COMPARISON OF COMBUSTION, CHEMICAL, AND NEAR-INFRARED SPECTROSCOPIC METHODS TO DETERMINE SOIL ORGANIC CARBON

Jason P Wight, Fred L. Allen, M. Z., Zanetti, and T. G. Rials
Department of Plant Sciences, University of Tennessee, 2431 Joe Johnson Drive 37996-4561
Knoxville

Corresponding Author: Jason Wight, email: Jwight@utk.edu

ABSTRACT

As interest in soil carbon dynamics and sequestration grows, so does the need for a rapid, accurate, and inexpensive method for quantifying soil organic carbon (SOC). Soils were collected from 14 sites and three depths. All samples were analyzed via dry combustion (CC) and Walkley-Black chemical (WB) methods. In addition, samples were air-dried and processed to give five surface roughness levels. Near infrared reflectance (NIR) spectra were obtained using a LabSpec Pro® near infrared spectrometer. The effect of surface roughness on signal quality was ascertained. Partial least squares regression was used to develop a model able to predict SOC as measured by NIR. Results from the three methods; CC, WB, and NIR, were compared to assess the reliability of NIR determination of SOC. Both NIR and WB analysis correlated well (greater than 0.9) with SOC as determined by combustion. NIR proved to be a viable alternative method of SOC analysis for the wide range of Tennessee soils used in this study.

INTRODUCTION

Due to increasing atmospheric CO_2 concentrations, interest in carbon dynamics and sequestration has increased. Soil carbon sequestration has the potential to be an inexpensive, widely utilized form of carbon storage. However, the size and nature of SOC pools can be affected by a variety of factors including local management practice, climate, and soil type. Therefore, studies across a wide array of systems must be undertaken to understand soil carbon sequestration. To accomplish this a rapid, accurate, and inexpensive method for quantifying SOC is needed.

One method that has recently demonstrated the potential to fulfill this demand is NIR. NIR-based technology has been successfully used in grain characterization for almost 35 years (Ben-Gera, and Norris, 1968) and has recently been expanded to other areas. In 1986, Dalal and Henry had used an NIR technique to predict organic matter in soil and in 1995, Ben-Dor and Banin had achieved high correlations between NIR signal intensity at certain wavelengths to specific soil organic matter functional groups. More recently Reeves and McCarthy (2002) presented refined analytical and statistical techniques resulting in a NIR model with r^2 value of 0.90 encompassing a range of Midwestern soils. However, one drawback of NIR is that machine signals require calibration using a library of soils with known carbon contents. It has also been shown that calibration accuracy is dependant on both precise NIR techniques and the local origin of the soil calibration library (Confalonieri, et. al., 2001). ***The objective of this research was to evaluate the potential of near infrared reflectance (NIR) spectroscopy to determine SOC content in a variety of soils collected from across Tennessee.***

METHODS

Sampling

Two soil sample subsets were used. Subset 1 consisted of a group of 55 samples taken from those obtained by landowners from across Tennessee and submitted to the University of Tennessee Soil Test Lab in Nashville. These were selected to represent a wide range of soil types and carbon levels. Subset 2 consisted of soil samples taken from specific, predetermined locations with a soil probe. These soils were sampled from 14 selected sites across Tennessee. They were taken from the following depths: 0-2”, 2-6”, and 0-6”. Samples were then air dried, lightly ground, and sieved into five particle size classes (see Table 1), resulting in 210 individual samples.

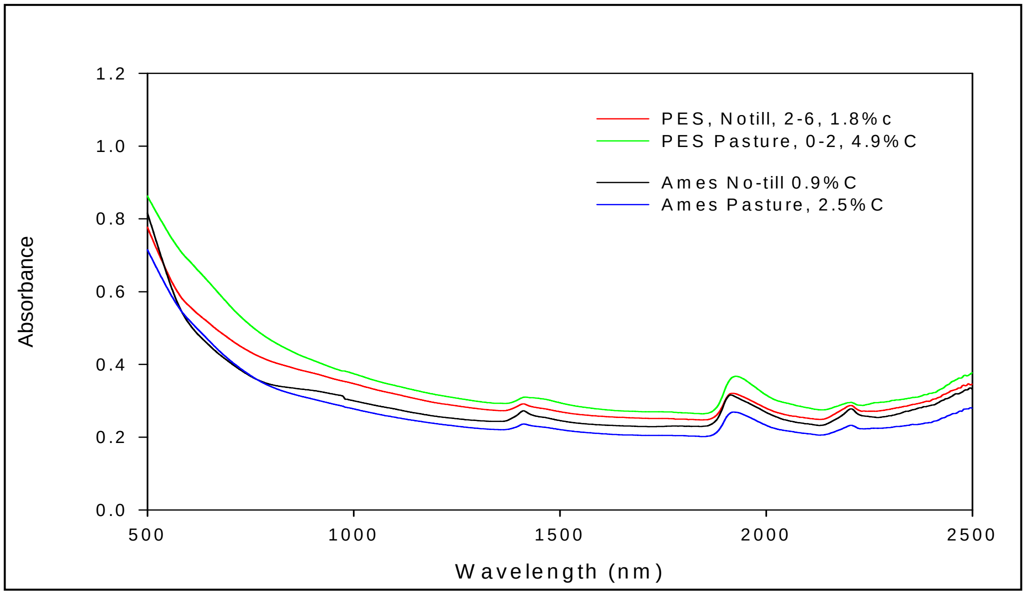
Table 1. Particle size separation treatment designations.

Particle Size (s)	Ground s<.01"	mix of s<0.08" and s<.01"	.01"<s> 0.08"	s<.08"	Sifted s<.01"
Treatment	A	B	C	D	E

Analysis

CC was measured using carbon combustion (FlashEA 1112 NC Analyzer, Thermo Electron Corp.). Organic matter (OM) was measured using a modified Walkley-Black chromic acid oxidation method (Walkley and Black, 1934). NIR spectra were made with an Analytical Spectral Devices (ASD) Field Spectrometer at wavelengths between 500-2400 nm, using a rotating sample cup. Light was provided by a DC lamp set at 30° above the sample, directed towards the samples’ center. A fiberoptic probe placed 2.76” above the surface gave an optical scanning field with 1.4” diameter. Captured spectra were then transferred from the ASD to an Unscrambler® file (CAMO technologies, 2003). Five spectra per sample were collected and averaged into one. The data set was further reduced by averaging spectral data collected from 1nm intervals to intervals of 4nm to reduce file size and time required to compute partial least squares (PLS) models. Then, reflectance (R) was transformed to absorbance, A=log (1/R) and a mean normalization transformation was performed. To improve peak discrimination, the Norris derivative was taken of each 4nm segment. PLS models were then constructed and a cross-validation was performed.

Figure 1. NIR spectra of four soils.



RESULTS

Figure 1 shows NIR spectra of selected soils. It can be seen that the spectra have unique but similar shapes, with signal peaks of different soils at the same wavelengths. These spectral characteristics allow correlations with soil chemical properties to be determined. Analysis resulted in a strong (r=0.90) overall relationship between CC and NIR (Figure 2). Early in the model development process it was observed that models for higher carbon (CC> 7%) samples did not apply well to those for lower carbon samples (CC<7%). Because most of the samples were low in carbon, further analysis was directed towards these low C samples only. This caused the omission of 9 of the 235 samples, but improved model performance greatly. Because model predictions are restricted to sample population, results do not apply to the omitted high carbon soils. Table 2 shows in detail the correlations, standard errors, and fitting parameters between the different sample groups, NIR signal, CC and OM. Generally, NIR correlated better with CC than OM. All particle size groups had very high (>0.95) model correlations for CC (Figure 3) while similar correlations for OM were lower (>0.80). Standard errors displayed trends similar to the correlations with those of CC being smaller (0.11%-0.25% C) than those of OM (0.36%-0.9%). The fully cross-validated models followed the same trends, with accordingly lower correlations and higher standard errors. Cross-validated NIR correlations with CC were 0.80 or above with standard errors of prediction ranging from 0.16% to 0.53%. NIR showed lower correlation with OM than CC (r>0.65) with standard prediction errors being higher (0.4% to 1% C).

It should be noted that while the subset 1 samples showed the same NIR prediction trends for CC relative to OM, overall model quality was much lower than those based on subset 2. This may be due to a number of factors including more variability within each individual sample in subset 1 or the fact that this subset represents a wider spatial and taxonomic variety than subset 2. However, when the subset 1 samples were combined with subset 2, overall model quality was improved to a 0.90 correlation and 0.42% C standard error of prediction for the validated model. Data for 0-2" and 2-6" depth increments were used for model development, but comparisons between C detection methods at depths are not shown. Accuracy between methods followed similar trends for each depth as that which was seen in the overall model development shown in Table 2.

The overall linear regression of Walkley-Black determined OM to WBC correlation was 0.87 with a standard error of 0.59%. All NIR predictions of CC, which had a correlation of 0.9 and a 0.42% standard error compared favorably to the Walkley-Black chemical method of soil carbon determination (Table 3, Figure 4).

Table 2. Model fit, error, and parameters.

	NIR Prediction of Combustion C				NIR Prediction of OM				OM Prediction of Combustion C			
Sample Set	**r**	**Slope**	**0ffset**	**RMSEC (%C)**	**r**	**Slope**	**0ffset**	**RMSEC (%C)**	**r**	**Slope**	**0ffset**	**RMSEC (%C)**
Subset 1	0.665	0.429	1.250	0.939	0.878	0.771	0.616	0.750	0.879	0.77	0.46	0.58549
Subset 2	0.952	0.906	0.152	0.277	0.864	0.746	0.700	0.693	0.870	0.756	0.391	0.444
Subsets 1+2	0.902	0.813	0.323	0.424	0.806	0.650	0.930	0.845	0.848	0.719	0.488	0.538

Cross-Wise Validation												
	NIR Prediction of Combustion C				NIR Prediction of OM				OM Prediction of Combustion C			
Model Set	**r**	**Slope**	**0ffset**	**RMSEP (%C)**	**r**	**Slope**	**0ffset**	**RMSEP (%C)**	**r**	**Slope**	**0ffset**	**RMSEP (%C)**
Subset 1	0.535	0.362	1.410	1.060	0.653	0.568	1.220	1.240	0.862	0.757	0.524	0.622
Subset 2	0.933	0.882	0.185	0.325	0.839	0.729	0.706	0.750	0.846	0.748	0.403	0.453
Subsets 1+2	0.866	0.785	0.371	0.492	0.765	0.617	1.017	0.919	0.840	0.712	0.499	0.550

† Abbreviations correspond to the following: near-infrared reflectance (NIR), carbon (C), organic matter (OM), correlation (r), Root mean standard error of correlation (RMSEC), and root mean standard error of prediction (RMSEP).

Table 3. Comparison of SOC determination methods.

Sample Site	Depth (in)	CC (%)	W-B OM (%)	OM Pred of CC (%)	NIR Pred of CC (%)
TES Upland Forest	0-6	2.21	3.5	2.41	2.35
TES Pasture Sideslope	0-6	1.44	2.7	1.32	1.36
TES Pasture Sideslope 2	0-6	1.75	3.2	1.76	1.76
TES Depression Pasture	0-6	1.69	3.0	1.67	1.68
TES Sideslope Tilled	0-6	0.98	1.9	0.68	0.78
TES Upland Tilled	0-6	0.90	1.3	0.56	0.68
Ames Forest	0-6	1.61	2.6	1.56	1.58
Ames 100 yr Pasture	0-6	1.49	2.3	1.40	1.43
Ames No-till Soy-corn	0-6	0.83	1.4	0.47	0.59
Ames Tilled Soy	0-6	0.98	1.5	0.68	0.78
PES Forest	0-6	2.74	3.8	3.15	3.02
PES Fescue Pasture	0-6	2.83	4.7	3.27	3.13
PES No-till Corn	0-6	1.83	3.3	1.86	1.85
PES Tilled Potatoes	0-6	1.16	1.8	0.93	1.01

†Abbreviations correspond to the following: UT Tobacco Experiment Station (TES), UT Plateau Experiment Station (PES), Walkley-Black (W-B), organic matter (OM), combustion carbon (CC), near-infrared reflectance (NIR) and prediction (Pred).

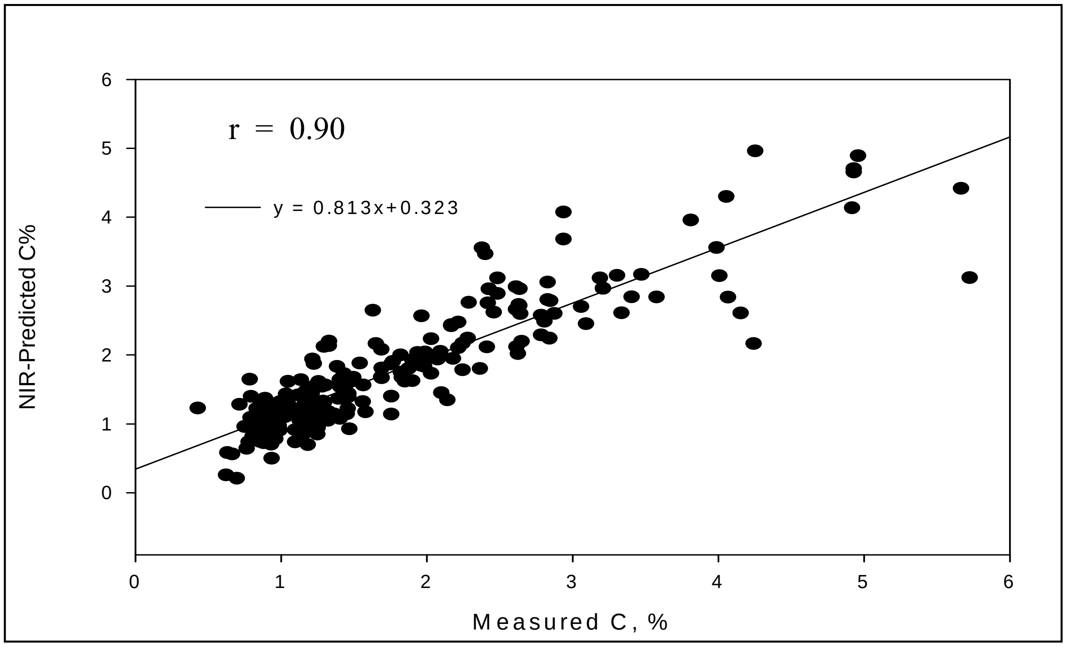


Figure 2. Plot of CC Vs. NIR predicted C.

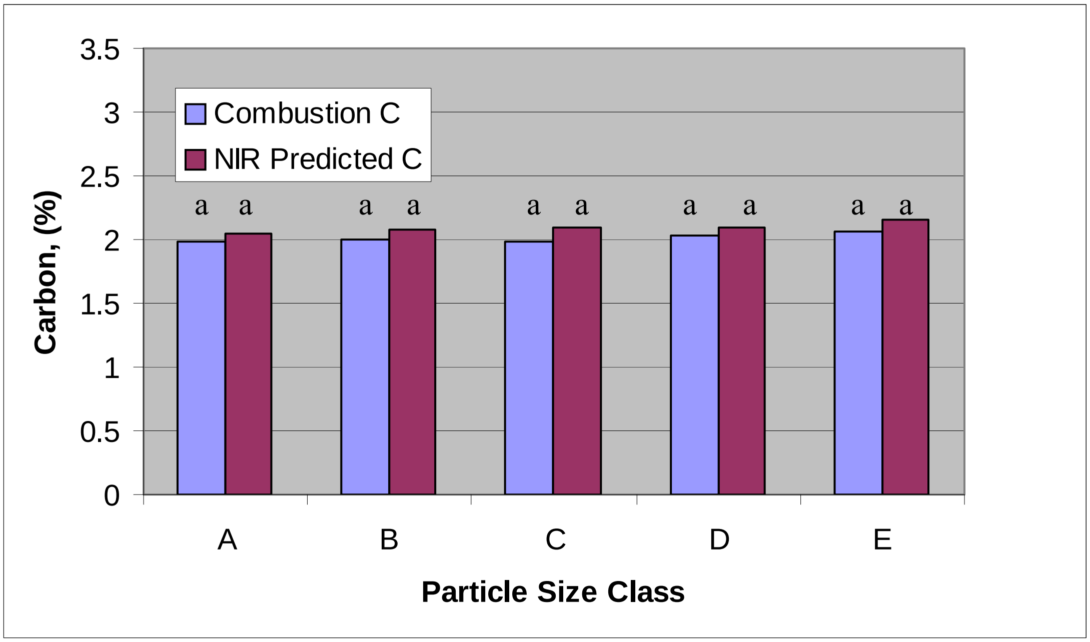


Figure 3. Effect of particle size class on NIR prediction of combustion carbon.
† Columns topped by the same letter in each pair are not significantly different.

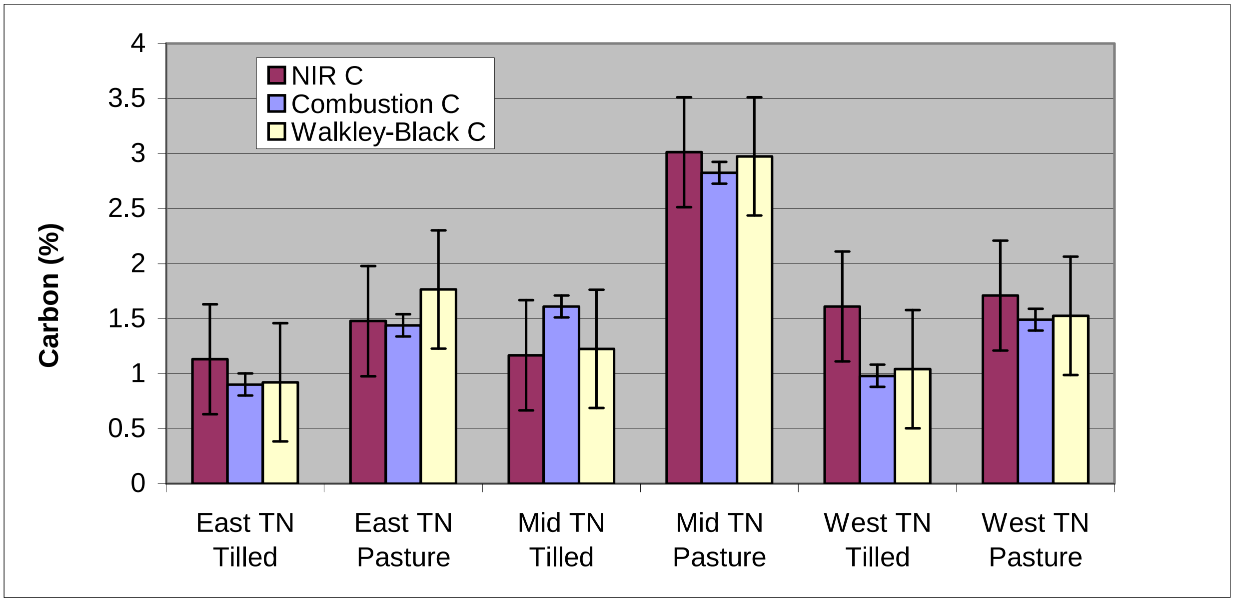


Figure 4. Comparison of SOC determination methods with six Tennessee soils at a depth of 0-6”.

CONCLUSIONS

- NIR derived model parameters were generally insensitive to sample particle size, so differing sample preparation techniques did not adversely effect the quality of NIR measurements.
- Combustion carbon can be more accurately predicted than Walkley-Black organic matter using this NIR technique.
- NIR presents a viable alternative to the Walkley Black method for carbon determination for the soils used in this study.

Benefits of NIR with respect to combustion and Walkley-Black methods:
-Faster analysis time
-No toxic chemical byproducts
-No reagents
-Equipment has proven to be durable and relatively low maintenance
Limitations of NIR:
-Model development requires some statistical knowledge to avoid over-fitting and interpretation errors.
-Analyses are restricted to soil types that are similar to those used in model creation

LITERATURE CITED

Ben-Dor, E. and A. Banin. 1995. Near-infrared Analysis as a rapid method to simultaneously evaluate several soil properties. Soil Sci. Soc. Am. J. 59:364-372.

Ben-Gera, I., and K.H. Norris. 1968. Determination of moisture content in soybeans by direct spectrophotometry, Isr. J. Agric. Res. 18:124-132.

CAMO Technologies. 2003. The Unscrambler® 8.0.5, CAMO Software, India Pvt. Ltd.

Confalonieri, M. F. Fornasier, A. Ursino, F. Boccardi, B. Pintus, and M. Odoardi. 2001. The potential of near infrared reflectance spectroscopy as a tool for the chemical characterization of agricultural soils. J. Near Infrared Spectrosc. 9:123-131.

Dalal, R.C. and R.J. Henry. 1986. Simultaneous determination of moisture, organic carbon, and total nitrogen by near infrared reflectance spectrophotometry. Soil Sci. Soc. Am. J. 50:120-123.

McCarty, G.W., J.B. Reeves III, R.F. Follett, and J.M. Kimble. 2002. Mid-infrared and near infrared diffuse reflectance spectroscopy for soil carbon measurement. Soil Sci. Soc. Am. J. 66:640-646

Walkley, A. and I.A. Black. 1934. An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37:29-37.