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ALP Program Report

2014 Spring - Cycle 23

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ALP Overview

The Agriculture Laboratory Proficiency (ALP) Program Spring 2014 Round cycle 23 was completed June 10, 2014, with eighty-five 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.

http://ag.udel.edu/dstp/images/030rev1.jpg

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 23.
- Fifty-one Laboratories provided soil pH (1:1) H_2O results.
- Cycle 23 soil NH_4OAc K ranged from 81 to 300 mg kg^{-1} with an MAD values ranging 6.8 - 32 mg kg^{-1} across the five soils.
- S04-S was highly inconsistent on the two soils with the highest concentration.
- Botanical Ca, ranged from 0.79 - 1.36 mg kg^{-1}, with three labs noted for low bias.
- Botanical Zn values ranged from 20.7 to 49.4 mg kg^{-1} across the tree samples.
- Soil SRW-1403 had a NO_3-N 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-1401 a Arisburg silt loam collected from Boone Cty, MO; SRS-1402 a sandy loam collected from near Westmoreland, NB, Canada; SRS-1403 a sandy loam, collected from Bookings Cty, SD; SRS-1404 a Brady silt loam from Wilson Cty, TN; and SRS-1405 Delhi loamy sand from Fresno Cty, CA. Chemical properties of the SRS materials concentration median ranges: pH (1:1) H_2O 5.60 - 7.03; NO_3-N 21.1 - 71.4 mg kg^{-1}; Bray P1 (1:10) 5.4 - 138 mg kg^{-1}; K NH_4OAc 81.4 - 316 mg kg^{-1}; Mehlich 3 P (ICP) 6.2 - 151 mg kg^{-1}; DTPA-Zn 0.50 - 27.4 mg kg^{-1}; SOM-WB 1.60 – 4.20 %; CEC 8.6 - 13.7 cmol kg^{-1}; clay 8.3 - 16.8% and Solvita CO_2 Respiration 4.7 - 43.2 mg kg^{-1}.

Standard Reference Botanical (SRB) materials were: SRB-1401 grape petiole from Washington state, SRB-1402 potato blend composite from Washington state and SRB-1403 corn leaves from Indiana. SRB material median concentrations ranged: NO_3-N 57 - 20180 mg kg^{-1}; Dumas N 1.07 - 3.88%; total P 0.29 - 0.39%; total K 1.80 - 9.64%; total S 0.17 - 0.22 %, total B 13.1 - 36.9 mg kg^{-1}; and total Cd 0.067 - 1.39 mg kg^{-1}.

Standard Reference Water samples represent an agriculture water sample collected: SRW-1401 an irrigation canal near Mountain view, Alberta, Canada; SRW-1402 from the San Miguel river in western Colorado; and SRW-1403 an irrigation well Sydney, NE. SRW median concentrations ranged: pH 7.68 - 8.80; EC 0.11 - 0.79 dSm^{-1}; SAR 0.35 - 0.92; Ca 0.28 - 4.02 mmolc L^{-1}; Cl 0.067 - 2.04 mmolc L^{-1}; and NO_3–N 0.007 - 3.3 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 23 met homogeneity standards."

Table 1. ALP soils homogeneity evaluation Cycle 23, 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-1401	7.60	*0.02*	0.25	*0.010*	13.4	*1.9*	19.6	*2.2*
SRS-1402	4.85	*0.03*	0.48	*0.043*	39.8	*1.4*	66.7	*5.9*
SRS-1403	4.94	*0.05*	0.30	*0.011*	5.7	*0.8*	26.5	*1.5*
SRS-1404	7.26	*0.02*	0.52	*0.028*	4.6	*0.4*	51.2	*1.8*
SRS-1405	5.03	*0.02*	0.66	*0.035*	8.4	*0.6*	57.2	*2.9*

[1] Statistics based on four soil replicates, each analyzed in triplicate ALP Cycle 23.

2014 Cycle 23 Observations

Results for soil pH (1:1) H_2O (test code 115) analysis MAD values for Cycle 24 averaged 0.058 pH units. Within lab pH standard deviation was 0.042 pH units. Soil CEC ranged 8.6 to 13.7 cmol kg^{-1} across the five soils. Soil Solvtia CO_2 respiration (test code 191) results were provided by seven laboratories with median results ranging from 4.7 - 43.2 mg kg^{-1} with a intra-lab precision, with s values averaging 0.6 for four of five samples. Sample SRS-1405 has the highest in sand content measured in the ALP Program, 80.1%. Soil ammonium acetate K (Test code 140) MAD values ranged 8.8 - 32 mg kg^{-1} and ammonium acetate Ca MAD values 96 to 235 mg kg^{-1} for the five soils. These results higher than those of cycles 21 and 22 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 0.025%. 0.039% and 0.035%, respectively. Across the three materials there was a greater inter-lab variability (MAD) in total potassium values than combustion N, P, Ca or total S concentrations for SRB-1401. Generally the potato blend sample SRB-1402 had high level median NO_3-N, Cl, K, Ca, Na, and Cd relative to the other two botanical samples of cycle 23. Also of significance sample SRB-1403 which had low quantities of As, Ba, Cd, Co, and Pb mg kg^{-1}.

Water EC results showed high consistency across samples. Across the three water samples EC MAD values ranged from 0.003 to 0.016 dSm^{-1}. NO_3-N values ranged from 0.007 - 3.30 mmolc L^{-1} across the three water samples.

SRS Results - pH

Fifty-one laboratories provided ALP results for soil pH (1:1) H_2O (test code 115). Soils ranged from acid to alkaline, median range 5.60 to 7.03. Lab results were ranked low to high based on sample SRS-1401 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally soils SRS-1404 and SRS-1405 were very similar in pH, and 94% of labs found no differences between the two soils. Labs #1, #6, #7, #27 and #46 and #47 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.

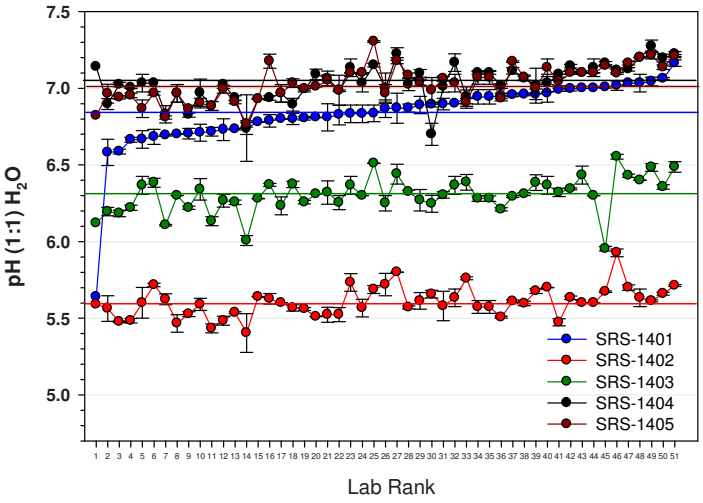

Figure 1. pH (1:1) H_2O distribution plots for SRS materials, ALP 2014 Cycle 23.

pH precision across the five ALP soils indicates very high precision, with intra-lab standard deviation (*s*) values ranging from 0.031 to 0.051 pH units, the highest noted for SRS-1401. For specific labs poor precision was noted for three laboratories, exceeding by 2 times that noted for consensus intra-lab *s*. Specifically *s* for lab #14 exceeded 0.10 pH units for 2 of five soils. Soil SRS-1401 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-eight labs. Median soil Bray P1 values ranged from 5.4 to 138 mg kg^{-1} PO_4-P; Mehlich 1 P 8.3 to 20.6 mg kg^{-1} P and M-3-P ICP ranged from 8.6 to 73.9 mg kg^{-1} P, across the five soils. Ranking lab results based on sample SRS-1401, median Bray P concentrations are shown in indicated in Figure 2. A saw tooth trend was noted for soils SRS-1403 and SRS-1404 associated with moderate soil P concentrations and high sand content with three of twenty-two labs (#15, #19, and #20) having large inconsistency. Inconsistency is likely related to extraction, analysis instrument and/or method compliance. MAD values were the lowest for soil SRS-1405 and highest for SRS-1402 of the five soils.

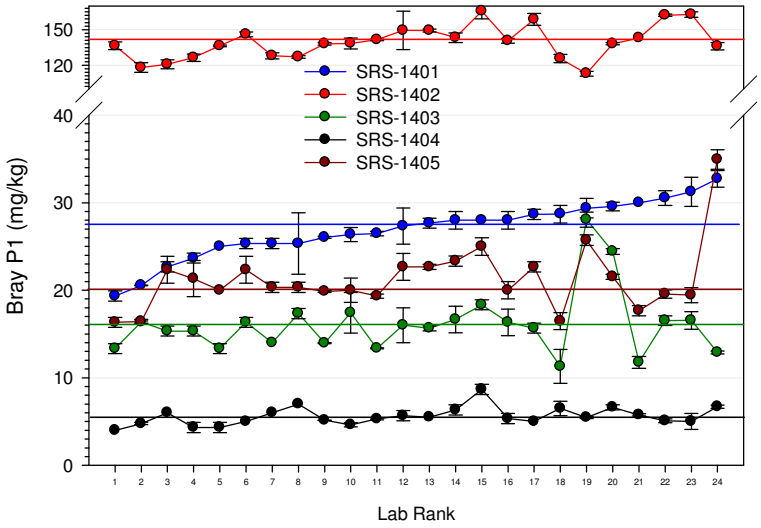

Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2014 Cycle 23.

Twenty-four laboratories provided ALP results for Olsen P (test code 134), for the five soils which medians ranged from 1.6 to 43.4 PO_4-P mg kg^{-1}. Mehlich 3 P–SPEC median concentrations were 3.0 to 133 mg kg^{-1} PO_4-P reported by ten labs. Strong Bray (P2) was reported by eight laboratories ranging from 18.5 to 234 mg kg^{-1} PO_4-P with the highest P concentration noted for SRS-1402.

SRS - Potassium

Forty-one laboratories provided ALP soil M3-K (test code 150) results. These were ranked low to high based on sample SRS-1401 (see Figure 3). Soil SRS-1405 was the most inconsistent across labs. Across soils, lab #1 had consistent low bias and labs #38 through #41 high bias. Labs #3, #18, #23, and #25 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-1404, with a consensus intra-lab value of 4.8 mg kg^{-1} K and highest for SRS-1405 with a value of 12.8 mg kg^{-1} K. Potassium within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 160 mg kg^{-1} K. Precision was poor (based on intra-lab *s*) for labs #28, #34 and #37 which exceeded 31.5 mg kg^{-1} K on SRS-1403; and lab #27 the value exceeded 48 mg kg^{-1} K on SRS–1405. Poor precision is attributed to extraction and/or analysis instrument operation.

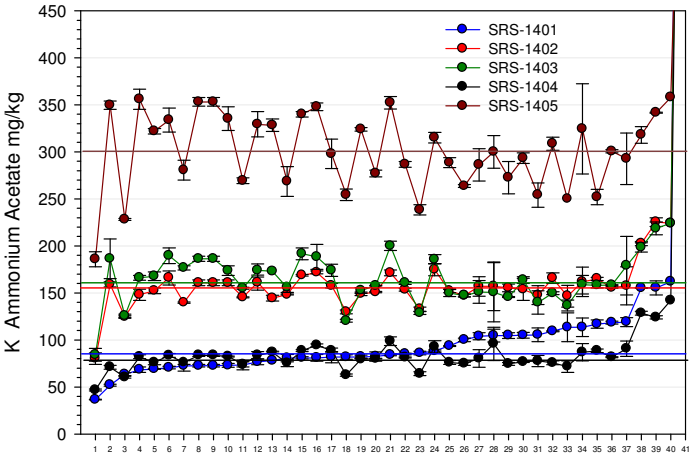

Figure 3. Extractable K distribution plots for SRS materials, ALP 2014 Cycle 23.

SRS SOM-LOI

Forty-five laboratories provided ALP results for soil SOM-LOI (test code 182). Soil Median SOM-LOI values ranged from 2.20 to 4.45%. Results were ranked based on sample SRS-1401 (see Figure 4). Labs #41 though #44 were noted having consistent high bias. Labs #7, #14, and #39 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 0.15% SOM-LOI, the highest for SRS-1402. Across labs *s* values for SRS-1401 ranged from 0.010 - 0.37 %. Across soil materials low precision was noted for several laboratories. Specifically *s* for labs #9, #14, #16, #21, #39 and #40 exceeded 0.15 for SRS-1402 and lab #39 exceeded 0.22 % SOM for four of five soils evaluated in ALP cycle 23. Poor precision may be associated with muffle furnace crucible position and furnace heating time.

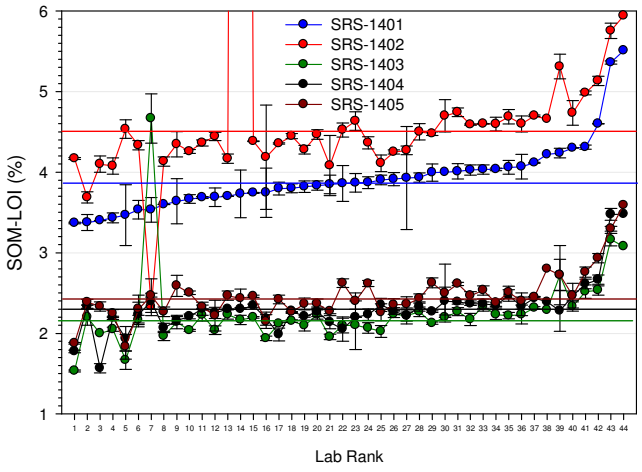

Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2014 Cycle 23.

Soil SO_4-S

Twenty laboratories provided ALP soil extractable SO_4-S, (test code 139) results. These were ranked low to high based on sample SRS-1401 (see Figure 5). Soil SRS-1404 was the highest in concentration and the most inconsistent across labs. Across soils, labs #1 and #2 had low bias on all soils, labs #15 through #20 high bias. Labs #4, #11 and #14, were inconsistent across a majority of soils. Source of this inconsistency is likely related to instrument calibration or method compliance.

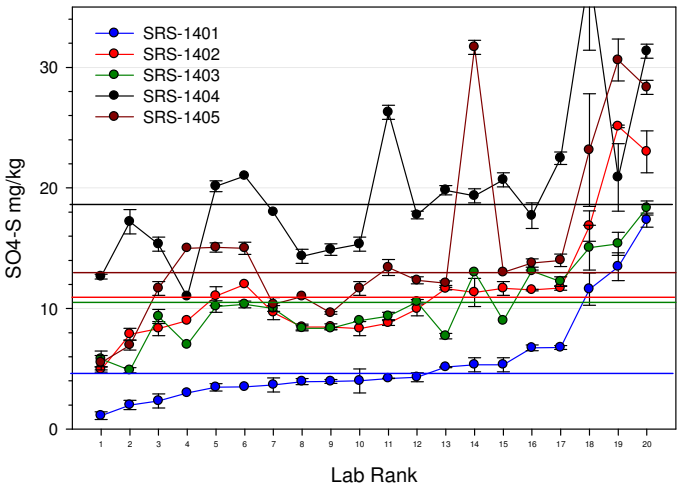

Figure 5. Soil SO_4-S distribution plot, ALP 2014 Cycle 23.

Soil SO_4-S intra-lab *s* values were lowest for ALP soil SRS-1403. with a consensus intra-lab value of 0.56 mg kg^{-1} and highest for SRS-1404 with a value of 1.7 mg kg^{-1}. Individual lab precision across the ALP soil materials indicates very high precision, generally, for soils with SO4-S less than 8 mg kg^{-1}. Intra-lab precision was poor for lab #18 on three of five soils; lab #19 on SRS-1404. 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-1401 (see Figure 6). Data plots show labs #20 has a high bias for two of three botanical samples. Lab #3 showed high bias on SRB-1402. Labs #4, #5, #15 and #17 were inconsistent.

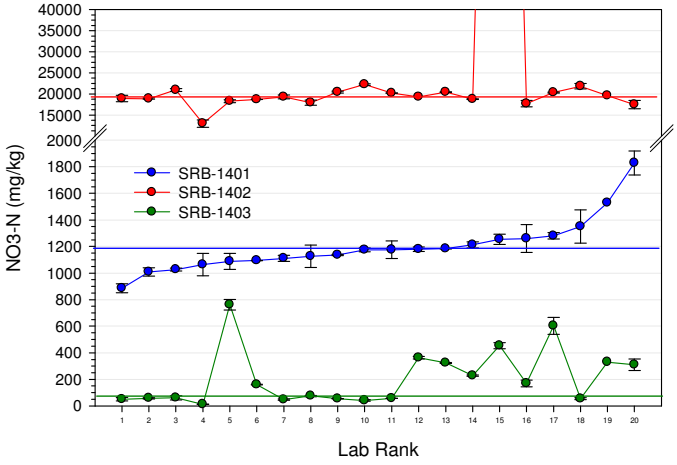

Figure 6. Nitrate distribution plots for SRB materials, ALP 2014, Cycle 23.

Botanical NO_3-N results for cycle 23 indicate very high precision, with intra-lab standard deviation (*s*) values ranging from 22 to 950 mg kg^{-1} for test code 202 for the three samples. Individual lab NO_3-N intra-lab *s* values for SRB-1401; ranged from 2 – 104 mg kg^{-1}; SRB-1402 ranged from 10 - 3070 mg kg^{-1}, and SRB-1403 ranged from 1.0 – 63 mg kg^{-1}. Lab #18 had consistently high standard deviation across one of three botanical samples.

SRB - Dumas Nitrogen and TKN

Twenty laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and nine 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-1402 (see Figure 7). It is note worthy that TKN was lower than Dumas for SRB-1402. Labs #1 showed low bias for Dumas N SRS-1402, whereas labs #13 through #15 showed inconsistency across all three botanical samples. Lab #1 for TKN showed low bias for SRB-1307.

Dumas N and TKN results indicate very high precision across all labs for all samples. Individual lab Dumas N *s* values for SRB-1401, ranged from 0.003 to 0.582 % N, SRB-1402 ranged from 0.006 to 0.091 % N and SRB-1403 ranged from 0.004 to 0.102 % N. Lab #5 had consistently high standard deviation for one of three botanical samples. Individual lab TKN *s* values for SRB-1401 ranged from 0.011 to 0.17 %, SRB-1402 ranged from 0.036 to 0.37 % and sample SRB-1403 ranged from 0.026 to 0.22 % TKN nitrogen.

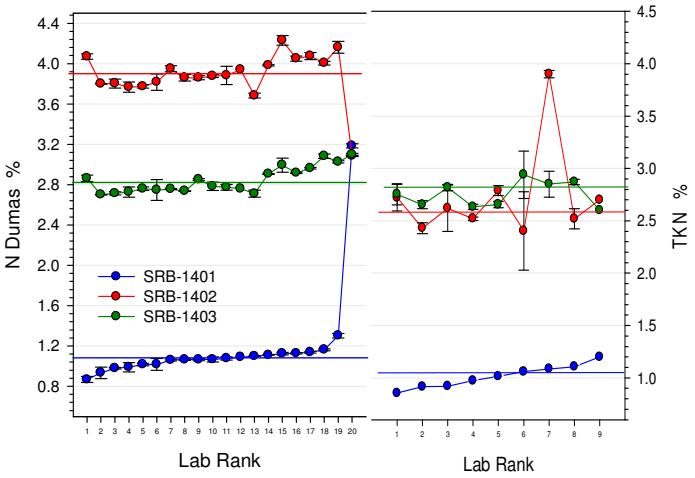

Figure 7. N distribution plots for SRB materials, ALP 2014 Cycle 23.

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-1401 for test code 213 (see Figure 8). Laboratory #1, and #2 showed low bias on two of three samples, whereas lab #25 indicate high bias. Labs #7, #16, and #19 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 0.02 to 0.15 %K for test code 213 across the three samples. Individual lab intra-lab *s* values for SRB-1401; ranged from 0.008 to 0.29 % K and SRB-1402 0.010 — 0.92 % K. Lab #24 had consistently high standard deviations exceeding 0.12 %K for two of the three botanical samples.

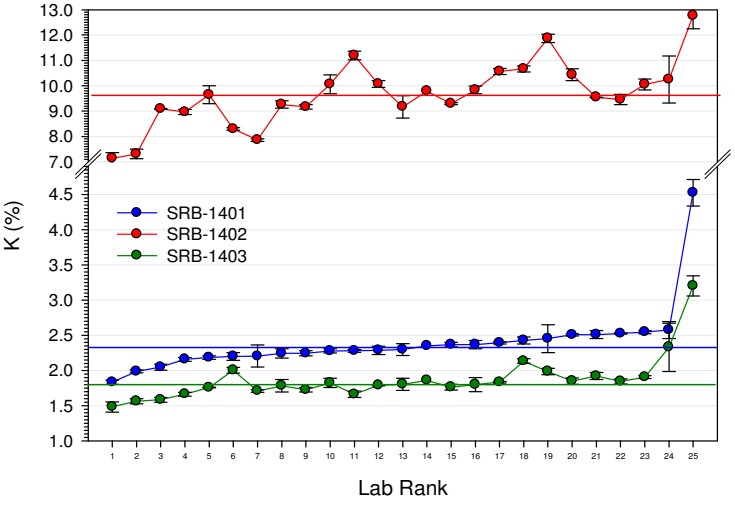

Figure 8. Potassium (code 213) distribution plots for SRB materials, ALP 2014 Cycle 23.

SRB - Calcium

Thirty laboratories provided ALP results for cycle 22 calcium (Ca) combined test codes 214 and 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-1401 (see Figure 9). Consistent bias was noted for labs #1 through #3. Lab #30 showed high bias on two of three samples. Labs #21 and #24 had high bias on SRB-1402. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Ca results indicate very high precision, with intra-lab standard deviation (*s*) values ranged 0.007 tp 0.067 % Ca for test code 214 across the three botanical samples. Individual lab intra-lab *s* values for SRB-1401; ranged from 0.006 - 0.13 % Ca; SRB-1402 ranged from 0.007 – 0.12 % Ca and SRB-1403 0.006 - 0.43 % Ca. Lab #27 had a high standard deviations exceeding 0.40 % Ca for botanical sample SRB-1403.

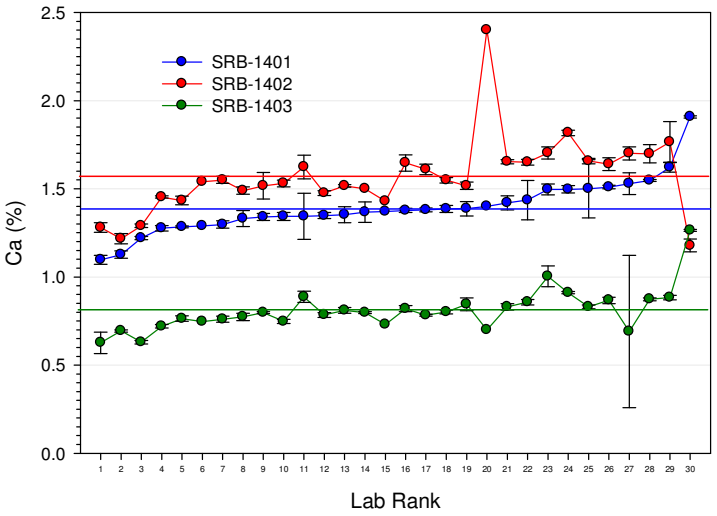

Figure 9. Calcium distribution plots for SRB materials, ALP 2014 Cycle 23.

SRB - Zinc

Thirty laboratories provided ALP results for zinc (Zn) (test codes 220 and 232). Results median values are designated by horizontal lines for each botanical material and labs results are ranked low to high based on sample SRB-1401 (see Figure 9). Laboratories #1, #2 and #3showed low bias, whereas lab #30 indicated high bias. Lab #14 was inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical S results indicate very high precision, with intra-lab standard deviation (*s*) values ranged from 3.6 to 4.1 mg kg^{-1} Zn for test code 220 across the three botanical samples. Individual lab intra-lab *s* values for SRB-1401; ranged from 0.44 - 15.7 mg kg^{-1} Zn; SRB-1402 ranged from 0.33 – 16.2 mg kg^{-1} Zn and SRB-1403 0.23 - 19.3 mg kg^{-1} Zn. Lab #30 had consistently high standard deviations exceeding 15 mg kg^{-1} Zn for all three samples, the highest for botanical sample, SRB-1403, which exceeded 19 mg kg^{-1} Zn.

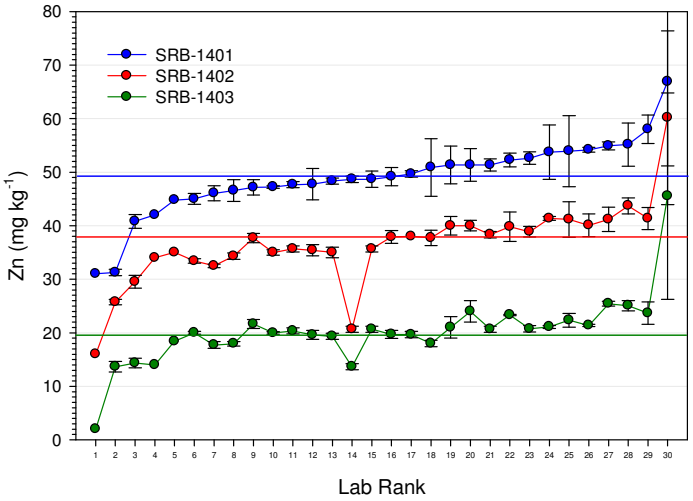

Figure 10. Zinc distribution plots for SRB materials, ALP 2014 Cycle 23.

SRW - Water pH

Nine laboratories provided ALP results for water pH (test code 301). Ranking lab results low to high based on sample SRW-1401 (see Figure 11). Labs #1 and #2 indicated consistent low bias on all three samples. Labs #5, 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 0.03 0.04 and 0.09 pH units, respectively. Precision for sample SRW-1402 was the most consistent across the nine laboratories. Across water samples poor precision was noted for one laboratory. Specifically intra-lab the *s* values for lab #8 exceeded 0.20 pH on SRW-1401. Highest precision was noted for lab #3 with intra-lab *s* values of < than 0.02 pH units.

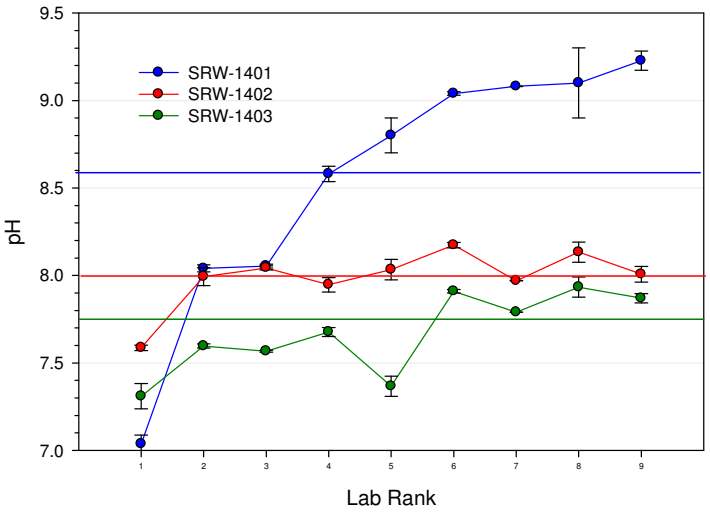

Figure 11 . Water pH distribution plots for SRW materials, ALP 2014 Cycle 23.

SRW - NO_3-N Results

Nine laboratories provided ALP results for water NO_3-N (test code 303). Lab results were ranked low to high based on sample SRW-1401 (see Figure 12). Median values are designated by horizontal lines. Lab #9 had consistent high bias on all samples. Labs #2, #7 and #8 showed high consistency across all samples.

NO_3-N precision across the three water solution matrices indicates excellent precision, with intra-lab *s* values of 0.011, 0.012, and 0.47 mmolc L^{-1} for SRW-1401, SRW-1402, and for SRW-1403, respectively. Water NO_3-N precision was excellent for all individual labs with only lab #8 exceeding 0.15 mmolc L^{-1} on sample SRW-1402. Across samples intra-lab *s* was less than 0.030 mmolc L^{-1} for lab #3.

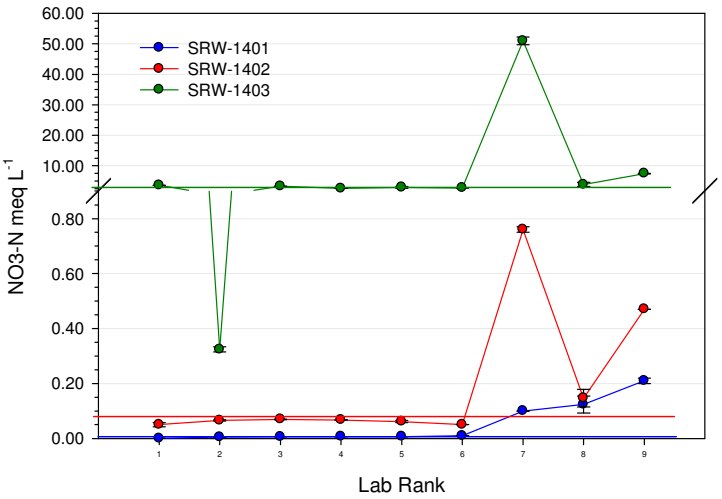

Figure 12. Water EC distribution plots for SRW materials, ALP 2014 Cycle 23.

Announcements

- ALP will be a sponsor of the Southern Extension and Research Meeting in Lexington Kentucky, June 22-24, 2014.
- ALP collected five proficiency soils in April and May 2014 from across Arizona, North Dakota and South Dakota representing a diverse range of textures and chemical properties. Additional collections are planned for the Canadian Maritimes in July.
- 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.
- The ALP Environmental Soils program has been restructured. Specific changes include the use of two certified reference soil standards for evaluating laboratory proficiency each proficiency cycle.
- ALP has developed a large archive of standard reference soils and botanical materials available for purchase from past ALP cycles. If there is specific soil type, soil properties or plant sample that you believe should be considered please contact the ALP Program Technical Director, rmiller@lamar.colostate.edu.

Summary

ALP 2014 Cycle 23 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 23. 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

June 28, 2014

"The saddest aspect of life right now is that science gathers knowledge faster than society gathers wisdom. "

- Isaac Asimov

ALP
Agricultural Laboratory Proficiency Program