2016 Volume 3

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2016 Volume 3

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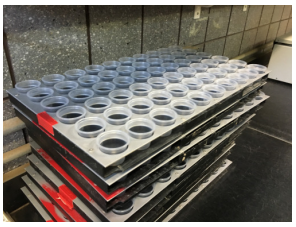
ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 31.
- Sixty-two Laboratories provided soil pH (1:1) H_2O results and medians ranged from 4.60 - 6.65.
- Cycle 31 soil M3-P Spec ranged from 7.0 to 106 mg kg^{-1} with MAD values ranging 0.9 - 9.3 mg kg^{-1} across the five soils.
- Lab results for Mehlich-3 Zn were inconsistent on four of five proficiency soils for cycle 31.
- Botanical P, ranged from 0.140 - 0.382% with one of thirty-eight labs noted for high bias.
- Botanical B results showed high consistency across the four samples for twenty-eight of thirty-three labs for PT Cycle 31.
- Water EC content showed very high consistency by fifteen of seventeen labs across all samples.

The Agriculture Laboratory Proficiency (ALP) Program spring 2016 Round Cycle 31 was completed November 18, 2016, with one-hundred eight labs enrolled from the United States, Canada, South Africa, Italy, Serbia, Ukraine, Philippines and Guatemala. 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

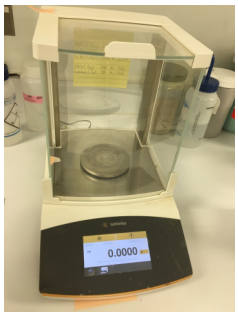
Standard Reference Soils (SRS) materials utilized for cycle 31 were: SRS-1611 a Osco silt loam collected from Ogle Cty, IL; SRS-1612 a Calloway silt loam collected from St Francis, AR; SRS-1613 a sandy loam collected Middlesex Cty, ON, Canada; SRS-1614 a Palouse silt loam collected Walla Walla Cty, WA; and SRS-1615 Ade loamy fine sand collected Vigo Cty, IN. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 4.60 - 6.65; NO_3-N 25.2 - 67.3 mg kg^{-1}; Bray P1 (1:10) 6.2 - 107 mg kg^{-1}; K NH_4OAc 66 - 617 mg kg^{-1}; SO_4-S 5.6 - 21 mg kg^{-1}; Mehlich 3 P (ICP) 7.2 - 117 mg kg^{-1}; DTPA-Zn 0.50 - 2.51 mg kg^{-1}; SOM-LOI 1.78 – 4.41%; CEC 5.2 - 18.4 cmol kg^{-1}; clay 9.3 - 25.2% and Solvita CO_2 Burst Respiration 12 - 90 mg kg^{-1}.

Standard Reference Botanical (SRB) materials for Cycle 31 were: SRB-1609 a grape petiole composite from CA; SRB-1610 corn stalk composite from CT; SRB-1611 buck wheat grain from ND; and SRB-1612 citrus leaves from CA. SRB material median analytes ranged: NO_3-N 33 - 6600 mg kg^{-1}; Dumas N 0.94 - 2.27%; total P 0.14 - 0.38%; total K 0.53 - 3.82%; total Mg 0.21 - 0.56%; total S 0.08 - 0.24 %, total Zn 15.1 - 81.9 mg kg^{-1}; and total Cd 0.007 - 0.28 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-1607 a water sample collected from a water source near Cut Bank, MT; SRW-1608 from a Ashton, ID; and SRW-1609 is irrigation Fremont WY. SRW median concentrations ranged: pH 8.04 - 8.56; EC 0.25 - 0.93 dSm^{-1}; SAR 0.47 - 7.35; Ca 0.63 - 4.11 mmolc L^{-1}; Mg 1.47 - 4.07 mmolc L^{-1}; SO_4 0.47 - 7.35 mmolc L^{-1}; and NO_3 0.011 - 0.063 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 31 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 31, 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-1611	6.10	*0.01*	0.46	*0.033*	15.9	*0.5*	46.6	*1.4*
SRS-1612	4.97	*0.03*	0.34	*0.019*	4.2	*0.5*	37.6	*1.2*
SRS-1613	6.51	*0.02*	0.34	*0.022*	8.7	*0.6*	26.8	*0.8*
SRS-1614	4.46	*0.04*	0.69	*0.027*	54.2	*1.3*	71.8	*2.1*
SRS-1615	5.69	*0.03*	0.29	*0.012*	7.3	*0.7*	24.4	*0.9*

[1] Statistics based on five soil replicates, each analyzed in triplicate ALP Cycle 31.

2016 Cycle 31 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 31 averaged 0.065 pH units across the soils. Within lab pH standard deviation was 0.05 pH units. Soil displacement CEC ranged 5.2 to 19.2 cmol kg^{-1} across the five soils. Soil Solvtia CO_2 respiration (test code 191) results were provided by six laboratories with median results ranging from 12 - 90 mg kg^{-1} with MAD values averaging >20 for three of five samples. Sample SRS-1615 had a large discrepancy in M3-P values: Spec 24 ppm and ICP of 64 mg kg^{-1}, which generally similar M3-P values. Soil ammonium acetate K (Test code 140) MAD values ranged 6 - 34 mg kg^{-1} and ammonium acetate Mg MAD values ranged 9 to 43 mg kg^{-1} for the five soils. These results for K and Mg were improved relative to cycle 30 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 0.058% nitrogen with intra-lab *s* of 0.032%, 0.048%, 0.027% and 0.034%, respectively. There was a greater inter-lab variability (MAD) in total boron values than for combustion N, P, K, Ca, Mg, Zn, Mn, Fe or total Cu concentrations across all samples. Generally the buck wheat grain sample SRB-16011 had lower median concentrations of NO_3-N, K, Ca, Mg, Na, S, As, Ba and Sr relative to the other four botanical samples. One observation on Cycle 31, intra-lab variability was higher for S than all other macro elements for all four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.002 to 0.014 dSm^{-1}. NO_3-N values ranged from 0.011 - 0.063 molc L^{-1} across the three water samples with MAD values ranging 0.007 to 0.014 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 - 6.65. Lab results were ranked low to high based on sample SRS-1611 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1611, SRS-1613 and SRS-1615 showed good consistency across labs. Labs #1, #2, #3, #19, #58 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.

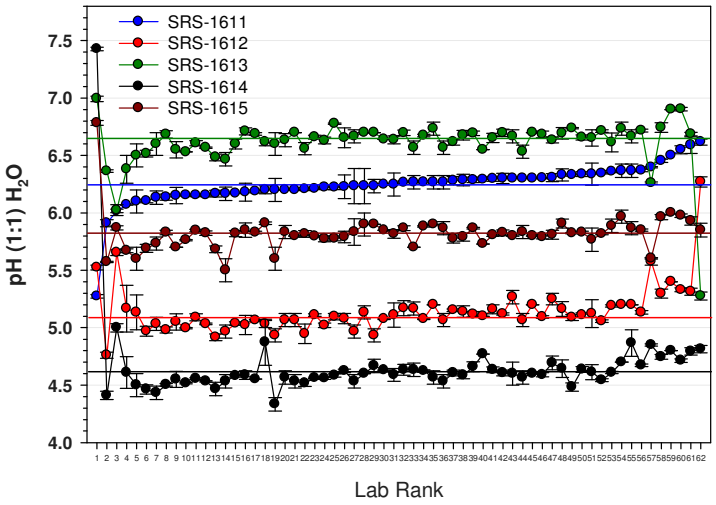


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2016 Cycle 31.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.021 to 0.032 pH units, the lowest noted for SRS-1615. For specific labs poor precision was noted for SRS-1612 for six laboratories, exceeding by three times that noted for consensus median intra-lab *s*. Specifically *s* for lab #27 exceeded 0.05 pH units for four of five soils. Soil SRS-1614 was the least variable with respect to intra-lab variance for Cycle 31.

SRS - Phosphorus: Bray P1, Bray P2, Olsen, Modified Morgan, M1, and M3

Bray P1 results were reported by twenty-four labs. M3-P ICP was reported by 33 labs. Median soil M3-P values ranged from 7.2 - 117 mg kg^{-1} PO_4-P; Olsen P 5.8 to 63 mg kg^{-1} P and Bray P2 ranged from 10.7 to 193 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1611, median M3-P ICP concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1614 and SRS-1615 associated with the highest P concentrations. Soils SRS-1612, lowest in concentration, showed low intra-lab variability with a range of 0.1 - 3.6 ppm. Lab #1 showed low bias on three samples. Labs #3, #8 #17, #22, #27, #32 and #33 were inconsistent across the five soils. Inconsistency is likely related to extraction, analysis instrument and/or method compliance.

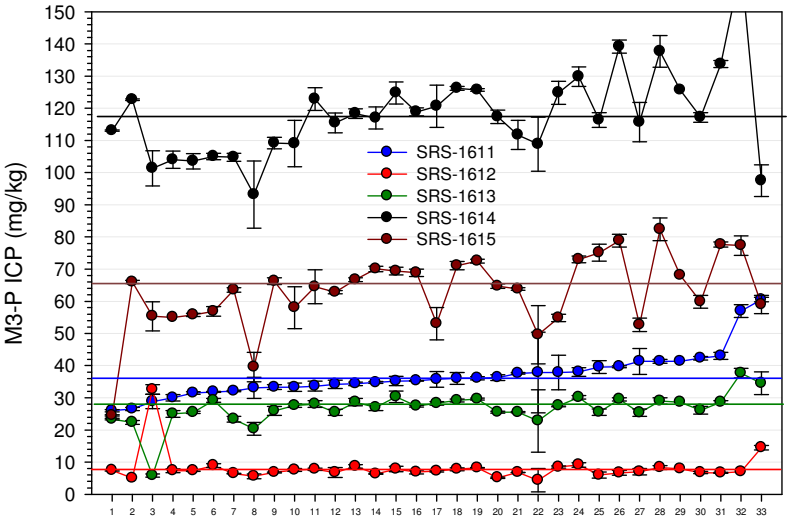


Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2016 Cycle 31.

Seven laboratories provided ALP results for Mehlich 1 P, with medians ranging from 3.8 to 57 mg kg^{-1} PO_4-P . Bray P1 (1:7) median concentrations were 6 to 90 mg kg^{-1} PO_4-P reported by five labs. Modified Morgan was reported by four laboratories ranging from 1 to 8 mg kg^{-1} PO_4-P with the highest concentration noted for SRS-1614.

SRS - Potassium

Forty-four laboratories provided ALP results for soil K (test code 141) results. Results were ranked low to high based on sample SRS-1611 (see Figure 3). Soils SRS-1613 and SRS-1615 were the most inconsistent across labs. Lab #44 showed high bias on 4 of 5 five soils. Labs #6, #9, #17, #18, #26, #36 and #43 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-1612, with a median intra-lab value of 1.7 mg kg^{-1} Kg and highest for SRS-1614 with a value of 9 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} K. Precision was poor (based on intra-lab *s*) for labs #23, #25, #40, and #42 which exceeded 10 mg kg^{-1} K on SRS-1611; and labs #25, #29, and #36 the value exceeded 20 mg kg^{-1} K for SRS-1613. Poor precision is attributed to extraction and/or analysis instrument operation.

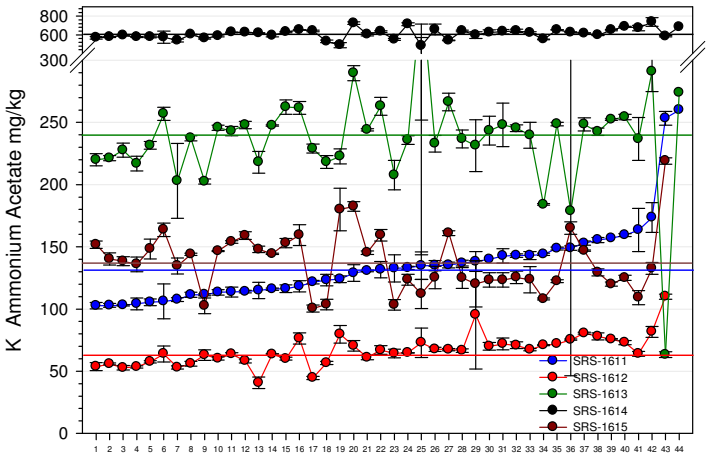


Figure 3. Extractable K distribution plots for SRS materials, ALP 2016 Cycle 31.

SRS SOM-LOI

Fifty laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.78 to 5.47%. Results were ranked based on sample SRS-1611 (see Figure 4). Labs #1 and #2 were noted having high bias on two of five soils. Sample SRS-1614 shows moderate inconsistency likely associated with the highest SOM 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 0.04 to 0.08% SOM-LOI, the highest for SRS-1614. Across labs, *s* values for SRS-1613 ranged from 0.01 - 0.35 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #1, #9, #13, #14, #23 and #37, exceeded 0.20 % SOM for SRS-1611. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

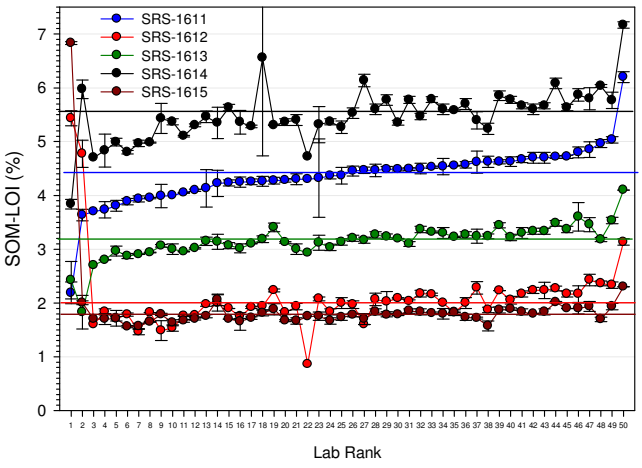


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2016 Cycle 31.

SRS - Mehlich 3 Zn

Twenty-eight laboratories provided ALP results for Mehlich 3 Zinc (M3-Zn, test code 165). Results were ranked low to high based on sample SRS-1611 (see Figure 5). Soil SRS-1612 was the lowest in concentration and the most consistent across labs. Soil SRS-1613 was highly erratic across labs. Across soils, labs #7 #18, #22 and #27 were inconsistent across soils and #1 and #2 had low bias. Source of this inconsistency is likely related to instrument calibration or method compliance.

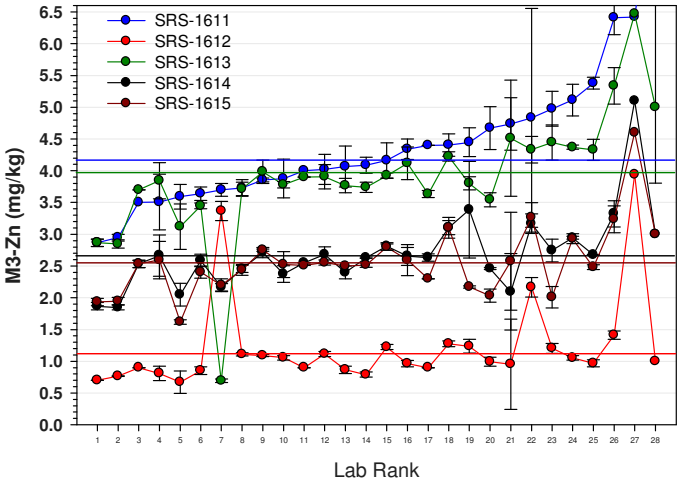


Figure 5. Soil M3-Zn distribution plot, ALP 2016 Cycle 31.

M3-Zn median intra-lab *s* values were lowest for ALP soil SRS-1613 with an intra-lab median value of 0.006 dSm^{-1} and highest for SRS-1611 with a value of 0.016 dSm^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1611. Intra-lab precision was poor for labs #4, #21, and #22 on three of five soils. Poor precision maybe associated with M3 extraction and/or ICP-OES instrument operation.

SRB Nitrate-Nitrogen

Twenty-seven laboratories provided ALP results for NO_3-N by cadmium reduction (test code 202 203 and 204). New for Cycle 31 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-1609 (see Figure 6). The data plot shows labs #26 and #27 had high bias for SRB-1609. Labs #3, #19, #23, and #25 were inconsistent.

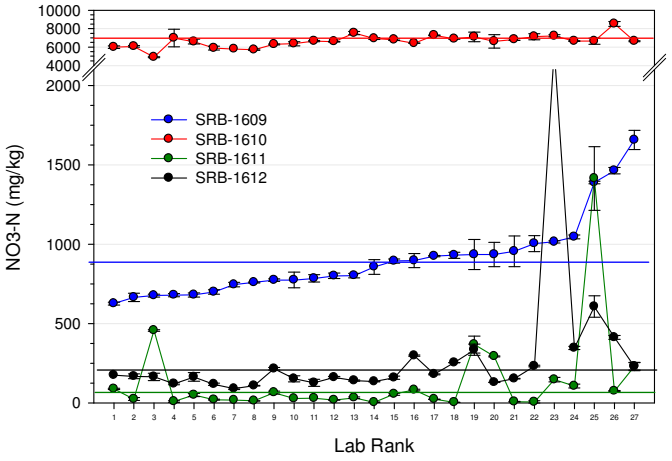


Figure 6. Nitrate distribution plots for SRB materials, ALP 2016, Cycle 31.

Botanical NO_3-N (test code 202) results for Cycle 31 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 5 to 115 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-1609 ranged from 2.8 – 96 mg kg^{-1}; SRB-1610 ranged from 25 - 950 mg kg^{-1}, SRB-1611 ranged from 0.5 – 200 mg kg^{-1} and SRB-1612 ranged from 1.4 - 67 mg kg^{-1} Lab #25 had consistently high standard deviations for two of three samples. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty-two laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and nine labs for TKN (Test code 209) for Cycle 31. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1609 (see Figure 7). It is note worthy that TKN was lower than Dumas for two of four samples. Labs #31 showed high bias for Dumas N for three samples, whereas labs #6 and #12 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-1609, ranged 0.004 to 0.095% N, SRB-1610 ranged from 0.002 to 0.136% N, SRB-1611 ranged from 0.002 to 0.092 % N, and SRB–1612 from 0.003 to 0.125 % N. Lab #11 had consistently high standard deviations. Lab TKN *s* values for SRB-1609 ranged from 0.002 to 0.076% TKN, SRB-1610 ranged from 0.003 to 0.087% TKN, SRB-1611 ranged from 0.011 to 0.170% TKN nitrogen and SRB-1612 ranged from 0.011 to 0.145% TKN nitrogen.

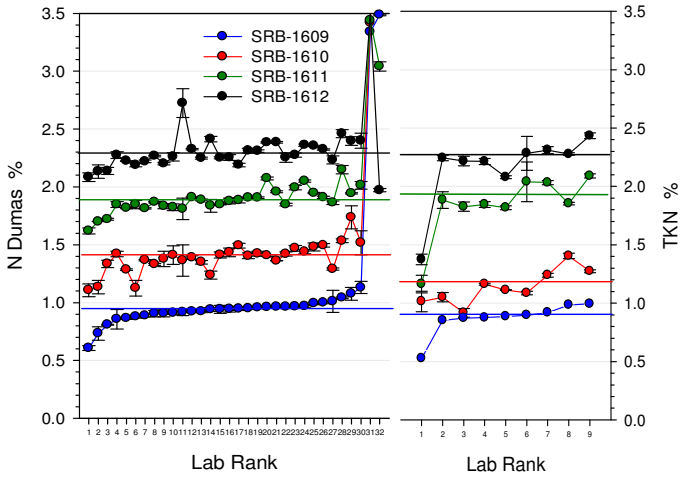


Figure 7. N distribution plots for SRB materials, ALP 2016 Cycle 31.

SRB - Potassium

Thirty-eight 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-1609 (see Figure 8). Laboratories #37 and #38 showed high bias. Labs #1, #9, #10 #18 and #35 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical K results indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 0.016 to 0.076 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-1609, ranged from 0.010 to 0.59 % K; SRB-1610, 0.005 — 0.41 % K; SRB-1611, 0.005 - 0.18 % K; and SRS-1612, 0.003 to 0.11 % K. Five labs had high standard deviations exceeding 0.20 %K for SRB-1610. Five labs were flagged for poor K precision.

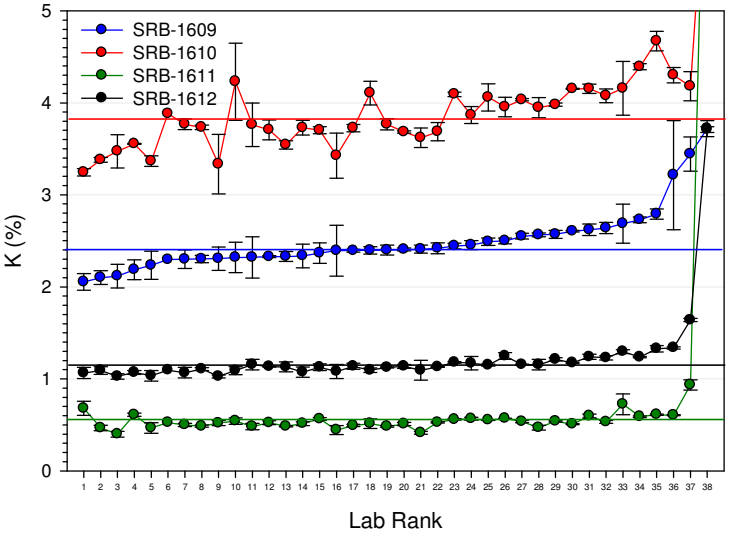


Figure 8. Potassium (code 213) plots for SRB materials, ALP 2016 Cycle 31.

SRB - Phosphorus

Thirty-eight laboratories provided ALP results for Cycle 31 phosphorus (P) combined (test codes 212). 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-1609 (see Figure 9). Consistent high bias was noted for labs #37 and #38. Labs #3 and #4 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 median intra-lab standard deviation (*s*) values ranged 0.003 to 0.009 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-1609; ranged from 0.001 - 0.10 % P; SRB-1610 ranged from 0.001 – 0.026 % P and SRB-1611 0.001 - 0.041 % P; and SRB-1612 0.002 - 0.034 % P. Labs #13 had a high standard deviation exceeding 0.025 % P for three of four botanical samples. Five labs were flagged for poor precision for botanical P.

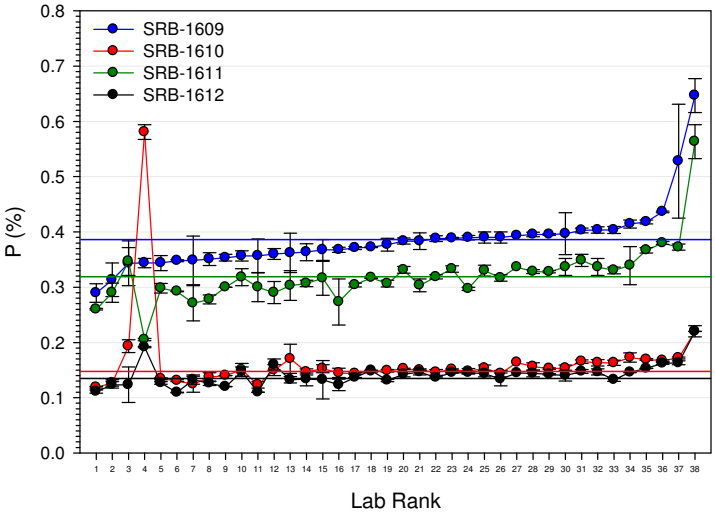


Figure 9. Phosphorus distribution plots for SRB materials, ALP 2016 Cycle 31.

SRB - Boron

Thirty-three laboratories provided ALP results for boron (B) (test code 219). Result median values are designated by horizontal lines for each botanical material and individual labs results are ranked low to high based on sample SRB-1609 (see Figure 10). Labs #1 and #2 showed low bias on all samples. Labs #23, #32, and #33 were inconsistent and data suggests that samples may have switched during analysis. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical B results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.88 to 1.57 mg kg^{-1} B for across the four botanical samples. Individual lab intra-lab *s* values for SRB-1609; ranged from 0.10 - 8.4 mg kg^{-1} B; SRB-1610 ranged from 0.03 – 1.7 % S; SRB-1611 0.05 - 2.3 mg kg^{-1} B; and SRB-1612 0.16 - 7.7 mg kg^{-1} B. Labs #5 and #11 had consistently high standard deviations for two of four botanical samples.

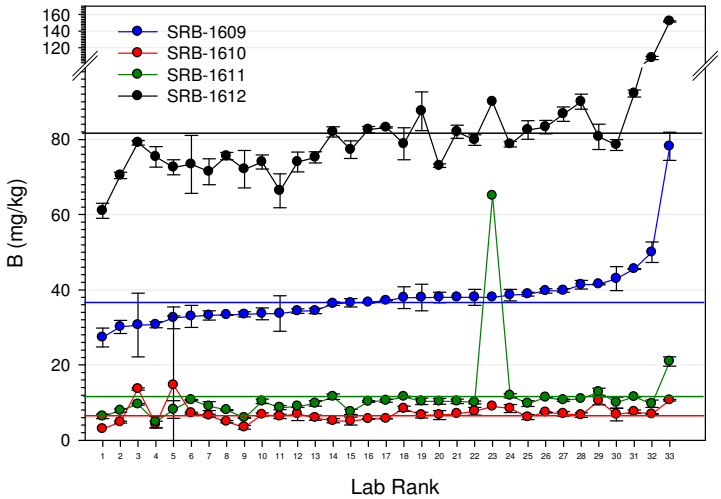
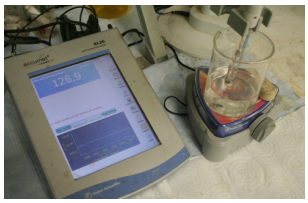


Figure 10. Boron distribution plots for SRB materials, ALP 2016 Cycle 31.

SRW - Water EC



Seventeen laboratories provided ALP results for water EC (test code 302). Lab result were ranked low to high based on sample SRW-1607 (see Figure 11). Lab #1 indicated consistent low bias on all three samples. Lab #17 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 0.002, 0.001 and 0.004 dSm^{-1}, respectively. Precision for sample SRW-1608 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 #12 exceeded 0.004 dSm^{-1} on SRW-1609. Highest precision was noted for lab #5 with intra-lab *s* values of < than 0.002 dSm^{-1}.

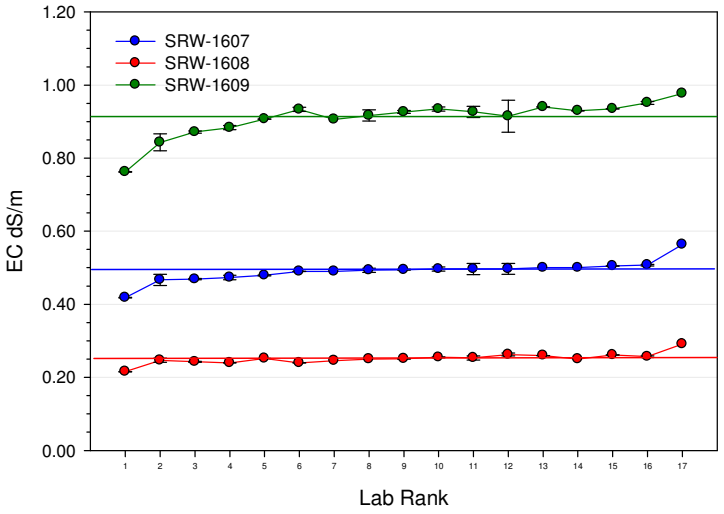


Figure 11 . Water EC distribution plots for SRW materials, ALP 2016 Cycle 31.

SRW - Ca Results

Fifteen laboratories provided ALP results for water Na (test code 303). Lab results were ranked low to high based on sample SRW-1609 (see Figure 12). Median values are designated by horizontal lines. Lab #3 had high bias. Labs #1 and #14 showed inconsistency across samples.

Ca precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.031, 0.009, and 0.027 meq L^{-1} for SRW-1607, SRW-1608, and for SRW-1609, respectively. Water Ca precision was excellent for all individual labs with only lab #15 exceeding 0.12 meq L^{-1} on two of the three samples. Across samples intra-lab *s* was less than 0.027 meq L^{-1} for lab #9. Four labs were flagged for poor precision on ALP Cycle 31 for Ca content.

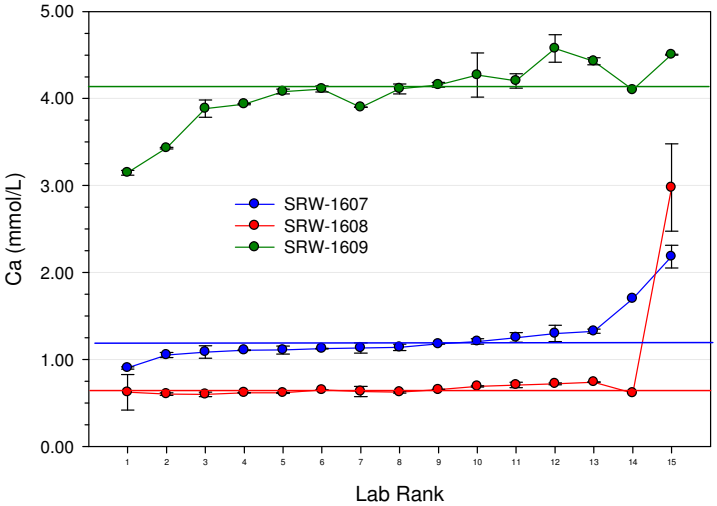


Figure 12. Water Ca distribution plots for SRW materials, ALP 2016 Cycle 31.

Announcements

- The new soil jaw crusher has been installed for 2017 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.

- Collaborative Testing Services will be initiating a new proficiency testing program for greenhouse media and nutrient solutions in February 2017. The program will be based on three proficiency cycles annually covering standard inorganic analytes (pH, EC, NO_3-N, NH_4-N, PO_4-P, SO_4-S, K, Ca, Mg, Na, Zn, Mn, Fe, Cu, Mo). Program specifics will be announced pending finalization of the program outline.

- ALP collected new proficiency soils this fall, with six from Alberta, Canada; two from Montana, and one Indiana 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 data and evaluate on a yearly basis. A sub committee is to develop a program outline March 1, 2017.

- 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 31. Since 2006 we have completed the analysis of 155 soils, 96 plant samples and 93 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 31. As the coordinators of the program we appreciate your consideration and participation in the proficiency program. We continually seek feedback from laboratory participants to improve the service and function of the program. Please forward all comments to info@cts-interlab.com.

Cycle 32 Ship

March 10, 2017

"Discovery consists of seeing what everybody has seen, and thinking what nobody has thought."

— I.J. Good, The Scientist Speculates , 1963

ALP
Agricultural Laboratory Proficiency Program