

ALP Program Report



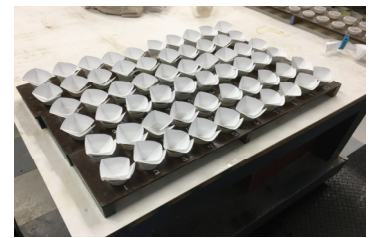
Robert O. Miller, PhD, ALP Technical Director, Windsor, CO
Christopher Czuryca, Collaborative Testing Services, Inc, Sterling, VA

ALP Overview

Special points of interest:

- An assessment soil homogeneity indicate ALP reference soil materials were highly uniform for Cycle 53.
- Sixty-four laboratories provided soil pH (1:1) H₂O results, medians ranged from 5.32 - 7.60.
- Soil M3-P ICP for Cycle 53 ranged from 21.9 to 102 mg kg⁻¹ with MAD values ranging 1.8 - 6.3 mg kg⁻¹ across the five soils.
- Soil M3-K values ranged from 81 - 568 mg kg⁻¹ for the five ALP soils of PT Cycle 53.
- Botanical N by combustion was reported by 41 labs, with two labs showing bias across the four PT materials for Cycle 53.
- Botanical Total Mn content , ranged from 9.3 - 121.4 mg kg⁻¹ for forty-five labs, with two noted having high bias.

The Agriculture Laboratory Proficiency (ALP) Program spring 2024 Round Cycle 53 was completed May 20, 2024, with results from one-hundred eight labs enrolled from the US, Canada, South Africa, Italy, 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 seventeen 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 53 were: SRS-2401 Nora-Crofton complex loam, collected Minnehaha Cty, SD; SRS-2402 Hagerstown silt loam Centre Cty, PA; SRS-2403 a Appling sandy loam collected from Granville Cty, NC; SRS-2404 is Shano silt loam collected Grant Cty, WA; and SRS-2405 a sandy loam collected near Osoyoos, BC, Canada. Chemical properties of the SRS materials ranges: pH (1:1) H₂O 5.32 - 7.60; SMP Buf 5.95 - 7.46 mg kg⁻¹; Bray P1 (1:10) 10.1 - 78 mg kg⁻¹; M3-K 81 - 568 mg kg⁻¹; M3-Ca 487 - 2362 mg kg⁻¹; DTPA-Zn 0.36 - 2.04 mg kg⁻¹; SOM-LOI 0.84 - 5.73%; CEC 4.4 - 22.9 cmol kg⁻¹; clay 3.6 - 27.3% and NO₃-N 4.0 - 109.7 mg kg⁻¹.

Standard Reference Botanical (SRB) materials for Cycle 53 were: SRB-2401 avocado leaf composite from CA; SRB-2402 soybean leaf composite from NE; SRB-2403 grape petiole composite from WA and SRB-2404 spinach leaf composite from CA. SRB median analytes concentrations: NO₃-N 73 - 2978 mg kg⁻¹; Dumas N 0.115 - 3.41 %; wet digestion total P 0.035 - 0.404 %; total K 0.17 - 3.80 %; total Ca 0.031 - 1.63 %; total S 0.021 - 0.65 %, total B 1.8 - 36 mg kg⁻¹; and Zn 4.0 - 47.2 mg kg⁻¹.

Standard Reference Water (SRW) samples represent an agriculture water samples collected: SRW-2401 a water sample collected from a domestic well Alpina, SD; SRW-2402 collected irrigation supply canal Butte, NE; and SRW-2403 from a domestic water supply watertown, WI. SRW median concentrations: pH 7.88 - 8.23; EC 0.29 - 0.139 dSm⁻¹; SAR 0.50 - 53.8; Ca 0.048 - 6.32 mmolc L⁻¹; Na 0.54 - 8.70 mmolc L⁻¹; HCO₃ 1.58 - 3.73 mmolc L⁻¹; and NO₃ 0.01 - 0.17 mmolc L⁻¹.

Inside this issue:

Soil homogeneity evaluation	2
2024 Cycle 53 observations	2
SRS Results: pH, P, K, SOM	3
SRS NO ₃ -N results Cd Reduction	5
SRB NO ₃ -N results	5
SRB: N, P, K and Mn	6
SRW Results	8
Announcements	9

Homogeneity Evaluations



*“..soil pH, Buf pH
A&E, Olsen P and
SOM-WB analysis Stdev
values for Cycle 53 met
homogeneity standards.”*

SRS material homogeneity was evaluated based on soil test codes pH (1:1) H₂O, buffer pH Adams Evans, EC (1:1), P Olsen, K Olsen, NO₃-N and SOM-WB on analysis of six 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 H₂O, Table 1. Proficiency soil antecedent moisture contents were 4.20, 3.05, 0.90 2.08 and 0.84 % . respectively.

Homogeneity was also evaluated on SRB and SRW matrix samples. Botanical results indicate all samples were well homogenized for N, P, Zn and C, with RSD values less than 0.5% of N and C on three of botanical samples, Table 2. Water results for EC, Ca, NO₃ and NH₄ were well homogenized with RSD values for EC less than 1% for two of the samples, Table 3.

Table 1. ALP soils homogeneity evaluation Cycle 53, 2024.

Sample	pH (1:1) H ₂ O		EC (dS m ⁻¹)		P Olsen (mg kg ⁻¹)		SOM-WB (%)	
	Mean ¹	Std	Mean	Std	Mean	Std	Mean	Std
SRS-2401	5.25	0.02	0.26	0.01	3.5	0.4	5.78	0.15
SRS-2402	6.64	0.01	0.23	0.01	11.6	0.7	2.50	0.06
SRS-2403	6.08	0.01	0.21	0.01	12.0	1.0	2.38	0.14
SRS-2404	7.26	0.02	1.19	0.02	30.2	1.8	0.89	0.08
SRS-2405	7.58	0.01	0.20	0.01	25.6	1.2	0.87	0.15

¹ Statistics based on five randomly selected soil replicates, each analyzed in triplicate.

Table 2. ALP botanical homogeneity evaluation Cycle 53, 2024.

Sample	N (%)		P (%)		Zn (mg kg ⁻¹)		C (%)	
	Mean ¹	Std	Mean	Std	Mean	Std	Mean	Std
SRB-2401	0.149	0.003	0.030	0.001	7.37	0.67	42.91	0.17
SRB-2402	2.93	0.009	0.310	0.002	36.7	0.84	39.56	0.08
SRB-2403	1.03	0.004	0.379	0.007	46.1	0.70	39.79	0.10
SRB-2404	3.47	0.047	0.397	0.008	46.1	0.99	37.01	0.05

¹ Statistics based on three randomly selected botanical replicates analyzed.

Table 3. ALP water homogeneity evaluation Cycle 53, 2024.

Sample	EC (dS m ⁻¹)		Ca (meq L ⁻¹)		NO ₃ (meq L ⁻¹)		NH ₄ (meq L ⁻¹)	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std
SRW-2401	0.257	0.010	1.61	0.018	0.128	0.008	1.26	0.16
SRW-2402	0.816	0.005	0.033	0.010	0.009	0.001	1.65	0.49
SRW-2403	1.312	0.008	6.21	0.98	0.009	0.001	1.40	0.16

¹ Statistics based on three randomly selected soil replicates, each analyzed in triplicate.

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

Sixty-four laboratories provided ALP results for soil pH (1:1) H₂O (test code 115). Soils ranged from acid to alkaline, median range 5.32 - 7.60. Lab results were ranked low to high based on sample SRS-2401 (see Figure 1) with median pH designated by horizontal lines for each soil. Generally across labs all soils showed good consistency across labs. Labs #1 through #4 showed low bias across all five soils. Labs #19, #32 and #58 were inconsistent across the three soils for cycle 53. Source of bias is likely associated with ISE performance and/or method compliance. Inconsistency could be result of extract carry-over.

pH precision across the five ALP soils indicates very high precision, with median intra-lab standard deviation (*s*) values ranging from 0.021 to 0.034 pH units, the lowest noted for SRS-2301. Six labs had poor precisions, with standard deviations exceeding consensus median intra-lab *s*. Specifically *s* for labs #3, #11, #19, #20, #27, #32, #57, #58 and #64 exceeded 0.06 pH units for SRS-2401. Soil SRS-2403 was the least variable with respect to intra-lab variance.

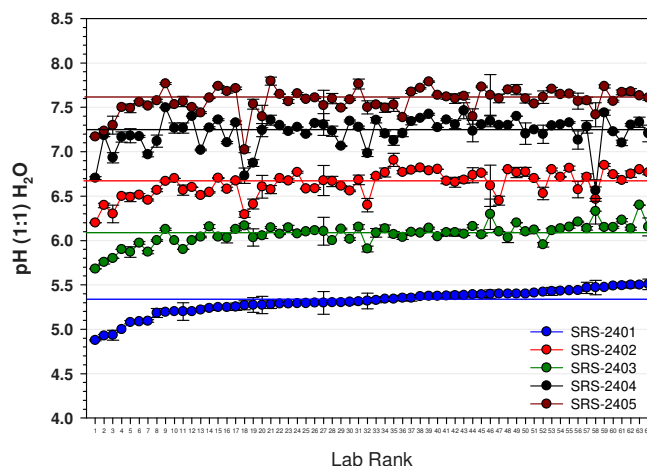


Figure 1. pH (1:1) H₂O distribution plots for SRS materials, ALP 2024

SRS - Phosphorus: Bray P1, M3-P, Olson P

Bray P1 results were reported by thirty labs. M3-P ICP was reported by 47 labs. Median soil Bray P1 values ranged from 10.1 - 77.9 mg kg⁻¹ PO₄-P; Olsen P 4.8 to 32.9 mg kg⁻¹ P; Bray P2 ranged from 19 to 210 mg kg⁻¹ P; and M1-P from 14 to 212 mg kg⁻¹ P, across the five soils. Ranking lab results based on sample SRS-2401, median M3-P ICP concentrations are shown in indicated in Figure 2. Soil SRS-2403, moderate in concentration was variable between labs. Soils SRS-2404 and SRS-2405 had near identical concentrations of 100 mg kg⁻¹ P. Soils SRS-2402 and SRS-2403 had similar Bray P1 concentrations. Lab #1, #44 and #45 had in consistent results across all five soils. Labs #27 and #30 had M3-P ICP high bias for soils SRS-2404 and 2402.

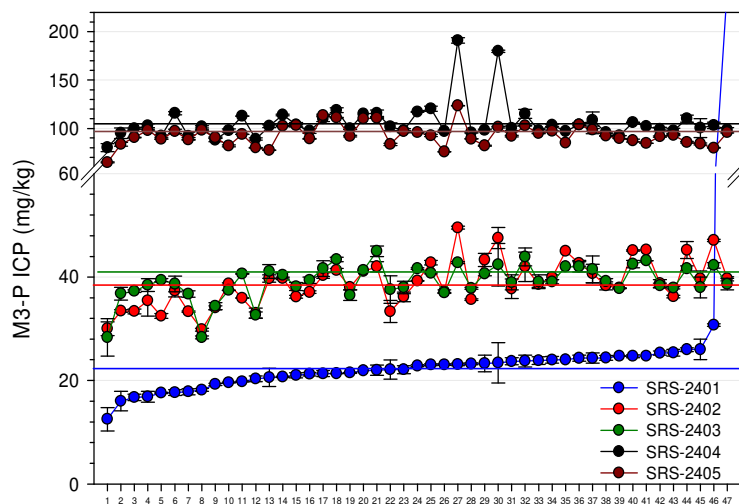


Figure 2. M3-P ICP distribution plots for SRS materials, ALP 2024 Cycle 53.

Eleven labs reported M3-P Spec median concentrations ranging 10.3 - 89.2.7 mg kg⁻¹ P. Thirteen laboratories reported Bray P2, six labs for M1-P and two results for Modified Morgan P, with medians ranging from 3.7 - 29.0 mg kg⁻¹ PO₄-P. Modified Kelowna was reported by two laboratories ranging from 0.7 - 58.8 mg kg⁻¹ P and total P (US-EPA 513) ranged 330 - 661 mg kg⁻¹ P with the highest concentration noted for SRS-2404.

SRS - Potassium

Forty-eight laboratories provided ALP results for soil M-3 K (test code 159) results. Results were ranked low to high based on sample SRS-2402 (see Figure 3). Soil SRS-2404 and SRS-2405 were the most inconsistent across labs. The source of the variability is unknown. Laboratory #32 showed low bias on two of five soils. Across all soils labs #4, #4, #20 and #45 were inconsistent across the five soils for M3-K. Source of inconsistency is likely related to extraction, analysis instrument and/or method compliance.

M3-K intra-lab *s* values were lowest for soil SRS-2402, with a median intra-lab value of 3.5 mg kg⁻¹ K and highest for SRS-2404 with a value of 19.2 mg kg⁻¹. M3-K within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 200 mg kg⁻¹ K. Precision was poor (based on intra-lab *s*) for five labs which exceeded 10 mg kg⁻¹ K on SRS-2401. Across the five soils for Cycle 53 eight labs were flagged for poor precision. Poor precision is attributed to extraction and/or analysis instrument operation.

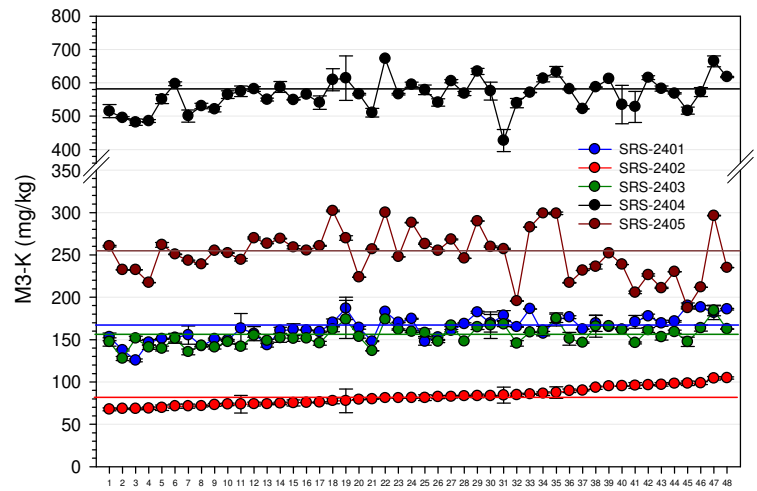


Figure 3. Extractable M3-K distribution plots for SRS materials, ALP 2024 Cycle

SRS - SOM-LOI

Forty-six laboratories provided ALP results for soil SOM-LOI (test code 183). Soil Median SOM-LOI values ranged from 1.07 to 4.43%. Results were ranked based on sample SRS-2405 (see Figure 4) and had high consistency. Lab #1 had consistent low bias across all soils. Labs #2, #34, and #44 were inconsistent across the five soils. Source of bias is likely related to muffle furnace operation and/or method compliance.

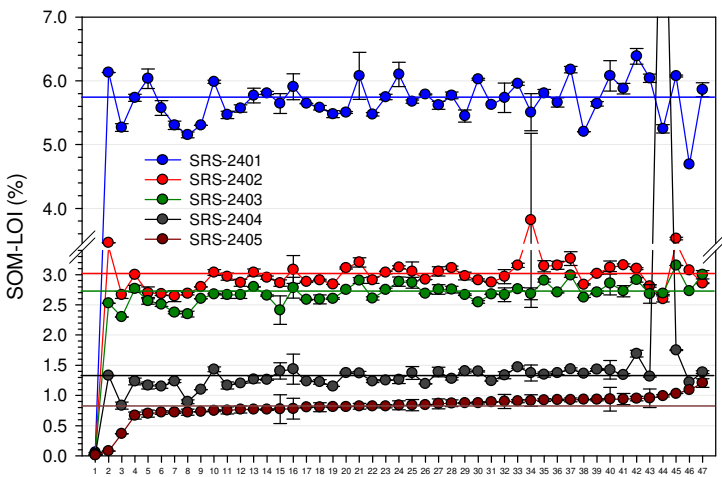


Figure 4. SOM-LOI distribution plots for SRS materials, ALP 2024 Cycle 53.

Source of bias is likely related to muffle furnace operation and/or method compliance.

SOM-LOI precision across the five soils indicates high median intra-lab precision *s* values ranging from 0.049 to 0.114% SOM-LOI, highest for SRS-2401. Across labs, *s* values for SRS-2401 ranged from 0.006 - 0.37%. Across soils low precision was noted for several laboratories. Specifically *s* for labs #5, #16, # 25, #32, #34, #37 and #40 exceeded 0.10% SOM-LOI for SRS-2402. Lab #34 had poor precision on SRS-2402. Poor precision may be associated with the muffle furnace and heating time.

ALP soil comparison

Fifty-five laboratories provided ALP results for soil extractable NO₃-N (test code 127) results. Results were ranked low to high based on sample SRS-2405 (see Figure 5). Soil SRS-2404, highest in NO₃-N concentration was the most inconsistent across labs. The source of the variability is unknown. Laboratory #2 showed low bias on all soils. Across all soils labs #12, #25, #31 and #49 were inconsistent across three of five soils. Source of inconsistency is likely related to extraction, analysis instrument and/or method compliance.

Soil NO₃-N intra-lab *s* values were lowest for soil SRS-2403, with a median intra-lab value of 0.3 mg kg⁻¹ and highest for SRS-2404 with a value of 6.1 mg kg⁻¹. Soil NO₃-N within-lab precision across the ALP soil materials indicates very good precision, generally, for soils with less than 30 mg kg⁻¹. Precision was poor (based on intra-lab *s*) for three labs which exceeded 2 mg kg⁻¹ NO₃-N on SRS-2405. Across the seven soils for Cycle 53 eight labs were flagged for poor precision. Poor precision is attributed to extraction and/or analysis instrument operation.

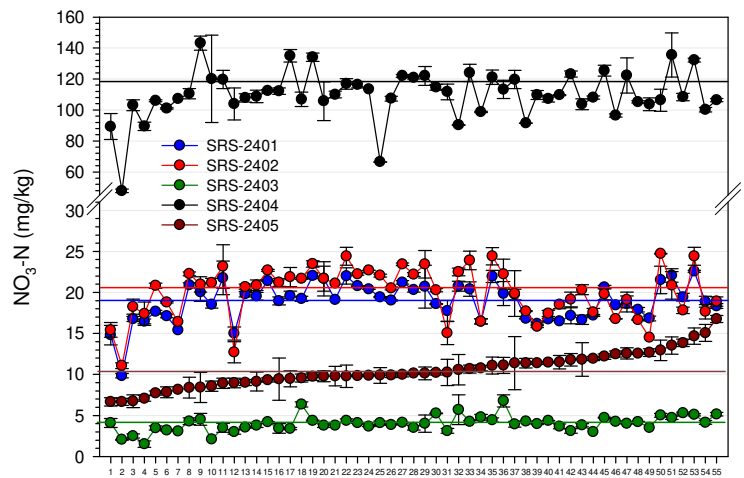


Figure 5. Soil NO₃-N distribution plots for SRS materials, ALP 2024 Cycle 53.

SRB - NO₃-N

Twenty-eight laboratories provided ALP results for NO₃-N by cadmium reduction and ISE (test codes 202, 203 and 204). Median values are designated by horizontal lines for each of the four botanical materials labs based on sample SRB-2402 (see Figure 6). Labs #1 - #3 had low bias results for all four materials. The data plot shows labs #4, #19, #20 and #28 were inconsistent on two of four samples.

Botanical NO₃-N (test code 202) results for Cycle 53 indicate very high precision, with intra-lab median standard deviation (*s*) values ranging from 28 to 1224 mg kg⁻¹ across the four samples. NO₃-N (test code 202) intra-lab *s* values for SRB-2401 ranged from 2 - 80 mg kg⁻¹; SRB-2402 ranged from 4 - 104 mg kg⁻¹, SRB-2403 ranged from 2 - 183 mg kg⁻¹ and SRB-2404 ranged from 58 - 4130 mg kg⁻¹. Labs #6, #14, 19 had consistently high standard deviations for samples SRB-2402 and SRB-2404 highest NO₃-N content. Five of 28 labs were flagged for poor precision for cycle 53.

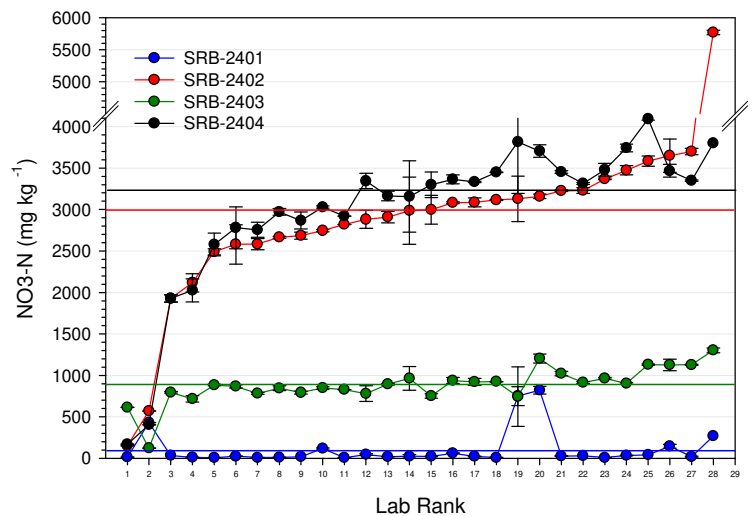


Figure 6. Nitrate distribution plots for SRB materials, ALP 2024, Cycle 53.

2024 Volume 1

SRB - Dumas Nitrogen and TKN

Forty-two laboratories provided ALP results for botanical Dumas (Combustion) Nitrogen (test code 210) and twelve labs for TKN (Test code 209) for Cycle 53. Median values are designated by horizontal lines for each material and labs results ranked low to high based on sample SRB-240 (see Figure 7). Labs #1 and #478 were inconsistent for Dumas N the four samples. Its note worthy that TKN was consistently lower than Dumas for three of four samples.

Dumas N results indicate very high intra-lab precision across all labs for all samples. Intra-lab median N lab s values were 0.023% N for SRB-2401; 0.044 % N for SRB-2402; 0.035% for SRB-2403; and 0.043% for SRB-2404. Lab #2, #39, and #42 had consistently high standard deviations on three of four PT samples. TKN median intra-lab s values for SRB-2401 were 0.002%, SRB-2402 0.012%, SRB-2403 0.004% and SRB-2404 0.006% TKN nitrogen, respectively.

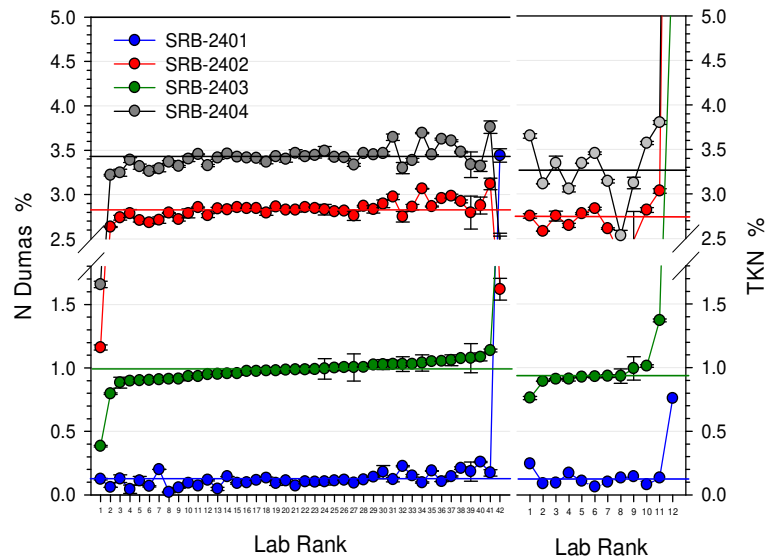


Figure 7. N distribution lab plots for SRB materials, ALP 2024 Cycle 53.

SRB - Phosphorus

Forty-eight laboratories provided ALP results for Cycle 53 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-2402 (see Figure 8). Labs #1, #1, #2, #15, #47 and #48 showed inconsistency. Source of inconsistency is likely related to sample digestion, analysis instrument and/or test code method compliance.

Botanical P results indicate very high precision, with median intra-lab standard deviation (s) values ranged 0.005 to 0.019 % P for test code 212 across the four botanical samples. Individual lab intra-lab s values for SRB-2401; ranged from 0.001 - 0.014% P; SRB-2402 ranged from 0.001 - 0.061 % P and SRB-2403 0.001 - 0.031 % P; and SRB-2404 0.001 - 0.107 % P. Seven labs were flagged for poor precision for botanical P for Cycle 53.

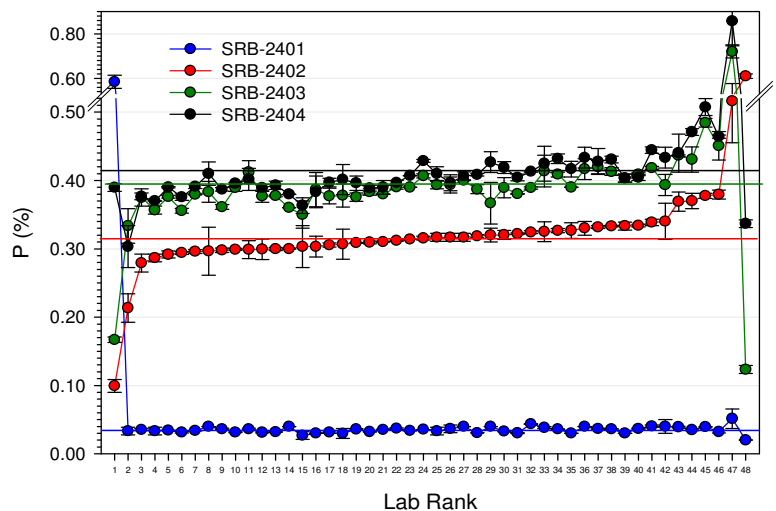


Figure 8. Phosphorus distribution lab plot for SRB materials, ALP 2024 Cycle 53.

SRB - Potassium

Forty-seven 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-2403 (see Figure 9). Labs #1, #2, and #47 were inconsistent. 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 0.059 to 0.242 % K for test code 213 across the four samples. Individual lab intra-lab *s* values were: SRB-2401, ranged from 0.001 - 0.391 % K; SRB-2402, 0.012 - 0.771 % K; SRB-2403, 0.006 - 0.385 % K; and SRS-2405, 0.006 - 0.313 % K. Labs #1 and #47 had high standard deviations exceeding 0.20 % K on two of four samples. Across samples five labs were flagged for poor K precision for Cycle 53.

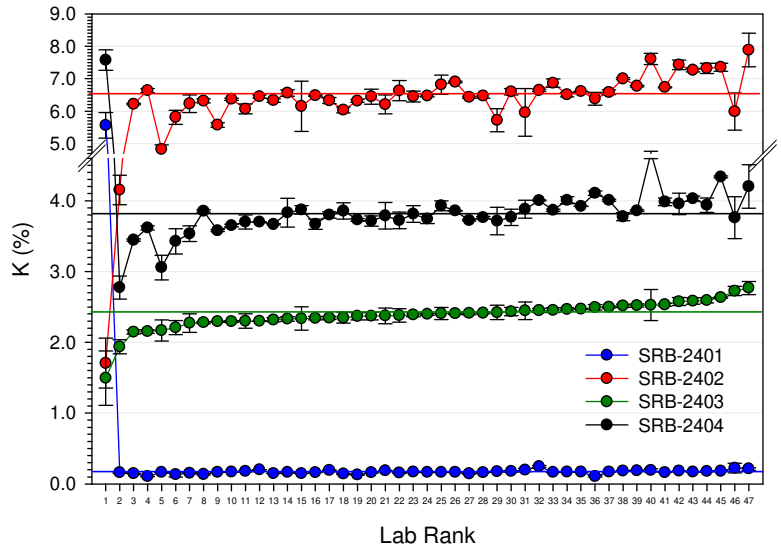


Figure 9. Potassium lab plot for SRB materials, ALP 2024 Cycle 53.

SRB - Manganese

Forty-five laboratories provided ALP results for Manganese (Mn) (test code 221). 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-2401 (see Figure 10). Across samples labs #11 had low bias on 3 of 4 samples. Labs #42 - #45 were inconsistent. Source of bias is likely related sample digestion, analysis instrument and/or method compliance.

Botanical Mn results indicate very high precision, with median intra-lab standard deviation (*s*) values ranged from 0.22 to 1.53 mg kg⁻¹ Mn for across the four botanical samples. Individual lab intra-lab *s* values for SRB-2401; ranged from 0.05 - 38 mg kg⁻¹ B; SRB-2402 ranged from 0.05 - 42 mg kg⁻¹B; SRB-2403 0.6 - 37 mg kg⁻¹B; and SRB-2404 0.3 - 6.0 mg kg⁻¹ B. Lab #44 had consistently high standard deviations for three samples.

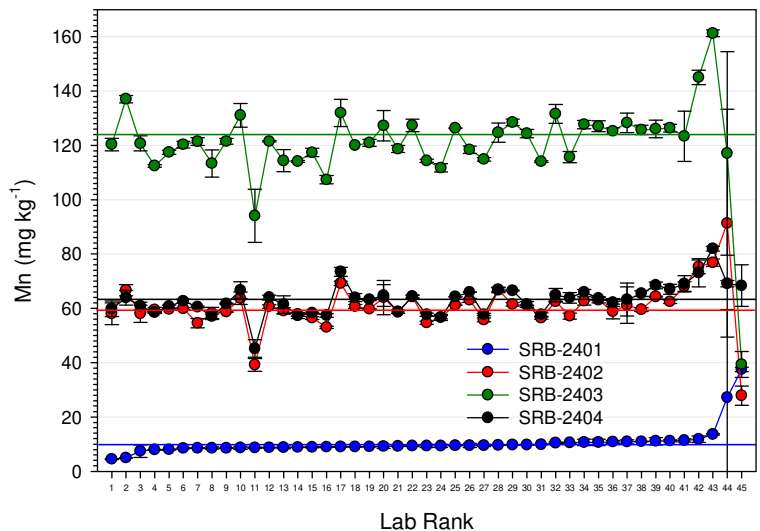
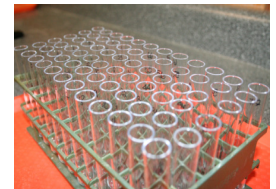


Figure 10. Manganese (code 219) lab plots for SRB materials, ALP 2024 Cycle 53.

SRW - Water EC

Twenty-one laboratories provided ALP results for water pH (test code 302) and EC. Lab results were ranked low to high based on sample SRW-2403 (see Figure 11). Sample SRW-2401 had the highest EC in for Cycle 53. Labs #2 and #19 indicated inconsistency across 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 s values of 0.015, 0.008 and 0.0035 dSm^{-1} , for the three water samples, respectively. Precision for sample SRW-2403 was the most consistent across the nineteen participating laboratories. Intra-lab s values for lab #20 exceeded 0.042 dSm^{-1} on SRW-2401. Highest precision was noted for lab #16 with intra-lab s values of < than 0.003 dSm^{-1} for all three samples. Two labs were flagged for precision for EC.

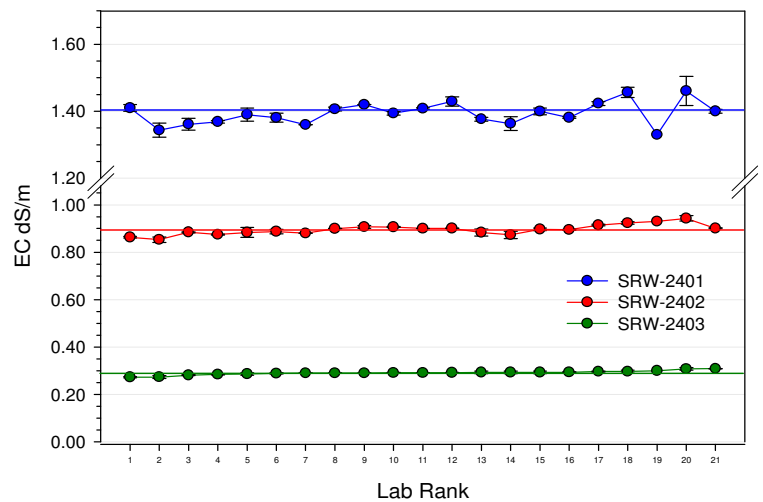


Figure 11. Water EC distribution plots for SRW materials, ALP 2024 Cycle 53.

SRW - Mg

Nineteen laboratories provided ALP results for water Mg (test code 304). Lab results were ranked low to high based on sample SRW-2403 (see Figure 12). Median values are designated by horizontal lines. Labs #1 and #2 showed consistent low bias on all two samples, and is likely a result of a calibration error.

Magnesium precision across the three water solution matrices indicates excellent precision, with intra-lab s values of 0.19, 0.007, and 0.027 mmolc L^{-1} for SRW-2401, SRW-2402, and for SRW-2403, respectively. Water Mg precision was excellent for all individual labs with only labs #5, #11, and #19 exceeding 0.06 mmolc L^{-1} Mg on sample SRW-2403. One lab was flagged for poor precision on ALP Cycle 53 for water Mg content.

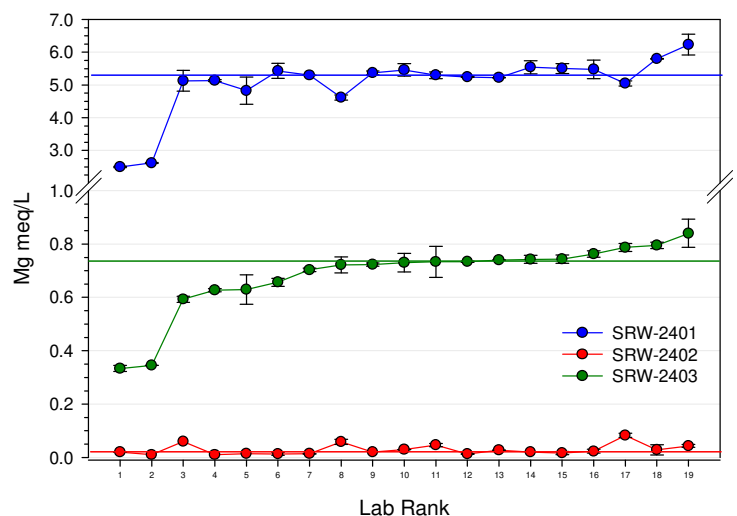


Figure 12. Water Mg distribution plots for SRW materials, ALP 2024 Cycle 53.

Announcements

- ▶ The ALP Program welcomes Kassidy Taylor, Program operations specialist. Kassidy will oversee the data management, statistical analysis and lab reports.

The start of ALP soil carbon proficiency program has been delayed till September 2024. Test parameter include, total Soil Carbon (SC), soil organic carbon (SOC), soil inorganic carbon (SIC), pH and moisture content. The program will consist three cycles per year each with four soils. The soil carbon proficiency program will be required for labs seeking ALTA-SC certification.

- ▶ ALTA will have their summer meeting the August 19-20, in Bloomington, Illinois. Topics include presentations on lab analysis, soil carbon analysis, Modus soil and plant codes and the Enhance Quality Assurance (EQA) program serving Iowa. For more information can be found at ALTA.Ag.

- ▶ The 18th International Symposium on Soil and Plant Analyses (ISPPA) will be held in June 9-13, 2025 in Durham, North Carolina. Topics include soil, plant and water analysis, soil health, and plant nutrition. More information and enrollment can found at: <https://www.isspasymposium.org/>

- ▶ ALP has standard reference soils and plant tissue samples available for purchase. For more information on these methods contact the ALP Technical Director, Robert.Miller@cts-interlab.com.

Summary

ALP is has provided nineteen years of service with the completion of Cycle 53. Since 2005 ALP has completed the analysis of 265 soils, 184 plant samples and 171 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 53. 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 54 Ship
June 25, 2024

**“All problems become smaller if
you don’t dodge them, but con-
front them.”**

- William Halsey, 1947

