2014 Volume 2

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ALP Program Report

2014 Summer - Cycle 24

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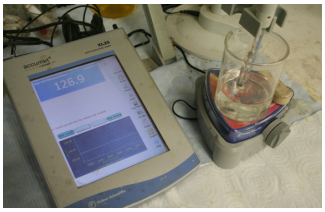
ALP Overview

The Agriculture Laboratory Proficiency (ALP) Program Spring 2014 Round cycle 24 was completed September 15, 2014, with eighty-seven 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,

Special points of interest:

- Soil homogeneity assessment indicate ALP reference materials were highly uniform for Cycle 24.
- Fifty-five Laboratories provided soil pH (1:1) H_2O results and medians ranged from 5.93 - 7.47.
- Cycle 24 soil NH_4OAc K ranged from 83 to 658 mg kg^{-1} with MAD values ranging 8.2 - 60 mg kg^{-1} across the five soils.
- DTPA-Cu was highly inconsistent on soil SRS-1406 highest in Cu concentration.
- Botanical P, ranged from 0.09 - 0.32 mg kg^{-1}, with three of twenty-six labs noted for low bias.
- Botanical B values ranged from 11.1 to 34.5 mg kg^{-1} across the tree samples.
- Soil SRW-1406 had a Ca concentration of 3.2 mmolc l^{-1}.

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Proficiency Materials

Standard Reference Soils (SRS), materials used for the soils and environmental programs were: SRS-1406 a Brios sandy loam collected from Maricopa Cty, AZ; SRS-1407 a Tifton loamy sand collected from Grady Cty, GA; SRS-1408 a Elkton silt loam, collected from Price George Cty, MD; SRS-1409 a Canisteo silty clay loam from Palo Alto Cty, IA; and SRS-1410 Saranac silty clay from Randolph Cty, IN. Chemical properties of the SRS materials concentration median ranges: pH (1:1) H_2O 5.93 - 7.47; Sat. Paste SAR 0.10 - 15.4; NO_3-N 9 - 293 mg kg^{-1}; Bray P1 (1:10) 39.8 - 190 mg kg^{-1}; K NH_4OAc 83 - 658 mg kg^{-1}; Mehlich 3 P (ICP) 51.7 - 549 mg kg^{-1}; DTPA-Zn 0.37 - 28.6 mg kg^{-1}; SOM-WB 1.77 – 4.78 %; CEC 4.2 - 29.3 cmol kg^{-1}; clay 15.3 - 32.7% and Solvita CO_2 Respiration 10 - 56 mg kg^{-1}.

Standard Reference Botanical (SRB) materials were: SRB-1404 potato petiole from Washington state, SRB-1405 grass hay composite from Minnesota and SRB-1406 olive leaves from California. SRB material median concentrations ranged: NO_3-N 76 - 1650 mg kg^{-1}; Dumas N 1.66 - 3.41%; total P 0.097 - 0.227%; total K 1.00 - 8.40%; total Mg 0.26 - 0.807%; total S 0.14 - 0.22 %, total B 11.1 - 32.4 mg kg^{-1}; and total Sr 4.3 - 273 mg kg^{-1}.

Standard Reference Water samples represent an agriculture water sample collected: SRW-1404 an irrigation canal near Montrose, Colorado; SRW-1404 from an irrigation well in central New Mexico; and SRW-1406 an irrigation canal, Windsor, Colorado. SRW median concentrations ranged: pH 7.85 - 8.02; EC 0.28 - 0.93 dSm^{-1}; SAR 0.50 - 4.78; Ca 1.86 - 3.19 mmolc L^{-1}; Cl 0.15 - 3.22 mmolc L^{-1} ; and NO_3–N 0.009 - 0.125 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 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 24 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 24, 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-1406	7.44	*0.03*	5.65	*0.18*	107	*15*	314	*15*
SRS-1407	6.67	*0.05*	0.23	*0.01*	13.1	*2.3*	17.2	*1.1*
SRS-1408	6.24	*0.01*	0.25	*0.01*	18.1	*1.1*	10.9	*0.3*
SRS-1409	5.75	*0.01*	0.69	*0..03*	29.2	*1.5*	59.6	*5.3*
SRS-1410	7.23	*0.01*	0.73	*0.06*	38.1	*0.8*	61.9	*0.9*

[1] Statistics based on four soil replicates, each analyzed in triplicate ALP Cycle 24.

2014 Cycle 24 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 24 averaged 0.08 pH units. Within lab pH standard deviation was 0.062 pH units. Soil CEC ranged 4.7 to 29.3 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 10 - 55.7 mg kg^{-1} with an intra-lab precision, with s values averaging 2.4 for four of five samples. Sample SRS-1406 has the highest in EC (1:1) measured in the ALP Program at 5.4 dS m^{-1}. Soil ammonium acetate K (Test code 140) MAD values ranged 8.2 - 60 mg kg^{-1} and ammonium acetate Ca MAD values 58 to 390 mg kg^{-1} for the five soils. These results lower than those of cycles 23 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 combustion N MAD values averaged 0.07% nitrogen with intra-lab *s* of 0.034%. 0.033% and 0.027%, respectively. There was a greater inter-lab variability (MAD) in total potassium values than combustion N, P, Ca or total S concentrations for SRB-1404. Generally the olive leaf sample SRB-1406 had lower level median N, P, K, Ca, Mg, Zn and Mo relative to the other two botanical samples of cycle 24. Also of significance sample SRB-1404 which had the highest concentrations of Ba, Cd, and Co mg kg^{-1}.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.011 to 0.045 dSm^{-1}. NO_3-N values ranged from 0.009 - 0.12 mmolc L^{-1} across the three water samples.

SRS Results - pH

Fifty-five laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.93 to 7.47. Lab results were ranked low to high based on sample SRS-1406 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1406 and SRS-1410 were very similar in pH, and 92% of labs found no differences between the two soils. Labs #1, #2, #4, #5, #13, #21 and #53 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.

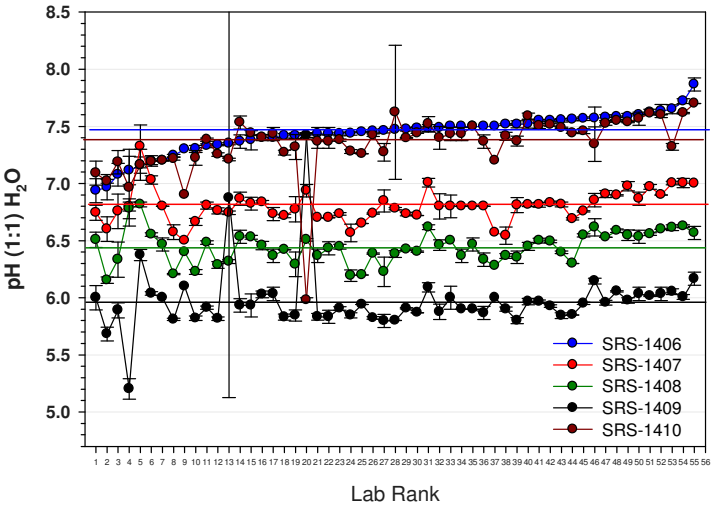

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2014 Cycle 24.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.017 to 0.025 pH units, the highest noted for SRS-1409. For specific labs poor precision was noted for two laboratories, exceeding by 2 times that noted for consensus intra-lab *s*. Specifically *s* for lab #14 exceeded 0.20 pH units for 2 of five soils. Soil SRS-1409 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-one labs. Median soil Bray P1 values ranged from 40 to 190 mg kg^{-1} PO_4-P; Mehlich 1 P 19.5 to 210 mg kg^{-1} P and M-3-P ICP ranged from 52 to 550 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1407, median M3-P ICP concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1410 and SRS-1406 associated with moderate soil P concentrations and high sand content with four of twenty-six labs (#4, #8, #9and #11) having large inconsistency. Inconsistency is likely related to extraction, analysis instrument and/or method compliance. MAD values were the lowest for soil SRS-1407 and highest for SRS-1406 of the five soils.

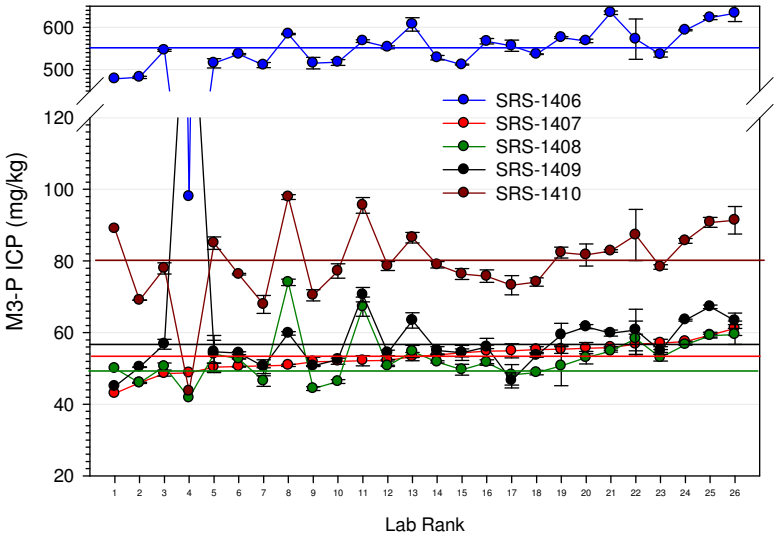

Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2014 Cycle 24.

Thirty laboratories provided ALP results for Olsen P (test code 134), for the five soils which medians ranged from 15 to 115 PO_4-P mg kg^{-1}. Mehlich 3 P–SPEC median concentrations were 43.6 to 460 mg kg^{-1} PO_4-P reported by eight labs. Strong Bray (P2) was reported by seven laboratories ranging from 31 to 330 mg kg^{-1} PO_4-P with the highest P concentration noted for SRS-1406.

SRS - Potassium

Thirty eight laboratories provided ALP results for soil K (test code 140) results. These were ranked low to high based on sample SRS-1408 (see Figure 3). Soil SRS-1410 was the most inconsistent across labs. Across soils, lab #2 had consistent low bias and labs #38 high bias. Labs #1, #9, #16, #17, #19 #32, and #34 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-1408, with a median intra-lab value of 2.3 mg kg^{-1} K and highest for SRS-1406 with a value of 7.5 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 #36 and #37 which exceeded 10 mg kg^{-1} K on four of five soils; and lab #19 the value exceeded 25 mg kg^{-1} K on all samples. Poor precision is attributed to extraction and/or analysis instrument operation.

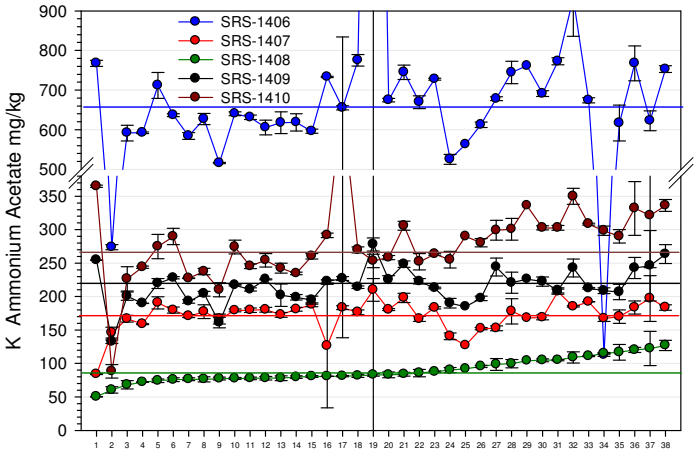

Figure 3. Extractable K distribution plots for SRS materials, ALP 2014 Cycle 24.

SRS SOM-LOI

Forty-four laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 1.77 to 4.78%. Results were ranked based on sample SRS-1406 (see Figure 4). Lab #1 was noted having consistent high bias. Labs #6, #13, #15, #17 and #44 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 *s* values ranging from 0.08 to 0.21% SOM-LOI, the highest for SRS-1408. Across labs *s* values for SRS-1407 ranged from 0.008 - 0.27 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #12, #25, #26, #28, #31 and #32 exceeded 0.12 for SRS-1406 and lab #39 exceeded 0.22 % SOM for four of five soils evaluated in ALP cycle 24. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

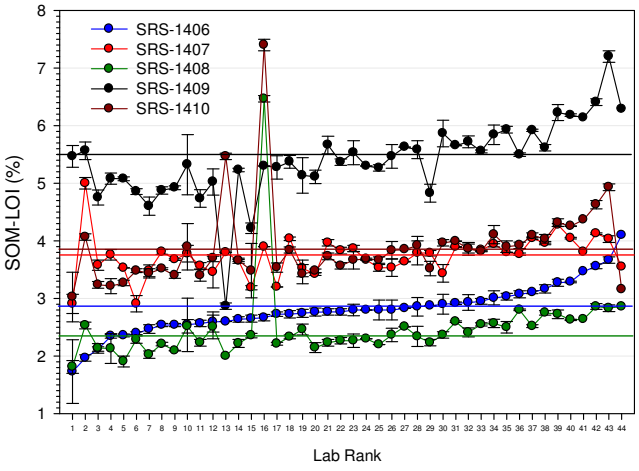

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2014 Cycle 24.

Soil DTPA-Cu

Seventeen laboratories provided ALP results for soil extractable DTPA-Cu, (test code 172) results. These were ranked low to high based on sample SRS-1408 (see Figure 5). Soil SRS-1406 was the highest in concentration and the most inconsistent across labs. Across soils, labs #1 had low bias on all soils, labs #27 high bias on three of five soils. Labs #2, #10 and #19, were inconsistent across a majority of soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

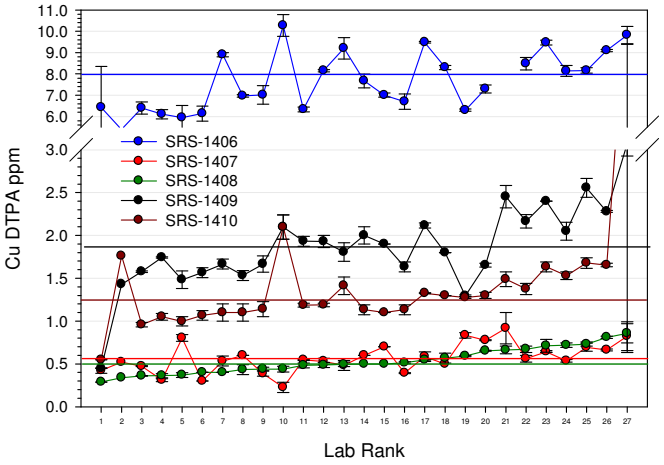

Figure 5. Soil DTPA-Cu distribution plot, ALP 2014 Cycle 24.

Soil DTPA-Cu median intra-lab *s* values were lowest for ALP soil SRS-1408 with a consensus intra-lab value of 0.02 mg kg^{-1} and highest for SRS-1406 with a value of 0.21 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, for soils with DTPA-Cu less than 2.0 mg kg^{-1}. Intra-lab precision was poor for lab #27 on three of five soils. Poor precision maybe associated with instrument detection limit 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-1406 (see Figure 6). Data plots show labs #1 has a high bias for one of three botanical samples. Lab #10 showed high bias on SRB-1404. Labs #8, #15, #17 and #18 were inconsistent.

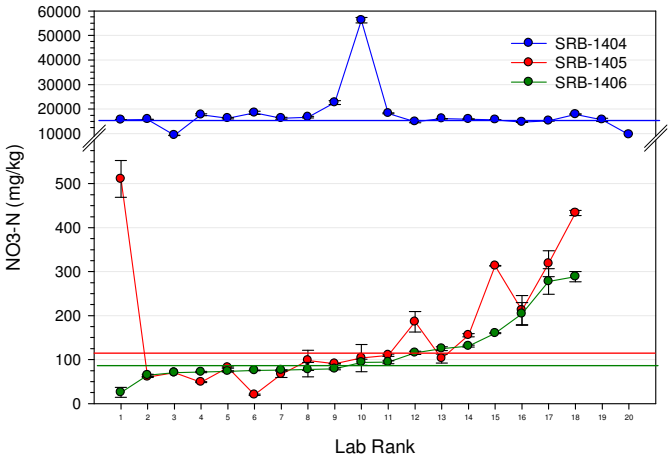

Figure 6. Nitrate distribution plots for SRB materials, ALP 2014, Cycle 24.

Botanical NO_3-N results for cycle 24 indicate very high precision, with intra-lab standard deviation (*s*) values ranging from 74 to 475 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-1404; ranged from 57 – 1103 mg kg^{-1}; SRB-1405 ranged from 1 - 42 mg kg^{-1}, and SRB-1406 ranged from 1 – 29 mg kg^{-1}. Lab #1 had consistently high standard deviation for botanical sample SRB-105. Five labs were flagged for poor precision.

SRB - Dumas Nitrogen and TKN

Twenty-two 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-1404 (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-1404, whereas lab #10 showed inconsistency across all three botanical samples. Lab #7 for TKN showed high bias for SRB-1406.

Dumas N and TKN results indicate very high precision across all labs for all samples. Individual lab Dumas N *s* values for SRB-1404, ranged from 0.001 to 0.071 % N, SRB-1405 ranged from 0.006 to 0.104 % N and SRB-1406 ranged from 0.001 to 0.101 % N. Lab #2 had consistently high standard deviation for two of three botanical samples. Individual lab TKN *s* values for SRB-1404 ranged from 0.017 to 0.18 %, SRB-1405 ranged from 0.005 to 0.075 % and sample SRB-1406 ranged from 0.010 to 0.085 % TKN nitrogen.

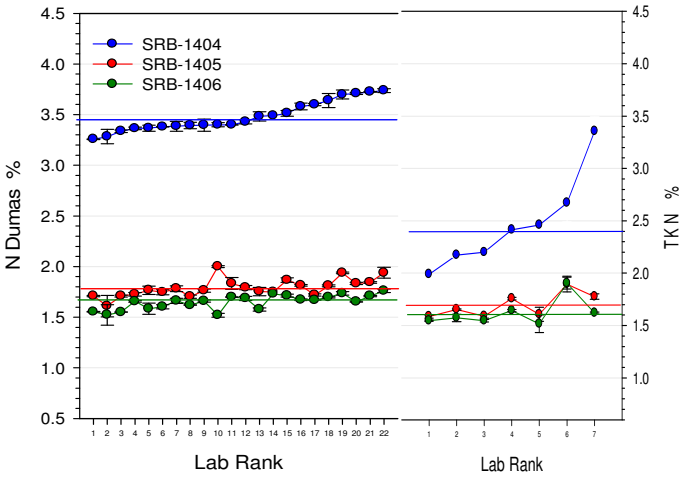

Figure 7. N distribution plots for SRB materials, ALP 2014 Cycle 24.

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-1404 for test code 213 (see Figure 8). Laboratory #1, and #2 showed low bias on two of three samples, whereas lab #28 indicate high bias. Labs #4, #6, and #17 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 0.056 to 0.25 %K for test code 213 across the three samples. Individual lab intra-lab *s* values for SRB-1404; ranged from 0.011 to 0.73 % K and SRB-1405 0.010 — 0.34 % K. Lab #34 had consistently high standard deviations exceeding 0.30 %K for two of the three samples. Four labs were flagged for poor precision.

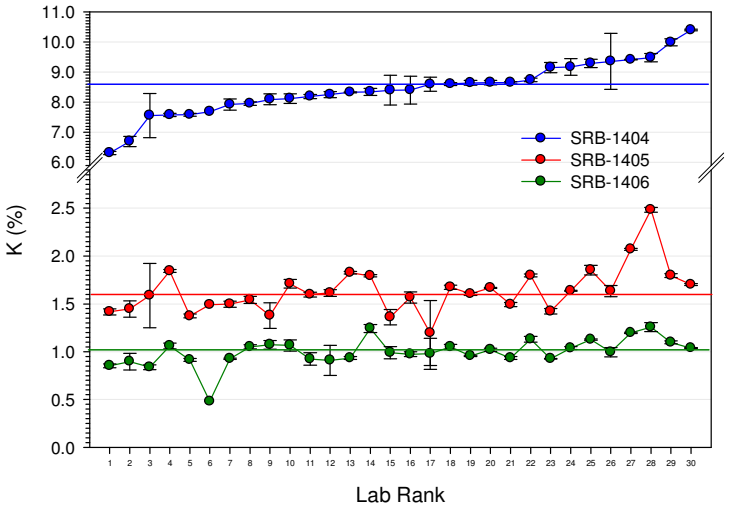

Figure 8. Potassium (code 213 and 223) plots for SRB materials, ALP 2014 Cycle 24.

SRB - Phosphorus

Twenty-six laboratories provided ALP results for cycle 24 phosphorus (P) combined (test code 227). 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-1404 (see Figure 9). Consistent bias was noted for labs #1 through #3. Lab #26 showed high bias on one of three samples. 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 0.007 % P for test code 212 across the three botanical samples. Individual lab intra-lab *s* values for SRB-1404; ranged from 0.003 - 0.044 % P; SRB-1405 ranged from 0.001 – 0.026 % P and SRB-1406 0.001 - 0.020 % P. Lab #26 had a high standard deviations exceeding 0.02 % P for all three botanical samples. Two labs were flagged for poor precision.

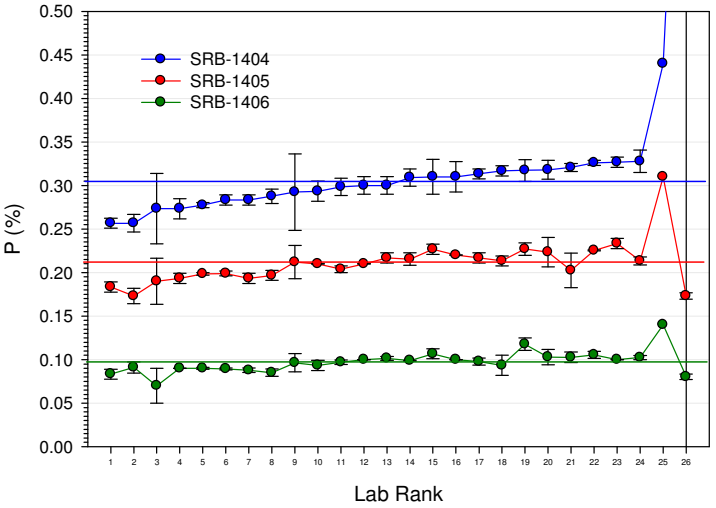

Figure 9. Phosphorus distribution plots for SRB materials, ALP 2014 Cycle 24.

SRB - Boron

Twenty-one laboratories provided ALP results for boron (B) (test code 219). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1404 (see Figure 10). Laboratories #1, and #2 showed low bias on two fo thee samples, whereas lab #20 indicated high bias all samples. Labs #13 and #17 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical B results indicate very high precision, with intra-lab standard deviation (*s*) values ranged from 0.96 to 1.6 mg kg^{-1} B for across the three botanical samples. Individual lab intra-lab *s* values for SRB-1404; ranged from 0.08 - 2.6 mg kg^{-1} B; SRB-1405 ranged from 0.11 – 2.5 mg kg^{-1} B and SRB-1406 0.12 - 4.2 mg kg^{-1} B. Lab #21 had consistently high standard deviations exceeding 2.4 mg kg^{-1} B for all three samples, the highest for botanical sample, SRB-1404.

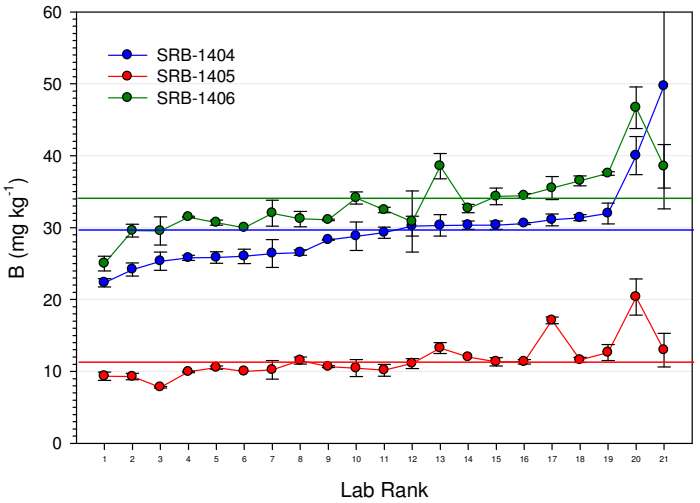

Figure 10. Boron distribution plots for SRB materials, ALP 2014 Cycle 24.

SRW - Water pH

Ten laboratories provided ALP results for water pH (test code 301). Ranking lab results low to high based on sample SRW-1404 (see Figure 11). Labs #1 and #2 indicated consistent low bias on all three samples. Labs #8, 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 0.003, 0.01 and 0.05 pH units, respectively. Precision for sample SRW-1405 was the most consistent across the ten laboratories. Across water samples poor precision was noted for two laboratories. Specifically intra-lab the *s* values for lab #8 exceeded 0.06 pH on SRW-1406. Highest precision was noted for lab #1 with intra-lab *s* values of < than 0.02 pH units.

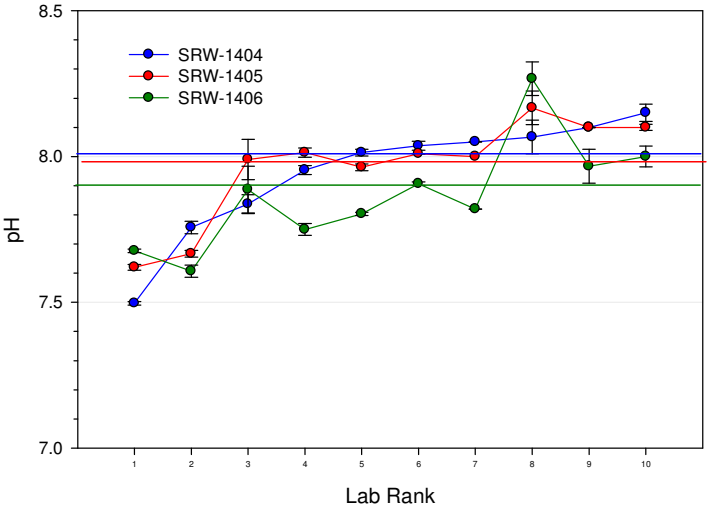

Figure 11 . Water pH distribution plots for SRW materials, ALP 2014 Cycle 24.

SRW - Ca Results

Ten laboratories provided ALP results for water Ca (test code 303). Lab results were ranked low to high based on sample SRW-1404 (see Figure 12). Median values are designated by horizontal lines. Labs #1 and #2 had consistent high bias on all samples. Labs #3 - #10 showed high consistency across all samples.

Ca precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.100, 0.065, and 0.115 mmolc L^{-1} for SRW-1404, SRW-1405, and for SRW-1406, respectively. Water Ca precision was excellent for all individual labs with only lab #5 exceeding 0.21 mmolc L^{-1} Ca on sample SRW-1404. Across samples intra-lab *s* was less than 0.030 mmolc L^{-1} for lab #6. Two labs were flagged for poor precision.

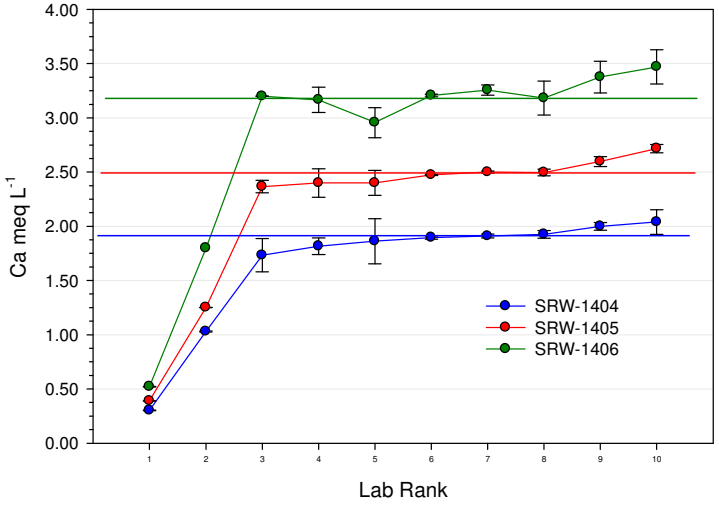

Figure 12. Water EC distribution plots for SRW materials, ALP 2014 Cycle 24.

Announcements

- ALP collected fifteen proficiency soils in July 2014 from five New England States and the provinces of Quebec, Nova Scotia, and Prince Edward Island representing a diverse range of textures and chemical properties. Additional collections are planned for Ontario and Michigan in October.

- ALP was a sponsor at the Southern Extension and Research Meeting in Lexington Kentucky, June 22-24, 2014.

- Data Submission. CTS will revamping the ALP data submission, to use a direct file upload via a data portal, later this year. This will replace emailing the proficiency data file to CTS each ALP cycle.

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

- ALP has developed a large archive of standard reference soils and botanical materials available for purchase from past ALP cycles. 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.

Summary

ALP 2014 Cycle 24 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 24. 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 24 Ship

September 26, 2014

"Geology differs from physics, chemistry, and biology in that the possibilities for experiment are limited. "

- Reinout Willem van Bemmelen, 1961

ALP
Agricultural Laboratory Proficiency Program