RELIABILITY OF SOIL AND PLANT ANALYSES FOR MAKING NUTRIENT RECOMMENDATIONS

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ABSTRACT

Nutrient management is dependent on the collection of soil and plant samples for analytical testing and assessment. The quality of the analytical test are subject to bias and precision of the measurements made by the testing laboratory. Failure to understand lab analyses uncertainty can lead to over confidence in the management recommendation. Test uncertainty varies by soil and plant test methods utilized and by performance capability of the testing laboratory. Generally soil methods that provide the most reliable test data, based on the level of within lab proficiency uncertainty are: pH, EC, nitrate, and potassium. Those with the lease reliability are boron, calcium carbonate and soil organic mater. Generally plant methods are very reliable with total nitrogen and phosphorus the most reliable test methods. Laboratory testing is a dynamic process, relative to chemical reagents, instrumentation, laboratory staff and laboratory sample workload, each of which can contribute to bias and increased uncertainty.

INTRODUCTION

Fundamental to agriculture nutrient management is the collection and testing of soil and plant samples for the assessment of salinity and nutrient status of the crop. A majority of soil methods used in the Western United States (Gavlak et al., 1994) as for salinity and nutrient management are based on semi-quantitative analyses which are correlated with crop nutrient response. Interpretation of the lab test values are based on probability of deleterious crop impacts as is the case with electrical conductivity (EC) and boron (B) and probability of crop response to a nutrient application as is the case with phosphorus (P) or potassium (K). For plant analyses these methods have focused on correlative relationships between quantitative plant petiole or leaf blade nutrient contents and the probability of crop response to applied nutrients. Generally plant nutrients are measured as soluble forms such as nitrate (NO_3-N) and phosphate (PO_4-P) in leaf petioles or as total quantities such as nitrogen (N), potassium (K) and zinc (Zn), in leaf blades.

An inherent component of any laboratory test is the measurement error of the test value. Measurement error is comprised of two components, bias and precision. Bias is the relative overall inaccuracy consistently high or low of the actual or true test value. It can be used to compare equivalent test methods or assess a testing laboratory's performance. Precision is the measure of repeatability of the test value and can be expressed as the method uncertainty, and increases as the test concentration decreases. Method bias and precision are endemic to all testing, however the amount of bias and the overall repeatability of a test value is function of the specific method and the laboratory conducting the analysis. A majority of modern commercial

laboratories employ a quality control program to minimize bias and maximize analysis precision. In addition they participate in laboratory proficiency programs such as the Agricultural Laboratory Proficiency Program (ALP) or the North American Proficiency Program (NAPT) to verify lab test quality. However, lab testing is a dynamic process, relative to chemical reagents, instrumentation, laboratory staff and laboratory sample workload, each of which can contribute to a loss of precision and/or lead to bias.

SAMPLES AND METHODS

Soil and plant test reliability is for the most part a function of three components: the sample; the test method, and the laboratory. Poor sample collection cannot be overcome by the best test method or the most proficient laboratory. And inherent soil variability across the field or at a specific location is a factor that needs to be addressed prior to collection. Soil sample test variation generally increases with decreases in soil tillage, which can to a limited extent be reduced by increasing the number of sub samples collected. Nutrient stratification by depth can increase variability. It is advised that a minimum of 20 soil cores be composited for whole fields (40 acres) and 10-12 cores for grid points samples. For plant samples it is recommended 20-40 plants over a uniform area be collected. Collecting a representative sample in the field helps assure a reliable test lab test data.

With regard to soil test methods, these are divided into three classes: soil salinity/sodicity, nutrient assessment and physio-chemical properties. Soil salinity test methods in the Western United States are well characterized and for the most part quantitative for tests of interest. For soil salinity/sodicity: pH; EC; saturated paste cations and anions; sodium absorption ratio (SAR); and boron are the dominate test methods. Results from proficiency lab programs indicate the uncertainty of soil saturated paste moisture is generally within ± 1.3%, while that for pH is ± 0.12 units, and that of saturated paste EC is ± 0.07 dS/m for soil containing 0.5 - 1.5 dS/m soluble salts (see table 1). Please note these ranges represent consensus industry test performance values obtained from proficiency testing programs and not those of any specific testing laboratory.

Saturated paste soluble cations test method indicate laboratory uncertainty is generally ± 0.4 mmolc/L for calcium (Ca) and 0.2 mmolc/L of magnesium (Mg) for soils containing 1.0 - 10 mmolc/L of these cations, while that of sodium (Na) is ± 0.1 mmolc/L for soils within this range. Results for soil saturated paste chloride (Cl) indicate an uncertainty of ± 0.10 mmlc/L for soils with less than 2.0 mmolc/L and ± 0.05 mmolc/L for soils with less than 0.50 mmolc/L Cl. For soils very low in saturated paste B (< 0.3 mg/L) uncertainty is ± 0.15 mg/L and ± 0.05 mg/L for soils with > 1.0 mg/L.

Table 1. Soil salinity/sodicity within laboratory test method uncertainty.

Soil Salinity/Sodicity Test	Concentration Range	Uncertainty
Saturated Paste Percent (%)	20 - 50	± 1.3
pH	4.0 - 9.0	± 0.12
EC (dS/m)	0.5 - 2.0	± 0.07
Ca (mmolc/L)	1.0 - 20.0	± 0.4
Mg (mmolc/L)	1.0 - 10.0	± 0.2
Na (mmolc/L)	0.5 - 5.0	± 0.1
SAR	0.1 - 4.0	± 0.1
Cl (mmolc/L)	0.2 - 2.0	± 0.10
HCO3 (mmolc/L)	1.0 - 10.0	± 0.20
SO4 (mmolc/L)	0.5 - 5.0	± 0.20
B (ppm)	0.01 - 0.20	± 0.05

[1] Uncertainty based on 95% confidence, from 95 soils samples evaluated in the ALP Program 2006-2012.

Table 2. Soil nutrient within laboratory test method uncertainty.

Soil nutrient method	Concentration Range	Uncertainty
NO3-N (ppm)	10 - 40	± 1.8
Bray P 1 (ppm)	10.0 - 50.0	± 2.0
Olsen P(ppm)	5.0 - 30.0	± 1.5
K ammonium acetate (ppm)	80 - 300	± 15
Zn - DTPA (ppm)	0.50 - 1.0	± 0.12
Cu (DTPA (ppm)	0.20 - 1.00	± 0.08
B Hot water (ppm)	0.20 - 1.80	± 0.12

[1] Uncertainty based on 95% confidence, from 95 soils samples evaluated in the ALP Program 2006-2012.

Soil test nutrient test methods indicate laboratory uncertainty is generally of ± 1.2 ppm for soils with less than 10 ppm NO_3-N and ± 1.8 ppm for soils with 10 - 40 ppm NO_3-N (Table 2). Soil extractable PO_4-P uncertainty as determined by Bray P-1 (1:10 and 1:7 methods), generally is ± 1.1 ppm for soils with less than 10 ppm and ± 2.0 ppm for soils with a soil test of 10 - 50 ppm. The Olsen soil test method (dominantly used in the Western US for phosphorus) has an uncertainty of 1.5 ppm. Results for extractable cations indicated that these have differing levels of

uncertainty. For ammonium acetate extractable X-K and X-Mg, method uncertainty ranges from ± 15 - 25 ppm across soils. Method uncertainty of extractable soil DTPA Zn and Cu is generally within ± 0.12 ppm for Zn and ± 0.08 ppm for Cu for soils with less than 2.0 ppm of these elements. Across soils hot-water B uncertainty was ± 0.12 ppm soils ranging from 0.20 to 1.8 ppm.

Table 3. Soil physio-chemical within laboratory method uncertainty.

Soil physio-chem method	Concentration Range	Uncertainty
SOM - WB (%)	0.50 - 5.0	± 0.15
SOM-LOI (%)	0.5 - 5.0	± 0.20
CEC (cmol/kg)	4.0 - 20.0	± 0.5
CaCO3 (%)	0.50 - 15.0	± 0.20
Sand (%)	2.0 - 60.0	± 1.5
Silt (%)	5.0 - 60.0	± 1.6
Clay (%)	5.0 - 40.0	± 1.1

[1] Uncertainty based on 95% confidence, from 95 soils samples evaluated in the ALP Program 2006-2012.

With regard to plant test methods, results indicate that plant NO_3-N uncertainty is generally ± 80 ppm for samples containing 500 - 5000 ppm while that for PO_4-P was within ± 90 ppm for units, see Table 4. Only 15% of the laboratories typically had a bias across the plant sample tested, and it tended to occur on plant samples that had less than 100 mg/kg NO3-N. Total Nitrogen uncertainty averaged ± 0.10 % N for samples containing 0.7 to 5.4% N. For K lab uncertainty was generally ± 0.10 % K across the samples evaluated with less than 12% of the laboratories indicating a significant bias.

CONCLUSIONS

Method bias performance of individual laboratories cannot be discussed here. Generally speaking 80% of the participating laboratories provide analysis results that are within the 95% confidence interval true analysis value for the proficiency test method, indicating no bias. All participating laboratories occasionally provide analytical results which are flagged for bias, however, approximately 30% of the laboratories have fewer than 5% of sample test results flagged for bias.

For the client selecting an analytical laboratory, it's important to carefully scrutinize the laboratory as part of the nutrient management decision process. However, the means of assessing a laboratory's performance is often outside the scope of their expertise. The first step in selecting a laboratory is to develop a working relationship with the manger or agronomist, and verify they are actively participating in a proficiency program. Secondly the client should inquire as to their quality control program and the frequency of the use of standard reference samples. A quality control program that evaluates analytical quality using 1 sample every 20 indicates a consistent quality monitoring program. Finally for growers, consultants and researchers sincerely interested in the quality of their analytical work, it is recommended they purchase reference standard materials of known analysis to fully evaluate lab performance based on a blind evaluation.

LITERATURE

Gavlak, R., D. Horneck and R.O. Miller. 1994. Plant, Soil and Water reference methods for the Western Region. Western Region Extension Publication WREP 125.

Miller, J.N. 1993. Outliers in experimental data and their treatment. Analyst. 118:455-461.

Dixon, W.J. and J. Massey. 1951. Ratios involving extreme values. Annals of Mathematical Statistics pp. 68-78.

Miller, R.O. and D. Hansen. 1997. The impact of laboratory accuracy and precision on of nutrient recommendation systems. Proc. of the 1998 Great Plains Soil Fertility Conference, March 3-4, 1998, Denver Colorado.