

# IR assessment of C in tropical soils

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## Abstract

Calibrations for soil carbon content measured by dry combustion (Total Carbon, TC) and chromate oxidation (Organic Carbon, CORG) of soils from the Brazilian National Soil Collection were made using Fourier Transform Near- and Mid-Infrared Diffuse Reflectance Spectroscopy combined with PLS statistics. Calibration sets of sample populations of different carbon ranges, soil taxonomic classes, and soil textural groups were established. Calibrations obtained for the largest TC and CORG ranges were better, compared to the lower ones, but lower RMSD and RD were found for the lower carbon ranges. Taxonomic soil class was not an adequate criterion for calibration set formation. Soil texture had effects on calibrations, especially using NIRS, because of the particular size effect to which NIRS was more sensitive than Mid-IR. In general, DRIFTS showed better performance than NIRS. NIRS only outperformed DRIFTS when used with a calibration set that was fairly homogeneous in its particle size distribution. Results demonstrated that while calibrations can be developed using either DRIFTS or NIRS for even a very diverse set of soil samples, which will determine C over a wide range of concentrations inherent in such a diverse set, it is desirable to separate sample populations by soil textural properties for calibration development to achieve more accurate results.

## Key Words

Chemometrics, granulometric composition, bulk soil

## Introduction

The application of infrared spectroscopy (near- and mid-IR) for the quantitative analysis of soils has become of increased interest over the last one and a half decades or so. One of the main reasons is the need for new methodologies for the assessment of C forms in soils and the potential of the technique both for laboratory and field measurements. Potential future policies for C sequestration in agriculture (crop production systems and pasture grazing) and forestry (particularly eucalyptus and pine plantations) would require the measurement of soil C over time at many locations to evaluate how much C is being sequestered or lost from the soil. Standard methods such as chromate oxidation or high temperature combustion are slow, expensive or both. Loss-on-ignition, which is a fairly cheap and fast method, for highly weathered tropical soils suffers from accuracy problems (Nelson and Sommers 1996; Watson *et al.* 2000; Lal *et al.* 2001).

Infrared spectroscopy, in turn, is a technique that is able to measure large number of samples, and determine any number of analytes at a time, once calibrations are developed (Reeves *et al.* 1999). There is numerous literature about the types of soil parameters, such as total C (CTOT), organic C (CORG), forms of N, macroelements, texture etc., that can be potentially determined by IR spectroscopy (e.g. Viscarra-Rossel *et al.* 2006).

For application on soils, mid-IR Fourier-transform diffuse reflectance spectroscopy (DRIFTS) seems to be more robust than near infrared (NIRS) (Madari *et al.* 2005), however, the application of either of them is not always straightforward for the several possible levels of future application. Fairly accurate calibrations can be developed for the local level (e.g. plot or even farm) (Madari *et al.* 2006), but to achieve robust calibrations at regional or national level criteria for calibration development has to be investigated.

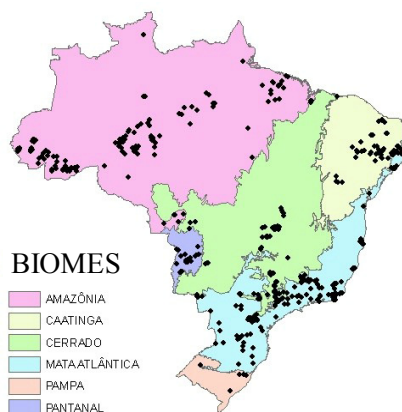
The objective of this study was to investigate what kind of major criteria could be applied when sample populations for calibration development are to be selected, in the case of soils, to determine TC and CORG with the highest accuracy possible using around 1000 samples from the National Soil Collection of the Brazilian Agricultural Research Corporation (Embrapa) complemented by some Ferralsol samples from the collection of the Institute of Agronomy (IAC-Campinas, São Paulo State of Brazil).

## Methods

### Samples

Three hundred and sixty seven soil profiles from all Brazilian biomes were selected from the National Soil

Collection of the Brazilian National Soil Research Center, Rio de Janeiro State, and from the soil collection of the Agricultural Institute of Campinas (IAC), São Paulo State, Brazil. The distribution of the soil profiles over Brazil is shown in Figure 1. Diagnostic soil horizons were selected, on average 3 horizons from each profile, resulting in 1135 soil samples for carbon measured by dry combustion (TC), and 1014 soil samples for carbon measured by dichromate oxidation (CORG). The TC values of the entire test set ranged between 0.4 and 555.0 g/kg, and for CORG from 0.2 to 401.9 g/kg.



**Figure 1. Distribution of the examined soil profiles in Brazilian biomes.**

#### *Sample preparation and conventional sample analysis*

All samples were bulk soil samples. Each sample was dried at 65 °C and finely ground to pass an 80-mesh sieve. The TC of these samples was measured by combustion at 925 °C (Nelson and Sommers 1996) using a Perkin Elmer CHNS/O Series II 2400 Analyzer. Coefficient of variation of the method was 3%. In this work we refer to the carbon that can be determined by chromate oxidation (CORG), the so-called Walkley-Black method, as organic carbon (Embrapa 1997). This involves oxidation of the soil organic matter by potassium dichromate solution ( $K_2Cr_2O_7$ , 0.4N mixed with cc.  $H_2SO_4$ ) combined with 5 minute heating and boiling. After that the solution was cooled down distilled water was added to it, followed by titration with ammonium sulphate ( $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ , 0.1N) in the presence of phosphoric acid (cc.  $H_3PO_4$ , 85%) using diphenylamine as indicator. These methods were used as reference for calibrations of the Mid-IR and NIR techniques.

#### *Infrared Analysis*

Mid (2,500-25,000 nm) and near (110-2,500 nm) infrared spectra of the soils were obtained by a Digilab (Bio-Rad) FTS-7000 spectrometer equipped with a KBr beamsplitter and a DTGS detector for the mid-IR region and with a quartz beamsplitter and InSb liquid nitrogen cooled detector for the near IR region. In both regions samples were scanned at  $4\text{ cm}^{-1}$  resolution with 64 co-added scans per spectrum. Samples, for both spectral regions, were ground (80 mesh) and non-diluted for the measurement (Reeves 2003). A Pike Autodiff autosampler /reflectance accessory was used. The blank reference standards were KBr and S for DRIFTS and NIRS respectively.

#### *Chemometrics*

Calibration development was carried out using SAS PLS with a custom made program testing 22 different spectral pretreatments for both analytes (Reeves and Delwiche 2004). Final calibrations were done using the entire spectral range and averaging every 4 data points, for both spectral regions. Calibrations were developed using the one-out cross-validation procedure with and without an independent test set. Calibration sets of sample populations of different carbon ranges, soil taxonomic classes, and soil textural groups were established (shown in footnote of Table 1).

## **Results**

The mid- (DRIFTS) and near-infrared (NIRS) calibration results are shown in Table 1. Results on the whole sample set demonstrated that either NIRS (CORG:  $R^2=0.809$ ; TC:  $R^2=0.930$ ) and DRIFTS ( $R^2=0.934$ ;  $R^2=0.948$ ) are promising techniques for the development of calibrations for quantitative soil C analysis. Making up calibration sets by soil C content and by soil taxonomic groups did not improve the accuracy of the calibrations, however, major improvement was achieved by calibration sets based on the texture (particle

size distribution) of the individual samples. Both NIRS (e.g. CORG:  $R^2=0.975$ ) and DRIFTS (CORG:  $R^2=0.967$ ) performed well on the calibration set that contained samples that had similar particle size distributions, such as the very clayey samples (>60% clay). The accuracy of NIRS, however, decreased when applied to more heterogeneous sample sets (clayey [CORG: NIRS  $R^2=0.938$ , DRIFTS  $R^2=0.962$ ] and medium texture [CORG: NIRS  $R^2=0.871$ , DRIFTS  $R^2=0.917$ ]), while DRIFTS kept showing good accuracy. The difference in accuracy was more evident for CORG.

**Table 1. Mid-infrared (DRIFTS) and near infrared (NIRS) calibration results for soil carbon.**

<sup>1</sup> Sample Data Sets	<sup>2</sup> MSC	Derivative	<sup>3</sup> GAP	<sup>4</sup> # Factors	$R^2$	<sup>5</sup> RMSE	<sup>6</sup> RD
NIRS, Total Carbon (TC)							
Carbon1	No	Second	8	15	0.931	17.66	0.574
Carbon2	No	First	16	13	0.739	7.90	0.473
Carbon 3	No	First	8	12	0.750	4.80	0.356
Carbon 4	No	Second	4	4	0.952	34.56	0.180
NIRS, Organic Carbon (CORG)							
Carbon 5	No	First	16	13	0.809	18.55	0.968
Carbon 6	No	Second	8	10	0.712	5.23	0.478
Carbon 7	No	Second	8	9	0.726	3.43	0.385
DRIFTS, Total Carbon (TC)							
Carbon 1	Yes	First	4	13	0.947	15.38	0.504
Carbon 2	Yes	First	8	12	0.856	5.87	0.352
Carbon 3	Yes	First	16	11	0.811	4.18	0.312
Carbon 4	No	Second	4	4	0.948	36.14	0.188
DRIFTS, Organic Carbon (CORG)							
Carbon 5	Yes	First	8	13	0.934	10.88	0.568
Carbon 6	Yes	First	4	12	0.810	4.24	0.400
Carbon 7	No	First	6	11	0.840	2.62	0.294
NIRS, Taxonomic Soil Class, Total Carbon (TC)							
Soilclass1	No	First	16	9	0.725	7.65	0.433
Soilclass 2	No	Second	4	5	0.854	5.72	0.383
NIRS, Taxonomic Soil Class, Organic Carbon (CORG)							
Soilclass 3	No	First	16	9	0.725	7.70	0.440
Soilclass 2	No	Second	4	4	0.784	6.75	0.470
DRIFTS, Taxonomic Soil Class, Total Carbon (TC)							
Soilclass 1	No	First	4	10	0.861	5.44	0.308
Soilclass 2	Yes	First	8	11	0.914	4.40	0.295
DRIFTS, Taxonomic Soil Class, Organic Carbon (CORG)							
Soilclass 3	No	First	4	10	0.862	5.45	0.312
Soilclass 4	Yes	Second	16	10	0.905	4.49	0.313
NIRS, Soil Textural Group, Total Carbon (TC)							
Texture1	No	First	8	10	0.961	6.42	0.293
Texture 2	No	First	8	12	0.930	7.26	0.359
Texture 3	No	Second	32	8	0.866	6.39	0.345
NIRS, Soil Textural Group, Organic Carbon (CORG)							
Texture 4	No	Second	4	8	0.975	5.33	0.309
Texture 5	No	First	8	12	0.938	7.00	0.487
Texture 6	No	Second	32	8	0.871	6.37	0.568
DRIFTS, Soil Textural Group, Total Carbon (TC)							
Texture1	Yes	First	16	5	0.953	7.05	0.322
Texture 2	Yes	First	4	12	0.954	5.89	0.291
Texture 3	Yes	First	8	12	0.905	5.39	0.291
DRIFTS, Soil Textural Group, Organic Carbon (CORG)							
Texture 4	Yes	Second	32	7	0.967	6.19	0.358
Texture 5	Yes	First	4	12	0.962	5.52	0.384
Texture 6	Yes	First	8	13	0.917	5.11	0.455

<sup>1</sup>Calibration sets Carbon1 to 4 are based on soil total carbon (TC) content ( $0.4 \leq C \leq 555.0$ ,  $0.4 \leq C \leq 99.1$ ,  $0.4 \leq C \leq 39.9$ , and  $0.8 \leq C \leq 555.0$  g/kg, respectively); Carbon5 to 7 are based on organic carbon (CORG) content ( $0.2 \leq C \leq 401.9$ ,  $0.2 \leq C \leq 66.0$ , and  $0.2 \leq C \leq 30.0$  g/kg, respectively); Soilclass1 and 3 and 2 and 4 are based on soil taxonomy class (Ferralsols and Acrisols, respectively) for TC and CORG calibration; Texture1 and 4, 2 and 5, and 3 and 6 are based on soil textural grouping (very clayey, clayey, and medium texture, respectively) for TC and CORG calibration.

<sup>2</sup>Multiplicative Scatter Correction;

<sup>3</sup>Number of data points skipped for derivatives;

<sup>4</sup>Number of Partial Least Squares Factors used in calibration;

<sup>5</sup>Rootmean Squared Deviation;

<sup>6</sup>Relative Difference. Adapted from Madari *et al.* (2005).

## Conclusions

Calibrations can be developed using either DRIFTS or NIRS for even a very diverse set of soil samples, which will determine C over a wide range of concentrations inherent in such a diverse set. However, to obtain more reliable predictions for soil C content using a very diverse set as calibration set does not appear to be the most useful approach. Developing calibrations for ranges of soil C content decreased the error of the calibrations (RMSD and RD), however, resulted in lower accuracy ( $R^2$ ). Calibrations based on soil textural classes also do not seem to be the right approach for soil carbon content prediction. The reason for this might be that calibrations using a set of samples of large variance in textural composition suffer from the sensitivity of infrared spectroscopy on particle size distribution of the samples, especially in the case of NIRS. Near infrared spectroscopy (NIRS) had excellent performance ( $R^2 = 0.961-0.975$ ) when applied for a calibration set that contained samples that had very similar particle size distribution, but its performance declined for more heterogeneous sample populations regarding particle size. Diffuse reflectance infrared spectroscopy (DRIFTS), by being less influenced by specular effects, showed reasonable performance ( $R^2 > 0.95$ ) for sample sets containing soils of a wide range of particle size distribution. For calibration purposes for soil carbon content (both TC and CORG) prediction, therefore, it seems to be desirable to create calibration sets based on soil textural properties and then to use the most adequate spectral region (NIR for the more homogeneous sets, or Mid-IR for the less homogeneous ones) for the calibration.

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