2016 Volume 2

28, August 2016

ALP Program Report

2016 Summer - Cycle 30

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

Special points of interest:

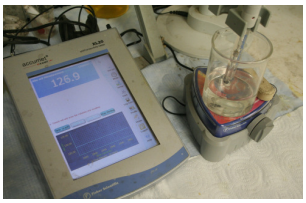
- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 30.
- Sixty-two Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.43 - 7.97.
- Cycle 30 soil M3-P ICP ranged from 15.3 to 147 mg kg^{-1} with MAD values ranging 1.9 - 13.5 mg kg^{-1} across the five soils.
- Lab results for Saturated Paste EC were highly consistent on soil SRS-1606, SRS-1608 and SRS-1609 .
- Botanical P, ranged from 0.241 - 0.814% with one of thirty-four labs noted for high bias.
- Botanical S results showed high consistency across the four samples for twenty-six of thirty labs for PT cycle 30 samples.
- Water Na content showed high consistency by thirteen of fifteen labs across all samples.

Inside this issue:

Soil Homogeneity Evaluation	2
2016 Cycle 30 Observations	2
SRS Results: pH, P, K, SOM	3
Sat. Paste EC	5
SRB NO3-N Results	5
SRB: N, P, K and S	6
SRW Results	8
Announcements	9

ALP Overview

The Agriculture Laboratory Proficiency (ALP) Program spring 2016 Round cycle 30 was completed August 12, 2016, with one-hundred eight 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. ALP is has completed ten years of service to Ag laboratory industry.



Data was compiled for each method (test code) and proficiency material. Data analysis of each material include: the number results; grand median value; median absolute deviation (MAD), (95% Confidence Interval); method intra-lab standard deviation (*s*); lab mean, and 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,

Proficiency Materials

Standard Reference Soils (SRS), materials used for the soils and environmental programs were: SRS-1606 a Kuma-Keith silt loam collected from Sherman Cty, KS; SRS-1607 a sandy loam collected from Prince Edward Island, PE; SRS-1608 a Pecos silty clay loam collected Chaves Cty, NM; SRS-1609 a Ruston fine sandy loam collected Pike Cty, MS; and SRS-1610 sand loam collected Sussex Cty, DE. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.43 - 7.97; NO_3-N 10.1 - 57.6 mg kg^{-1}; Bray P1 (1:10) 12.2 - 117 mg kg^{-1}; K NH_4oAc 95 - 764 mg kg^{-1}; SO_4-S 9.7 - 1076 mg kg^{-1}; Mehlich 3 P (ICP) 15.4 - 147 mg kg^{-1}; DTPA-Zn 0.30 - 1.71 mg kg^{-1}; SOM-LOI 1.62 – 3.46%; CEC 4.5 - 22.2 cmol kg^{-1}; clay 7.1 - 23.8% and Solvita CO_2 Burst Respiration 7.8 - 42.2 mg kg^{-1}.

Standard Reference Botanical (SRB) materials were: SRB-1605 a sugar beet leaf composite from Washington State; SRB-1606 corn leaf composite from Iowa; SRB-1607 Arugula leaves from California; and SRB-1608 potato petiole form Idaho. SRB material median analytes ranged: NO_3-N 349 - 14830 mg kg^{-1}; Dumas N 1.99 - 6.49%; total P 0.226 - 0.814%; total K 3.96 - 6.63%; total Ca 0.43 - 2.41%; total S 0.104 - 1.14 %, total B 4.6 - 44.3 mg kg^{-1}; and total Cd 0.07 - 1.25 mg kg^{-1}.

Standard Reference Water samples represent an agriculture water sample collected: SRW-1604 a water sample collected from a water source in the South Elkhorn river in NE; SRW-1605 from a Jackson, MN; and SRW-1606 is irrigation well Riverdale, WY. SRW median concentrations ranged: pH 7.71 - 8.07; EC 0.26 - 0.81 dSm^{-1}; SAR 0.19 - 0.80; Ca 1.36 - 6.03 mmolc L^{-1}; Mg 0.56 - 2.42 mmolc L^{-1}; SO_4 0.06 - 1.00 mmolc L^{-1} ; and NO_3 0.020 - 1.37 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 30 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 30, 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-1606	7.80	*0.028*	0.56	*0.024*	11.1	*0.9*	30.5	*1.2*
SRS-1607	5.74	*0.038*	0.64	*0.035*	17.9	*0.7*	73.4	*3.6*
SRS-1608	7.90	*0.058*	5.61	*0.212*	47.3	*1.7*	12.3	*1.1*
SRS-1609	5.30	*0.027*	0.40	*0.020*	8.5	*0.8*	31.4	*1.0*
SRS-1610	6.10	*0.091*	0.57	*0.018*	20.1	*0.7*	55.7	*1.7*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 30.

2016 Cycle 30 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 30 averaged 0.08 pH units. Within lab pH standard deviation was 0.12 pH units. Soil displacement CEC ranged 4.5 to 22.2 cmol kg^{-1} across the five soils. Soil Solvtia CO_2 respiration (test code 191) results were provided by eight laboratories with median results ranging from 7.8 - 42.2 mg kg^{-1} with an intra-lab precision, with s values averaging > 12 for three of five samples. Sample SRS-1608 had a saturated paste SAR of 5.96 with a within lab standard deviation of 0.19 and a MAD of 0.52. Soil ammonium acetate K (Test code 140) MAD values ranged 5 - 56 mg kg^{-1} and ammonium acetate Mg MAD values ranged 8.7 to 136 mg kg^{-1} for the five soils. These results for Mg were similar to cycles 29 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 0.078% nitrogen with intra-lab *s* of 0.047%, 0.074%. 0.074 and 0.087%, respectively. There was a greater inter-lab variability (MAD) in total potassium values than for combustion N, P, Ca, Mg, Na, or total S concentrations across all samples. Generally the arugula leaf sample SRB-1607 had higher level median N, P, K, Ca, S, Zn, and Cd relative to the other three botanical samples. One observation on Cycle 30, intra-lab variability was higher for K than all other macro 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 0.006 to 0.015 dSm^{-1}. NO_3-N values ranged from 0.020 - 1.37 molc L^{-1} across the three water samples with MAD values ranging 0.011 to 0.091 molc L^{-1}.

SRS Results - pH

Sixty-two laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.43 to 7.97. Lab results were ranked low to high based on sample SRS-1607 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1606, SRS-1607 and SRS-1608 showed good consistency across labs. Labs #39, #44, #46, #52, #56 and #61 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.

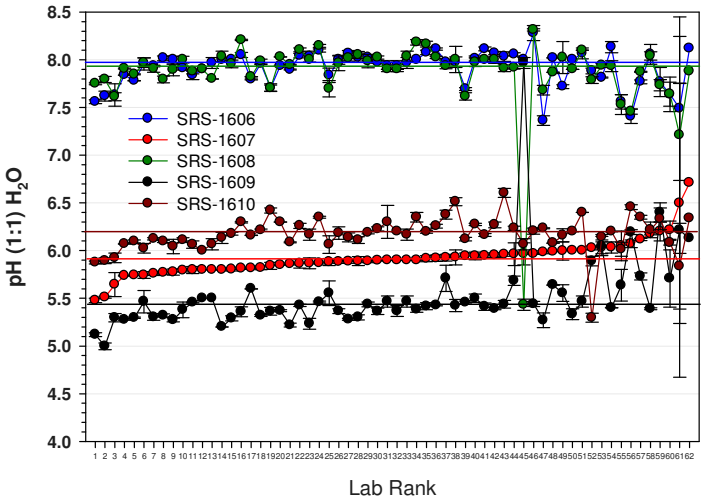


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2016 Cycle 30.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.020 to 0.035 pH units, the highest noted for SRS-1609. For specific labs poor precision was noted for SRS-1609 for six laboratories, exceeding by three times that noted for consensus intra-lab *s*. Specifically *s* for lab #56 exceeded 0.50 pH units for four of five soils. Soil SRS-1607 was the least variable with respect to intra-lab variance for cycle 30.

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 12.2 to 116 mg kg^{-1} PO_4-P; Olsen P 9.3 to 47 mg kg^{-1} P and M-3-P ICP ranged from 15.3 to 147 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1606, median Olsen P concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1608 and SRS-1610 associated with medium high P concentrations. Soils SRS-1609, lowest in concentration showed low intra-lab variability with a range of 8 - 20 ppm. Lab #2 was showed low bias on three samples. Labs #1, #6 #18, #25 and #28 were inconsistent across the five samples. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

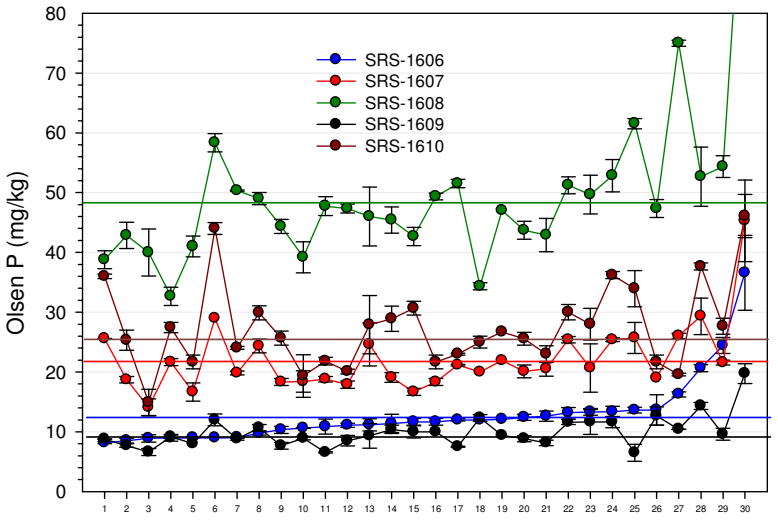


Figure 2. Olsen-P distribution plots for SRS materials, ALP 2016 Cycle 30.

Seven laboratories provided ALP results for Bray P1 (1:7) (test code 138), for the five soils with medians ranged from 69 to 190 PO_4-P mg kg^{-1}. Mehlich 1 median concentrations were 23.9 to 120 mg kg^{-1} PO_4-P reported by four labs. Strong Bray (P2) was reported by eight laboratories ranging from 69 to 190 mg kg^{-1} PO_4-P with the highest P concentration noted for SRS-1606.

SRS - Potassium

Forty-two laboratories provided ALP results for soil K (test code 141) results. These were ranked low to high based on sample SRS-1607 (see Figure 3). Soils SRS-1607 and SRS-1608 were the most inconsistent across labs. Labs #1 - #2 showed low bias on all five soils. Labs #3, #13, #23, and #38 were inconsistent across the five soils for Mg. 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-1610, with a median intra-lab value of 2.3 mg kg^{-1} Kg and highest for SRS-1606 with a value of 14 mg kg^{-1} Kg. Potassium within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 150 mg kg^{-1} Kg. Precision was poor (based on intra-lab *s*) for labs #2, #8, #31, and #40 which exceeded 35 mg kg^{-1} K on SRS-1606; and labs #10 and #26 the value exceeded 12 mg kg^{-1} K for SRS-1610. Poor precision is attributed to extraction and/or analysis instrument operation.

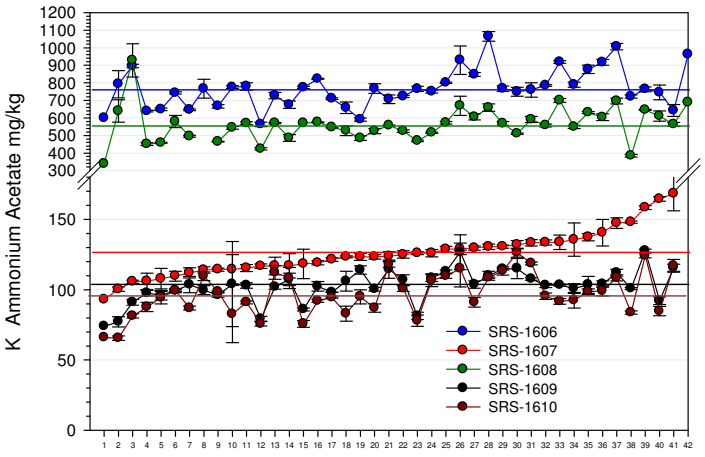


Figure 3. Extractable K distribution plots for SRS materials, ALP 2016 Cycle 30.

SRS SOM-LOI

Forty-four laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.62 to 3.49%. Results were ranked based on sample SRS-1606 (see Figure 4). Labs #43 and #44 were noted having high bias on four of five soils. Sample SRS-1608 shows great inconsistency likely associated with high gypsum content. Bias was noted in eight lab results. Source of bias is likely related to muffle furnace operation and/or method compliance.

SOM-LOI precision across the five materials indicates high intra-lab precision, with median *s* values ranging from 0.07 to 0.49% SOM-LOI, the highest for SRS-1608. Across labs *s* values for SRS-1606 ranged from 0.01 - 0.32 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #1, #17, and #25, exceeded 0.12 for three of five soils. Lab #8 exceeded 0.50 % SOM on soil SRS-1608 for ALP cycle 30. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

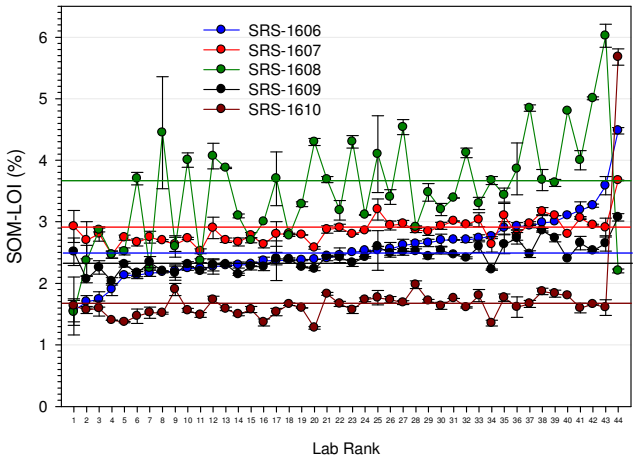


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2016 Cycle 30.

SRS - Saturated Paste EC

Twenty-five laboratories provided ALP results for Saturated paste EC (test code 103) results. These were ranked low to high based on sample SRS-1606 (see Figure 5). Soil SRS-1606 and SRS-1607 were the lowest in concentration and the most consistent across labs. Soil SRS-1610 was highly erratic across labs. Across soils, labs #1 #5, #17 and #23 were inconsistent across soils and #24 had high bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

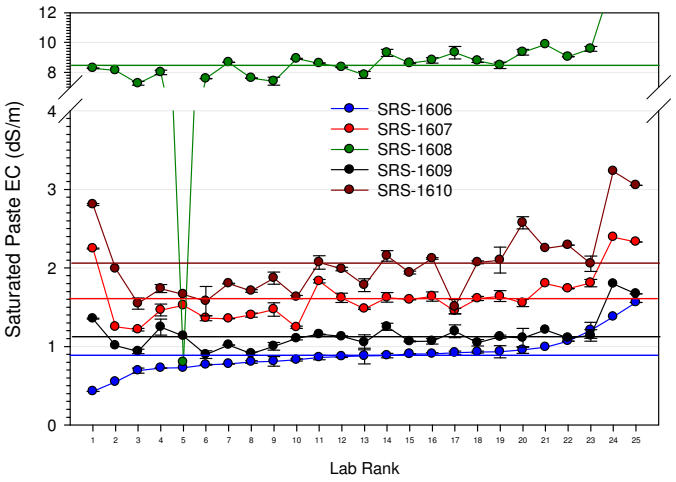


Figure 5. Soil Saturated Paste EC distribution plot, ALP 2016 Cycle 30.

Saturated Paste EC median intra-lab *s* values were lowest for ALP soil SRS-1606 with an intra-lab median value of 0.04 dSm^{-1} and highest for SRS-1610 with a value of 0.08 dSm^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1607. Intra-lab precision was poor for labs #4, #19, and #23 on three of five soils. Poor precision maybe associated with Saturated Paste EC extraction and/or conductivity instrument operation.

SRB Nitrate-Nitrogen

Twenty-three laboratories provided ALP results for NO_3-N by cadmium Reduction (test code 202 203 and 204). New for cycle 30 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-1605 (see Figure 6). The data plot shows labs #1 #2 had low bias all four botanical samples whereas, lab #23 had high bias. Labs #8, #14, and #19 were inconsistent.

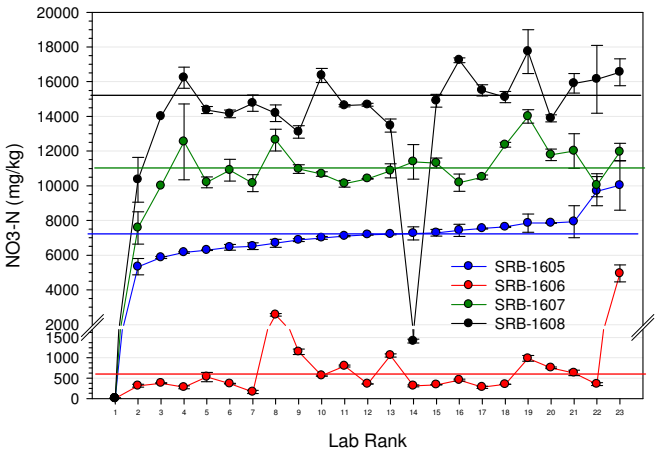


Figure 6. Nitrate distribution plots for SRB materials, ALP 2016, Cycle 30.

Botanical NO_3-N (test code 202) results for cycle 30 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 42 to 740 mg kg^{-1} for the four samples. Individual lab NO_3-N by Cadmium Reduction (test code 202) intra-lab *s* values for SRB-1605 ranged from 11 – 1425 mg kg^{-1}; SRB-1606 ranged from 2 - 480 mg kg^{-1}, and SRB-1607 ranged from 20 – 2200 mg kg^{-1}. Lab #24 had consistently high standard deviations for all samples , > 500 ppm. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Twenty-eight laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and seven labs for TKN (Test code 209) for cycle 30. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1606 (see Figure 7). It is note worthy that TKN was lower than Dumas for sample all four samples. Labs #1 showed low bias for Dumas N for three samples, whereas labs #27 and #28 showed inconsistency across the all four botanical samples.

Dumas N and TKN results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-1605, ranged 0.003 to 0.22% N, SRB-1606 ranged from 0.01 to 0.29% N, SRB-1607 ranged from 0.005 to 0.27 % N, and SRB–1608 from 0.013 to 0.38 % N. Lab #1 had consistently high standard deviations. Lab TKN *s* values for SRB-1605 ranged from 0.007 to 0.24% TKN, SRB-1606 ranged from 0.011 to 0.44% TKN, SRB-1607 ranged from 0.038 to 0.95% TKN nitrogen and SRB-1608 ranged from 0.017 to 0.13% TKN nitrogen.

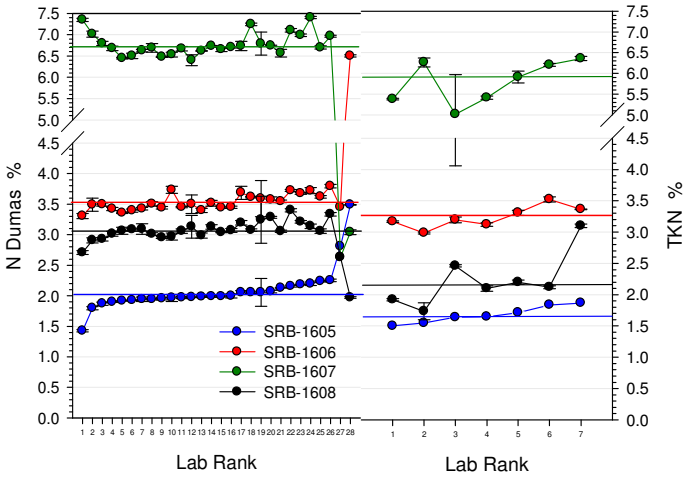


Figure 7. N distribution plots for SRB materials, ALP 2016 Cycle 30.

SRB - Potassium

Thirty-four 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-1606 (see Figure 8). Laboratories #1 and #2 showed low bias. Labs #3, #9, #21 and #32 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 0.019 to 0.37 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1606, ranged from 0.003 to 0.87 % K; SRB-1607, 0.006 — 0.85 % K; SRB-1608, 0.011 - 0.70 % K; and SRS-1609, 0.032 to 0.51 % K. Five labs had high standard deviations exceeding 0.20 %K for SRB-1603. Five labs were flagged for poor K precision.

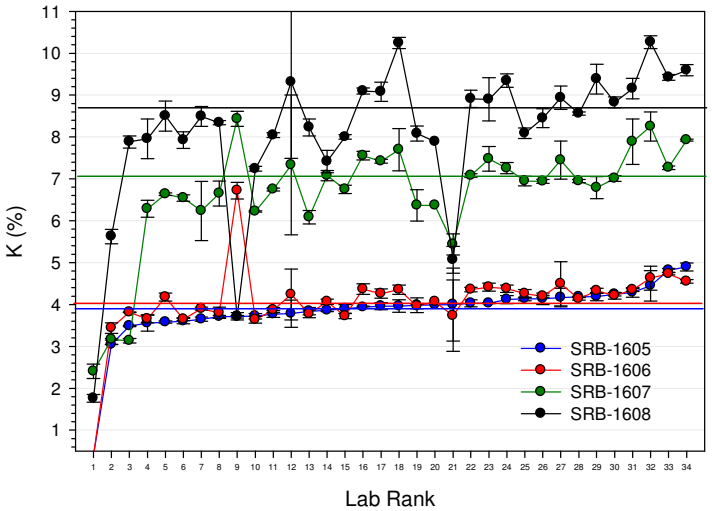


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2016 Cycle 30.

SRB - Phosphorus

Thirty-nine laboratories provided ALP results for cycle 30 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-1605 (see Figure 9). Consistent high bias was noted for labs #37 and #39. Labs #2, and showed inconsistency. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

Botanical P results indicate very high precision, with intra-lab standard deviation (*s*) values ranged 0.044 to 0.091 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1605; ranged from 0.003 - 0.030 % P; SRB-1606 ranged from 0.002 – 0.041 % P and SRB-1607 0.001 - 0.083 % P; and SRB-1608 0.002 - 0.042 % P. Labs #17 had a high standard deviations exceeding 0.010 % P for three of four botanical samples. Four labs were flagged for poor precision for botanical P.

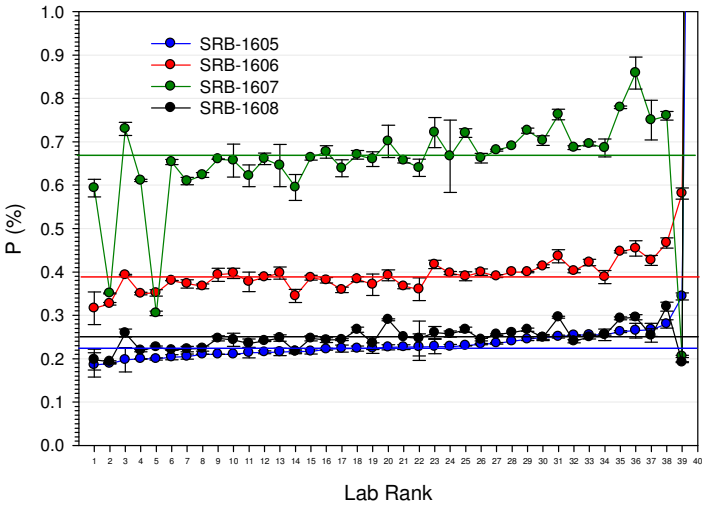


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2016 Cycle 30.

SRB - Sulfur

Thirty 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-1605 (see Figure 10). Labs #1 showed low bias on all four samples. Labs #27, #28, #29 and #30 were inconsistent and data suggests that sampels may have switched during analysis. 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 0.013 to 0.074 % S for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1605; ranged from 0.001 - 0.40 % S; SRB-1606 ranged from 0.0602– 0.040 % S; SRB-1607 0.003 - 0.147 % S; and SRB-1608 0.001 - 0.055 % S. Labs #13 and #27 had consistently high standard deviations for two of four botanical samples. For ALP cycle 30 three labs were flagged for poor S precision across the four botanical samples.

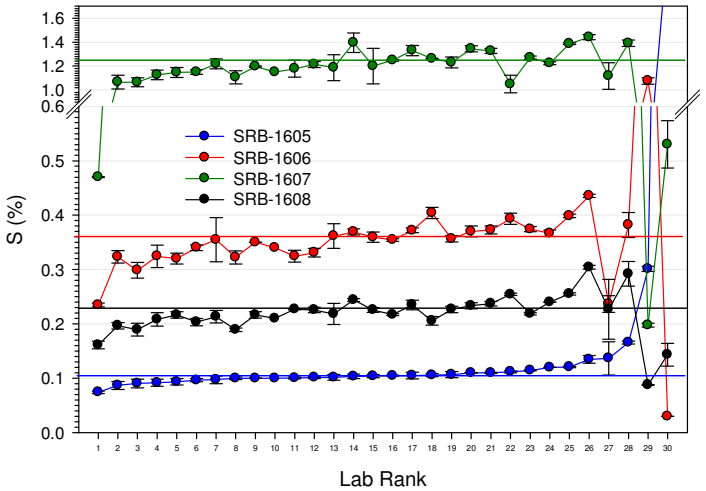


Figure 10. Sulfur distribution plots for SRB materials, ALP 2016 Cycle 30.

SRW - Water EC

Fifteen laboratories provided ALP results for water EC (test code 302). Ranking lab results low to high based on sample SRW-1604 (see Figure 11). Labs #1 and #2 indicated consistent low bias on all three samples. Labs #13 and #14 showed high bias consistently across the three samples. Source of bias is likely associated with EC probe performance and/or calibration.

EC precision across the three water materials indicates good high precision, with intra-lab median Std values of 0.003, 0.010 and 0.031 dSm^{-1}, respectively. Precision for sample SRW-1604 was the most consistent across the fifteen participating laboratories. Across water samples poor precision was noted for one laboratory. Specifically intra-lab the s values for lab #8 exceeded 0.20 dSm^{-1} on SRW-1605 and SRW-1606. Highest precision was noted for lab #4 with intra-lab s values of < than 0.005 dSm^{-1}.

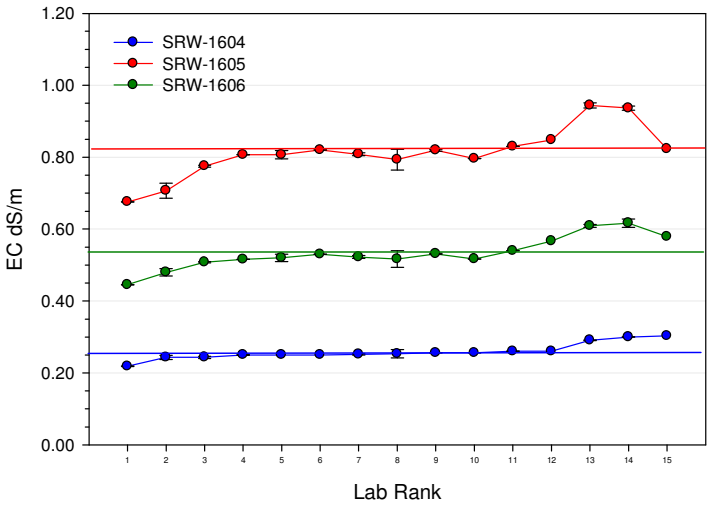


Figure 11 . Water EC distribution plots for SRW materials, ALP 2016 Cycle 30.

SRW - Na Results

Fifteen laboratories provided ALP results for water Na (test code 305). Lab results were ranked low to high based on sample SRW-1604 (see Figure 12). Median values are designated by horizontal lines. Labs #1 had low bias and #15 had consistent high bias. Lab #7 showed inconsistency across samples.

Na precision across the three water solution matrices indicates excellent precision, with intra-lab s values of 0.043, 0.026, and 0.066 meq L^{-1} for SRW-1604, SRW-1605, and for SRW-1606, respectively. Water Na precision was excellent for all individual labs with only lab #1 exceeding 0.10 meq L^{-1} on two of three samples. Across samples intra-lab s was less than 0.001 meq L^{-1} for lab #13. Three labs were flagged for poor precision on ALP Cycle 30 for Na content.

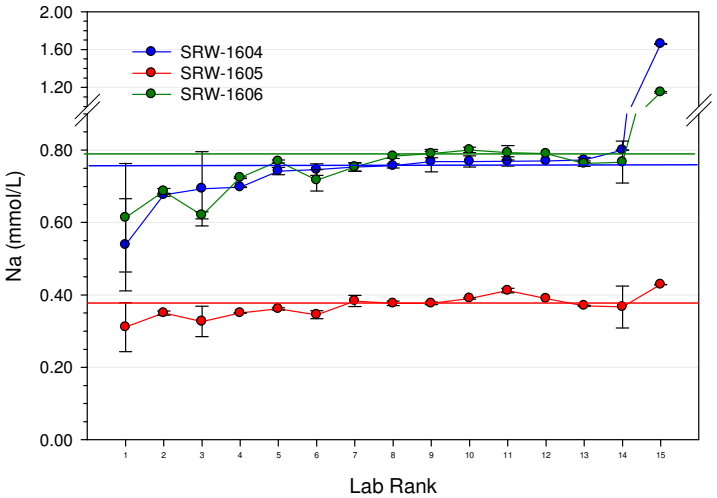


Figure 12. Water Na distribution plots for SRW materials, ALP 2016 Cycle 30.

Announcements

- The new soil jaw crusher has been placed on line a 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 systems.

- FOR soils method SOM-LOI, we have subdivided the method into two classes SOM–LOI Regressed (method code 183) and SOM-LOI Un-regressed (method code 184) due to difference noted by laboratories in the US Midwest.

- ALP collected two new proficiency soils this summer from Idaho and six from Alberta Canada 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 September 19, 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 is celebrating ten years of service with the completion of cycle 30. Since 2006 we have completed the analysis of 150 soils, 92 plant samples and 90 water samples providing comprehensive proficiency data on inter and intra laboratory performance across a range of analytical methods.

We thank all laboratories who participated in cycle 30. 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 31 Ship

September 19, 2016

"Service to others is the rent you pay for your room here on earth".

— Muhammad Ali, 1978

ALP
Agricultural Laboratory Proficiency Program