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ALP Program Report

2014 Fall - Cycle 25

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ALP Overview

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 25.
- Fifty-four Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.10 - 7.21.
- Cycle 25 soil NH_4OAc K ranged from 32 to 373 mg kg^{-1} with MAD values ranging 4.3 - 24 mg kg^{-1} across the five soils.
- Cl was highly consistent on soil SRS-1414 at 4.8 ppm concentration.
- Botanical P, ranged from 0.20 - 0.43 mg kg^{-1}, with three of twenty-six labs noted for low bias.
- Botanical Mg values ranged from 0.13 to 0.59 % across the three samples.
- Water Mg concentration showed high consistency by seven of eleven labs across all three samples.

The Agriculture Laboratory Proficiency (ALP) Program Fall 2014 Round cycle 25 was completed September 15, 2014, with ninety-two labs enrolled from the United States, Canada, Guatemala and South Africa. Proficiency samples consisted of five soils, three botanical and three water samples. Analytical methods evaluated are base on those published by AOAC, four regional soil work groups, the Soil Plant Analysis Council and Forestry Canada.

Data was compiled for each method (test code) and proficiency material. Data analysis of each material include: the number results; grand median value; median absolute deviation (MAD), (95% Confidence Interval); method intra-lab standard deviation (*s*); lab mean, and lab standard deviation. Additional information on the ALP program testing methods and statistical protocols can be found at the program web site: http://www.collaborativetesting.com/reports/default.aspx?F_CategoryId=12,

Proficiency Materials

Standard Reference Soils (SRS), materials used for the soils and environmental programs were: SRS-1411 a Warwick Channery fine sandy loam collected from Windham Cty, VT; SRS-1412 a Pulaski fine sandy loam collected from Payne Cty, OK; SRS-1413 a Del Rey silt loam, collected from Iroquois Cty, IL; SRS-1414 a Otoe silty clay loam from Cass Cty, NE; and SRS-1415 Danvers-Judith clay loam Judith Basin Cty, MT. Chemical properties of the SRS materials ranges: pH (1:1) H_2O 5.10 - 7.21; NO_3-N 2.5 - 59 mg kg^{-1}; Bray P1 (1:10) 11.7 - 351 mg kg^{-1}; K NH_4OAc 32 - 373 mg kg^{-1}; SO_4-S 4.3 - 96 mg kg^{-1}; Mehlich 3 P (ICP) 16.2 - 300 mg kg^{-1}; DTPA-Zn 0.67 - 3.57 mg kg^{-1}; SOM-WB 1.25 – 5.69 %; CEC 6.7 - 21.9 cmol kg^{-1}; clay 7.1 - 33.3% and Solvita CO_2 Respiration 9 - 25 mg kg^{-1}.

Standard Reference Botanical (SRB) materials were: SRB-1407 corn leaves from Indiana, SRB-1408 potato petiole composite from Washington State and SRB-1409 oat hay from California. SRB material median concentrations ranged: NO_3-N 57 - 21,200 mg kg^{-1}; Dumas N 1.29 - 4.08%; total P 0.20 - 0.43%; total K 0.96 - 10.5%; total Mg 0.13 - 0.59%; total S 0.11 - 0.24 %, total B 13.7 - 26.7 mg kg^{-1}; and total Cd 0.03 - 1.17 mg kg^{-1}.

Standard Reference Water samples represent an agriculture water sample collected: SRW-1407 a water sample collected from South Bend, NE; SRW-1408 from a irrigation ditch near Telluride, CO; and SRW-1409 a stream near Jackson, ME. SRW median concentrations ranged: pH 7.82 - 8.12; EC 0.15 - 0.72 dSm^{-1}; SAR 0.12 - 3.50; Ca 1.03 - 3.89 mmolc L^{-1}; K 0.01 - 0.26 mmolc L^{-1}; Cl 0.07 - 2.85 mmolc L^{-1} ; and NO_3–N 0.015 - 0.034 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 EC (1:1). Homogeneity was also evaluated on SRB and SRW matrix samples.

"..soil pH, EC and Olsen P analysis Stdev values for cycle 25 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 25, 2014.

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-1411	5.39	*0.04*	0.26	*0.007*	116	*4.6*	25.2	*1.3*
SRS-1412	5.84	*0.01*	0.44	*0.005*	35.7	*1.5*	38.5	*1.2*
SRS-1413	4.53	*0.02*	0.08	*0.007*	7.6	*0.4*	2.1	*0.6*
SRS-1414	5.13	*0.02*	0.37	*0..02*	7.3	*0.03*	26.0	*0.5*
SRS-1415	7.06	*0.02*	1.18	*0.03*	24.3	*0.9*	51.8	*3.2*

[1] Statistics based on four soil replicates, each analyzed in triplicate ALP Cycle 25.

2014 Cycle 25 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 25 averaged 0.06 pH units. Within lab pH standard deviation was 0.052 pH units. Soil CEC ranged 6.7 to 21.8 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 9.4 - 25 mg kg^{-1} with an intra-lab precision, with s values averaging 1.9 for four of five samples. Sample SRS-1415 has the highest in EC (1:1) measured in the ALP Program at 1.05 dS m^{-1}. Soil ammonium acetate K (Test code 140) MAD values ranged 4.3 - 24.3 mg kg^{-1} and ammonium acetate Ca MAD values 28 to 363 mg kg^{-1} for the five soils. These results lower than those of cycles 24 and represent a increase in MAD values that are attributed to: (1) issues in lab consistency; (2) soils generally higher in potassium; and (3) ICP operation.

Across the three botanical samples Dumas combustion N MAD values averaged 0.068% nitrogen with intra-lab *s* of 0.187%. 0.109% and 0.092%, respectively. There was a greater inter-lab variability (MAD) in total potassium values than combustion N, P, Ca or total S concentrations for SRB-1409. Generally the oat hay sample SRB-1406 had lower level median N, P, K, Ca, Mg, Zn and Mo relative to the other two botanical samples of cycle 25. Also of significance sample SRB-1408 which had the highest concentrations of Ba, Cd, Co, and Sr mg kg^{-1}.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.015 to 0.72 dSm^{-1}. NO_3-N values ranged from 0.015 - 0.034 mmolc L^{-1} across the three water samples.

SRS Results - pH

Fifty-four laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.10 to 7.21. Lab results were ranked low to high based on sample SRS-1411 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1413 and SRS-1414 were very similar in pH, and 83% of labs found no differences between the two soils. Labs #1, #4, #26, #51, and #54 were inconsistent across soils. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of soil extract carry-over.

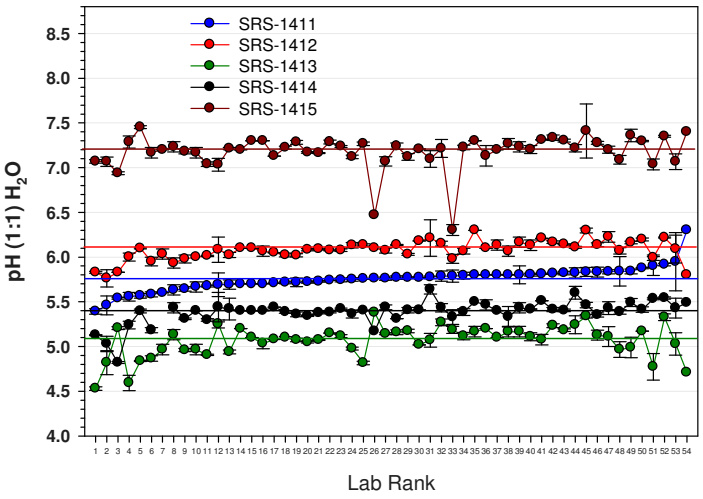

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2014 Cycle 25.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.016 to 0.023 pH units, the highest noted for SRS-1415. For specific labs poor precision was noted for two laboratories, exceeding by 1.5 times that noted for consensus intra-lab *s*. Specifically *s* for lab #12 exceeded 0.14 pH units for three of five soils. Soil SRS-1413 was the most variable with respect to intra-lab variance.

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

Bray P1 results were reported by twenty-four labs. Median soil Bray P1 values ranged from 11.7 to 351 mg kg^{-1} PO_4-P; Mehlich 1 P 4.9 to 110 mg kg^{-1} P and M-3-P ICP ranged from 6.2 to 300 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1411, median Bray P1 concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1412 associated with moderately high soil P concentrations. Soils SRS-1413 and SRS-1414 had near identical Bray P contents across all twenty-four labs. Four labs (#1 #4) had consistent low bias on SRS-1411. Inconsistency was noted for labs #2 and #3 is likely related to extraction, analysis instrument and/or method compliance.

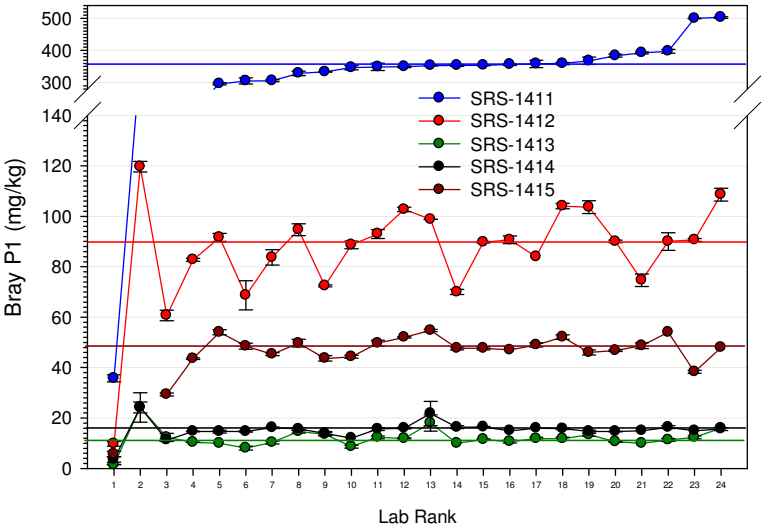

Figure 2. Bray P distribution plots for SRS materials, ALP 2014 Cycle 25.

Twenty-six laboratories provided ALP results for Olsen P (test code 134), for the five soils with medians ranged from 6.8 to 113 PO_4-P mg kg^{-1}. Mehlich 3 P–SPEC median concentrations were 11.8 to 287 mg kg^{-1} PO_4-P reported by eight labs. Strong Bray (P2) was reported by eight laboratories ranging from 15.5 to 528 mg kg^{-1} PO_4-P with the highest P concentration noted for SRS-1411.

SRS - Potassium

Thirty-nine laboratories provided ALP results for soil K (test code 140) results. These were ranked low to high based on sample SRS-1411 (see Figure 3). Soil SRS-1415 was the most inconsistent across labs. Across soils, lab #37 had consistent high bias. Labs #1, #2, #8, #9, #28, #36, and #39 were inconsistent across the five soils. 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-1411, with a median intra-lab value of 1.5 mg kg^{-1} K and highest for SRS-1414 with a value of 7.2 mg kg^{-1} K. Potassium within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 250 mg kg^{-1} K. Precision was poor (based on intra-lab *s*) for labs #1 and #36 which exceeded 9 mg kg^{-1} K on three of five soils; and lab #28 the value exceeded 170 mg kg^{-1} K on all samples. Poor precision is attributed to extraction and/or analysis instrument operation.

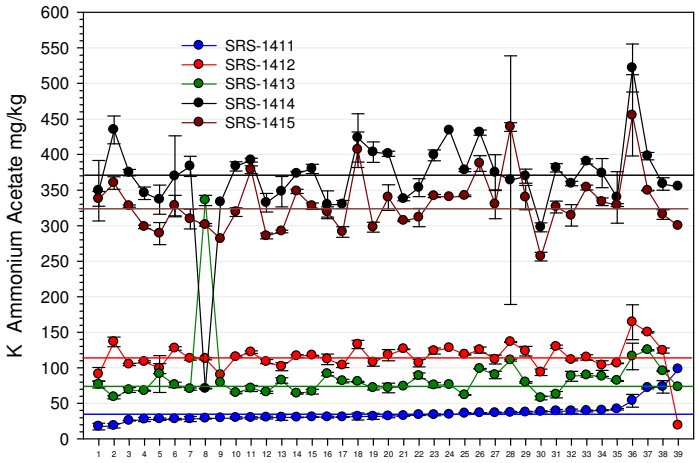

Figure 3. Extractable K distribution plots for SRS materials, ALP 2014 Cycle 25.

SRS SOM-LOI

Forty-eight laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.25 to 5.69%. Results were ranked based on sample SRS-1411 (see Figure 4). Lab #48 was noted having consistent high bias. Labs #8, #17, #30, #40, and #46 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 0.056 to 0.078% SOM-LOI, the highest for SRS-1415. Across labs *s* values for SRS-1411 ranged from 0.008 - 0.37 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #8, #18, #24, #30, and #47 exceeded 0.12 for three of five soils. Lab exceeded 0.50 % SOM on one of five of five soils evaluated in ALP cycle 25. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

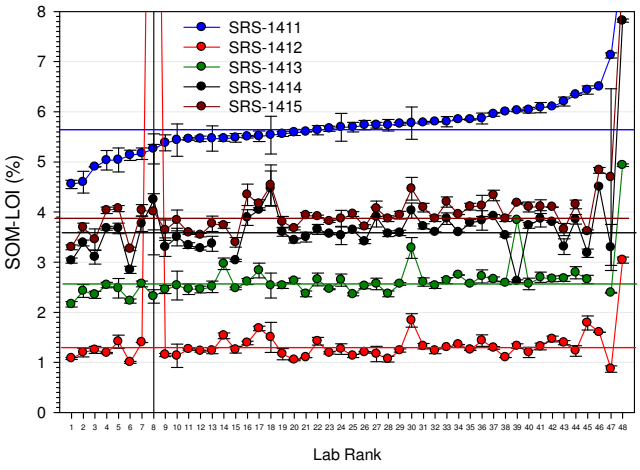

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2014 Cycle 25.

Sikora Buffer pH

Nineteen laboratories provided ALP results for Sikora Buffer pH, (test code 122) results. These were ranked low to high based on sample SRS-1411 (see Figure 5). Soil SRS-1415 was the highest in concentration and the most consistent across labs. Across soils, labs #1 had low bias on all soils, labs #19 high bias on three of five soils. Labs #2, #14 and #18, were inconsistent across a majority of soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

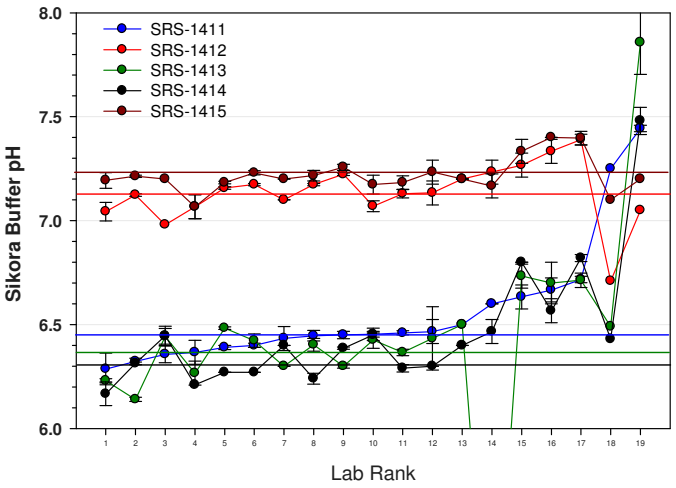

Figure 5. Soil DTPA-Cu distribution plot, ALP 2014 Cycle 25.

Soil Sikora buffer pH median intra-lab *s* values were lowest for ALP soil SRS-1414 with a consensus intra-lab value of 0.017 mg kg^{-1} and highest for SRS-1413 with a value of 0.032 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, with the exception of soil SRS-1413. Intra-lab precision was poor for labs #12 and # 16 on four of five soils. Poor precision maybe associated with instrument pH electrode issues.

SRB Nitrate-Nitrogen

Twenty laboratories provided ALP results for NO_3-N (all test codes 202, 203, 204). Results were combined for all methods as medians were nearly identical. Median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1407 (see Figure 6). Data plots show labs #1 has low bias for two of three botanical samples. Lab #13 showed high bias on SRB-1409. Labs #15, #16, #17, #18, and #19 were inconsistent.

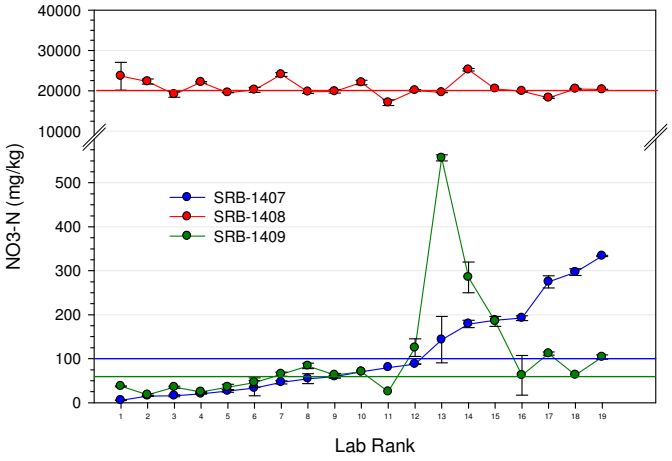

Figure 6. Nitrate distribution plots for SRB materials, ALP 2014, Cycle 25.

Botanical NO_3-N results for cycle 25 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 3.2 to 382 mg kg^{-1} for test code 202 for the three samples. Individual lab NO_3-N (test code 202) intra-lab *s* values for SRB-1407; ranged from 0.6 – 58 mg kg^{-1}; SRB-1408 ranged from 57 - 3468 mg kg^{-1}, and SRB-1409 ranged from 1 – 35 mg kg^{-1}. Lab #13 had consistently high standard deviation for botanical sample SRB-1407. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Twenty-one laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and seven for TKN (Test code 209). Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-1407 (see Figure 7). It is note worthy that TKN was lower than Dumas for all samples. Labs #1 and #2 showed low bias for Dumas N SRS-1407 and SRV-1408, whereas lab #19 showed inconsistency across all two of three botanical samples.

Dumas N and TKN results indicate very high precision across all labs for all samples. Individual lab Dumas N *s* values for SRB-1407, ranged from 0.005 to 0.850 % N, SRB-1408 ranged from 0.006 to 0.458 % N and SRB-1409 ranged from 0.004 to 0.404 % N. Lab #21 had consistently high standard deviation for two of three botanical samples. Individual lab TKN *s* values for SRB-1407 ranged from 0.007 to 0.055 %, SRB-1408 ranged from 0.012 to 0.125 % and sample SRB-1409 ranged from 0.006 to 0.079 % TKN nitrogen.

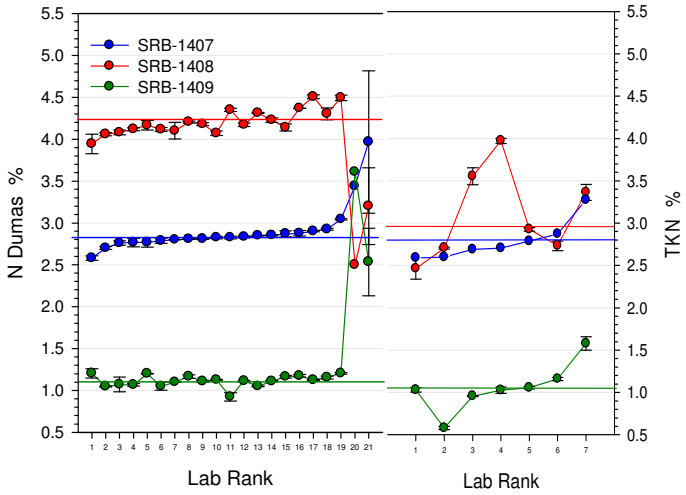

Figure 7. N distribution plots for SRB materials, ALP 2014 Cycle 25.

SRB - Potassium

Thirty-one laboratories provided ALP results for potassium (K) (test codes 213 and 226). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1407 for test code 213 (see Figure 8). Laboratories #1 and #2 showed low bias on two of three samples, whereas lab #32 indicate high bias. Labs #6, #7, #12 and #24 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 standard deviation (*s*) values ranging from 0.015 to 0.152 %K for test code 213 across the three samples. Individual lab intra-lab *s* values for SRB-1407; ranged from 0.01 to 0.40 % K; SRB-1408 and 0.010 — 0.89 % K; SRB-1409 0.003 - 0.134 %K. Lab #12 had consistently high standard deviations exceeding 0.30 %K for SRB-1407. Four labs were flagged for poor K precision.

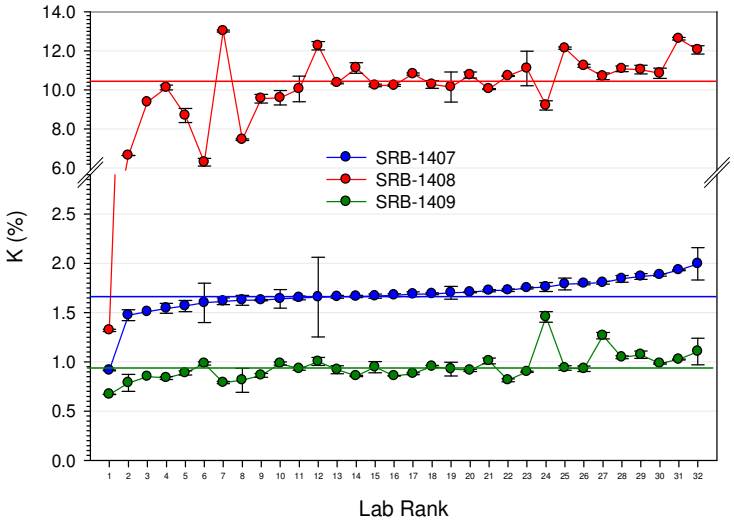

Figure 8. Potassium (code 213 and 223) plots for SRB materials, ALP 2014 Cycle 25.

SRB - Phosphorus

Thirty-one laboratories provided ALP results for cycle 25 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-1407 (see Figure 9). Consistent bias was noted for labs #1 through #3. Lab #32 showed high bias. Labs #25 had high bias on all samples. 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 0.006 to 0.008 % P for test code 212 across the three botanical samples. Individual lab intra-lab *s* values for SRB-1407; ranged from 0.001 - 0.037 % P; SRB-1408 ranged from 0.001 – 0.035 % P and SRB-1409 0.001 - 0.066 % P. Lab #10 had a high standard deviations exceeding 0.007 % P for two of three botanical samples. Two labs were flagged for poor precision.

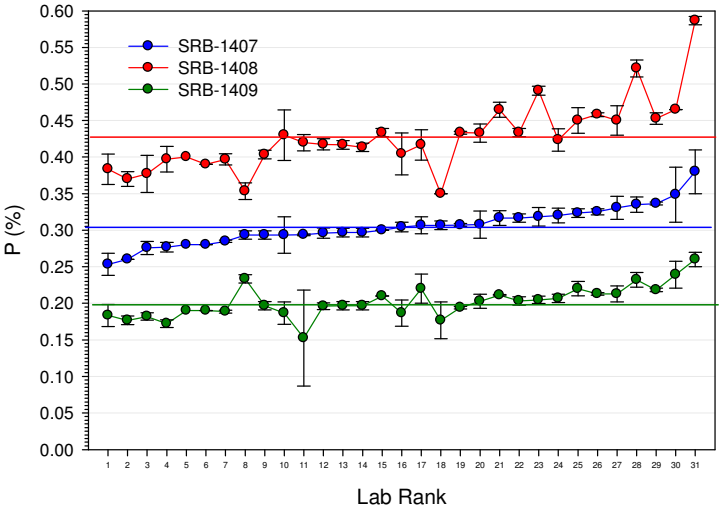

Figure 9. Phosphorus distribution plots for SRB materials, ALP 2014 Cycle 25.

SRB - Zinc

Twenty-five laboratories provided ALP results for Zinc (Zn) (test code 220). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1407 (see Figure 10). Laboratories #1, and #3 showed low bias on two of thee samples, whereas lab #25 indicated high bias all samples. Labs #4 and #23 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Zn results indicate very high precision, with intra-lab standard deviation (*s*) values ranged from 0.96 to 1.6 mg kg^{-1} Zn for across the three botanical samples. Individual lab intra-lab *s* values for SRB-1407; ranged from 0.08 - 2.6 mg kg^{-1} Zn; SRB-1408 ranged from 0.11 – 2.5 mg kg^{-1} Zn and SRB-1409 0.12 - 4.2 mg kg^{-1} Zn. Lab #21 had consistently high standard deviations exceeding 2.4 mg kg^{-1} Zn for all three samples, the highest for botanical sample, SRB-1404.

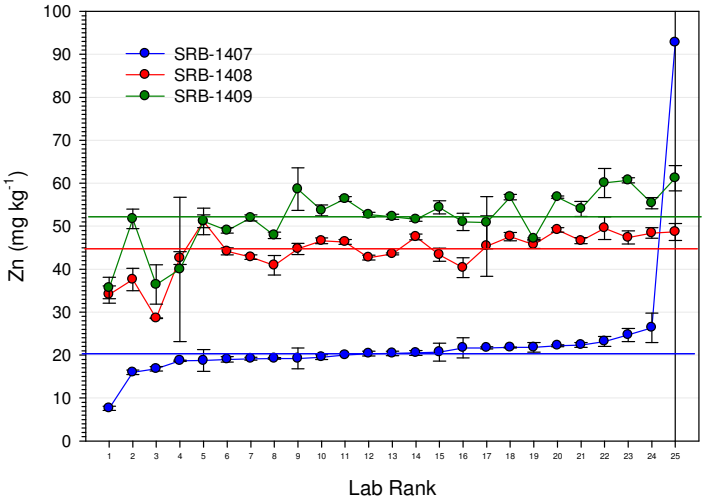

Figure 10. Zinc distribution plots for SRB materials, ALP 2014 Cycle 25.

SRW - Water pH

Ten laboratories provided ALP results for water pH (test code 301). Ranking lab results low to high based on sample SRW-1407 (see Figure 11). Labs #1, #2, and#3 indicated consistent low bias on all three samples. Labs #4, appeared 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 Std values of 0.020, 0.023 and 0.033 pH units, respectively. Precision for sample SRW-1408 was the most consistent across the ten laboratories. Across water samples poor precision was noted for three laboratories. Specifically intra-lab the *s* values for lab #1 exceeded 0.10 pH on SRW-1408. Highest precision was noted for lab #3 with intra-lab *s* values of < than 0.02 pH units.

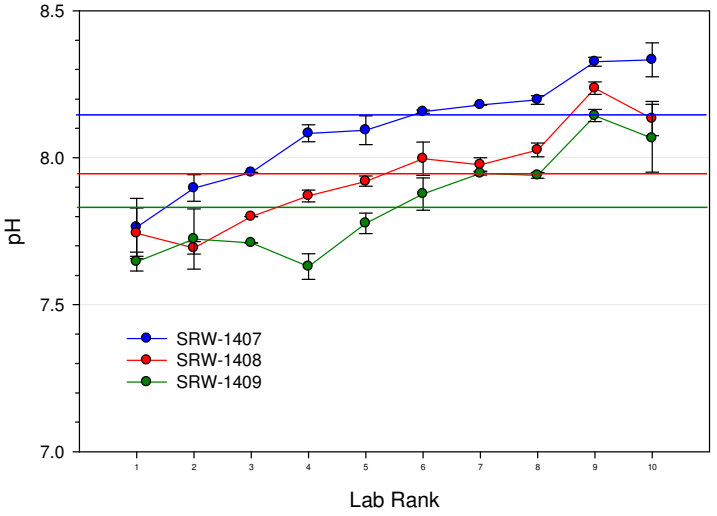

Figure 11 . Water pH distribution plots for SRW materials, ALP 2014 Cycle 25.

SRW - Mg Results

Eleven laboratories provided ALP results for water Mg (test code 304). Lab results were ranked low to high based on sample SRW-1407 (see Figure 12). Median values are designated by horizontal lines. Labs #1 and #2 had consistent low bias across all samples. Labs #3 - #10 showed high consistency across all samples.

Mg precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.014, 0.004, and 0.005 mmolc L^{-1} for SRW-1407, SRW-1408, and for SRW-1409, respectively. Water Mg precision was excellent for all individual labs with only lab #5 exceeding 0.06 mmolc L^{-1} Mg on sample SRW-1408. Across samples intra-lab *s* was less than 0.002 mmolc L^{-1} for lab #4. Two labs were flagged for poor precision.

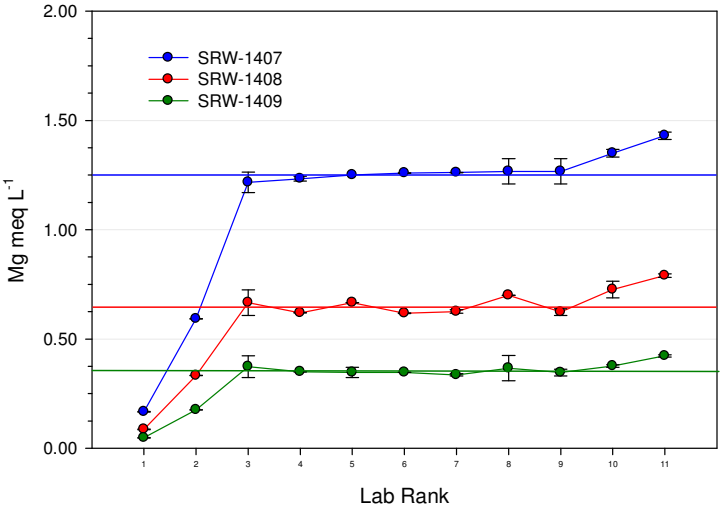

Figure 12. Water Mg distribution plots for SRW materials, ALP 2014 Cycle 25.

Announcements

- ALP is now an accredited proficiency provider for agricultural laboratory testing in North America under ISO 17043 by AClass, an accreditation board for Proficiency Providers (ANSI-ASQ National Accreditation Board). This is a major achievement and required an extensive audit of program standards, documentation and operation.

- ALP collected five proficiency soils in this fall from Illinois, Kansas and Nebraska representing a diverse range of textures and chemical properties. Additional collections are planned for British Columbia, Ontario, Michigan, and Indiana in the spring of 2015.

- ALP was a sponsor at the American Society of Agronomy Meetings in Long Beach California November 3-6, 2014.

- Plan to attend the ISSPA meeting in Kona, Hawaii January 26-30, 2015, and stop by the ALP sponsorship booth.

- If there is a specific soil type, soil properties or plant sample that you believe should be considered for the proficiency program please contact the ALP Program Technical Director, rmiller@lamar.colostate.edu.

- A special remembrance of Dr. Don Horneck of Oregon State University who passed away in September. He co-authored the Western States methods manual and was an active supporter of laboratory proficiency testing.

Summary

ALP 2014 Cycle 25 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 25. 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 26 Ship

March 20, 2015

"Equipped with his five senses, man explores the universe around him and calls the adventure Science. "

- Edwin Powell Hubble, The Nature of Science, 1954

ALP
Agricultural Laboratory Proficiency Program