Considerations for Carbon Soil Testing: Laboratory Perspective

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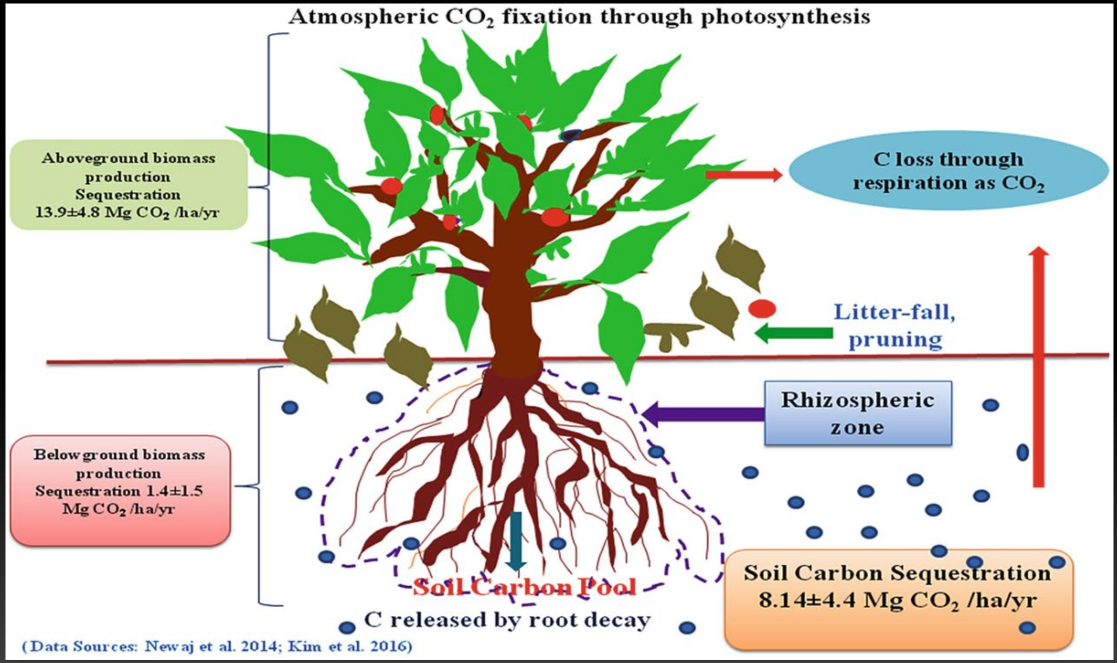
Importance of SOC Analysis

Increasingly soil carbon sequestration is discussed as one mechanism for modulating climate CO_2 flux. Estimates vary, but indicate potential soil C sequestration at 4 – 12 Mg C ha/yr.

Quantifying soil C flux is now a major focus of carbon modeling and improved methods of soil C quantification are needed.



https://media.springernature.com/original/springer-static/image/chp%3A10.1007%2F978-981-13-0253-4_4/MediaObjects/442951_1_En_4_Fig1_HTML.png

Sol carbon analysis

https://static.producer.com/wpcontent/uploads/2019/01/03140458/40-4col_RHB-Rogo-Ag-soil-sampler.jpg

With increase interest in carbon sequestration, new focus interest in soil carbon analysis for assessing sequestration. Traditionally, SOM analysis has measured for assessing SOM by:

> SOM Walkley- Black, dichromate / H_2SO_4 oxidation; and
> Loss-On-Ignition (LOI), gravimetric loss, thermic oxidation.

Neither quantifies C or provides accuracy required for the assessment of sequestered carbon.

Soil organic carbon (SOC) analysis, as measured by O_2 dry combustion, is the standard method for evaluating soil carbon and soil health research.

SOM vs SOC vs TIC

Soil organic matter (SOM) represents that fraction of soil comprised of organic C, H, S, and O.

Soil organic carbon (SOC) represents that fraction of the soil comprised of organic carbon, bound in cells, lignin and humus. Generally, SOC = 0.58 x SOM.

TIC (total inorganic carbon) represents inorganic carbon in soil, bound as $CaCO_3$, $MgCO_3$ and $NaCO_3$.

Total Soil Carbon = SOC + TIC

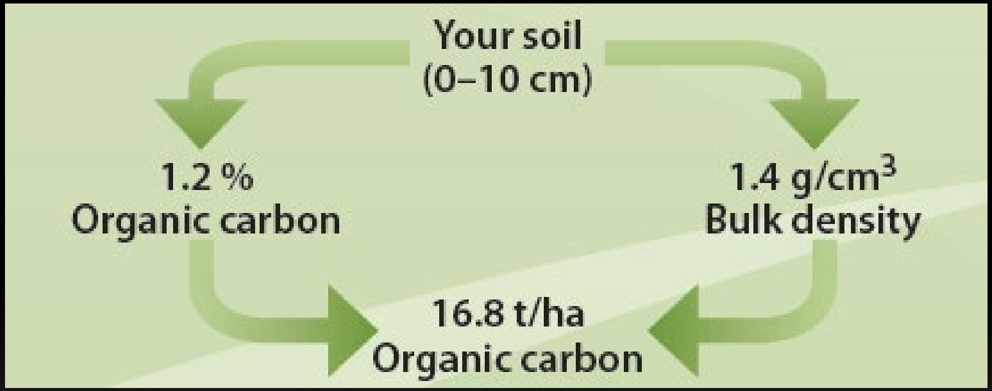
Quantifying SOC

Quantifying SOC requires three measurements:

- Measurement of bulk density
- Measurement of SOC
- Soil moisture (dry)

(Not to be confused with total soil carbon, Total carbon = organic C + inorganic C)

Requires accurate measurement of moisture, BD and SOC.



10,000 m^2 in one hectare x 0.1 m soil depth x 1.4 g/cm^3 bulk density x 1.2 % = 16.8 t/ha.

Soil cores

Quantifying SOC requires rigid control over core diameter and core depth to generate accurate soil bulk density values.

Diameter is easily controlled, but depth requires ridged control to avoid compaction and over estimate of BD.

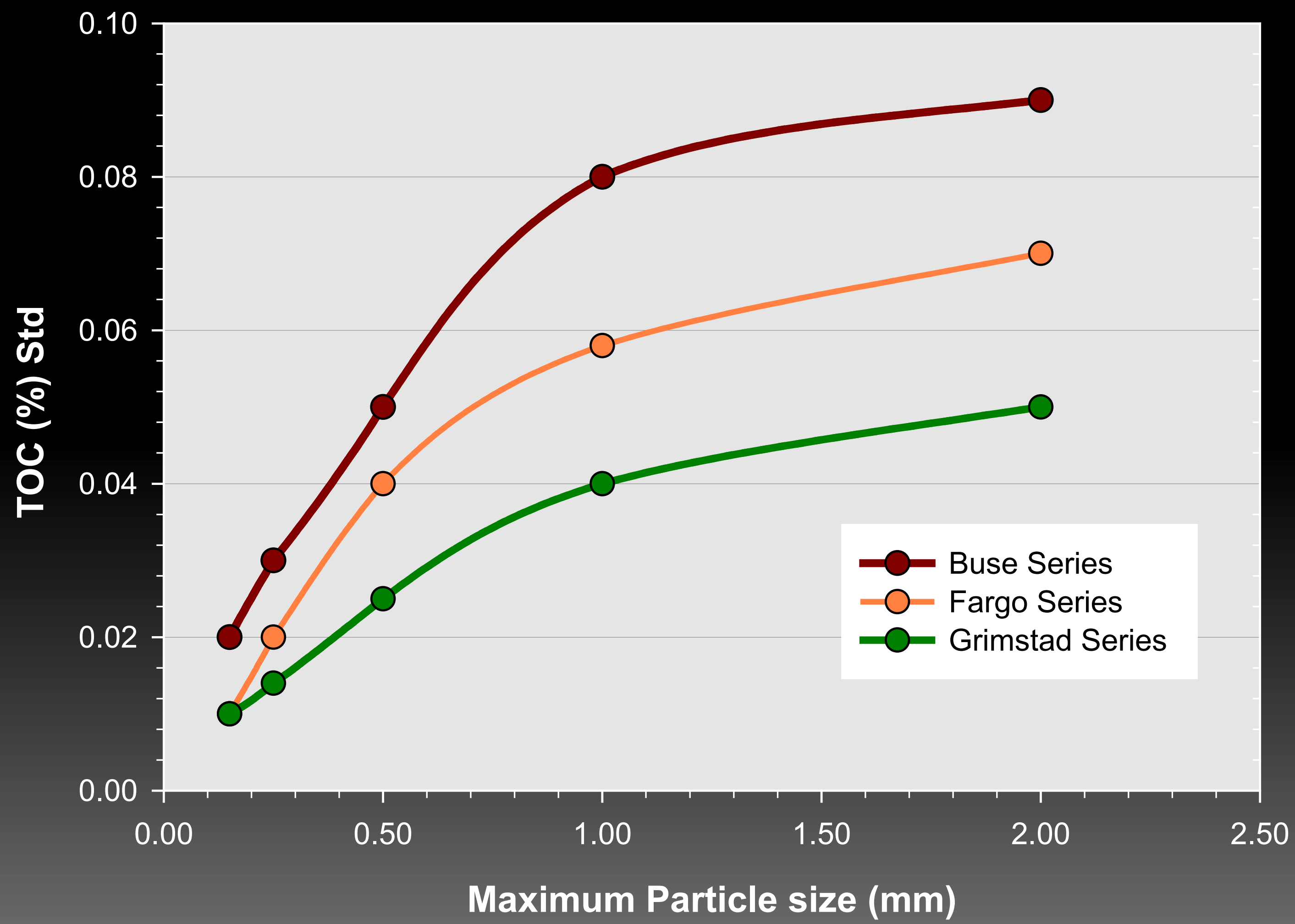
SOC / Combustion

O2 combustion analysis is the most accurate means of measuring SOC. Samples are place in high temperature and furnace in pure O2 environment, gases passed through catalyst and CO2 measured by IR cell.

Requires large sample size, or fine pulverized sample (< 0.25 mm). Multiple manufactures. May require pre-treatment to remove TIC (CaCO3).

[1] LECO 928 with robotic sampler.

Impact of soil particle size on SOC variation



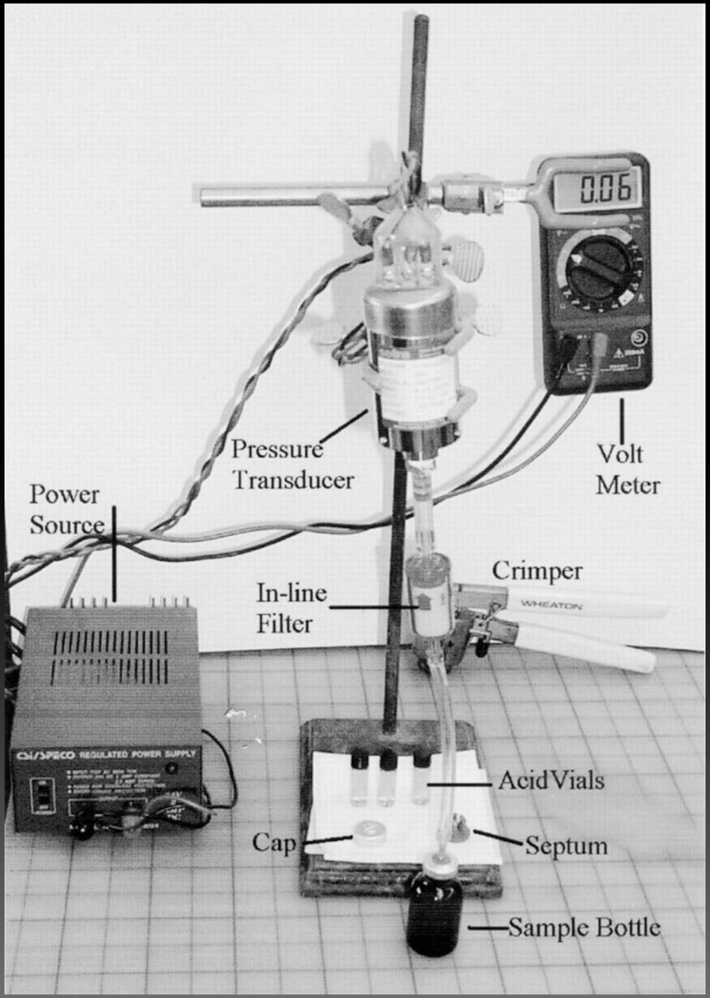
Cihacek and Jacobson, 2007

Measuring Inorganic Carbon ($CaCO_3$)

Pressure calcimetry is based on reaction of HCl with $CaCO_3$, generating CO_2 gas, and is quantified against known standards.

Utilizing a 2 g sample, the method is capable of an MDL of 0.01% TIC.

Bias, may occur on soils containing > 2% SOC, associated with the hydrolysis of organic carbon producing CO_2 .



Sherrod, L.A. et al 2002. Inorganic Carbon Analysis by Modified Pressure-Calcimeter Method

Automated TIC ($CaCO_3$)

Several auto samplers are on the market that offer robotic septum bottles, that provide automated measurement of VOC and sample pressure.

These include Hach, Gilson, Cetac and Skalar.

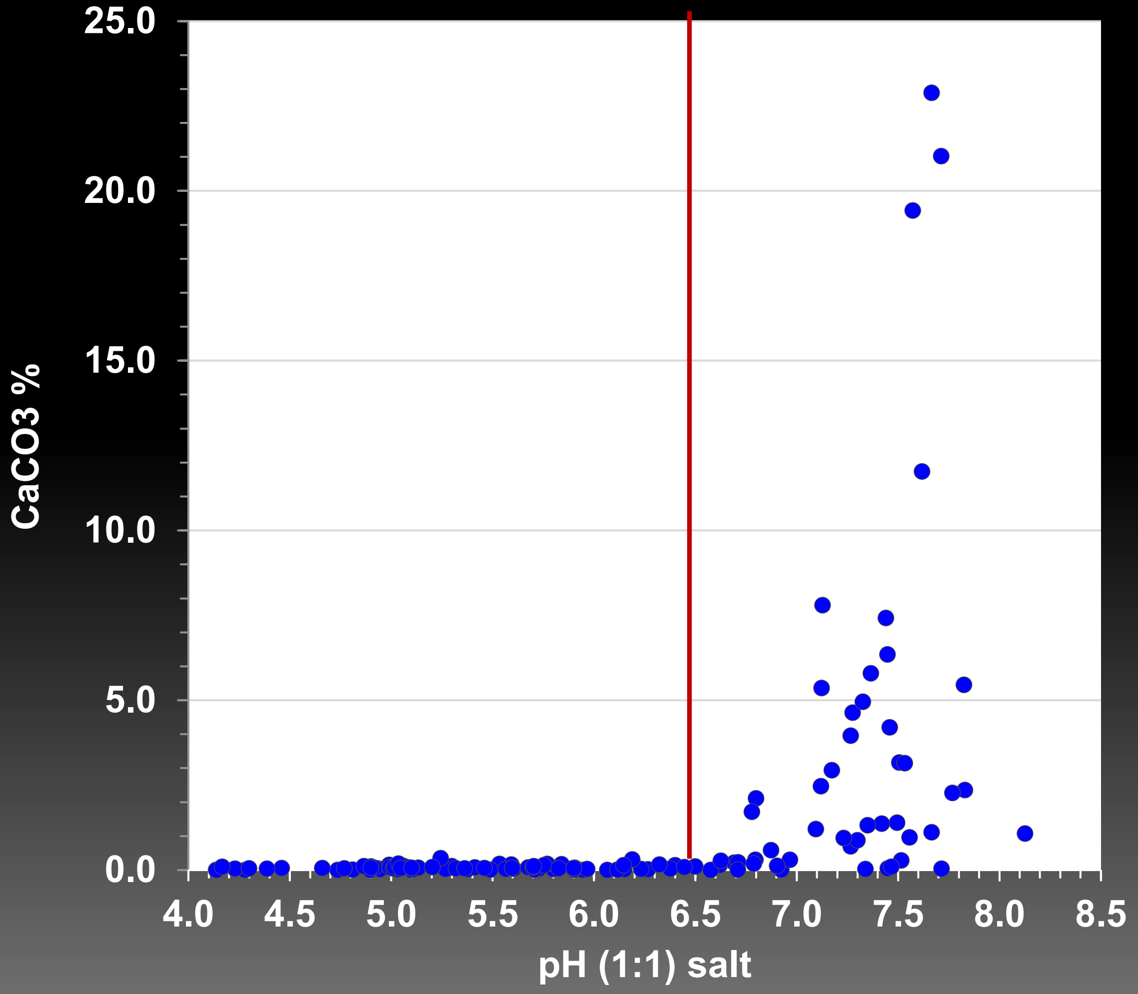
Sherrod, L.A. et al 2002. Inorganic Carbon Analysis by Modified Pressure-Calcimeter Method

pH vs $CaCO_3$ content

Soils below pH 6.5 have very low probability of containing significant quantities of $CaCO_3$.

Although many soils with pH 6.5 – 7.0 do not contain $CaCO_3$, the probability increases. On these soils there is greater likelihood of residual lime applications.

At left, 190 ALP soils 2006-2020, pH vs CaCO3 content.

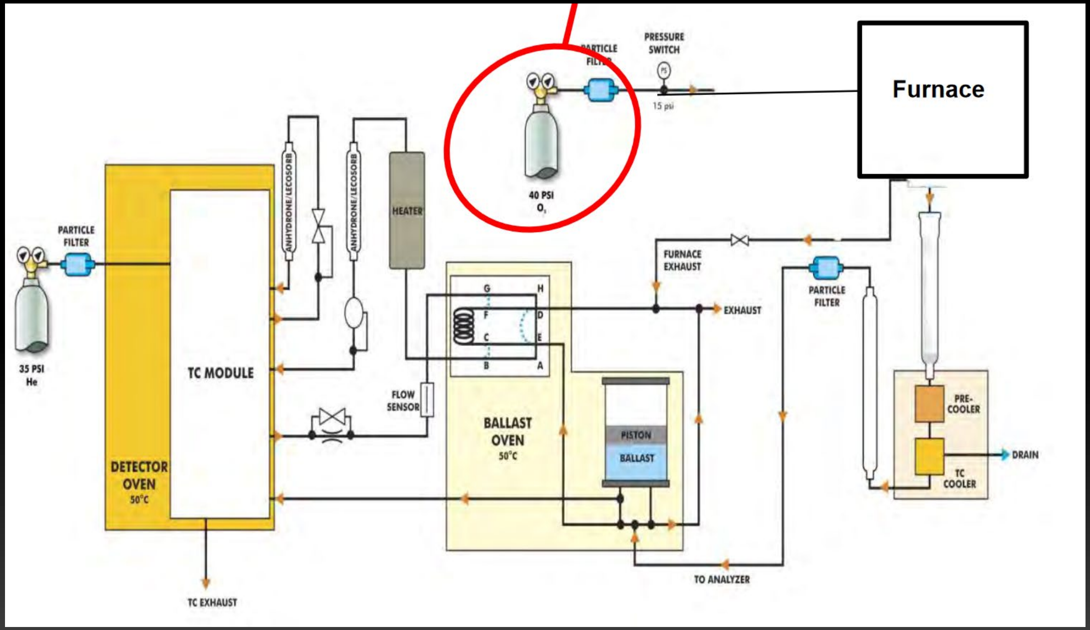


Removal of soil $CaCO_3$ with acid

For alkaline soils containing carbonates soils may be pretreated with acid to remove CO_2 though volatilization.

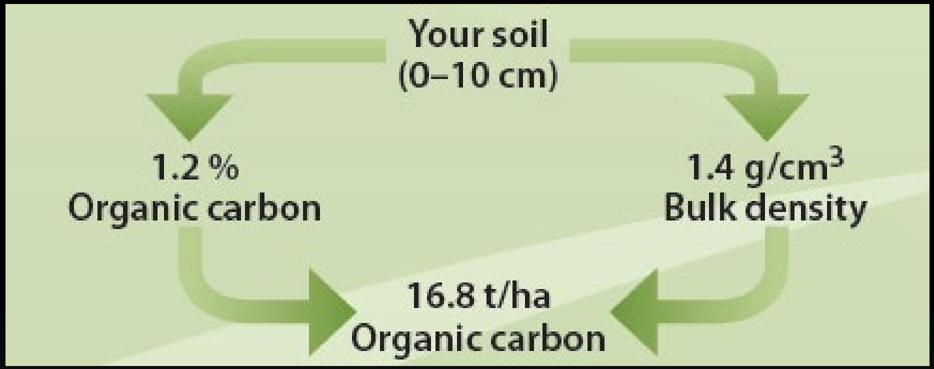
However, pro-long use of strong acids (HCL, SO_4 and NO_3) may damage the instrument catalyst and detection system.

Not recommended.



Quantifying SOC Measurement Uncertainty

For acid soils, two measurements are required to determine the soil mass of organic carbon, bulk density and SOC.



The use of to measurements will result in the propagation of uncertainty. For multiplication and division:

$$\partial_f = \pm\sqrt{\left(\frac{\partial_x}{X}\right)^2 + \left(\frac{\partial_y}{Y}\right)^2}$$

Where X is the uncertainty in SOC
And Y is the uncertainty in bulk density

http://www.physics.unc.edu/~deardorf/uncertainty/UNCguide.html

Propagation of SOC uncertainty: SOC x BD

Example #1

SOC %	2.00 ± 0.07 % SOC
Bulk density	1.21 ± 0.06 gm cm^{-3}

Final result: 24.2 ± 0.61 tons ha^{-1} ± 2.5 %

Example #2

SOC %	1.21 ± 0.12 % SOC
Bulk density	1.41 ± 0.18 gm cm^{-3}

Final result: 17.1 ± 1.62 tons ha^{-1} ± 9.5 %

Impact of uncertainty on SOC

Example, initial soil SOC 2.00% soil BD 1.40 gm cm^{-3} . Increase soil SOC content 0.15%, based on 10 cm depth.

Initial SOC content **28.0 tons ha^{-1}**

(2.00 % x 1.40 g cm^{-3})

Final SOC content **30.1 tons ha^{-1}**

Net gain: **2.01 tons ha^{-1}**

Uncertainty measurements

SOC: ± 0.12 % SOC

BD: ± 0.18 gm cm^{-3}

Uncertainty impacts subtraction

Initial SOC content **28.0 ± 1.42 tons ha^{-1}**

Final SOC content **30.1 ± 1.40 tons ha^{-1}**

Net gain: **2.01 ± 1.98 tons ha^{-1}**

Thus on cannot quantity an a 0.15% increase in SOC

Quantifying SOC sequestration

Quantification of SOC will require laboratory carbon measurement uncertainty < 0.07% and BD < 0.10 gm cm^{-3}.

This level of precision requires accurate collection and determination of soil BD, and highly pulverized samples, < 0.25 mm nominal particle size.

Consideration for soils with pH > 6.5, pretreatment of quantification of TIC.

The Laboratory challenge

Yes, lab methods and instrumentation are capable of accurately measuring SOC, and quantifying C sequestration.

However for SOC sequestration, the soil sampling process, lab sample prep, lab QC procedures require significant greater scrutiny to provide accurate results.

The issue, will the carbon market support the costs of quality results.

Thank you for your time and attention

ALP
Agricultural Laboratory Proficiency Program

ALP
Proficiency Testing Services

Robert Miller and Chris Czyryca

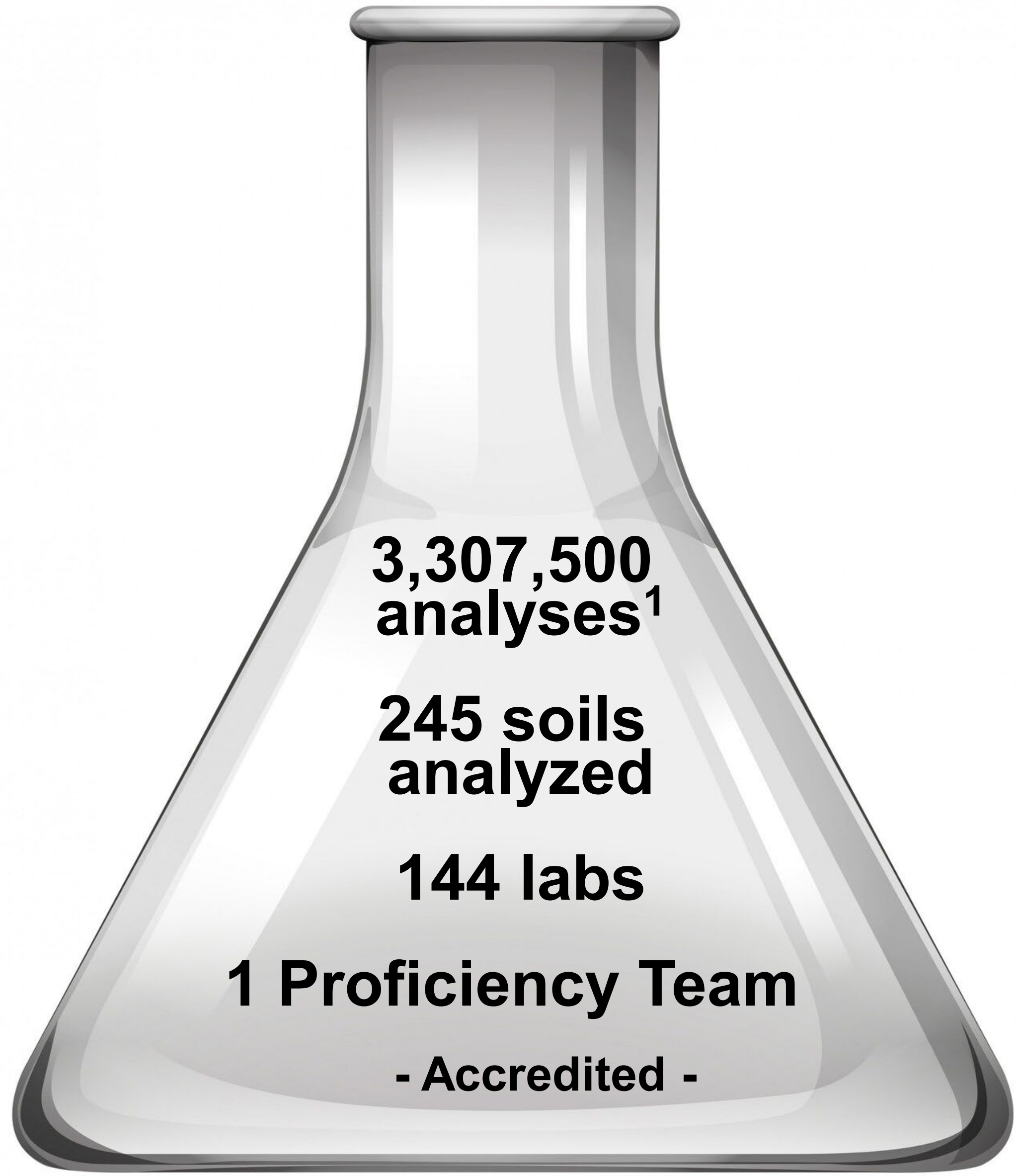
Celebrating 18 years of Service

ALP by the numbers

The ALP soils program is the most comprehensive lab PT program providing lab proficiency results on both method bias and lab precision.

Proficiency soils are diverse, collected across North America, representing a broad range of soil chemical and physical properties.

Reports are comprehensive listing method performance (bias and precision) each soil.



[1] Number of soils x analyses x labs x reps.

Miller and Czyryca, 2023

Proficiency soil consistency

Standard reference soil SRS-1812 was re-submitted after four years as SRS-2206. More than 98% of parameter medians, were within the measurement MAD.

EC, NO_3-N, M3-K, M3-Zn, SOM-LOI and SOC the median values were reproducible to two significant digits.

Results verify ALP standard reference soils proficiency median and MAD statistical results are highly reproducible and remarkedly stable over four years.

Analysis	Unit	SRS-1812	SRS-2206
		Median	Median
EC (1:1)	dS/m	0.647	0.643
pH (1:1) salt		6.94	7.01
NO_3-N	mg kg^{-1}	19.2	19.0
M3-P ICP	mg kg^{-1}	27.2	29.2
M3-K	mg kg^{-1}	419	422
M3-Zn	mg kg^{-1}	2.13	2.11
SOM-LOI	%	4.15	4.10
SOC	%	1.963	1.984

[1] Laboratory soil median values.

Miller and Czyryca, 2023

ALP - ALTA collaboration

ALP collaborates with the Agricultural Laboratory Testing Association, for certifying soil analysis laboratories and providing training webinars.

Certification. The ALTA-SAC program evaluates lab soil pH, P, K analysis each ALP cycle based on 80% passing score each parameter.

Lab Webinars: ALP has assisted in the development of seven ALTA training webinars.

- Laboratory quality management
- The laboratory SOP
- Basics of lab quality control
- Determining the method detection limit
- Soil scooping – part I and part II
- Lab PT failure analysis part I

SAC SOIL ANALYSIS CERTIFICATION

2022 ALTA-SAC Certified Test Procedures (Cycle 49*)

LABORATORY	ALTA Certified	pH Water 1:1 or 1:2	pH Salt 1:1 or 1:2	Buffer pH Sikora or SMP
A&L Great Lakes Laboratories	Yes	Passed	Passed	Passed
Agricultural Soil Management, Inc.	Yes	Passed		
AgSource Cooperative Services	Yes	Passed	Passed	Passed
AgSource Laboratories Ellsworth	Yes	Passed		Passed
Blacklog Services	Yes	Passed		
Brookside Labs	Yes	Passed	Passed	

ALTA March webinar

ALTA
AGRICULTURAL LABORATORY TESTING ASSOCIATION

ICP Analysis & Calibration, Jason Lessl, University of Georgia

March 7, 2023, 11:00 AM EST

Join Zoom Meeting
https://us02web.zoom.us/j/85448975779?pwd=VjF2MCsvekk2WVBGR3ZoS3ZOVXA1Zz09

Meeting ID: 854 4897 5779
Passcode: 834508

Contact Gary Fisher, ALTA Secretary: info@alta.ag

ALTA.ag

Scan for web site

2023 ALP update

- Sponsorship of the 17th International Symposium on Soil and Plant Analysis in Conception Chile, March 21-24, 2023.

- Addition of soil extractable metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se Zn) to standard soil proficiency tests, no additional charge.

- Adoption of AgGateway Modus v2 soil library method codes for the proficiency testing program.

To enroll: Chris: christopher.czyryca@cts-interlab.com

Modus library

Standardizing agricultural lab test data is an important enabler of principled decision-making in agriculture and its estimated ~70% of soil tests results are electronically-exchanged in the US.

AgGateway is a global, non-profit organization that helps agri-businesses expand their ability to exchange and use data and has been working on laboratory data information standard for farm management information systems (FMIS).

The laboratory methods library (Modus) was initially developed in 2013 focusing on Ag analyses using a controlled xml vocabulary across multiple Ag matrices. 2018 schema expanded: soil, plant, water, manure, nematodes.

Modus soil library structure

Example

- **Matrix**
- **Soil**
- **Analyte**
- **Method**

Phosphorus

- Mehlich 3
- Formulation
- Extraction basis
- Extraction ratio
- Extraction time
- Instrument ICP
- Reporting unit

Additional identifiers:

- Alternate reporting unit
- Method: measured or calculated
- Acceptance criteria: official, provisional, experimental, proprietary
- Regional work group approval
- Former Modus v 1.0 code ID
- Reference citation

806 Soil methods

Modus v2 soil P example

Matrix	Analyte	Extraction Name	Extraction reagent	Extraction Ratio	Extraction Basis	Extraction Time	Analyte Measurement	Aggregation Method	Reporting Unit	Alt Reporting Unit	Accept.	Status	Organization
SOIL	P	Mehlich 1	(0.05 M HCl + 0.0125 M H2SO4)	1:5	m/v	5 min	ICP-OES	Measured	mg/kg	ppm	Official	ACTIVE	SERA-6
SOIL	P	Mehlich 1	(0.05 M HCl + 0.0125 M H2SO4)	1:5	m/v	5 min	Spec	Measured	mg/kg	ppm	Official	ACTIVE	SERA-6
SOIL	P	Mehlich 2	(0.2N CH3COOH + 0.015N NH4F + 0.2N NH4Cl + 0.012N HCl)	1:10	m/v	5 min	ICP-OES	Measured	mg/kg	ppm	Official	ACTIVE	NCSU
SOIL	P	Mehlich 2	(0.2N CH3COOH + 0.015N NH4F + 0.2N NH4Cl + 0.012N HCl)	1:10	m/v	5 min	Spec	Measured	mg/kg	ppm	Official	ACTIVE	NCSU
SOIL	P	Mehlich 3	(0.2N CH3COOH + 0.25N NH4NO3 + 0.013N HNO3 + 0.015N NH4F + 0.001M EDTA)	1:10	v/v	5 min	ICP-OES	Measured	mg/dm3	mg/kg	Official	ACTIVE	SERA-6
SOIL	P	Mehlich 3	(0.2N CH3COOH + 0.25N NH4NO3 + 0.013N HNO3 + 0.015N NH4F + 0.001M EDTA)	1:10	v/v	5 min	Spec	Measured	mg/dm3	mg/kg	Official	ACTIVE	SERA-6
SOIL	P	Mehlich 3	(0.2N CH3COOH + 0.25N NH4NO3 + 0.013N HNO3 + 0.015N NH4F + 0.001M EDTA)	1:10	m/v	5 min	ICP-OES	Measured	mg/kg	ppm	Official	ACTIVE	SERA-6, NCERA-13, NEC-1812
SOIL	P	Mehlich 3	(0.2N CH3COOH + 0.25N NH4NO3 + 0.013N HNO3 + 0.015N NH4F + 0.001M EDTA)	1:10	m/v	5 min	Spec	Measured	mg/kg	ppm	Official	ACTIVE	SERA-6, NCERA-13, NEC-1812

52 soil P extraction methods, additional 12 calculated P methods.

AgGateway

WG04 Ag Lab Data Standardization Committee

Ben Cracker, AgGateway
Andres Ferreyra, Syngenta Digital
Randall Warden, A&L Great Lakes
Robert Miller, ALP Program
Jodi Jaynes, Sure-Tech
Jason Ellsworth, Wilbur Ellis
Brad Joern, Precision Planting
Corey Lacey, United Soils

ModusStandard.org

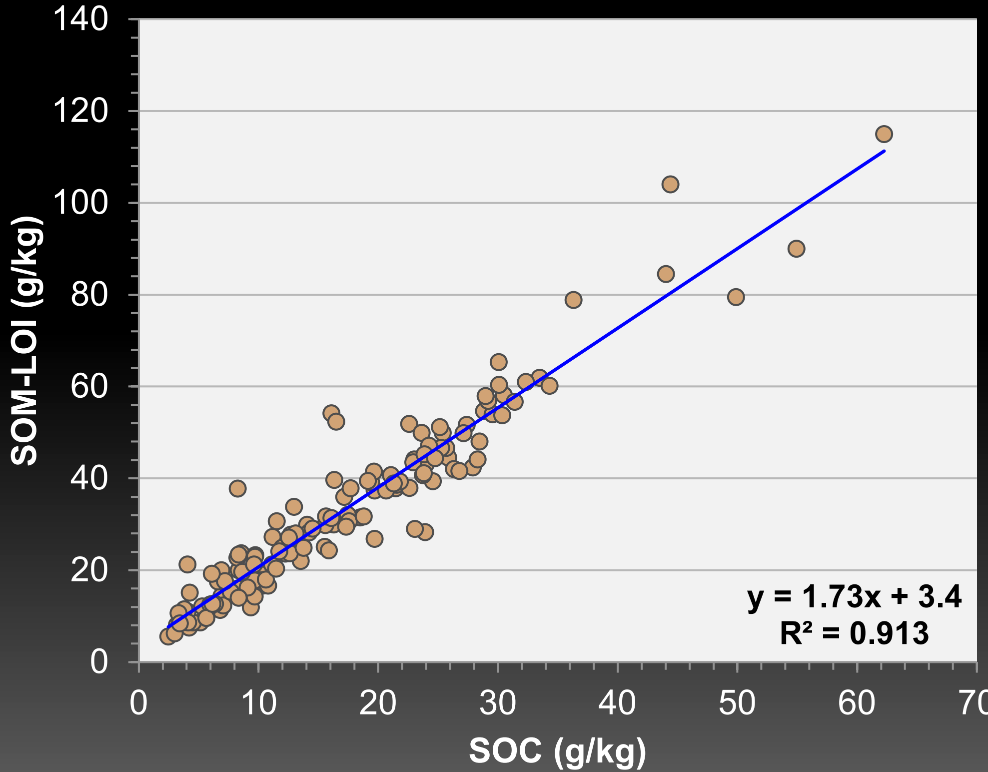
https://www.aggateway.org/Portals/1010/2020-04-07%20Soils%20Flyer-SR.pdf?ver=2020-04-07-114007-097

SOC vs LOI

Agricultural Laboratory Proficiency (ALP) program results show linear relation between SOC and SOM-LOI, from lab proficiency data.

Soil SOC ranged 2.0 - 70 g kg^{-1}, with pH $_{0.01\ M\ CaCl2}$ (1:1) < 7.3, n = 147.

Results for soils containing > 10 g kg^{-1} $CaCO_3$ are more variable.



[1] Data based on consensus median results of 117 labs.

ALP cost, service and support

Cost

- Low cost, basic soil PT program $540/yr, 3 cycles
- Three PT cycles per year, lower lab analysis cost.

Service

- Retest soil sample kits (14 shipped in 2022)
- Standard reference soils, quantities 0.5, 1.0, 20.0 kg
- Double blind PT soil evaluations

Support

- Laboratory technical consultation
    - Byron Vaughan, 20 years commercial lab experience
    - Mike Lindaman, 26 years experience managing commercial lab
    - Steve Meghan, 24 years lab director Univ of Idaho, A2LA assessor

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