

Emerging techniques for soil carbon measurements

Working Paper No. 2

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Abstract

Soil carbon sequestration is one approach to mitigate greenhouse gases. However, to reliably assess the quantities sequestered as well as the chemical structure of the soil carbon, new methods and equipment are needed. These methods and equipment must allow large scale measurements and the construction of dynamic maps. This paper presents results from some emerging techniques to measure carbon quantity and stability. Each methodology has specific capabilities and their combined use along with other analytical tools will improve soil organic matter research. New opportunities arise with the development and application of portable equipment, based on spectroscopic methods, as laser-induced fluorescence, laser-induced breakdown spectroscopy and near infrared, for *in situ* carbon measurements in different ecosystems. These apparatus could provide faster and lower cost field analyses thus improving soil carbon contents and quality databases. Improved databases are essential to model carbon balance, thus reducing the uncertainties generated through the extrapolation of limited data.

Keywords

Soil carbon; spectroscopic methods; LIFS; LIBS; NIRS; FTIR; soil organic matter; greenhouse effect; soil carbon sequestration; portable equipment.

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Acronyms

LIFS	Laser Induced Fluorescence Spectroscopy
LIBS	Laser Induced Breakdown Spectroscopy
NIR	Near-Infrared
NIRS	Near-Infrared Spectroscopy
SOM	Soil Organic Matter
NMR	Nuclear Magnetic Resonance
EPR	Electron Paramagnetic Resonance
FTIR	Fourier Transform Infrared
CS	Carbon Stocks
CDM	Clean Development Mechanism
IR	Infrared

Introduction

In the face of climate change and increasing CO₂ levels in the atmosphere, the global carbon cycle, soil organic carbon sequestration, and the role of different world biomes as potential sources and sinks of carbon are receiving increasing attention (Feller and Bernoux 2008). Carbon (C) sequestration in plant and soil systems offers an opportunity for mitigating the greenhouse effect (Lal 2004) but the relationship between soil carbon stocks (CS) and carbon fixation in natural and anthropic vegetation remains one of the least studied issues. Emphasis has been placed on measurements of carbon fixation by forests or measurements of carbon emissions following land-use changes (Schaefer et al. 2008). As agriculture represents one of the major land use systems, there is a close relationship between soil carbon capture and emissions and the allocation of land for agriculture. Many management practices can increase soil CS as well as above-ground carbon in biomass, including soil conservation practices (e.g., no-tillage, reduced tillage, terracing), incorporation of crop residues, increases in cropping intensity and fertilization, and conversion of cropland to permanent grasslands or forests. Although the Clean Development Mechanism (CDM) protocol has prioritized only aboveground carbon sequestration via reforestation and afforestation, the soil might represent even a larger carbon sink. In this respect, one of the challenges for the incorporation of agriculture into post-Kyoto agreements (after 2012) is to develop simple and effective methodologies for measuring, monitoring and verifying soil carbon in cropping, farming and land use systems.

The Brazilian Agricultural Research Corporation (EMBRAPA), through its National Centre for Instrumentation, has worked to address this challenge. Embrapa's team has used spectroscopic techniques, with high potential for field application, to analyse whole soil samples without sample preparation. Particularly, positive results have been obtained using Laser-Induced Breakdown Spectroscopy (LIBS), Laser-Induced Fluorescence Spectroscopy (LIFS) and Near-Infrared Spectroscopy (NIRS). Methodologies using LIBS and NIRS are being developed for soil C quantification and a LIFS equipment was developed to evaluate C stability in soil. A partnership between Embrapa and the International Potato Center (CIP) has

been conducive to the assessment of soil CS and C stability in different agroecosystems in the Southern Peruvian Andes, Kenya and Brazil, using state of the art non-destructive analytical methods. This chapter adds to our own work on emergent techniques through a review of the recent literature on the subject.

Soil carbon measurements

Determination of total carbon by dry combustion (measurement of CO₂ emitted from the oxidation of organic carbon and thermal decomposition of carbonate materials) is a common laboratory technique for carbon analysis (Nelson and Sommers 1996). However, these traditional methods (i.e., Walkley-Black, dry combustion) have limitations such as producing toxic residues and can be both time consuming and labour intensive (Walkley and Black 1934). Some laboratories base carbon measurements on weight change rather than CO₂ emitted, presenting discrepancies in results from different laboratories (Kimble et al. 2001). The weight loss-on-ignition method tends to overestimate soil organic matter (SOM) due to additional weight loss of inorganic constituents, primarily hydrated clays, during the heating process and is affected by ignition temperature and sample size (Cambardella et al. 2001). It can be stated that the accuracy of the quantification is heavily dependent on the reference method used (Segnini et al. 2008). In the case of soil organic carbon (SOC), total organic carbon (TOC) and CHNS methods are the most adequate since they enhance both accuracy and reproducibility.

Laser-Induced Breakdown Spectroscopy (LIBS) and Near-Infrared Spectroscopy (NIRS) are two of the contemporary alternative methods to quantify soil carbon (Cremers et al. 2001; Madari et al. 2006; Da Silva et al. 2008; Christy 2008; Ferraresi 2010; Martin et al 2010). The advantages of these techniques are: almost no sample preparation, quickness of the process and low cost of analyses. In addition, LIBS can be used for determining metals and the development of portable equipment is advantageous.

The actual uncertainty of climatic events and the expected changes call for new methods that deliver quick carbon quantification and qualitative organic matter (OM) information to advance in themes related to agricultural sustainability and the carbon cycle. The advent of *in situ* methods for determination of soil carbon are important due to the comparatively rapid and potentially cost-effective benefits of these methods, the reduction in sampling and laboratory errors and their potential to minimize soil disturbance while increasing the ability to analyze large areas of soil. Advanced field methods of carbon analysis should be capable of providing repetitive, sequential measurements for evaluation of spatial and temporal variation

at a scale that was previously unfeasible (Gehl and Rice 2007). Thus, spectroscopy becomes a clean and rapid alternative approach for this purpose (Ferraresi 2010).

Qualitative information can be provided by laboratory spectroscopic methods, for example, Nuclear Magnetic Resonance (NMR), Electron Paramagnetic Resonance (EPR), Fourier Transform Infrared (FTIR), NIRS, Raman, Ultraviolet-visible (UV-vis) Absorption and Fluorescence. However, only NIRS and fluorescence spectroscopy has the potential to be transformed into a field technique to produce quality SOM indicators (Martin-Neto et al. 2009; Milori et al. 2006).

In the following sections, basic fundamentals of such techniques for soil carbon determination and our main results obtained in different ecosystems are presented. In our research, significant correlations among fluorescence and other new and traditional methods have been found.

Carbon quantification and soil bulk density by NIRS

Infrared (IR) radiation refers broadly to that part of the electromagnetic spectrum between visible and microwave regions. IR spectroscopy is one of the most powerful tools available to the chemist for identifying organic and inorganic compounds because, with the exception of a few homomolecular molecules such as O₂, N₂, and Cl₂, all molecular species absorb infrared radiation.

NIRS is a reproducible and low-cost method that characterizes materials according to their reflectance in the NIR spectral region. However, NIRS has only relatively recently been tested for quantitative analysis of soils (Reeves and McCarty 2001) and it has a high potential for evaluating and characterizing large areas of soil, quickly, reliably and economically. In many areas of agriculture, NIRS has reduced the need for chemically and other instrumentally based methods of sample analysis (Madari et al. 2006; Shepherd and Walsh 2006, 2007). In this technique, calibrations are based on a representative sample set to relate spectral information to the analyte in question (Siesler et al. 2002; Roberts et al. 2004). Chemometrics tools are already necessary for quantitative analysis, since the equipment response is limited and in several wavenumbers.

Madari et al. (2006) showed that both Diffuse Reflectance Infrared Fourier Transform (DRIFT) and NIRS, when combined with chemometric methods could be useful for quantifying total carbon, nitrogen, sand and clay in soil samples. These techniques could also be calibrated to estimate parameters such as soil aggregation indices, which are not directly measurable by other means. Ferraresi (2010) evaluated the NIRS and DRIFTS on SOM, microbial biomass and texture determination in Brazilian soils. Clay, silt, sand, total organic carbon and microbial carbon contents as well as microbial quotient were accurately quantified by IR spectroscopy. Janik et al. (2007) showed a good correlation between mid-IR and total and particulate organic carbon.

Soil bulk density is needed to convert organic carbon content to mass of organic carbon per unit area. However, measurements of soil bulk density are labour-intensive, costly and tedious. The use of NIRS for characterizing the particle size distribution of SOM through

determinations based on bulk soil spectra has been suggested with promising results (Barthes et al. 2008; Moreira et al. 2009).

Christy (2008) presented an on-the-go spectrophotometer for *in situ* measurement of reflectance spectra and evaluated the potential of the system for making real-time predictions of various soil attributes using NIRS. A review by Cécillon et al. (2009) showed that NIRS can provide information related to many chemical and some physical and biological soil properties. The spectra can be used as an integrated measure of soil quality, so as to classify sites according to their degradation status or for monitoring the effect of a management factor on soil quality. However, several technological limitations, i.e., the need for robust quantification models based on large soil characteristics data (site, classification, texture, land use, etc.) and, friendly and cheaper devices for *in situ* analysis, must be addressed regarding large application of this very promising method. The use of soil spectra libraries seem to be a good step forward (Terhoeven-Urselmans et al. 2010).

LIBS and its potential to perform analysis *in situ*

LIBS is an emerging analytical technique based on atomic and ionic emission of elemental sample constituents that provides qualitative information about the sample composition. LIBS is able to perform multielemental direct analysis, dispensing the pre-treatment of samples, besides showing potential to perform analysis *in situ* (Cremers and Radziemski 2006).

Ferreira et al. (2009) evaluated the effect of three LIBS instrumental parameters (laser pulse energy, delay time and integration time gate) on signal-to-noise ratio (SNR) of seven elements in soil samples. To optimize LIBS parameters for each individual element response, a multivariate technique for multiple response optimization was used. They observed that the best compromise between high line intensity and low noise must be determined case by case, since analytes presents different physical behaviour and because they are differently bounded in each matrix. However, it is possible to combine the LIBS parameters aiming at multielemental analyses. Using a multiple response optimization method was a convenient strategy to find the best combination among parameters, which provides high SNR for several elements simultaneously, hence preserving the original multielemental feature of LIBS.

Elements emission lines in LIBS spectrum are closely related with the matrix in which they are embedded (Ferreira et al. 2009), thus quantitative analysis using LIBS is not a simple task. Several factors contribute to matrix effects: all of the elements in the plasma may not be equally ionizable, creating variations in the equilibrium between neutral and ionized atoms; and the mass of different elements ablated changes due to differences in heat capacity and vaporization temperatures (Anzano et al. 2006). Other drawbacks of LIBS include its dependence on the fulfilment of equilibrium conditions in the plasma; the possible saturation of the signal for high concentration elements due to self-absorption effects, even for high-energy lines, that makes their quantification difficult or impossible with LIBS; and, the large number of complex physical-chemical phenomena involved in the processes of ablation and plasma formation, evolution and interaction with the background ambient (Gaudiuso et al. 2010). These signal emission features make difficult the use of calibration standards for LIBS and researchers adapt univariate models constructed with classical least-squares regression (Da Silva et al. 2008, Trevizan et al. 2008). In some cases, the matrix effects could be reduced

by using multivariate calibration techniques (Vrenegor et al. 2005; Doucet et al. 2007). Artificial Neural Network (ANN) is a kind of multivariate technique which, due to its superior classification and prediction capabilities, has gained space in LIBS spectroscopy (Ferreira et al. 2008).

Quantitative carbon measurements in temperate soils have been reported by several research groups (Cremers et al. 2001; Ebinger et al. 2003; Gehl and Rice 2007; Martin et al 2010). However, there is only one study for tropical soil using a portable LIBS system (Da Silva et al. 2008).

Portable LIBS equipment

Portable LIBS equipment makes it possible to carry out quantitative field soil analysis. The main advantage is the fast and low-cost assessment with almost no sample preparation (Ferreira et al. 2008; Da Silva et al. 2008).

Ferreira et al (2008) determined Cu concentration in tropical soil samples using a portable LIBS system with ANN as a calibration strategy. Cross validation was applied, following ANN training, for verification of prediction accuracy. The ANN showed good efficiency for Cu predictions ($R=0.96$), despite features of the portable instrumentation employed. The proposed method presented a limit of detection (LOD) of 2.3 mg dm^{-3} of Cu and a mean squared error (MSE) of 0.5 for the predictions.

Da Silva et al. (2008) calibrated a portable LIBS system for quantitative measurements of carbon in whole soil samples from the Brazilian Savanna region. Tropical soils have large amounts of iron in their composition, so the carbon line at 247.86 nm presented strong interference of this element (iron lines at 247.86 and 247.95). For this reason, they used the carbon line at 193.03 nm. Simple and multivariate linear regressions plus cross validation showed correlation coefficients higher than 0.91, indicating the potential of using portable LIBS systems for quantitative carbon measurements in tropical soils.

Fluorescence and LIFS equipment

LIFS is one of the most sensitive devices available for analytical purposes. It is relatively easy to implement, phenomenologically straightforward and well investigated, and largely non-invasive so that it can be useful for environmental applications. The excitation of the fluorescence material is performed by a laser, which has the advantages of its high intensity, coherence and polarization. Hence, it produces a good SNR when compared to fluorescence induced by a lamp, gives greater selectivity in excitation, and reduces interference factors in the fluorescent signal.

Fluorescence is highly probable in molecular systems containing atoms with lone pairs of electrons such as C=O, aromatic, phenolic, quinone and more rigid unsaturated conjugated aliphatic systems. These functional groups are present in humic substances (HS) from soils (Senesi 1990; Senesi et al. 1991) and represent the main fluorophors of SOM. The extension of the π -electronic system, the level of heteroatomic substitution and type and number of substituting groups under the aromatic rings strongly affect the intensity and wavelength of molecular fluorescence.

LIFS of whole soils

NMR and EPR Spectroscopic techniques require extraction and chemical fractioning of HS from the soil (e.g. humic acids - HA, fulvic acids and humin). This chemical process results in the production of dangerous residues and causes modifications in OM structure (Feller and Beare 1997). In order to render SOM analysis viable at the closest to natural state possible and to carry out quick and low cost *in situ* analyses, methodologies using LIFS has been developed. Milori et al. (2006) developed a methodology using LIFS to assess the effect of soil management on the humification index of SOM at different depths. The excitation at near ultraviolet-blue radiation is more resonant with rigid and complex OM structures (Milori et al. 2002; Martin-Neto et al. 2009), such as condensed aromatic rings and unsaturated cyclic organic groups. Thus, the area under the fluorescence emission normalized by carbon content of soil was defined as the SOM humification index (H_{LIF}). The technique was used to assess the SOM humification index in different soil layers of the Brazilian Savanna (Cerrado) region and how it was affected by land management. In the conventional tillage treatment, H_{LIF} was

rather uniform along the profile, which was consistent with the homogeneity imparted by tillage disturbances on the 0-20 cm layer of these soils. The H_{LIF} for the native Cerrado and no-tillage soils showed a tendency to increase from top to deeper layers as the proportion of the particulate OM fraction, and thus of labile compounds like carbohydrates and peptides, decreased in depth (Milori et al. 2006). Similar results were observed by González-Perez et al. (2007) for subtropical Brazilian soils. The results concurred with other spectroscopic techniques such as Fluorescence spectroscopy of dissolved HS, EPR and NMR (González-Pérez et al. 2007; Dieckow et al. 2009).

Segnini et al. (2011) studied CS and stability in five Peruvian agroecologies, along a 1,000 km transect covering the arid Pacific coast, the Andean high plateau, and the Amazonian rainforest. Coffee plantations in the Amazon and alfalfa under irrigation in the dry valleys presented larger ($P > 0.05$) CS (83 Mg ha^{-1}) than primary rainforests. The dry lowlands showed the lowest CS (40 Mg ha^{-1}). SOC increased with elevation in the arid environments. In the high plateau potato systems, low CS (47 Mg ha^{-1}) were found. The soils in both the Amazonian site and the dry valleys presented lower H_{LIF} , when compared to other agroecologies. H_{LIF} increased with soil depth due to the presence of recalcitrant carbon, while at the surface the presence of labile carbon dominates as a result of a constant input of plant residues.

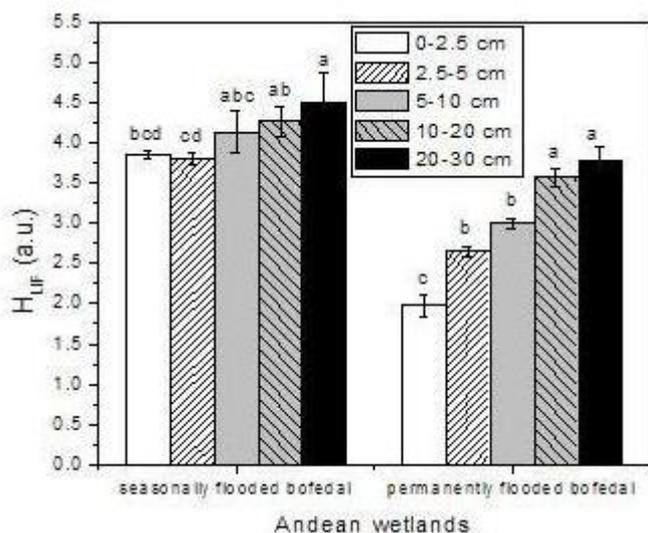
Undoubtedly, the humification index is a highly relevant factor in agroecosystems studies. LIFS allows affordable analyses of SOM humification since the technique measures stable carbon, which can be extremely useful in studies on carbon sequestration by soils and mitigation of CO_2 emissions.

Portable LIFS

The goal is to link a portable LIFS with GPS to evaluate the SOM and produce soil quality maps (EMBRAPA 2001). Segnini et al. (2010a) used EPR and a portable LIFS system developed by Embrapa Instrumentation for assessing SOM stability in whole soil samples from permanent and seasonally flooded wetlands in the Peruvian Andes (Figure 1). The results obtained by both techniques were comparable ($R^2 = 0.88$) and were reliable indicators of increased or reduced SOM stability through its humification index. Results from the portable LIFS system also showed significant correlations when compared to both the bench LIFS system ($R^2 = 0.88$) and EPR ($R^2 = 0.62$), showing the feasibility of using a portable

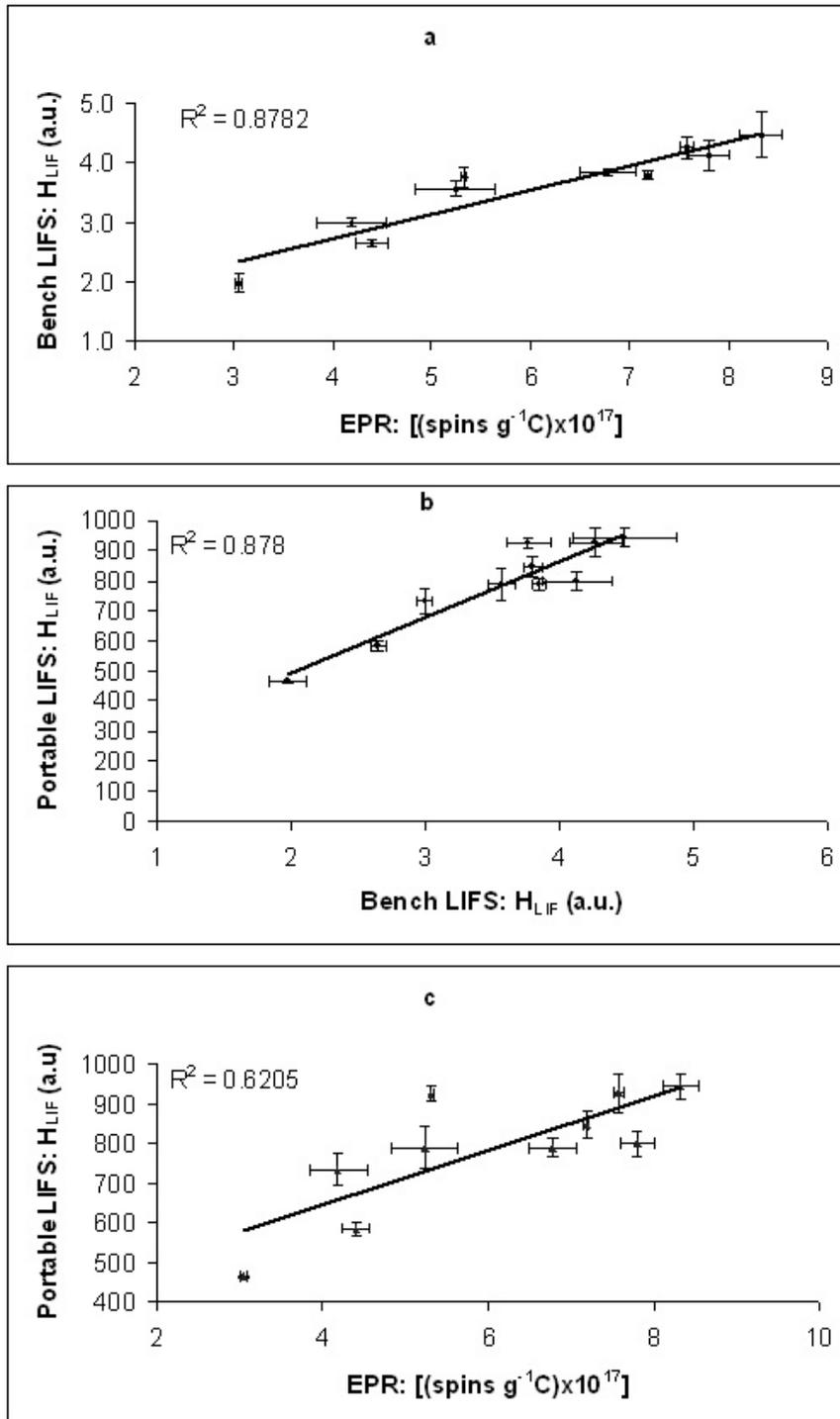
LIFS system and representing an improvement in speed and convenience for SOM stability evaluation across the landscape (Figure 2). The soil characterization can be done in the field with whole soil samples, thus avoiding transporting them through complex terrains like the Andean mountains. In another study, Segnini et al. (2010b) successfully used the portable LIFS equipment and powder soil instead of soil pellets for conducting a comparative soil carbon analysis of cropping systems and native vegetation areas in different agroecosystems in Kenya. The results showed wide variations in the levels and stability of carbon stored in the soil, depending on factors such as land use, crops grown, water content, elevation, native vegetation and agricultural practices.

Figure 1



Humification index (H_{LIF}) of soils determined through Laser-Induced Fluorescence spectroscopy (LIFS) of soils sampled at different depths: 0-2.5, 2.5-5, 5-10, 10-20 and 20-30 cm, in two areas of the Peruvian Andes: seasonally flooded bofedal and permanently flooded bofedal. Bars with different letters are statically different ($P < 0.05$).

Figure 2



Data showing the close relationship between (a) the concentrations of semiquinone-type free radicals, as measured by Electron Paramagnetic Resonance (EPR) and the results of the H_{LIF}, as measured by Laser-Induced Fluorescence Spectroscopy (LIFS); (b) bench and portable LIFS systems and (c) portable LIFS and EPR in the assessment to humification index of wetlands (bofedales) from the Peruvian Andes.

Priorities and recommendations for action

Relevant results from some emerging techniques based on NIRS, LIBS and LIFS, which measure carbon quantity and stability were presented. Each methodology has specific capabilities and their combined use along with other analytical tools will improve SOM research. Opportunities are provided by the development and application of portable equipment systems, based on spectroscopic methods, for *in situ* measurements of SOM content, in different ecosystems. These apparatus could provide faster and lower cost field analysis to improve the data basis of carbon content in soils and their compartments. These increased data are essential for carbon balance models and for reducing extrapolation risks from a reduced number of carbon analyses.

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