab #16 had consistently high standard deviations for all samples , > 50 ppm. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and nine labs for TKN (Test code 209) for cycle 29. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1601 (see Figure 7). It is note worthy that TKN was lower than Dumas for sample SRB-1601. Labs #1 - #2 showed low bias for Dumas N SRB-1601 and SRB-1602, whereas labs #2, #12, #20, #22 and #28 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-1601, ranged 0.001 to 0.085% N, SRB-1602 ranged from 0.002 to 0.12% N, SRB-1603 ranged from 0.004 to 0.07 % N, and SRB–1604 from 0.003 to 0.17 % N. Lab #1 had consistently high standard deviations. Lab TKN *s* values for SRB-1601 ranged from 0.012 to 0.085% TKN, SRB-1602 ranged from 0.016 to 0.21% TKN and sample SRB-1603 ranged from 0.003 to 0.25% TKN nitrogen.

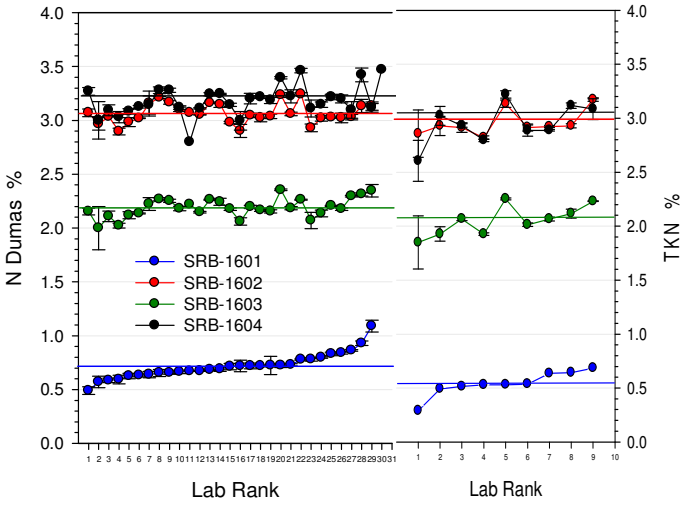


Figure 7. N distribution plots for SRB materials, ALP 2016 Cycle 29.

SRB - Potassium

Thirty-six 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-1601 (see Figure 8). Laboratories #1 and #2 showed low bias, whereas labs #32 - #36 showed high bias. Labs #3, #20, #21 and #31 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 0.081 to 0.20 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1601, ranged from 0.016 to 0.98 % K; SRB-1602, 0.005 — 0.24 % K; SRB-1603, 0.011 - 0.46 % K; and SRS-1604, 0.005 to 0.27 % K. Five labs had high standard deviations exceeding 0.20 %K for SRB-1603. One lab was flagged for poor K precision.

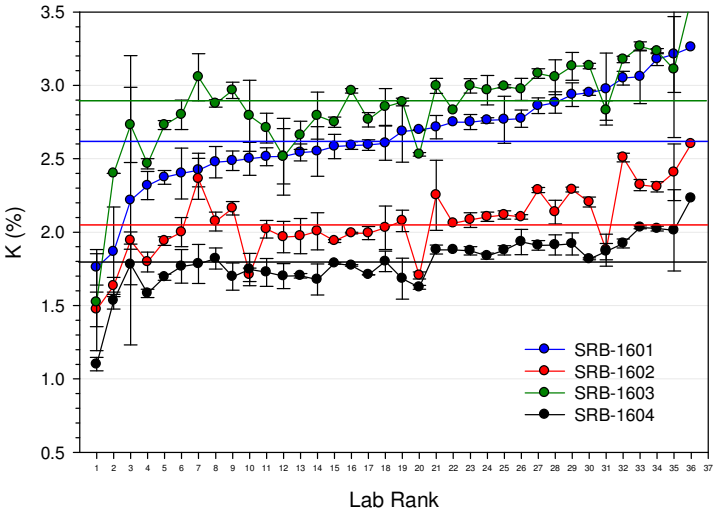


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2016 Cycle 29.

SRB - Phosphorus

Thirty-six laboratories provided ALP results for cycle 29 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-1602 (see Figure 9). Consistent high was noted for labs #30 - #36. Labs #7, #19, #26 and #27 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 0.007 to 0.016 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1601; ranged from 0.001 - 0.047 % P; SRB-1602 ranged from 0.001 – 0.015 % P and SRB-1603 0.001 - 0.040 % P; and SRB-1604 0.002 - 0.041 % P. Labs #15 had a high standard deviations exceeding 0.050 % P for three of four botanical samples. Four labs were flagged for poor precision for botanical P.

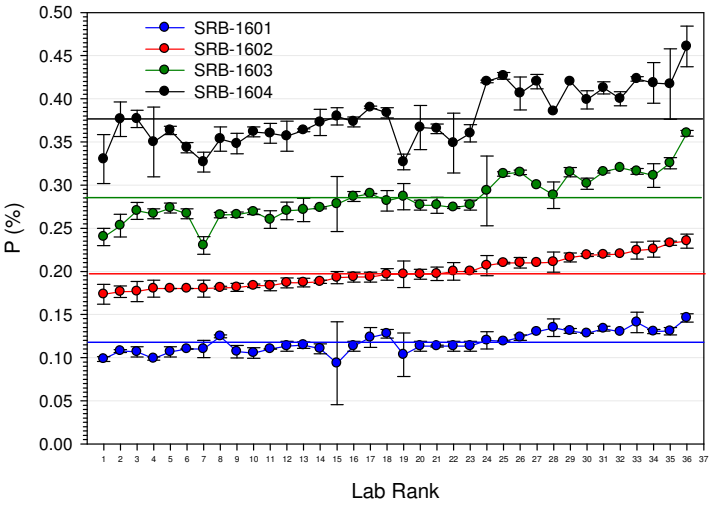


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2016 Cycle 29.

SRB - Copper

Thirty-four laboratories provided ALP results for manganese (Cu) (test code 223). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1601 (see Figure 10). Labsy #1 and #2 showed low bias on all four samples, whereas lab #34 indicated high bias. Labs #5, #16, #17, #18 and #33 were 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 0.56 to 4.4 mg kg^{-1} Cu for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1601; ranged from 0.01 - 2.4 mg kg^{-1} Cu; SRB-1602 ranged from 0.06 – 4.4 mg kg^{-1} Cu; SRB-1603 0.22 - 19.2 mg kg^{-1} Cu; and SRB-1604 0.06 - 3.4 mg kg^{-1} Cu. Labs #6 and #33 had consistently high standard deviations for tow of four botanical samples. For ALP cycle 20 Two labs were flagged for poor Cu precision.

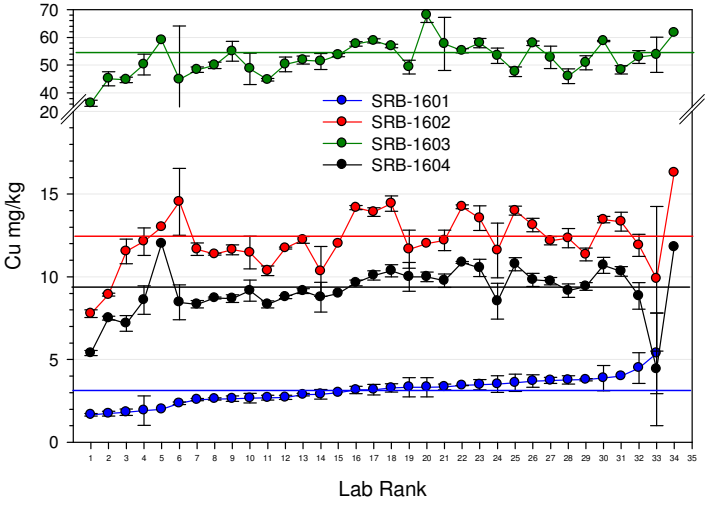
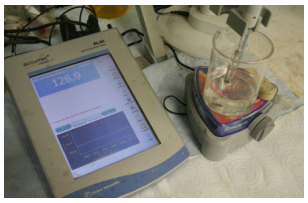


Figure 10. Copper distribution plots for SRB materials, ALP 2016 Cycle 29.

SRW - Water pH



Seventeen laboratories provided ALP results for water pH (test code 301). Ranking lab results low to high based on sample SRW-1601 (see Figure 11). Labs #2 indicated consistent low bias on all three samples. Labs #10 and #11 were 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 0.026, 0.045 and 0.062 pH units, respectively. Precision for sample SRW-1601 was the most consistent across the seventeen participating laboratories. Across water samples poor precision was noted for one laboratory. Specifically intra-lab the *s* values for lab #13 exceeded 0.21 pH on SRW-1601. Highest precision was noted for lab #9 with intra-lab *s* values of < than 0.01 pH units.

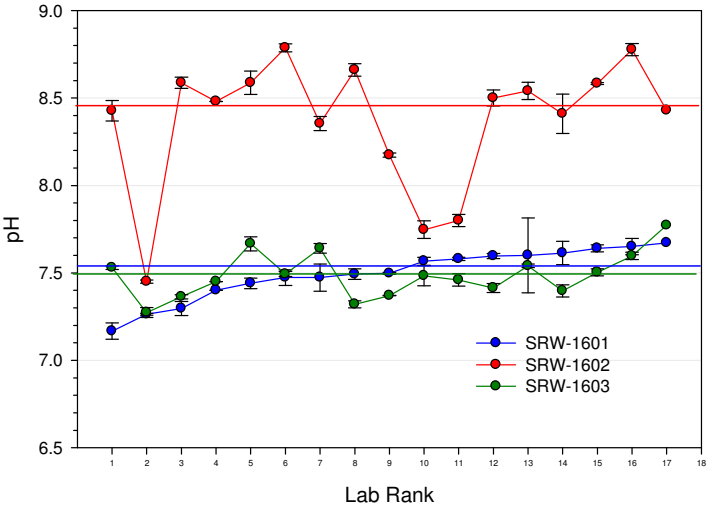


Figure 11 . Water pH distribution plots for SRW materials, ALP 2016 Cycle 29.

SRW - Ca Results

Fourteen laboratories provided ALP results for water Ca (test code 302). Lab results were ranked low to high based on sample SRW-1601 (see Figure 12). Median values are designated by horizontal lines. Labs #1 and #1 had low bias and #14 had consistent high bias. Lab #7 showed inconsistency across samples.

Ca precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.030, 0.041, and 0.026 meq L^{-1} for SRW-1601, SRW-1602, and for SRW-1603, respectively. Water Ca precision was excellent for all individual labs with only lab #4 exceeding 0.05 meq L^{-1} on sample SRW-1601. Across samples intra-lab *s* was less than 0.005 meq L^{-1} for lab #11. Three labs were flagged for poor precision on ALP Cycle 29 for Ca content.

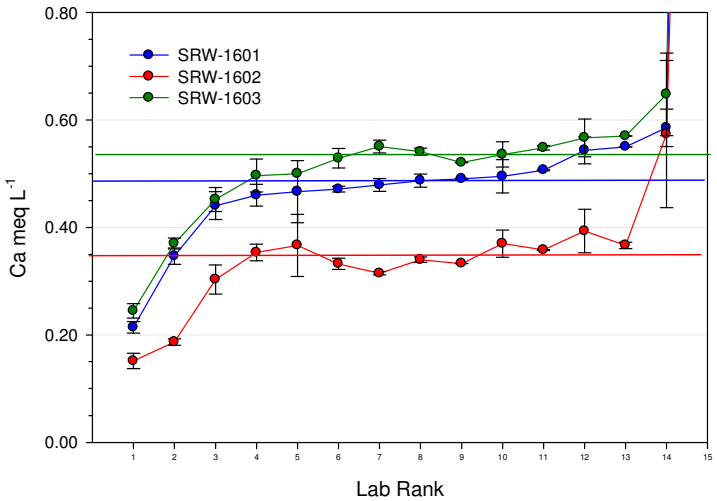


Figure 12. Water Ca distribution plots for SRW materials, ALP 2016 Cycle 29.

Announcements

- Several changes have been made in the ALP program for cycle 29. These include: the addition of a 4th proficiency material to the botanical program; update of the methods list to include soil water potentials and saturated paste K; and modification to the soil method listing to follow Modus library descriptions.

- The program has purchased a new soil jaw crusher for preparing PT soils. The Fritsch Jaw Crusher is capable of crushing heavy clayed soils to pass 0.8 mm sieve at a rate of 250 kg hr^{-1}. The use of this equipment will improve the processing of fine textured soils and minimize excessive grinding associated with disc and flail mill processing.

- ALP collected a four new proficiency soils in spring 2016 from Iowa, Illinois, Kansas and New Mexico representing a diverse range of textures and chemical properties.

- 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 August 1, 2016.

- 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@lamar.colostate.edu.

Summary

ALP 2016 Cycle 29 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 29. 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 29 Ship

June 26, 2016

"The recipe for perpetual ignorance is: be satisfied with your opinions and content with your knowledge".

— Elbert (Green) Hubbard (1902)

ALP
Agricultural Laboratory Proficiency Program