2020 Volume 3

1 December 2020

ALP Program Report

2020 Fall - Cycle 43

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ALP Overview

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 43.
- Fifty-nine Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.70 - 7.28.
- Soil M3-P ICP for Cycle 43 ranged from 28.6 to 218 mg kg^{-1} with MAD values ranging 1.6 - 29 mg kg^{-1} across the five soils.
- Soil M3-K values ranged from 78 - 429 mg kg^{-1} for the five ALP soils of PT Cycle 43.
- Botanical N by combustion was reported by 34 labs, with nine labs showing high bias values on the two materials with > 6% N for Cycle 43.
- Botanical K, ranged from 0.62 - 3.28% with four of forty labs noted for inconsistency across the four samples.

Inside this issue:

The Agriculture Laboratory Proficiency (ALP) Program fall 2020 Round Cycle 43 was completed December 1, 2020, with results from one-hundred seven labs enrolled from the US, Canada, South Africa, Italy, Ukraine, Guatemala and Philippines. Proficiency samples consisted of five soils, four botanical and three water samples. Analytical methods are base on those published by AOAC, regional soil work groups, the Soil Plant Analysis Council and Forestry Canada. ALP has completed fifteen 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 standard deviation. Additional information on methods and statistical protocols can be found at the program web site.

Proficiency Materials

Standard Reference Soils (SRS) materials utilized for Cycle 43 were: SRS-2011 a Nicolet clay, collected in Badger Cty, IA; SRS-2012 silt loam collected near Coaldale, AB, Canada; SRS-2013 an Abernathy silt loam collected in Limestone Cty, AL; SRS-2014 is a Marlette loam collected in Clinton Cty MI; and SRS-2015 a Mukilteo variant muck collected in Skagit Cty, WA. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.70 - 7.28; NO_3-N 49.6 - 138 mg kg^{-1}; Bray P1 (1:10) 20.2 - 136 mg kg^{-1}; M3-K 78 - 429 mg kg^{-1}; SO_4-S 4.3 - 54.7 mg kg^{-1}; DTPA-Mn 1.7 - 27 mg kg^{-1}; SOM-LOI 2.40 – 11.2%; CEC 6.6 - 25.9 cmol kg^{-1}; clay 9.4 - 30.7% and available water 6.5 - 17.3 %.

Standard Reference Botanical (SRB) materials for Cycle 43 were: SRB-2009 olive leaf composite from CA; SRB-2010 sorghum leaf composite from KS; SRB-2011 citrus leaf composite from CA; and SRB-2012 corn stalk leaf composite from IA. SRB median analytes ranged: NO_3-N 15 - 2690 mg kg^{-1}; Dumas N 0.65 - 2.45%; total P 0.075 - 0.35%; total K 0.62 - 3.28%; total Ca 0.12 - 3.91%; total S 0.03 - 0.23 %, total B 2.6 - 76.5 mg kg^{-1}; and total Mo 0.014 - 1.94 mg kg^{-1}.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2007 a water sample collected from the North county canal Weld Cty, CO: SRW-2008 was collected from a well Rumpus Ridge, SD; and SRW-2009 from the James River near Milltown, SD. SRW median concentrations: pH 7.80 - 8.43; EC 0.57 - 1.39 dSm^{-1}; SAR 0.75 - 4.50; Ca 1.95 - 2.63 mmolc L^{-1}; Na 1.2 - 5.73 mmolc L^{-1}; HCO_3 1.20 - 5.54 mmolc L^{-1} ; and NO_3 0.016 - 0.048 mmolc L^{-1}.

Soil Homogeneity Evaluation

SRS material homogeneity was evaluated based on soil test codes pH (1:1) H_2O, pH Adams Evans, EC (1:1), P Olsen, K Olsen, NO_3-N and SOM-WB on analysis of five jars of each PT soil, 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, Buf pH A&E, Olsen P and SOM-WB analysis Stdev values for Cycle 43 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation 2020, Cycle 43.

Sample	pH (1:1) H_2O		pH A&E Buffer		Olsen P (mg kg^{-1})		SOM-WB (%)	
	Mean [1]	*Std*	Mean	*Std*	Mean	*Std*	Mean	*Std*
SRS-2011	6.88	*0.029*	7.63	*0.02*	20.5	*1.0*	4.37	*0.09*
SRS-2012	7.24	*0.043*	7.66	*0.01*	13.6	*0.4*	2.91	*0.15*
SRS-2013	6.04	*0.033*	7.59	*0.02*	16.6	*0.6*	1.32	*0.23*
SRS-2014	5.56	*0.021*	7.64	*0.02*	7.2	*0.8*	2.61	*0.09*
SRS-2015	6.14	*0.113*	7.57	*0.02*	79.9	*8.1*	11.3	*0.54*

[1] Statistics based on five randomly selected soil replicates, each analyzed in triplicate ALP Cycle 43.

2020 Cycle 43 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 43 averaged 0.06 pH units across the soils. Median within lab pH standard deviation was 0.042 pH units. SRS-2013 had an abnormally low extractable Cl of 4.6 mg kg^{-1}, likely associated with Abernathy silt loam soil series. Soil TOC values for the cycle 43 ranged form 0.78 to 5.83 % organic carbon. Soil ammonium acetate Ca (Test code 140) MAD values ranged 36 - 523 mg kg^{-1} and ammonium acetate Mg MAD values ranged 4.7 to 35.7 mg kg^{-1} for the five soils. Soil SRS-2015 had abnormally high inter-lab variability for EC (1:1), NO_3-N, M3-K, M3-Mg, M3-Mn and SO_4-S, whereas results for pH, Bray-P1, Olsen-P, TOC, SOM-LOI, and CEC were within previously observed ranges. The source of the high inter-lab variability maybe related to the high OM content of the soil and/or cropping history of the collection site, a potato field in Skagit County, WA.

Across the four botanical samples Dumas combustion N MAD values averaged 0.052% nitrogen with intra-lab median *s* of 0.026%, 0.027%, 0.022% and 0.028%, respectively. Botanical sample SRB-2012 had a very low median B with a concentration of 2.6 ppm and with a MAD of 1.3 ppm. The olive leaf composite sample SRB-2009 had lower median concentrations of NO_3-N, PO4-P, K, Mg, Cl, Co and Mo and relative to the other three botanical samples. Consistent with past ALP cycles for 2020, cycle 43 intra-lab relative variability results were lowest for N than other macro elements for all four botanical samples.

Water EC results showed high consistency across samples. Across the three water samples EC Median values ranged from 0.057, 01.38 and 0.90 dSm^{-1}, respectively. Na values ranged from 1.22 - 5.73 molc L^{-1} across the three ALP water samples with MAD values ranging 0.03 to 0.18 molc L^{-1}. Sample SRW-2009 had and SAR of 4.49 with a MAD of 0.21.

SRS - pH (1:1)$_{H2O}$

Fifty-nine laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.70 - 7.28. Lab results were ranked low to high based on sample SRS-2014 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-2012 and SRS-2014 showed good consistency across labs. Lab #59 showed consistent high bias across all five soils. Labs #1, #40, #53, and #55 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.

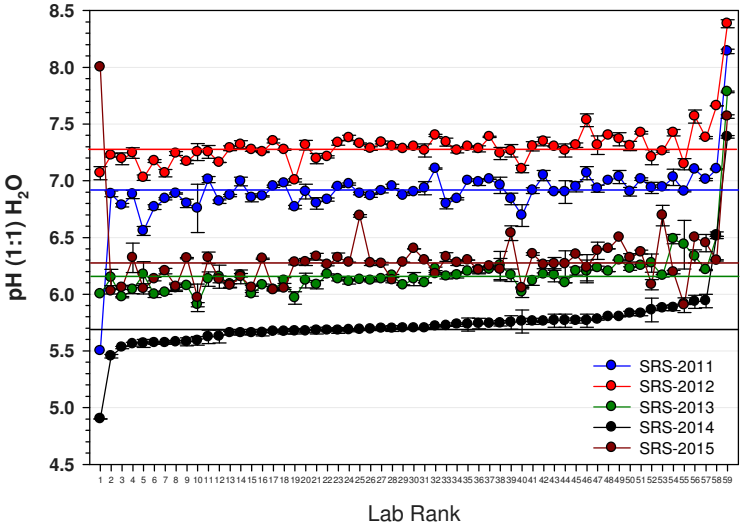


Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2020 Cycle 43.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.034 to 0.051 pH units, the lowest noted for SRS-2012. Five labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #4, #10, #38, #44, and #46 exceeded 0.10 pH units for SRS-2015. Soil SRS-2012 was the least variable with respect to intra-lab variance.

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

Bray P1 results were reported by thirty labs. M3-P ICP was reported by 40 labs. Median soil Bray P1 values ranged from 20.1 - 137 mg kg^{-1} PO_4-P; Olsen P 6.3 to 67.7 mg kg^{-1} P; Bray P2 ranged from 18.3 to 363 mg kg^{-1} P; and M1-P from 16.9 to 93.3 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-2011, median Bray P1 concentrations are shown in indicated in Figure 2. Soil SRS-2015, highest in concentrations was highly variable between labs. Soils SRS-2012 and SRS-2014 had near identical concentrations of 20 mg kg^{-1} P; soils SRS-2011 and SRS-2013 had ear identical concentrations of 39 mg kg^{-1} P. Lab #1 had low bias and labs #29 and #30, had consistent high bias all five samples. Soil SRS-2012, lowest in concentration, showed low intra-lab variability.

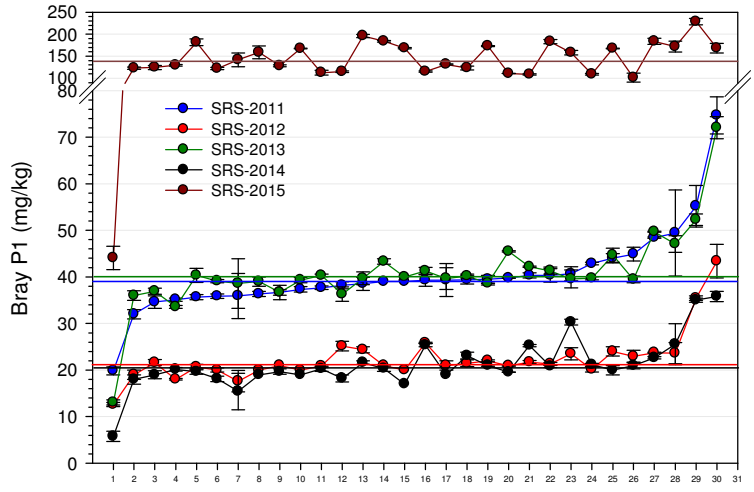


Figure 2. Bray P1 distribution plots for SRS materials, ALP 2020 Cycle 43.

M3-P Spec median concentrations were 21 - 202 mg kg^{-1} P reported by eight labs. Two laboratories provided ALP results for Modified Morgan P, with medians ranging from 1.9 - 14.6 mg kg^{-1} PO_4-P. Modified Kewlona was reported by two laboratories ranging from 14.4 - 166 mg kg^{-1} P and total P (US-EPA 503) ranged 350 - 1625 mg kg^{-1} P with the highest concentration noted for SRS-2015.

SRS - Potassium

Thirty-nine laboratories provided ALP results for soil M-3 K (test code 159) results. Results were ranked low to high based on sample SRS-2014 (see Figure 3). Soil SRS-2015 was the most inconsistent across labs with the lowest value reported by lab #20 of 83 mg kg^{-1} and the highest by lab #35 a value of 399 mg kg^{-1}. The source of the variability is unknown. Labs #1, #3, #16, #19, #20, #26, #36 and #41 were inconsistent across the five soils for M3-K. Source of inconsistency is likely related to sample extraction, analysis instrument and/or method compliance.

M3-K intra-lab *s* values were lowest for soil SRS-2014, with a median intra-lab value of 3.6 mg kg^{-1} Kg and highest for SRS-2015 with a value of 40.1 mg kg^{-1}. M3-K within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 300 mg kg^{-1} K. Precision was poor (based on intra-lab *s*) for three labs which exceeded 15 mg kg^{-1} K on SRS-2013. Poor precision is attributed to extraction and/or analysis instrument operation.

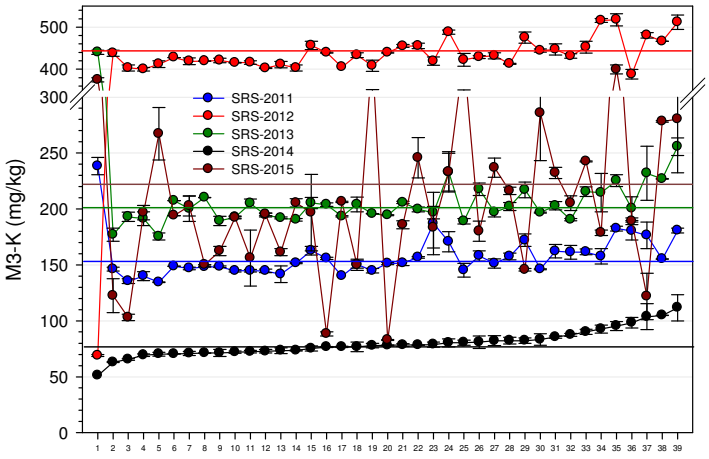


Figure 3. Extractable K distribution plots for SRS materials, ALP 2020 Cycle 43.

SRS - SOM-LOI

Forty-four laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 2.48 to 11.3%. Results were ranked based on sample SRS-2014 (see Figure 4). Sample SRS-2014 had high consistency. Labs #4, #12, #27 and #44 had inconsistency three of five soils. Lab #12 appears to have swapped samples four of five PT soils. Source of bias is likely related to muffle furnace operation and/or method compliance.

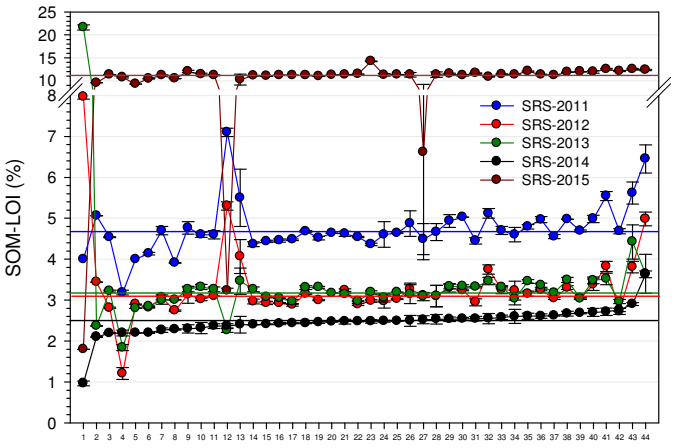


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2020 Cycle 43.

SOM-LOI precision across the five soils indicates high intra-lab precision, with median *s* values ranging from 0.07 to 0.26% SOM-LOI, highest for SRS-2015. Across labs, *s* values for SRS-2014 ranged from 0.005 - 0.13%. Across soils low precision was noted for several laboratories. Specifically *s* for labs #9, #13, #24, #27, #34, #44, and #45, exceeded 0.15% SOM-LOI for SRS-2011. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

SRS - Total Organic Carbon (TOC)

Fourteen laboratories provided ALP results for soil TOC (test code 181). Results were ranked low to high based on sample SRS-2011 (see Figure 5). Soil SRS-2013 was the most consistent across labs. Lab #14 had consistent high bis on two of five soils. Across soils, labs #5, and #13 were inconsistent across soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

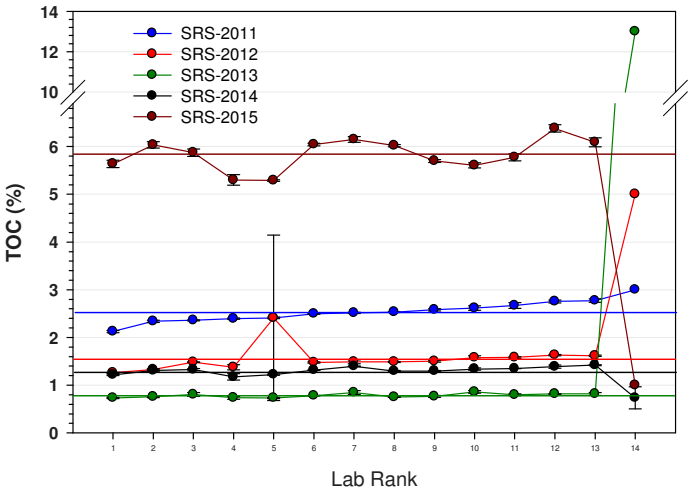


Figure 5. Soil TOC distribution plot, ALP 2020 Cycle 43.

Soil TOC median intra-lab *s* values were lowest for ALP soil SRS-2011 and SRS-2013, averaging 0.026 % and highest for SRS-2012 with a value of 0.48 %. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-2012 for lab #5. Intra-lab precision was very good for labs #2, #3, and #7—12, on all five soils. The high level of precision is likely associated with sample preparation and the combustion carbon instrument operation. Three labs were flagged for poor precision over the five soils.

SRB - NO_3-N

Twenty-four laboratories provided ALP results for NO_3-N by cadmium reduction, ISE and other (test codes 202, 203 and 204). Median values are designated by horizontal lines for each of the four botanical materials used and labs results are ranked low to high for twenty-two labs (codes 202-203) based on sample SRB-2009 (see Figure 6). The data plot shows labs #16 and #19 - #22 were inconsistent.

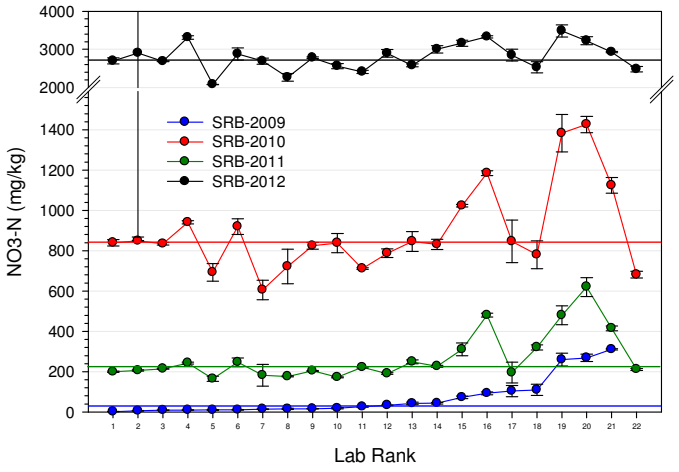


Figure 6. Nitrate distribution plots for SRB materials, ALP 2020, Cycle 43.

Botanical NO_3-N (test code 202) results for Cycle 43 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 2.6 to 1211 mg kg^{-1} for the four samples. Individual lab NO_3-N by cadmium reduction (test code 202) intra-lab *s* values for SRB-2009 ranged from 0.5 – 6.7 mg kg^{-1}; SRB-2010 ranged from 2.5 - 86 mg kg^{-1}, SRB-2011 ranged from 2.1 – 54 mg kg^{-1} and SRB-2012 ranged from 3.5 - 4390 mg kg^{-1} Lab #18 had consistently high standard deviations for three of four samples. Six labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Thirty-four laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and eight labs for TKN (Test code 209) for Cycle 43. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-2009 (see Figure 7). Labs #18, #22 and #31 were inconsistent for SRB-2012 relative to SRB-2009. It is note worthy that TKN was inconsistent and lower than Dumas for two samples. Samples SRB-2010 and SRB-2012 were inconsistent for TKN.

Dumas N results indicate very high precision across all labs for all samples. Individual lab Dumas N lab *s* values for SRB-2009, ranged 0.005 to 0.087% N, SRB-2010 ranged from 0.004 to 0.076% N, SRB-2011 ranged from 0.002 to 0.118 % N, and SRB–2012 from 0.003 to 2.19 % N. Lab #17 had consistently high standard deviations on all samples. Lab TKN *s* values for SRB-2009 ranged from 0.005 to 0.121%, SRB-2010 ranged from 0.004 to 0.248% TKN, SRB-2011 ranged from 0.002 to 0.234% TKN nitrogen and SRB-2012 ranged from 0.003 to 0.058% TKN nitrogen.

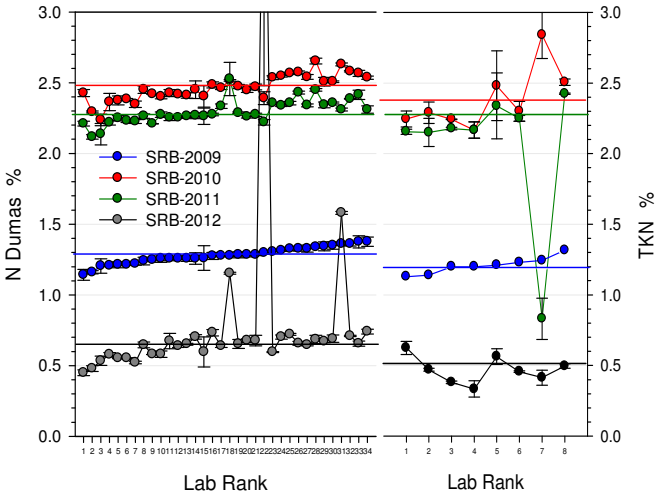


Figure 7. N distribution lab plots for SRB materials, ALP 2020 Cycle 43.

SRB - Phosphorus

Thirty-eight laboratories provided ALP results for Cycle 43 phosphorus (P) (test code 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-2012 (see Figure 8). Consistent high bias was noted for labs #37, and. Labs #15, #16, #35, and #36 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 0.005 to 0.013 % P for test code 212 across the four botanical samples. Individual lab intra-lab *s* values for SRB-2009; ranged from 0.001 - 0.255 % P; SRB-2010 ranged from 0.001 – 0.036 % P and SRB-2011 0.001 - 0.040 % P; and SRB-2012 0.001 - 0.372 % P. Lab #21 had a high standard deviation exceeding 0.04 % P on two of four botanical samples. Ten labs were flagged for poor precision for botanical P for Cycle 43.

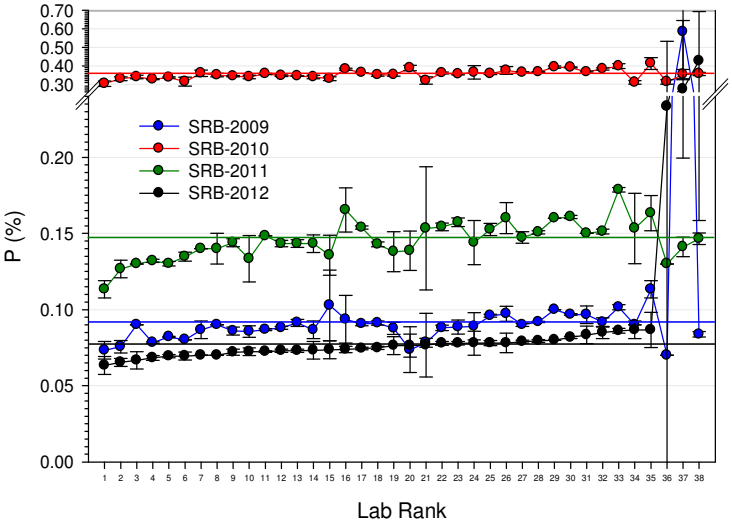


Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2020 Cycle

SRB - Potassium

Thirty-nine laboratories provided ALP results for potassium (K) (test code 213). Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-2012 (see Figure 9). Labs #27, #37, and #39 were inconsistent. Laboratories #27 swapped results for SRB-2009 and SRB-2010. Source of bias is 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 0.022 to 0.099 %K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2009, ranged from 0.001 - 0.167 % K; SRB-2010, 0.001 - 0.350 % K; SRB-2011, 0.001 - 0.218 % K; and SRS-2012, 0.001 - 4.18 % K. Lab #37 had high standard deviations exceeding 1.0 %K on three of four samples. Five labs were flagged for poor K precision for Cycle 43.

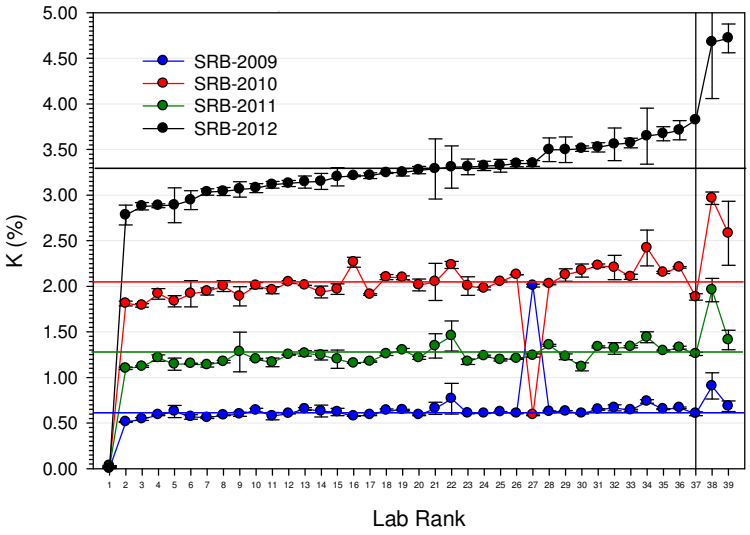


Figure 9. Potassium lab plot for SRB materials, ALP 2020 Cycle 43.

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-2012 (see Figure 10). Across samples labs #1 and #2 exhibited low bias. Labs #5, #31, #32 and #43 were inconsistent. 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 0.92 to 2.8 mg kg^{-1} B for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2009; ranged from 0.1 - 13.4 mg kg^{-1} B; SRB-2010 ranged from 0.1 – 3.9 mg kg^{-1} B; SRB-2011 0.1 - 15.0 mg kg^{-1} B; and SRB-2012 0.1 - 9.3 mg kg^{-1} B. Lab #31 had consistently high standard deviations for three samples. Five labs were flagged for poor B precision for Cycle 43.

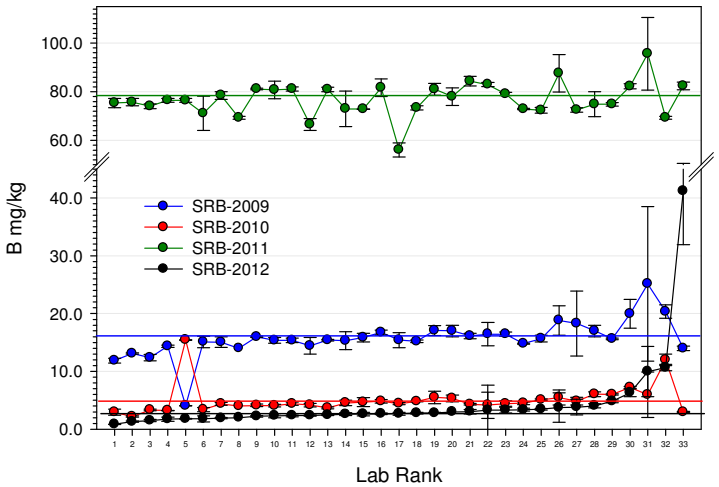
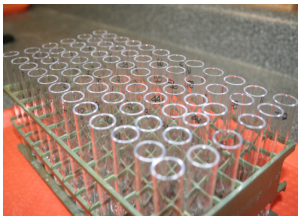


Figure 10. Boron (code 219) lab plots for SRB materials, ALP 2020 Cycle 43.

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-2007 (see Figure 11). Sample SRW-2008 had the highest EC in Cycle 43. Lab #14 indicated consistent high bias on all samples. Lab #15 and #17 showed inconsistently 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 very high precision, with intra-lab median Std values of 0.007, 0.015 and 0.008 dSm^{-1}, respectively. Precision for sample SRW-2007 was the most consistent across the thirteen participating laboratories. Intra-lab *s* values for lab #3 exceeded 0.020 dSm^{-1} on SRW-2008. Highest precision was noted for lab #14 with intra-lab *s* values of < than 0.0006 dSm^{-1} for all three samples.

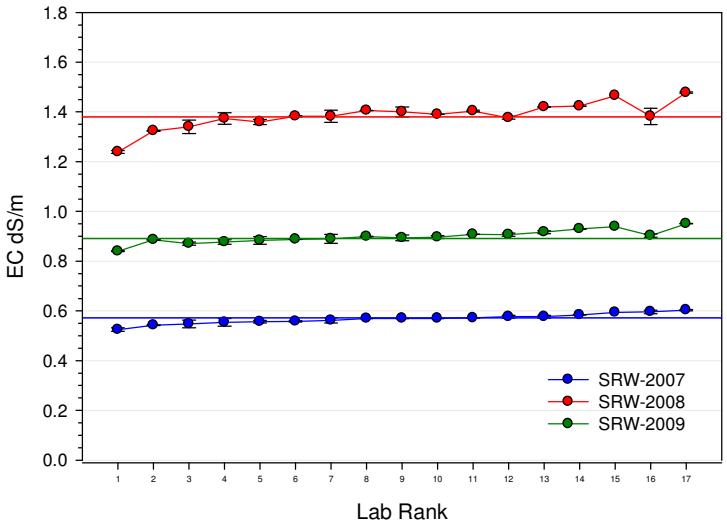


Figure 11 . Water EC distribution plots for SRW materials, ALP 2020 Cycle 43.

SRW - Na Results

Sixteen laboratories provided ALP results for water Na (test code 304). Lab results were ranked low to high based on sample SRW-2007 (see Figure 12) lowest in Na concentration. Median values are designated by horizontal lines. Labs #1 showed consistent low bias on two of thee samples, and is likely a result of a calibration error.

Na precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.028, 0.084, and 0.091 meq L^{-1} for SRW-2007, SRW-2008, and for SRW-2009, respectively. Water Na precision was excellent for all individual labs with only labs #1 and #10 exceeding 0.14 meq L^{-1} on two of the three samples. Four labs were flagged for poor precision on ALP Cycle 43 for Na content.

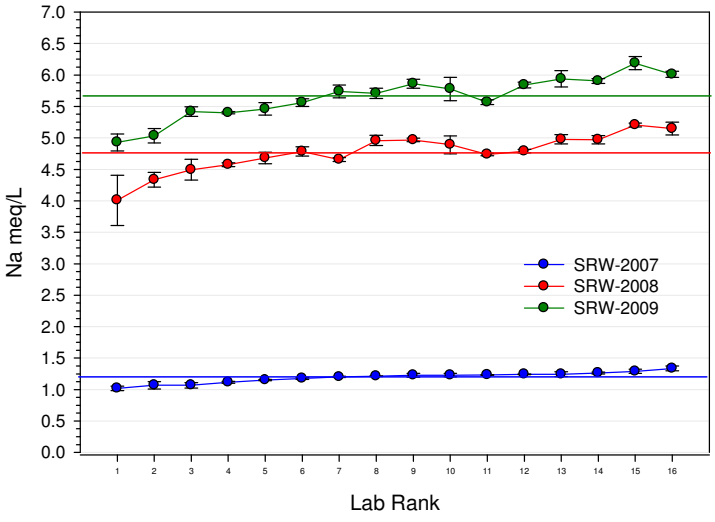


Figure 12. Water Mg distribution plots for SRW materials, ALP 2020 Cycle 43.

Announcements

- The Soil and Plant Analysis Council (SPAC) and Agricultural Laboratory Testing Association (ALTA) have developed an international plant analysis certification program (PAC) for laboratories. Analyses include: N, P, K, S, Ca, Mg Zn, B, Mn, Fe, and Cu. The PAC program will be based exclusively on ALP proficiency testing data evaluated on a yearly basis. For more information can be found at ALTA.Ag.

  The Agricultural Laboratory Testing Association (ALTA) is planning a webinar on laboratory Quality Management for January 19, 2021. For more information contact the ALTA secretary, gfisher@unitedsoilsinc.com.

- A new ALP web site: www.alpprogram.net/home/ . Generally information on the program is available, and a special section on method specific topics and lab quality control quality control will be offered.

- ALP has added new test methods to the soil proficiency program in 2020. Methods include Soil pH (1:1) 1.0 N KCL, Sikora 2 buffer pH. For more information on these methods contact the ALP Technical Director, Robert.Miller@cts-interlab.com.

- 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.

Summary

ALP is has provided fifteen years of service with the completion of Cycle 43. Since 2005 ALP has completed the analysis of 215 soils, 136 plant samples and 122 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 43. 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 44 Ship

March 17, 2021

"If a cluttered desk is a sign of a cluttered mind, of what, then, is an empty desk a sign?"

– Laurence J. Peter

ALP
Agricultural Laboratory Proficiency Program