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Review Article

EVALUATION OF LABORATORY AND SPECTROSCOPY METHOD AND SOC ESTIMATION CHALLENGES

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ABSTRACT
SOC is a critical indicator of soil quality which does stand for Soil organic carbon. There are two commonly used methods for estimating the spatial pattern of SOC. In this paper description of three methods, laboratory, field and satellite measurements are discussed. General or generic models are designed using a set of model parameters that are expected to provide accurate SOC estimates over large spatial extents. Mapping SOC directly through remote sensing may be challenging especially in locations where the soil surface is partially or wholly covered. All methods have pros and cons and they should be matched to specific measurement needs and applications before they are selected or rejected. The choice of an instrument or measurement techniques will depend upon the researchers' need and resources, such as the project objective and funding allotted for the project. Generic models can integrate data such as management practices, land cover, climate and soils.

Keywords*: SOC Estimation Challenges, Laboratory Method, Satellite Measurements, Soil Quality*

INTRODUCTION

Soil organic carbon (SOC) is a critical indicator of soil quality (Lal, 2004a, b; Lal, 2009; Stevens *et al.*, 2008). Tan *et al*. (2004) argued that the spatial variation in soil quality is the result of changes in SOC concentration. Soil quality as a factor which is influenced by Inherent features and soil management is intended and will be assessed by determining soil quality indicators (Doran and Parkin, 1994). Those measurable soil properties that affect the capacity of the soil for crop production capabilities are called soil quality indicators (Arshad and Martin, 2002). Soil quality indicators are defined as processes and characteristics of the soils that are susceptible to soil use changes (Aparico and Costa, 2007).

Soil quality is different in different geographical regions because of differences in climate, topography, parent material, vegetation and land use (Brejda *et al*, 2000). Different characteristics of the soil are considered as indicators of soil quality. A soil quality index should have the following features:

A. Including environmental process
B. Including physical, chemical and biological characteristics of soil
C. Sensitive to environmental changes and management
D. Be measurable, accessible and have quantitative processing

For a global soil C monitoring program representing the main types of ecosystems and allowing both the SOC stocks and the stock changes to be estimated, several challenges remain to be solved (Robert Jandl *et al*, 2014) :

1. The information on SOC is geographically unbalanced. An immediate challenge is the harmonization of already existing regional soil monitoring programs and soil databases.
2. The identification of a universal metric for SOC monitoring is needed. Typically, information is available for the total C concentration, which is then converted to the total SOC pool. For a valid estimation of the SOC pool, the measurement of the soil bulk density and the content of rock fragments are equally important.
3. A standardized approach to the reported soil depth for SOC pool estimations is required. SOC can be unevenly distributed over varying soil depths. Existing soil C maps are often based on data that poorly reflect the C pool of deeper soil horizons. The effect of land use changes on deep C stocks has been poorly addressed.

4. The understanding of SOC stabilization processes is incomplete. No general agreement on soil C fractionation methods to estimate the degree of stabilization has been achieved.
5. Specific fieldwork protocols for the assessment of SOC dynamics are needed. The large spatial heterogeneity of SOC in comparison to its moderate temporal change calls for cost-effective sampling protocols in order to properly capture SOC dynamics on a landscape scale and to identify small SOC changes in a highly variable pool.
6. SOC monitoring programs need to liaise with long-term soil experiment (LTSE). LTSEs offer a baseline for the SOC pool and can comprise a set of sites where targeted research on soil processes and their impacts on soil C can be performed. They can serve as a backbone for SOC monitoring.
7. Mechanistic SOC simulation models are expected to play an important role in monitoring programs. They can assist in the estimation of temporal trends in the SOC pool, but they are not yet adequate for the extrapolation of existing soil information over space and time.

Development of Methods for SOC Estimation

Rapid, accurate, and inexpensive measurement of the soil's carbon pool is essential to detect and quantify change in the ecosystem dynamics of C. A comparative assessment of present determination methods is needed urgently to identify promising techniques that reduce uncertainty in measuring the soil's C pool and flux at the farm and watershed scale.

Ex Situ Methods

Methods involve collecting representative soil samples and measuring the C concentration via dry or wet combustion techniques. The latter process involves the oxidation of organic matter by an acid mixture and measuring the evolved CO2 by gravimetric, titrimetric, or manometric methods. In the 19th century, Rogers and Rogers reported that dichromate sulfuric acid solution could oxidize organic substances. After unsuccessful attempts by Warrington and Peake, Cameron and Breazeale, Ames and Gaither accomplished the higher recovery of organic substances by the dichromate-sulfuric mixture. Schollenberger in 1927 introduced the titrimetric determination of unused chromic acid in the oxidation reaction with ferrous ammonium sulfate using several indicators (diphenylamine, o-phenanthroline, or Nphenylanthranillic acid. Walkley and Black and Tyurin in 1934 and 1935 developed a complete quantification method of SOC by wet oxidation without necessitating external heating. However,

Laboratory methods such as the Walkley and Black (1934) and the dry combustion (DC) (Nelson and sommers, 1982) have been the standard approaches for SOC determination. The SOC pool can also be quantified in situ, for example through the Inelastic Neutron Scattering (INS) method (Wielopolski *et al.*, 2011).

However, determination of SOC using laboratory or field based methods may be expensive and time consuming especially for C inventory over large spatial extents.

In Situ Methods

New in situ soil C methods promise high precision without as much sample processing time and their subsequent analysis. In situ methods mainly are based on remote sensing and spectroscopic measurements in the field. Spectroscopic methods include infra-red reflectance near-infra-red (NIR) and mid-infra-red, laser-induced breakdown spectroscopy (LIBS) and inelastic neutron scattering (INS). Potential of these methods are being calibrated with reference to soil sampling and subsequent analysis with automated dry combustion method.

Remote sensing exploits the fact that objects on the earth's surface reflect, absorb, and emit electromagnetic radiation in a different way (i.e., each object has a specific spectral response) depending on their molecular composition, texture, size and shape. A major limitation in most remote sensors especially when used to acquire information in-situ is that they provide only spectral response of objects on the earth's surface. However, analytical spectral devices (ASD) e.g., the Field Spec exist which may be used to acquire spectral reflectance of soils below the earth surface in the laboratory. Depending on the energy sources involved in the data acquisition, remote sensing imaging instruments may be classified as active (i.e. emits and detects own energy, to and from target), or passive (i.e. sun is the energy source). The use of passive optical remotely sensed spectral band data from the visible and near infra-red is being proposed to characterize soil quality (Brick lemyer and Brown, 2010; Croft *et al.,* 2012; McCarty *et al.,* 2002; Stevens *et al.,* 2008).

The SOC, a proxy of soil quality may be measured in the laboratory or field and upscale to cover large spatial extents using aerial or satellite data. This can be undertaken for example, by measuring the spectral reflectance of surface and sub-surface soils in the laboratory, and then developing models that relate SOC concentration at different depths with reflectance. These developed models can then be applied directly on to the satellite data to extrapolate over large spatial extents.

Alternately, the temporal variability in crop yield may also be a useful indicator of soil quality variability across space and time. Validation of remotely sensed products with actual field measurements may be conducted through statistical analysis, for example by regression analysis or analysis of variance (ANOVA). If a large disagreement exists between modeled estimates and actual measurements, the algorithmormodel is modified and re-applied to generate another SOC estimate which is evaluated, and the process of model and product development repeated until satisfactory results are achieved.

Laboratory Methods

The Walkley and Black (1934) method is a chemical oxidation procedure for measuring SOC concentration. Although the Walkley– Black procedure is simple, rapid with minimal equipment needs, the results may vary depending on the land uses, soil depth, and soil texture (De Vos *et al.,* 2007). Alternately, the weight loss on ignition method is a DC approach that gravimetrically determines SOC from soil samples heated in a furnace at 430 °C, for 24 h (Chatterjee *et al.,* 2009).

Tivet *et al*. (2012) demonstrated that the DC method provides less uncertainty in SOC estimates for different land uses and depth compared with Walkley–Black, and proposed conversion equations from Walkley–Black to DC. Laboratory methods such as the DC compute SOC as mass fraction by weight (g kg−1) (Smith and Tabatabai, 2004a). For estimating the spatial variation in SOC, it is important to initially determine the soil bulk density (ρb), so as to express C on volume basis (g m−2 or Mg ha−1). The requirement to analyze SOC and evaluate ρb is time consuming, and labor intensive (Chatterjee *et al.,* 2009; Lal, 2006).

Spectroscopic methods permit a rapid and non-destructive means for quantifying SOC with high precision, reduced cost and processing times (Cohen *et al.,* 2007), although considerable sample preparation (collection, grinding, sieving, and drying) is still required (Stevens *et al.,* 2008).

Laboratory spectroscopy may be useful for calibration of aerial and satellite reflectance measurements (Stevens *et al.,* 2008), and for investigating the relationship between SOC decomposition processes and soil reflectance.

Field Based Methods

The determination of SOC directly in the field may not only be cost effective, but appropriate in circumstances where a laboratory is not readily available (Reeves, 2010).

Satellite Measurements

The application of sensors mounted on satellite platforms for measuring SOC is still at its infancy (Croft *et al.,* 2012).

Although satellite derived reflectance data may provide spatially continuous SOC maps at high temporal resolutions, issues such as data acquisition costs, preprocessing requirements, and technical complexity have hampered their development (Croft *et al.,* 2012; Hansen *et al.,* 2008; Moran *et al.,* 1997).In addition, satellite borne remote sensors only detect the surface reflectance, which is correlated to SOC.

Other issues to contend with when determining SOC with satellite borne sensors include variable soil moisture for different localities, and vegetation which may obscure the remote sensors from acquiring soil reflectance.

However, for cropping systems, air or space borne sensors may be used to measure the soil reflectance during the times of the year when the crops are absent from the field, or begun growing.

The SOC modeled using data from optical sensors mounted on aerial platforms have yielded strong correlation with the ground data (Croft *et al.,* 2012; Stevens *et al.,* 2008). In contrast, Gomez *et al*. (2008) reported a weaker correlation between Hyperion satellite modeled SOC, and ground or laboratory determined SOC, which was attributed to the low signal/noise ratio. Spectral reflectance data must be processed to reduce noise or errors (Moran *et al.,* 1997).

Generic Models for SOC Determination

General or generic models are designed using a set of model parameters that are expected to provide accurate SOC estimates over large spatial extents. Mapping SOC directly through remote sensing may be challenging especially in locations where the soil surface is partially or wholly covered (e.g., by other vegetation or buildings).

For scenarios of partial coverage of the soil surface, SOC may be modeled through a combination of field, remotely sensed datasets, and analyzed through a GIS.

Examples of GIS based models for quantifying SOC at various scales include the General Ensemble biogeochemical Modeling System (GEMS), CENTURY, DayCent (Daily Century model), Rothamsted Carbon Model (RothC), and the Erosion Depositional Carbon Model (EDCM) (Liu *et al.,* 2004a, 2011; Tan *et al.,* 2009; Wielopolski *et al.,* 2011).

The RothC model is a soil decomposition model that requires plant productivity parameters as input (Coleman and Jenkinson, 1996). Generic models can integrate data such as management practices, land cover, climate and soils (Liu *et al.,* 2004a, 2008; Ojima *et al.,* 1994; Parton *et al.,* 2004; Zhao *et al.,* 2010).

The common model inputs include monthly precipitation, monthly maximum and minimum temperatures, soil texture, ρb, drainage, initial SOC level, water holding capacity, cropping system, cultivation, atmospheric N deposition, fertilization, harvesting, grazing, tree removal, land cover data, and natural disturbances such as erosion or fire (Dieye *et al.*, 2012; Liu *et al.*, 2008; Parton *et al.*, 2004).

The major output variables are NPP, grain yield, C decomposition, C exchange rates between ecosystems and atmosphere, biomass removal by harvesting, and the C pool in vegetation and soils. Generic models also provide the uncertainty of predicted variables in space and time (Liu *et al.,* 2004a, 2008).

Challenges in SOC Estimation

Developing accurate, rapid and systematic approaches for estimating SOC over large spatial scales constitutes a significant challenge. For example, the requirement of a high sampling density with point data and the high spatial variability of ρb influence interpolation accuracy (Moran *et al.,* 1997).

Unlike with point data, interpolation based on remotely sensed satellite data has the advantage of continuity of data in space and time (Duveiller and Defourny, 2010).In highly variable environment mixed pixels, which represent a weighted average of spectral reflectance signals of the different land cover types within a pixel may occur (Foody, 2000).

Approaches such as the sub-pixel mapping can minimize the mixed pixel problem (Roberts *et al.,* 1993).

Sub pixel mapping methods may be performed through methods such as the regression tree, spectral mixture analysis, or a combination of both. Regression tree concept was earlier introduced in this article, under the subsection dealing with non-parametric classification.

Spectral Mixture Analysis (SMA) technique uses information from all the spectral reflectance bands, to divide each ground resolution element into its constituent materials through decomposing the DN, or reflectance values into fraction images or components using end members (Garcia-Haro *et al.,* 1999).

End members are spectral reflectance generated from pure target surface classes.The SMA technique has been used to characterize the spatial distribution of surface crop residue cover which is a major source of SOM (Obade *et al.,* 2011).Mismatches between spatial, spectral and temporal resolution of remotely sensed data also create difficulty in the remote sensing based assessment of SOC changes (Lobell, 2010).

To minimize errors attributed to differing spatial resolution between sensors, an approach that is resolution independent should be used in map comparisons. Methods such as Map curves can be useful for comparing maps having different spatial resolutions without necessarily conducting rigorous geo-referencing.

The spectral reflectance of soil varies depending on the chemical or physical factors, such as soil mineralogy, soil moisture, SOM content, soil texture, and particle size (Croft *et al.,* 2012; Wielopolski *et al.,* 2011), which makes it difficult to acquire the pure spectral reflectance signals of SOC. The drawback

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of generic models such as CENTURY, GEMS is that they operate effectively for only soil systems on which they were created, and require historic datasets which are rare as part of the inputs (Dieye *et al.*, 2012; Liu *et al.*, 2011). The knowledge on variation of SOC with depth is also limited, because most SOC inventories focus on the first 1 m below the soil surface, although a substantial amount of C can occur at greater depths (Batjes, 2008).

DISCUSSION

Remote sensing data has a high spatial and temporal resolution and can be used for estimating ecosystem carbon sequestration. There are two commonly used methods (i.e. Ex situ methods and In situ methods**)** for estimating the spatial pattern of SOC.

Determination of SOC using laboratory or field based methods may be expensive and time consuming especially for C inventory over large spatial extents. The Walkley– Black procedure is simple, rapid with minimal equipment needs, the results may vary depending on the land uses, soil depth, and soil texture. DC method provides less uncertainty in SOC estimates for different land uses and depth compared with Walkley–Black, and proposed conversion equations from Walkley–Black to DC. Although satellite derived reflectance data may provide spatially continuous SOC maps at high temporal resolutions, issues such as data acquisition costs, preprocessing requirements, and technical complexity have hampered their development.

Although there is a strong relationship between remotely sensed spectral data and SOC content, prediction at different spatial scales has not been achieved. Moreover, to draw inferences of SOC content from satellite imagery on a large scale necessitates having surrogate indices such as vegetation type and species or soil moisture. Beside these shortcomings, remote sensing with its high resolution monitoring abilities is applicable for predicting SOC distribution, which is not feasible by any other means.

All methods have pros and cons and they should be matched to specific measurement needs and applications before they are selected or rejected. The choice of an instrument or measurement techniques will depend upon the researchers' need and resources, such as the project objective and funding allotted for the project.

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