



## Review

## Current and emerging methodologies for estimating carbon sequestration in agricultural soils: A review



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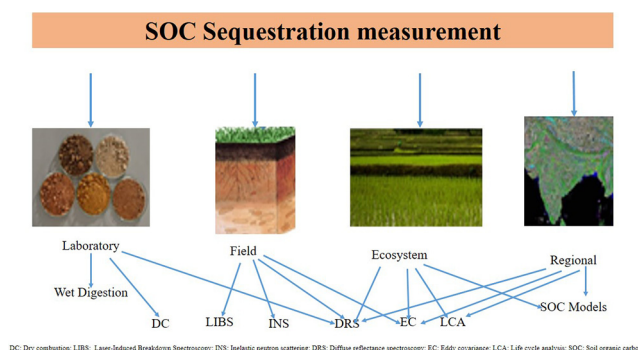
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## HIGHLIGHTS

- Methodologies for the measurement of soil carbon sequestration at point, field, ecosystem and regional level reviewed.
- Recent developments in spectroscopic techniques are discussed.
- Eddy-covariance and indirectly LCA methodological approaches are reviewed.
- Methodological potentials and uncertainties of soil carbon research sequestration are highlighted.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This review covers the current and emerging analytical methods used in laboratory, field, landscape and regional contexts for measuring soil organic carbon (SOC) sequestration in agricultural soil. Soil depth plays an important role in estimating SOC sequestration. Selecting appropriate sampling design, depth of soil, use of proper analytical methods and base line selection are prerequisites for estimating accurately the soil carbon stocks. Traditional methods of wet digestion and dry combustion (DC) are extensively used for routine laboratory analysis; the latter is considered to be the “gold standard” and superior to the former for routine laboratory analysis. Recent spectroscopic techniques can measure SOC stocks in laboratory and in-situ even up to a deeper depth. Aerial spectroscopy using multispectral and/or hyperspectral sensors located on aircraft, unmanned aerial vehicles (UAVs) or satellite platforms can measure surface soil organic carbon. Although these techniques’ current precision is low, the next generation hyperspectral sensor with improved signal noise ratio will further improve the accuracy of prediction. At the ecosystem level, carbon balance can be estimated directly using the eddy-covariance approach and indirectly by employing agricultural life cycle analysis (LCA). These methods have tremendous potential for estimating SOC. Irrespective of old or new approaches, depending on the resources and research needed, they occupy a unique place in soil carbon and climate research. This paper highlights the overview, potential limitations of various scale-dependent techniques for measuring SOC sequestration in agricultural soil.

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## 1. Introduction

Soil can be a potential source or sink of atmospheric carbon dioxide ( $\text{CO}_2$ ) and play a key role in climate regulation according to the nature of management practices adopted. Soil acts as an important compartment for carbon sequestration (Lal, 2014; Minasny et al., 2017), depending on its quality and ability to support biomass production (Bispo et al., 2017). In the top 1 m of its surface, soil stores 1500–2400 pg (peta gram =  $10^{15}$  g) of organic C (Ciais et al., 2013). Soil organic carbon (SOC) sequestration is one of the key cost-effective options for mitigating climate change with additional co-benefits of improving soil fertility and other ecosystem services. At the Conference of Parties (COP21) of the United Nations Framework on Climate Change (UNFCCC) in Paris, the stakeholders have voluntarily committed to promote soil carbon enhancing agricultural practices (Chambers et al., 2016). Maintaining or enhancing SOC stocks was recognized as part of Sustainable Development Goal 15 (ADG 15) (UNCCD, 2015). Agriculture constitutes one third of the global arable land (World Bank, 2015). For this reason it is imperative to devise appropriate soil and land management practices to increase SOC stocks and utilize agricultural soil as a sink (ITPS, 2015). A few optimistic estimates suggest that by enhancing the root growth of agricultural crops, sufficient soil carbon can be stored in the ground and thereby equal the expected amount of anthropogenic emissions in the next two decades (Kell, 2012). Conversely, Sommer and Bossio (2014) opined that agriculture soil may become saturated upon reaching equilibrium and may not sequester carbon at a predicted

rate. Irrespective of the different opinions about the total potential of agricultural soil carbon sequestration, overwhelming evidence suggests that carbon sequestration is conceivable in agricultural soil and its co-benefits for improving soil quality and productivity are numerous.

For climate change research, an accurate and reliable measurement method is required to estimate C stock over time so that the impact of management practices can be monitored and verified. This requires harmonization of measurement methods and protocols for exchange of data (Paustian et al., 2016). Guidelines and recommendations for scale dependent sampling design, sampling methods and baseline selections are required for accurate SOC stocks calculation. Although at the laboratory and point scale or context, standard procedures are available (Bispo et al., 2017), a standard method for the spatial scale is still lacking (Miller et al., 2016; Maillard et al., 2017). Sometimes presence of inorganic carbonate and bicarbonate minerals may be present as background of organic carbon (OC) in the soil (Schmidt et al., 2012) giving variety of organic chemical structures with varying levels of protection and chemical attractions. This explains why it is difficult to find a universal single laboratory method that works efficiently analyzing SOC in all soils. The SOC fractions and their stability often indicate the potential of soil to sequester carbon (Dignac et al., 2017). The standard fractionation methods should also correctly explain the SOC pools' stabilization mechanism.

The measurement standards for rapid and cost-effective measurement of soil carbon concentration and carbon sequestration on a large scale (Lobsey and Viscarra, 2016; Ramifehiarivo et al., 2017) at the

landscape and regional level and on a vertical scale at profile are still evolving. A recent attempt has been made to estimate carbon sequestration at the ecosystem level by using eddy-covariance flux towers and agricultural life cycle analysis. Keeping in mind the importance of soil carbon estimation and monitoring at the point-field-regional and ecosystem scales, it is critical to synthesize past and current SOC sequestration methodologies. This paper reviews current and emerging research findings on scale dependent methods for the estimation of SOC sequestration underpinned by fundamental mechanisms. Furthermore, we identify where improvements can be made to help decision-making. This is particularly pertinent when wanting to use a particular method, depending on their situation and resources. Gaps in knowledge are highlighted here in an effort to promote further research.

## 2. Critical pre-estimation parameters for accurate assessment of SOC

### 2.1. Defining boundary lines and appropriate planning of experiments

The SOC sequestration is calculated within a defined and meaningful boundary line that provides a clear and important finding. It was suggested that SOC sequestration calculation should not consider carbon that originates from the land unit and not directly from the atmosphere (Olson, 2013). Thus, the SOC sequestration definition should be adjusted and the term “land unit” requires to be added (Olson, 2010). Doing so will provide better clarity and to the ability to differentiate the accretion of SOC to soil either from internal or external sources. Hence, depending on the land unit, clearly defined and identified boundaries should be drawn for the plot area, field, farm, and landscape under study.

### 2.2. Establishing the baseline

The SOC sequestration varies with the land use change (LUC) and land management change (LMC) in a particular agricultural system. Several researchers have compared and reported the alteration in SOC sequestration, principally between treated and non-treated plots while considering the non-treated as the baseline (Franzuebbers, 2010; Nayak et al., 2012; Shahid et al., 2017) without reporting the initial SOC level (before treatment is implemented). In two comparison plots - one treated and the other non-treated - it is possible that the rate of loss of the SOC over the pre-treated plot may be different; one plot is losing at a slower rate than the other. In that case, if the SOC level for the pre-treated plot is compared with the treated and not-treated plots, apparently no SOC is sequestered. Conversely, at the end of the experiment a comparison between the treated and non-treated plots will report an instance of SOC sequestration. Hence determination of SOC in the initial soil before treatment is required for fixing it as a boundary line so that SOC change, steady state, retention and loss of SOC within the soil can be assessed (Olson, 2013). In recent studies, however, researchers have compared the pre-treated plots as baseline with different treated plots at the end of the experiment period, in order to determine the SOC change in the form of build-up or erosion from the soil in agriculture. Therefore, the baseline is related to the scope, objective and structure of the system and invariably has to be fixed by researchers.

### 2.3. Time line/time horizon

Fixing a time line is essential for measuring the SOC sequestration after the treatments have been administered. It is established that SOC changes take place slowly and this is characterized by the higher degree of variability at spatial scale and inconsistently lower instance of variability at a temporal scale. For this reason it is very difficult to detect the absolute quantifiable change in SOC relative to its real initial value. By modelling SOC dynamics over different soil types and land use, it is reported that a minimum of 6–10 years is required to detect a 15%

SOC increase (Smith, 2004). Yet the IPCC (2006) reported that SOC stocks are stabilized or reach a steady state of equilibrium only after 20 years with different management practices. It is also argued that for soils containing large amounts of clay and SOC, a 20-year fixed time horizon is too short to establish SOC equilibrium by following any land use or land cover change. Sometimes traditionally managed soils continue to lose C within a time period lasting 50 to 100 years (Sanderman and Baldock, 2010). Spatial variability and very slow rate of C changes are the key challenges for correct assessment of SOC change (Kumar et al., 2012). In light of the above constraints, long-term field experiments lasting many years or decades are suggested for detecting any change in SOC sequestration within various land and soil management options.

### 2.4. Sampling design and number

The ability to obtain unbiased SOC data from a given area and drawing correct inferences is compromised in the absence of proper sampling designs (EPA, 2002). Sampling can be done by following the systematic or random method or by convenience, and these methods have been widely used to measure the C stock in soil (Rhoton et al., 2002; IPCC, 2006). However, in some cases the above sampling designs failed to capture the variability present in soil (USDA, 2006). In such cases, a combination of stratified as well as random sampling design can be used, by dividing the plots into possible homogenous sub-plots or strata followed by random sampling within these zones to get unbiased estimates of SOC (de Gruijter et al., 2006; Brus et al., 2011). For example, sub-plotting or stratification can be done on the basis of salinity and clay content of soil through electromagnetic survey, yield map and remote sensing (Dang et al., 2009; Fisher et al., 2009). A systematic grid sampling (de Gruijter et al., 2006) and nested sampling (Webster and Oliver, 2001) design have also been suggested so that estimates improve. Advances have been made in geostatistics and the sampling design can be further improved by applying the concept of autocorrelation, variogram and range in the model-based approach (Allen et al., 2010). This strategy ensures that the target variables show auto correlation and the samples are collected at intervals less than the range (de Gruijter et al., 2006) obtained from the experimental semi variogram.

Along with sample design, sample numbers must be determined before samples are actually collected. Sample number should be adequate enough to estimate the mean of SOC with a greater confidence interval so that a reliable SOC change is detected and correct inferences are made. The sample number can be calculated from the sample variance of SOC and allowable error (that can be tolerated in the study) utilizing the method proposed by Zar (1999). The sample design used for a single farm to assess the effect of different management practices will be different from that used for a regional level study involving simulation models (Davis et al., 2018). Scaling up the point SOC data to regional or landscape level magnifies the error of estimation, an increase in coefficient of variation by 30% (Goidts et al., 2009). It is obvious that sampling in a large area involves cost and time, hence optimum sample numbers can be arrived at by using appropriate methods that are required for producing statistically accurate results.

### 2.5. Sampling method

Following the selection of sampling design and number, the ways in which samples are collected often depend on the objective (i.e., short- or long-term storage change). Several sampling methods used for SOC change measurement are: digging open pits, core sampling with a punch core, core drill method, etc. However, large-excavation of soil pits and core sampling methods are commonly used for the measurement of SOC change experiments (Liebig et al., 2010; Rau et al., 2011). The core sampling method is more efficient than pit sampling because it consumes less time, thus making possible to collect more samples with greater accuracy, particularly in spatially heterogeneous sites

(Davis et al., 2018). There is an acceptable trade-off between increased sample numbers and soil compaction caused by coring (Rau et al., 2011; Wolf et al., 1994). Although methods are available to address the compaction issue, inaccuracies still exist due to underestimating the coarse soil fractions (>2 mm) which persist if coring equipment is unable to sample large rocks (Vadeboncoeur et al., 2012). This may not be a problem in agricultural soil because these soils usually have low rock content.

Soil structure and horizon development is better revealed by excavating the pit than coring (Erkins et al., 2013). Sampling by pits makes it possible to measure the mass, which is required for bulk density determination and enhance the estimated accuracy that coring cannot do (Vadeboncoeur et al., 2012). Re-sampling at a later date from the same point is not possible in pit sampling as it involves site disturbance, which affects the precision of estimation (Erkins et al., 2013). Some researchers suggest taking an additional auger sample close to the pit, but there are a couple of difficulties: firstly, identifying the appropriate depth from which the core samples were collected; and secondly, arresting cross-contamination of soil strata upon auguring. A core barrel sampler attachment technique has been suggested to solve this problem (Mason, 1992; Jandl et al., 2014).

To detect change in SOC in an agricultural system, appropriate space and time sampling arrangement as per the study's objectives is suggested (de Gruijter et al., 2006). Augurs can be used in agricultural soil to take undisturbed cores, however, in a landscape containing variable quantities of stones and coarse roots (for example, in a forest), auger sampling should be avoided and new sampling methodologies such as the rotary core device employed (Rau et al., 2011). We suggest for conducting more comparison studies with coring methodology combining soil pit and auger sampling technique under different soil, topography and cropping system. Newer sampling devices need to be developed that can help collect samples quickly, without disturbing the site much, preventing compactions, and are inexpensive.

## 2.6. Sampling depth

Sampling depth is one of the major criteria for SOC measurement. Many researchers considered the depth from soil surface for their sample design and found that the SOC concentration in soil is a function of depth of sampling (Wuest, 2009). About 50% of the soil carbon recorded in 1 m soil depth of the entire land surface of the world is present in subsoil below 30 cm (Batjes, 1996). Deciding sampling depth is equally important because SOC variation over the soil depth is uneven (Jandl et al., 2014) and long-term SOC accumulation can occur in deeper soil layers up to a depth of 100 cm (Da Silva Oliveira et al., 2016). Usually, SOC measurements are done in the top 30 cm depth, a recommended sampling depth according to the IPCC's (2006) recommendation. However, the Kyoto Protocol specified top 30 cm soil depth for accounting SOC inventories and as a consequence, current assessments are mostly confined to this depth (Stolbovoy et al., 2007), and poorly reflect SOC stocks in the deeper horizon (Jandl et al., 2014). SOC accumulation in the deeper horizon plays an important role in its sequestration (Olson and Al-Kaisi, 2015), therefore suggestions have been made to include the entire root zone in SOC measurements (VCS, 2012; Olson and Al-Kaisi, 2015).

Measuring SOC only within the top layer of the soil profile could yield inaccurate results (Olson, 2013), because high and low temporal changes mostly occur in this horizon due to soil erosion (Hobley and Willgoose, 2010). Thus, nearly all SOC sampling protocols (e.g., GRACE net) recently advised to take samples from a minimum depth of 100 cm (Resende et al., 2006; Cerri et al., 2013). However the subsoil carbon accumulation depends on soil type, for example Spodosol in Austria's forest land accumulates SOC at a shallower depth where as in rangeland Vertisol of Hunter Valley, New South Wales, Australia, it continues to the deeper horizon (Jandl et al., 2014). Referring to SOC measurements, samples can be collected either by fixed depth or horizon-

wise (Allen et al., 2010). Horizon-based sampling is appropriate to assess profile SOC stock only when horizon depths are demarked accurately and samples are collected at the center of the horizon or samples of the whole horizons are bulked (Zhang and Hartemink, 2017).

In order to assess the horizontal variation, two or three vertical cores can be collected in vertical transect, and if horizontal variation is higher, more representative depth-wise stratified random sampling is suggested to increase the accuracy of assessment (Zhang and Hartemink, 2017). When comparing the fixed depth-based and horizon-based sampling, Wang et al. (2017) reported 16–22% and 30–40% higher SOC stocks in 0–20 cm and 0–80 cm (whole profile), respectively, in horizon-based sampling. Sampling by fixed depth interval is an inexpensive, simple and a preferred method for stock estimation at the regional scale, whereas horizon sampling is preferred in pedogenesis studies (Grüneberg et al., 2010). To capture the profile variations, raster sampling (Davis et al., 1995), fine grid sampling on soil monoliths (Roudier et al., 2016) and fuzzy c-means sampling (Zhang and Hartemink, 2017) methods can also be used. Undoubtedly, for stock estimation or SOC sequestration analyses, deeper sampling is an ideal option, but there is a trade-off between accuracy versus cost and labor resources. The science of depth and SOC sequestration is still evolving.

## 2.7. Bulk density corrections

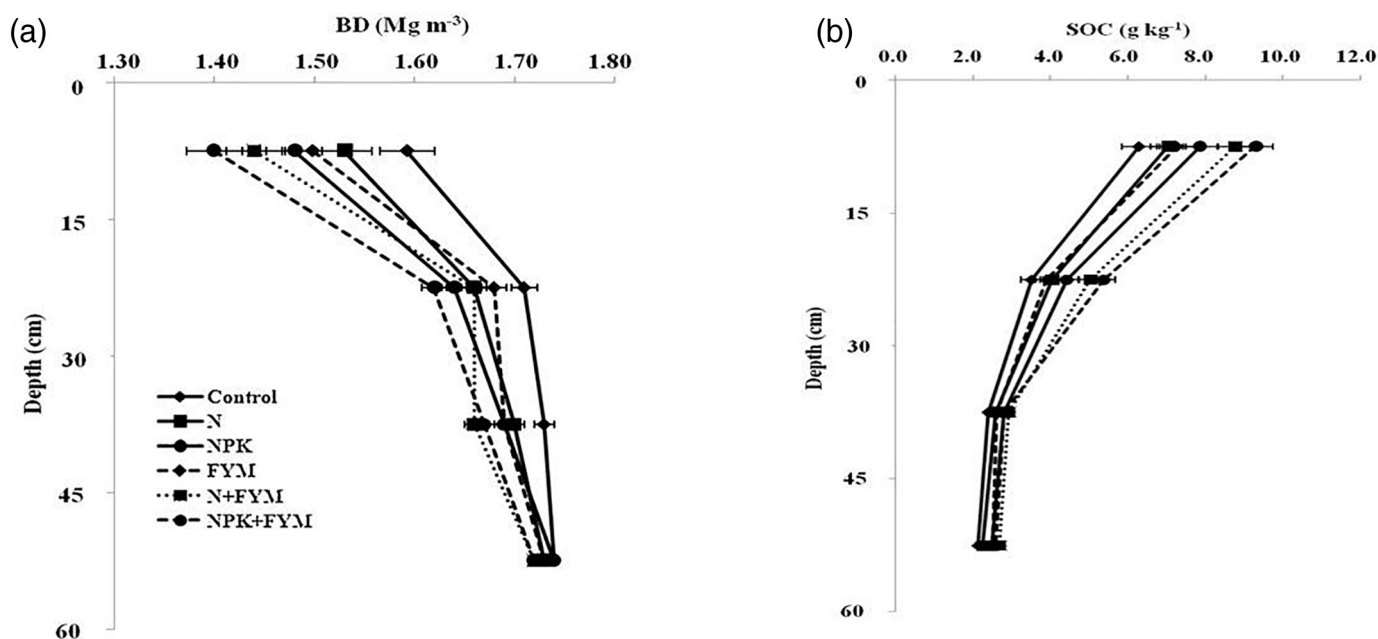
The SOC stock for a given depth is calculated from SOC concentration, bulk density (BD) and soil depth. The variations in BD across the depth of sampling in treated and non-treated plots introduce bias, more so in the surface horizon due to the prevalence of root and stubble biomass. In agricultural soil, SOC variability is also caused by depth of ploughing (Goedts et al., 2009) and other changes in management strategies (Olson and Al-Kaisi, 2015; Shahid et al., 2017) and associated BD change (Fig. 1). Despite several methods being available for correcting SOC data that arise due to concomitant variation of BD with SOC over the depth in response to soil management change (Lee et al., 2009), comprehensive evaluations of these methods are still lacking. To overcome this problem, the equivalent soil mass (mass-depth) approach in place of linear depth is suggested (Lee et al., 2009). Equivalent soil mass is defined as “the reference soil mass per unit area chosen in a layer” and equivalent C mass is “C mass stored in an equivalent soil mass” (Ellert et al., 2001). This approach for comparing the SOC change over time and depth has been well recognized (Gifford and Roderick, 2003; VandenBygaart and Angers, 2006).

The change in soil mass and its direction across the soil depth and C-concentration associated with it, is a tricky issue in the accurate estimation of SOC stocks and stock change. The material coordinate system that compares collective C density on a temporal scale on the basis of initial sampled cumulative mineral mass, is suitable for agricultural soil subject to frequent disturbances (Lee et al., 2009). However, it cannot detect SOC change in an individual layer, requires unreasonably larger sample numbers for a meaningful comparison at lower layer (Franzluebbers and Stuedemann, 2008), and is prone to error magnification due to integration of SOC stock.

## 3. Ex-situ SOC measurements

After addressing all factors responsible for the collection of soil samples for SOC quantification, the next decision to be made for which opinions vary, is the method of laboratory analysis. Much effort has been made by researchers to measure the amount of SOC using a variety of techniques involving ex-situ methods (Chatterjee et al., 2009). Several ex-situ methods are now available to determine SOC and total organic carbon (TOC) in soils. These include wet digestion, loss-on-ignition technique and dry combustion (DC) in an elemental analyzer. Ex-situ methods, i.e. dry combustion, have long been regarded as the ‘gold standard’. However, SOC sequestration in agricultural ecosystems requires





**Fig. 1.** Variation of (a) bulk density and (b) distribution of SOC in different soil layers under a 41 years of chemical and organic fertilization in a sub-humid tropical rice-rice system (Source: Shahid et al., 2017). (N: Nitrogen; NPK: Nitrogen, Phosphorus and Potassium; FYM: Farmyard manure; BD: Bulk density; SOC: Soil organic carbon).

accurate and cost-effective methods for measuring SOC and can verify and authenticate the SOC stocks. Some other ex-situ methods are discussed in Section 5.1.1.

### 3.1. Wet digestion

Generally, TOC is estimated directly by using a mixture of dichromate and sulfuric acid to oxidize the carbon supplied with or without heat (Schwartz, 1995). Heat is supplied as an accelerator to complete the reaction (Rosell et al., 2001). The oxidation process is based on the “Walkley-Black” (WB) method, where the residual oxidant is calculated through back titration after completing the reaction with the SOC (Walkley and Black, 1934). The WB method is widely used because it is easy, rapid and involves minimal equipment. The WB method is extensively used more so in the developing countries for quantification of SOC, because it is simple and cheap (Grewal et al., 1991). However, this method oxidizes only the active SOC in the sample, and this is deemed to be its major drawback (Nelson and Sommers, 1996). A correction factor of 1.33 (based on 76% organic C recovery) is often used to compensate for the partial oxidation (Walkley and Black, 1934). However, depending on the soil type and properties of SOC, the oxidation is quite variable and so is the recovery (Neal and Younglove, 1993). It is also reported that the manual titration and use of correction factors can affect accuracy (Metson et al., 1979). The correction factor depends on soil types, matrices, depths (Kimble et al., 2001), textural class (De Vos et al., 2007), horizons and SOC fractions (Rosell et al., 2001). Therefore, the correction factors have to be determined by conducting experiments with soil types existing in different areas.

The deeper horizons are considered to be the most appropriate sample for organic matter oxidation due to low accumulation of fulvic acid and less plant residue content. Organic carbon fractions such as “humus” (Nelson and Sommers, 1996), lipids, and proteins are possibly not fully oxidized (Komy, 1995). Some researchers have considered the elemental carbon able to resist chromate oxidation (Leong and Tanner, 1999), whereas others reported differential quantity of oxidation (Nelson and Sommers, 1996). However, the oxidation may vary from 60 to 86% in different soils (Dias et al., 1991; Nelson and Sommers, 1996; Cantarella et al., 2001). In their study, Chatterjee et al. (2009), while reviewing the recovery percentage in the soils of different

countries, reported a correction factor varying from 1.69 to 1.14. Bhattacharyya et al. (2015) suggested a correction factor of 1.29 for sub-humid and 1.31 for both semi-arid and arid bioclimatic systems for calculating SOC while using the WB method. In the WB method, the digestion temperature is controlled by the water and acid mixture ratio; temperature decreases due to the loss of vapor during the heating process (Nelson and Sommers, 1996). Thus, a supply of exterior heat can help to improve the recovery (Heanes, 1984).

The presence of chloride ( $\text{Cl}^-$ ), ferrous iron ( $\text{Fe}^{2+}$ ), higher manganese oxides ( $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$ ) and coal dust also interferes with SOC estimation (Nelson and Sommers, 1996). In pyritic acid sulfate soils, pyrite is oxidized during the dichromate wet oxidation digestion and results in overestimation of SOC; the interference of pyrite can be corrected by pre-estimation of pyrite sulfur (Willett and Beech, 1987). The WB method understates SOC content in the soil affected by fire. Trends for overestimating SOC content have been observed in Oxisols with high iron content when employing the WB method (Segnini et al., 2008). Authors found that C content was underestimated by 18% when compared to the elemental analyzer (EA) method, which is discussed below in more detail. A few studies (Hussain and Olson, 2000; Mikhailova et al., 2003) using the WB method did not find any significant variation among different tillage or management practices applied to an identical area of Typic Hapludoll in Argentina. Contrary to this, Nayak et al. (2012) using the WB method reported significant variation of SOC in response to different nutrient management practices. Nevertheless, the wet digestion method has limitations due to variable recovery percentage, despite still being widely used globally to measure SOC concentration. We recommend the development of site-specific correction factors or using exogenous heat during digestion to accurately estimate SOC when applying the WB method.

### 3.2. Dry combustion

Incinerating the SOC and thermal decomposition of carbonate minerals generates  $\text{CO}_2$  which is calculated by: (1) measuring the difference in mass loss-on-ignition (LOI) after dry combustion; and (2) collecting and analyzing the evolved  $\text{CO}_2$  by automated instruments after dry oxidation of SOC. Both methods involve oxidizing the SOC at a high temperature. The LOI method involves heating the sample in a muffle

furnace between 200 and 500 °C, whereas dry oxidation is carried out between 950 and 1150 °C with an automated analyzer.

### 3.2.1. Loss-on-ignition method (LOI)

The loss-on-ignition method is routinely used to measure SOC content based on the difference in weight of pre- and post-ashing treated dry soils (Nelson and Sommers, 1996). The method is based on the premise that, at the pre-determined temperature, all SOC is transformed into CO<sub>2</sub>, whereas carbonates remain unchanged. In fact, a negligible quantity of CO<sub>2</sub> and water is lost from carbonates and clay minerals, respectively (Grewal et al., 1991; Soon and Abboud, 1991; David, 1988). The SOC is calculated from individual conversion factors or equations developed from the LOI and SOC relationship (David, 1988), where SOC is analyzed/estimated by an auto-analyzer or by the multiplication factor (0.58), considering that SOM constitutes 58% of the SOC (Chatterjee et al., 2009).

These relationships and conversion factors vary with the soil type, the nature of SOC, soil depth and soil horizons. Sample size is another source of variation in LOI measurements. Schulte et al. (1991) reported that LOI value significantly decreased with increase in sample weight. A single regression equation cannot be used universally due to problems involving accuracy (Fagbenro and Oyeleye, 1999), so knowledge about the nature of the soil and the correction factor is essential before analysis can commence (David, 1988). Clay content in soil plays an important role in determining the nature of the LOI-SOC relationship (De Vose et al., 2005). Predictive potential of the regression equation can be improved by applying bivariate function of LOI and clay content (Spain et al., 1982).

In most of the literature, a temperature in the 375–800 °C range is given for the LOI combustion (David, 1988) with a value of 600 °C being reported as the most appropriate temperature for measuring the SOC by ashing. A large amount of humified SOC resists oxidizing at <500 °C temperatures. Some authors also indicated that even higher temperatures are required for complete oxidation of organic carbon. However, contrary to the reported literature, the carbonates do decay at the ashing temperature. Both temperature and the duration of ignition are crucial factors since they govern: (1) the loss of CO<sub>2</sub> and from carbonates decomposition and the compositional water from primary and secondary minerals; (2) the oxidation of Fe<sup>2+</sup>; and (3) the breakdown of hydrated salts (Ben-Dor and Banin, 1989; Schulte and Hopkins, 1996). Varying amounts of hygroscopic water are evaporated during the ignition of soil at 105 °C, so consequently the SOC value may be overestimated. Also, at temperatures >105 °C water present as a chemical constituent in different salts in the soil is released. Therefore, ignoring the loss of water in soils having lower SOC (Komy, 1995) and/or higher clay content (Dean, 1974) may create serious errors.

Temperatures ranging from 430 to 500 °C avoid the loss of carbonates (Rosell et al., 2001). However, Mg-rich calcite samples even decompose at temperatures <400 °C. Moreover, extended heating at 400 °C can decay carbonates (Ben-Dor and Banin, 1989). The particle size, weight and SOC content of the soil are responsible for the thermal instability of carbonates. Therefore, it is not easy to predict the most suitable temperature and extent of ignition for full recovery of SOC and minimize the loss by clays' dehydration or constituent's degradation. A higher (about 90%) LOI at 300 °C is reported during the first 30 min and 10% in the following one hour (Abella and Zimmer, 2007). In contrast, Ben-Dor and Banin (1989) suggested 400 °C for 8 h as the optimum for natural and synthetic soils. Donkin (1991) reported that 450 °C for 6 h is the most favorable temperature for ignition and no additional recovery will occur with further increase in temperature.

The LOI method implemented in Brazil involves heating at 550 °C (Lanarv, 1988) while in countries of Western Europe it is at 375 °C for 16 h (Ball, 1964). In the United States, lower temperatures are used; several laboratories there have carried out LOI at 360 °C (Schulte and Hopkins, 1996). Davies (1974) advised a temperature in the range

between 375 and 450 °C, while Nelson and Sommers (1996) suggested that <440 °C temperatures should be maintained during ignition. However, combustion at 550 °C is considered to produce and/or increase the losses of inorganic compounds and result in overestimation of SOC content (Silva et al., 1999). Because of the concern about decomposition of inorganic compounds and structural water losses, results obtained using this method are considered to be only tentative estimates of SOC content. Despite these restrictions, the LOI and SOC contents of soil are highly correlated as calculated from SOC data of various locations (Chatterjee et al., 2009).

However, the TOC content measured using this method by some researchers has produced ambiguous results (Krom and Berner, 1983). Natural soil inorganic carbon (SIC) and SOC cannot be precisely segregated by this method due to overlapping of the combustion and decomposition temperatures (Gibbs, 1977; Froelich, 1980; Leong and Tanner, 1999). For an improved segregation of SIC and SOC with diverse temperatures, it was thus recommended using the CO<sub>2</sub> and the H<sub>2</sub>O signals. The idea is that, if SOC is combusted, the CO<sub>2</sub> and the H<sub>2</sub>O signals appear at the same time, whereas for SIC, only a CO<sub>2</sub> signal is recorded. Nevertheless, the LOI is a simple, rapid, and cheap procedure for calculating SOC content, and each soil type and depth need a separate LOI-SOC regression equation. Finally, consistency should be assured for ignition temperatures, exposure times, and sample size. Information on these three parameters should be reported at the time a report is published (Heiri et al., 2001; Konen et al., 2002).

### 3.2.2. Dry combustion in an elemental analyzer

The content of total soil C (TC) is determined by DC using an EA, and TC in a typical non-calcareous soil becomes SOC. In a calcareous soil, SOC can be measured by subtracting the inorganic carbon determined with a modified pressure calcimeter (Sherrod et al., 2002; Al-Kaisi and Grote, 2007; Apesteguia et al., 2018) from the TC determined by an EA. Alternatively, it can be measured by removing SIC from samples through HCl pre-treatment to eliminate SIC before measurement, where the TC becomes SOC (Harris et al., 2001). At a high concentration of SIC in soil, the estimation error will be probably very large and may need a correction factor (Ramnarine et al., 2011). It was reported that when carbonate content is high, it can be measured, and subtracted from TC to calculate the SOC by the difference from the dry combustion (Soil Survey Staff, 2004).

In the Scheibler method, samples are treated with HCl and the soil's carbonate content is calculated from the amount of CO<sub>2</sub> released in a volumetric analysis (Tatzber et al., 2007). In the case of acid pretreatment, adequate care must be taken to eliminate acids by centrifugation (Yamamuro and Kayanne, 1995), and filtration and drying (Nieuwenhuize et al., 1994). Caughey et al. (1995) recommended a temperature of 40 °C; a temperature higher than this will lead to considerable loss of volatile organic carbon (VOC). Special attention must be paid to sample weight and size, the latter should be adequate enough to create a detectable signal and generate representative data within its combustibility limit (Chatterjee et al., 2009).



Elemental analyzer (EA) for determining total carbon content through dry combustion (DC).

Researchers are advised not to ignore SIC sources in the soil samples, and should consider the pedogenic and geogenic carbonate and liming practice of farmers even if soil pH is neutral and report the TC based on the DC as SOC without any pretreatment with HCl (Mulvaney et al., 2010). Based on the information available in the literature, dry combustion analysis using EA is the most correct method for measuring the soil C content. The elemental analyzers are more accurate and advantageous as: all forms of carbon are decomposed in this method; there is minimal sample requirement; and it requires only a short time for analysis. Nonetheless the initial purchase of the required equipment is expensive (Nelson and Sommers, 1996; Gatto et al., 2009) as are the maintenance costs.

#### 4. Soil organic carbon fractionation

Long-term SOC stabilization mechanisms in different soils require proper understanding (Lützow et al., 2007) of the consequences of land use and soil management change on SOC sequestration. For sequestration to happen, the soil carbon needs to be stable, non-labile and resist loss in a reasonable time frame when changes in management occur (Powlson et al., 2012), temperature changes (Lal, 2004) and there is small C input (Liu et al., 2013). The stable part of the SOC persists in the soil for a longer period (Baisden and Amundson, 2003; Bruun et al., 2007) and plays a significant role in climate change science. In this review, we consolidated different SOC stabilization mechanisms, and methods for extraction of SOC fractions with distinct chemical and physical characteristics formed by a specific stabilization mechanism. Their advantages and disadvantages are pointed out as well.

##### 4.1. SOC stabilization mechanism

A holistic understanding of SOC stabilization mechanisms is required for predicting the impacts of global climate change, and for developing management practices to improve SOC sequestration in soils (Marschner et al., 2008). Various mechanisms proposed for the stabilization of SOC are: (1) physical stabilization by protecting SOC within the aggregate that make SOC inaccessible to soil microbes (Krull and Skjemstad, 2003; Stockmann et al., 2013); (2) chemical protection by surfaces of minerals and metal ions (Six et al., 2004; Lützow et al., 2006; Jagadamma and Lal, 2010); and (3) selective preservation of certain recalcitrant organic molecules (Sollins et al., 1996). The spatial arrangement effect of organo-mineral associations on SOC explains the physical protection, whereas molecular-level interactions explain the chemical protection of SOC (Olk and Gregorich, 2006; Lützow et al., 2007). However, climatic factors, management practices, soil properties, and mineralogy decide which mechanism will play a dominant role in SOC stabilization (Sollins et al., 2006; Basile-Doelsch et al., 2009).

Molecular structures of soil organic carbon (SOC) fractions are inherently recalcitrant because of the aromatic nature of their chemical composition (Melillo et al., 1982). These fractions are stabilized by humification processes known as humic substances and are considered to be refractory, thus recalcitrant (Hayes and Clapp, 2001). Such an inherently chemical recalcitrant nature has been questioned (Piccolo, 2002), since its residence time in soil does not depend on chemical composition (Amelung et al., 2008) and fails to explain the SOC turn over on a long-time scale (Stockmann et al., 2013). Many studies have challenged the dominant role of molecular structure in predicting SOC cycling (Berhe and Kleber, 2013; Basile-Doelsch et al., 2015; Fang et al., 2015; O'Rourke et al., 2015). Some studies suggest that the SOC with lower molecular weight (carbohydrate and proteins) are more likely to stay in the soil for a longer period of time (Gleixner et al., 1999; Berhe et al., 2012).

SOC mineralization is often directly associated with soil micro biota composition, diversity, and activity (Marschner and Kalbitz, 2003; Fontaine and Bardot, 2005). These findings support the importance of microbes in SOC stabilization (Chabbi and Rumpel, 2009). Very

differently, however, Kemmitt et al. (2008) proposed the 'Regulatory Gate' hypothesis but this has not been generally accepted (Kuzakov et al., 2009). They argue that - rather than by microbial processes - the rate controlling step in SOC mineralization is regulated by abiotic processes such as adsorption, desorption and diffusion from soil surfaces, oxidation or stabilized extracellular enzymes. Although different mechanisms for SOC stability have been proposed, the pivotal role of interaction with soil mineral surface and metal ions has been widely recognized (Wissing et al., 2014; Throckmorton et al., 2015). It is worth noting here that the interaction of SOC with silt, clay and other minerals through various kinds of bonding such as van der Waal's and hydrogen bonding, ligand exchange at the mineral surfaces stabilizes SOC (Kleber et al., 2007; Lehmann et al., 2008). However, the possible mechanisms of SOC stabilization in diverse soils are not yet fully understood (Lützow et al., 2007). The key to a clear understanding of the mechanisms that are responsible for SOC stabilization lies in efficient extraction of their fractions of diverse stability.

##### 4.2. SOC fraction/pools

The SOC has generally been categorized into different pools - labile, stable, refractory and inert - based on their biological stability. Chan et al. (2001) classified the SOC based on the extent of their oxidation by sulfuric acid and reported the SOC fractions as being very labile, labile, less labile, and non-labile. The soil C fractions having fast turnover time ranging from a few days to months, which helps in nutrient cycling by promoting the microbial activity, are known as labile pools (Kaye and Hart, 1997). These are very sensitive to management change and suggested as soil quality indicators (Cambardella et al., 1998; Rudrappa et al., 2006; Blanco-Moure et al., 2016). Labile C fraction is determined as the following: microbial biomass carbon (MBC), particulate organic C (POC, <53  $\mu\text{m}$  organic C fraction) and/or light fraction (<1.6–2  $\text{g}/\text{cm}^3$  density) of soil (Parton et al., 1987; Cambardella and Elliott, 1992), readily mineralizable carbon, water soluble C or carbohydrate (WSC), acid hydrolysable carbon (AHC) and permanganate oxidizable C (PMOC).

MBC is the biologically active fraction of SOC and it has a rapid turnover rate and is responsible for releasing nutrients into the soil (Smith et al., 1993). This fraction is very sensitive to crop management practices such as tillage, residue recycling and application of organic matter, etc. (Nayak et al., 2012; Shahid et al., 2017), and it is used for routine evaluation of long-term fertilizer experiments (Li et al., 2013). The WSC is readily bio-available (Marschner and Kalbitz, 2003), <0.45  $\mu\text{m}$  size and most mobile, and therefore can move through the processes of diffusion and convection. WSC is the most dynamic C pool and it is either sorbed on soil or sediment particles or dissolved in interstitial pore water (Herbert and Bertsch, 1995). It accounts for only 0.05–0.4% of SOC in typically field-moist soils and 0.25–2% in forest soils, but can be considerably higher (Haynes, 2005). Permanganate oxidizable C (POSC) is known as active C fraction or readily oxidizable carbon (Weil et al., 2003) and is strongly correlated with SOC (Culman et al., 2012). Non-labile C can be determined from the subtraction of SOC and  $\text{KMnO}_4\text{-C}$  (Blair et al., 2006).

Humus or clay sorbed C is considered to be a slow pool (Parton et al., 1987) while C associated with organo-mineral-metal complex and charcoal C is a resistant or passive pool (Skjemstad et al., 1999; Kögel-Knabner et al., 2008). Based on the mean residence times of SOC, it can be grouped into active (1–5 years), slow (20–40 years) and passive (400–2000 years) pools (Parton et al., 1987). These 'divisions' is both originated from and led to further development of SOC fractionation methods so as to have holistic division of SOC pools that can explain properly its stability in the soil. Although substantial advances have been made in SOC stability research (Six et al., 2000a; Christensen, 2001), a complete picture on the role of different SOC pools on overall stability of SOC has not yet been developed.



### 4.3. SOC fractionation

#### 4.3.1. Physical fractionation

Accurate identification and estimation of the various SOC pools are essential for ecosystem soil C modelling (Saviozzi et al., 2014). Several physico-chemical methods are available to separate SOC fractions of different stabilities. However, these methods are not free from limitations on the basis of which the dominant stabilization mechanism can be identified (Olk and Gregorich, 2006; Paul et al., 2006). Physical fractionation methods (Table 1) include particle size, density and aggregate separation (Lützw et al., 2007; Stockmann et al., 2013) by using dry and wet sieving, slaking, dispersion (ultrasonic vibration in water), sedimentation and density separation. Methods and procedures of physical separation have been described in detail (Elliott and Cambardella, 1991; Christensen, 1992, 2001; Lützw et al., 2007). Through aggregate fractionation, the free SOC and protected SOC that is occluded in soil aggregates and organo-mineral assemblages are separated. Based on particle size, aggregates can be roughly divided into two categories: macro aggregates (>250  $\mu\text{m}$ ) and micro aggregates (<250  $\mu\text{m}$ ) (Sollins et al., 1996). In a typical surface soil nearly 90% of SOC is associated with aggregates (Jastrow et al., 1996); 20–40% of SOC as intra-micro aggregate SOC (Carter, 1996). The turnover time usually increases with decreasing aggregate size (Puget et al., 2000; Six et al., 2002; John et al., 2005). In a temperate climate SOC serves as an intra-macro aggregate binding agent and therefore the macro aggregates contain more SOC than micro-aggregates (Jastrow et al., 1996; Six et al., 2000b). This is unlike in tropical soil where other binding agents stabilize the macro aggregates (Six et al., 2000c; Zotarelli et al., 2005).

In a tropical rice-rice system under long-term fertilizer management treatments both macro as well as micro-aggregates contained similar percentages of total organic carbon (Tripathi et al., 2014). However, when exogenous organic matter was applied, macro-aggregates retained more TOC (Fig. 2). Sorption being the stabilization mechanism, higher SOC is associated with smaller particle size such as clay and silt as intermediate or passive pool where less SOC is associated with sand serving as the active pool (Christensen, 2001). Nonetheless, a higher allocation in a smaller fraction may not always end up with a higher turnover time (Lützw et al., 2007). Density fractionation separates the light fractions that are loosely attached with soil minerals from the heavy fraction that is held in organo-mineral complexes. Often the term light fraction (LF) is used as a synonym for POC (Sikora et al., 1996; Vanyushina and Travníková, 2003). The SOC fractions separated by density fractionation can be grouped as active, intermediate and passive SOC pools (Lützw et al., 2007).

Dispersion of aggregates and separation of POC fraction have been included in most of the fractionation methods (Zimmermann et al.,

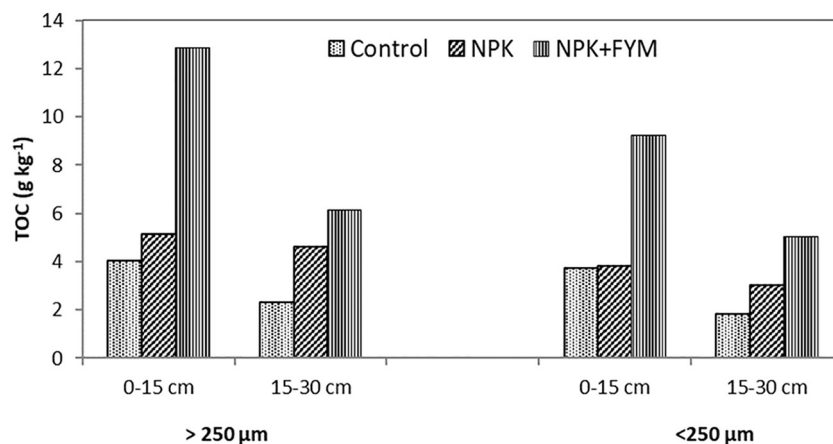
2007a). The POC plays a vital role in the development of aggregates (Six et al., 2001), and is sensitive to management change (Franzluebbers and Stuedemann, 2002; Nayak et al., 2012). The SOC is also stabilized by Fe oxides because of its ability to form bonds by ligand exchange due to having a higher surface area (Kahle et al., 2003; Kleber et al., 2004). This can be separated by high-gradient magnetic separation (HGMS). Pool sizes and turnover times of SOC in the soil clay fractions are strongly influenced by the amount, size and crystallinity of Fe oxides (Lützw et al., 2007). Separation of light from heavy fraction and silt fraction from clay-stabilized SOC is required to detect any changes with response to climate and management practices (Marzaioli et al., 2010).

The physical fractionation breaks down the SOC pools into smaller units. Hence this helps detect changes in the fractions and interpret what the long-term changes mean (Del Galdo et al., 2003). Nevertheless, the physical method is generally time-consuming and involves many pre-treatments. Moreover this approach alone cannot resolve the exact nature of the bonding between organic and mineral compounds. Thus, alone it cannot perform a satisfactory recovery of the stable SOC fraction.

#### 4.3.2. Chemical fractionation

Numerous wet chemical methods involving the principle of solubility and mineralogy separation are available depending on the nature and degree of interactions between organic and mineral phases of soil (Table 1). Based on solubility properties: humic substances are extracted using alkali dissolution by NaOH and  $\text{Na}_4\text{P}_2\text{O}_7$  (Stevenson, 1994); organic carbon (DOC) is dissolved by cold water or aqueous solution of different ionic strength and from in-situ by using a suction cup in the field; MBC is extracted by chloroform fumigation (Jenkinson, 1976; Vance et al., 1987); alkanes and fatty acids by repeated extractions with n-hexane (Schnitzer and Schuppli, 1989); long-chain alcohols and wax esters are extracted by chloroform (Schnitzer and Schuppli, 1989); and lipid is extracted by dichloromethane/methanol through the use of Soxhlet apparatus (Naafs et al., 2004; Wiesenberger et al., 2004). Hydrolysis involves quantifying SOC associated with protein and carbohydrate and oxidation involves separation of labile and active organic fractions (Lützw et al., 2007).

Through the process of acid hydrolysis, carbohydrate and protein can be separated by disruption of hydrolytic bonding through stepwise digestion with HCl and  $\text{H}_2\text{SO}_4$  (Leavitt et al., 1996; Paul et al., 1997; Silveira et al., 2008); hemi cellulose by 2% HCl; and crystalline cellulose is only hydrolysable with 80%  $\text{H}_2\text{SO}_4$  (Waksman, 1938). The chemical oxidation process involves various oxidizing agents including: potassium permanganate (Blair et al., 1995) to determine  $\text{KMnO}_4$ -oxidizable SOC (PMO-C); high-energy ultraviolet photo-oxidation



**Fig. 2.** Total organic carbon (TOC,  $\text{g kg}^{-1}$ ) in micro- and macro-aggregates of soil under different nutrient management at different depth (adopted and modified from Tripathi et al., 2014). (NPK: Nitrogen, Phosphorus and Potassium; FYM: Farmyard manure).



**Table 1**  
Features of soil organic carbon physical and chemical fractionations methods.

Methods	Principle	Fractions separated	Merits/Demerits	References
Physical fractionation				
Aggregate fractionation	Dis-aggregation by dry or wet sieving and slaking	Protected SOC that is occluded in secondary organo–mineral assemblages	Not possible to separate SOC occluded in clay microstructures	Cambardella and Elliot, 1993
Particle size fractions	Dispersion and sedimentation	Active, intermediate and passive fractions	Particle size fractions are not homogeneous in terms of their turnover time	Christensen, 2001
Density separation	Densitometry	Light fraction) from heavy fraction	Only a tentative differentiation of active and passive SOC	Lützow et al., 2007
High-gradient magnetic separation	Based on difference in magnetic susceptibilities	Clay fractions with different contents and crystallinity of Fe oxides	Very useful for differentiating the SOC fraction stabilized by Fe oxides	Golchin et al., 1997; Balesdent et al., 1998
Chemical fractionation				
Water soluble separation	Dissolution and centrifugation/suction cup extraction in-situ	Dissolve organic carbon	DOC has high ecological relevance but not a homogenous pool	Shang and Tiessen, 1998
Chloroform-fumigation extraction		Microbial biomass carbon	Extract major part of the active pool or labile pool	Haynes, 2005; John et al., 2003; Kaiser and Ellerbrock, 2005;
Alkali and acid soluble fractionation	Sieving or flotation and extraction	Humic material (fulvic acid, humic acid, humin fraction)	NaOH extractable SOC is not a homogeneous soil fraction	Jenkinson, 1976; Vance et al., 1987
Organic solvent soluble	Extraction by n-hexane, chloroform and methanol	Alkane, Fatty acids, Long chain alcohols, wax and esters, lipids	Lipids are involved in various stabilization mechanisms,	Stevenson, 1994
Hot water hydrolysis	Hot water extraction	Readily decomposable soil organic carbon pools	Carbohydrates and N-containing compounds	Schnitzer and Schuppli, 1989; Naafs et al., 2004
Acid hydrolysis	Reflux with 6 M HCl or step-wise chemical digestion with cold and hot H <sub>2</sub> SO <sub>4</sub>	Carbohydrates and proteins	Not able to separate functional SOC pools	Haynes, 2005
Oxidation with KMnO <sub>4</sub>	Enzymatic break down with mild oxidizing agents	Labile SOC	KMnO <sub>4</sub> can reacts with aromatic structures and humic substances	Leavitt et al., 1996
Photo-oxidation	UV photo oxidation by forming free radicals	Intermediate/passive pool	Does not differentiate stabilization due to recalcitrance and that due to occlusion within micro-aggregates	Blair et al., 1995; Tirol-Padre and Ladha, 2004
Oxidation with hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	Destruction of SOC through Oxidation	Active SOC pool	Less effective because of its less dispersing effect on clay micro-aggregates	Skjemstad et al., 1993.
Oxidation with disodium peroxo-disulfate (Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> )	Destruction of SOC through Oxidation	Pool stabilized by interactions with the mineral matrix	Incomplete SOC removal by oxidation with Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> was reported in acid soils rich in secondary minerals	Mikutta et al., 2005
				Eusterhues et al., 2003

(Skjemstad et al., 1993) to separate passive and inert SOC pool; hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (Theng et al., 1999; Eusterhues et al., 2005) to separate SOC accessible to exoenzymes (active OM pool); disodium peroxodisulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) (Eusterhues et al., 2003; Lorenz et al., 2006); sodium hypochlorite (NaOCl) to separate SOC pool stabilized by interaction with mineral matrix (Kleber et al., 2005; Siregar et al., 2005; Zimmermann et al., 2007a); and chemo-thermal oxidation at 375 °C (CTO-375) for pyrogenic carbon (PyC) quantification (Gustafsson and Gschwend, 1997).

The photo oxidation-based fractionation procedure does not differentiate between SOC stabilization due to recalcitrance and occlusion within micro aggregates (Lützow et al., 2007). The SOC that can resist oxidation with H<sub>2</sub>O<sub>2</sub> is found to be rich in N-containing compounds (Schulten et al., 1996; Cheshire et al., 2000). It is evident that pyrogenic materials lignite, charcoal and ash cannot be separated by H<sub>2</sub>O<sub>2</sub> oxidation (Schmidt et al., 1999). Incomplete SOC removal by oxidation with Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was reported in secondary mineral-rich acid soils (Eusterhues et al., 2003). There are indications that long-chain aliphatics are present in the oxidation product of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Cuyper et al., 2002). In soils where microporous Fe- and Al-oxides and other poorly crystalline constituents are bound to larger portion of SOC, oxidation by NaOCl and by Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was less efficient in extracting SOC. This is because it is protected by reactive micro porous sites (Kaiser and Guggenberger, 2003; Mikutta et al., 2005).

Among these methods, chemical oxidation is regarded as the most efficient at preferentially removing the young SOC inputs, simulating the microbial degradation that happens in nature (Kleber et al., 2005;

Bruun et al., 2007). Nevertheless, the chemical methods are not free from limitations. Luft and Stöfler (1998) reported that organic acids of low molecular weight produced through oxidative treatments are comparatively resistant to subsequent degradation and thus become enriched all through oxidative treatments. On the other hand, labile organic fractions of plant origin are resistant to many chemical oxidizing agents (Helfrich et al., 2007; Lützow et al., 2007). Therefore neither fractionation method alone can accurately differentiate SOC fractions with distinct turnover time and stabilization processes.

The methods in combination can precisely isolate various fractions from the soils with different mineralogy (Lützow et al., 2007; Lorenz et al., 2008). This will lead to a better understanding of SOC pools and their stabilization processes. These fractionation methodologies generally are prolonged in typical investigations; thus, researchers need to develop quick methods for analyzing SOC fractions that can explain their stabilization mechanism. Developments in the mid-infrared (MIR) spectroscopic measurement combined with partial least-squares regression (PLS) is a promising method for predicting various stabilized soil C fractions (Cozzolino and Moron, 2006; Janik et al., 2007; Zimmermann et al., 2007b; Calderón et al., 2011).

## 5. SOC measurement using spectroscopic methods

The spectroscopic method could be a comparatively rapid and less time-consuming technique for measuring and monitoring SOC in the laboratory, field and regional contexts. Traditionally, employing these methods was confined to the laboratory, but subsequently some of

these are increasingly applied for in-situ measurements (Viscarra et al., 2009) and air-borne monitoring (Ben Dor et al., 2009) using platforms such as unmanned aerial vehicles (UAV), aircraft and satellites. Some relatively recent advances in spectroscopic methods of soil C determination are presented below.

### 5.1. Visible and near-infrared (VNIR) and mid-MIR spectroscopy

#### 5.1.1. Measurement in laboratory

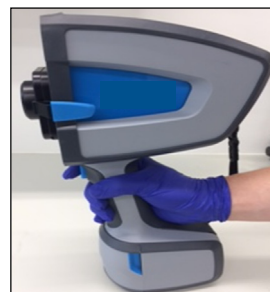
Visible near-infrared (VNIR), shortwave infrared (SWIR) mid-infrared (MIR) diffuse reflectance spectroscopic (DRS) methods have been developed to estimate SOC. The VNIR (400–1100 nm), SWIR (1100–2500 nm) and MIR (2500–25,000 nm) spectra can be taken either in the laboratory or in the field (e.g. Stevens et al., 2008). Being one of the main chromophores (Ben-Dor et al., 1999) of the soil, SOC can be determined using VNIR-SWIR laboratory spectroscopy (Reeves III et al., 2006; Rossel et al., 2006). Nocita et al. (2013) reported a SOC data of moist soil using VNIR spectroscopy because it is more accurate than that obtained in the laboratory for drier soil. The VNIR spectra have been modeled for SOC in the soils covering 8.1–19.8 g kg<sup>-1</sup> (Viscarra et al., 2006), 6.1–33.0 g kg<sup>-1</sup> (Reeves et al., 2002), 2.3–55.8 g kg<sup>-1</sup> (Shepherd and Walsh, 2002), 1.3–285.8 g kg<sup>-1</sup> (Chang et al., 2001), and 0.1–536.8 g kg<sup>-1</sup> (Brown et al., 2006) soil C, suggesting a wider applicability of models.

MIR spectroscopy can also predict SOC and TC, often with more accuracy than VNIR spectroscopy. Studies carried out by McCarty et al. (2002), Reeves III et al. (2006), and Reeves (2010) have confirmed the success of MIR in SOC prediction. The diffuse reflectance spectroscopy can also accurately estimate total organic carbon (TOC) and POC while charcoal-C fraction can be estimated employing photo-oxidation and NMR (Janik et al., 2007). Currently, several bench-top spectroradiometers covering a wide spectral range, and measurement resolution with different measurement principles are available (Table 2) (Mouazen et al., 2005). Nevertheless, there are several issues associated with laboratory spectroscopy, these being spectral configuration, detector performance, optical characteristics, calibration quality, sample homogeneity, reference method and measurement condition. Other uses of laboratory spectroscopy include the development of calibration models in larger contexts (i.e. aerial and satellite) reflectance measurements (Stevens et al., 2008).

#### 5.1.2. Measurement in field

Both the VNIR and MIR portable instruments can be used for on-site analysis of SOC in the field, however for field conditions, appropriate correction methods are required in order to remove the effects of soil water on the spectra (Minasny et al., 2011; Ji et al., 2015). The VNIR is better than MIR spectroscopy at predicting in-situ estimation of SOC because strong water absorption in the MIR may blur or mask the

absorption of SOC. In turn this will lead to inaccurate calibration and validation (England and Viscarra, 2018). Some commercially available spectrometer models like AgriSpec (400–2500 nm) have been successively used for in-situ estimation of SOC (Udelhoven et al., 2003; Stevens et al., 2006; Viscarra et al., 2009). The Veris (350–2200) ‘on-the-go’ spectroscopy device which was developed to hasten the data acquisition, predicted SOC having good correlation with laboratory value ( $R^2$  of 0.67) (Christy, 2008). The Soil Condition Analysis System (SCANS) is a VNIR (350–2500 nm) model equipped with a core sensing system and an AGA (Active gamma-ray attenuation) densitometer. It can measure SOC content, SOC composition and BD of both dry and wet samples in the intact cores at a defined depth interval up to 1.2 m depth (Viscarra et al., 2017).



Hand held VNIR spectroscopy



Mid-MIR spectroscopy

However, the surface roughness and spatial averaging of data (on the basis of speed and time of movement) introduces error in SOC estimation in this kind of mobile device (Morgan et al., 2009). Under such situations, these devices may not capture field level SOC variations (Bricklemeyer and Brown, 2010). Moreover, AGA has problems in measuring BD in the presence of gravels (England and Viscarra, 2018). Nevertheless prediction using portable spectroscopy can match laboratory results through appropriate spectral pre-processing and implementing suitable methods to model SOC from VNIR-MIR spectra.

#### 5.1.3. Aerial measurement

In comparison to in-situ estimation of SOC, only a few studies have been conducted for the prediction/estimation of SOC contents, where reflective spectroscopy using air-borne (aircraft or unmanned aerial vehicle) or satellite platform (Ben Dor et al., 2009) can be exploited. This is because of complexities involved in the acquisition of reflectance data. Several studies tried to predict SOC content in soil by using aerial photography (Chen et al., 2000), Hymap sensor (Selige et al., 2006; Gomez et al., 2012), GER DAIS-7915 air-borne sensor (Ben Dor et al., 2002), CASI-2 images (Stevens et al., 2006), and AHS-160 images

**Table 2**  
Spectrometer model with their spectral characteristics, and spectral characteristics for laboratory and field.

Spectrometer model	Spectral range (nm)	Spectral resolution	Output	Maker <sup>b</sup>
FTS7000	1000–2500	8 cm <sup>-1</sup> or 4 cm <sup>-1</sup> for solids and liquids; 2 cm <sup>-1</sup> for gases	Reflectance	Varian Inc.
NIR Systems 6500	400–2498	–0.5 nm at 835 nm and 4.5 nm at 2500 nm	Absorbance	FOSS
Labspec 5000	350–2500	3 nm @ 700 nm 6 nm @1400/2100 nm	Reflectance	ASD
FieldSpec Pro	350–2500	3 nm @ 700 nm 10 nm @1400/2100 nm	Reflectance	ASD
Veris	350–2200	8 nm	Reflectance	Veris Technologies, Inc
AgriSpec	450 to 2200	350 nm–1000 nm	Reflectance	ASD
DRIFT <sup>a</sup> (FTS7000)	2500 to 25,000	4 cm <sup>-1</sup>		
Scimitar 2000 FTIR spectrometer	1666–5000	4 cm <sup>-1</sup>	Reflectance	Varian Inc

<sup>a</sup> Mid-infrared (mid-IR) Fourier transform (FT) diffuse reflectance spectroscopy (DRIFTS).

<sup>b</sup> ASD: Analytical Spectral Devices Inc., Boulder, Colorado, USA; Foss: Foss NIRSystems, Inc., Denmark; Varian, Inc., now Agilent Technologies, Santa Clara, CA; Veris Technologies, Inc. 1925 Clay Ridge Court Salina, KS 67401.

(Denis et al., 2014). These attempts yielded varying level of success; the accuracy of prediction can be further enhanced at the regional level by following stringent appropriate calibration and validation procedures when using hyperspectral as well as multispectral data (Stevens et al., 2012; Vaudour et al., 2013).

By using the data of AISA-Eagle Vis-NIR (400–1000 nm) sensor (Spectral Imaging Ltd., Finland) and the bootstrapped partial least squares regression (PLSR) method, Vaudour et al. (2016) could accurately predict SOC content with limited bias ( $<0.6 \text{ g kg}^{-1}$ ). Castaldi et al. (2016) compared the current systems such as ALI and Hyperion on EO-1, OLI, Sentinel-2 MSI on Landsat 8 and forthcoming PRISMA, EnMAP, and HyspIRI satellite imagers using PLSR predictive models for estimating SOC content in soil. They found that in the absence of noise (low signal noise ratio), the performance of hyperspectral imagers was significantly better than that concerning multispectral imagers. In fact the next generation hyperspectral imagers performed better than the current imagers. Strict scanning protocols, appropriate selection of spectral processing and models that correspond with soil data obtained from reference method is required for accurate prediction of SOC from the VNIR and MIR spectra (England and Viscarra, 2018). A standardized SOC spectral library containing spectral and analytical data representing local variability will further enhance SOC prediction by reflectance spectroscopy.

### 5.2. Laser-induced breakdown spectroscopy (LIBS)

The LIBS is a recent method based on the principle of atomic emission spectroscopy; it can be used for determining soil carbon (Cremers et al., 2001; Ebinger et al., 2003). Some available portable models can be used as rapid alternative approaches for in-situ SOC estimation. Several researchers have reported a very good correlation between LIBS and conventional dry combustion that determined total SOC (Cremers et al., 2001; Ebinger et al., 2003). Different calibration models viz. partial least squares regression (PLSR) (Sirven et al., 2006), projection to latent structures (PLS) (Martens and Naes, 1989; Wold et al., 2001; Naes et al., 2002), the least absolute shrinkage and selection operator (LASSO) (Tibshirani, 1996) and the sparse multivariate selection regression with covariance estimation (MRCE) (Rothman et al., 2010), etc., can now analyze the LIBS data and improving the prediction efficiency.

The presence of Fe and Si (Nicolodelli et al., 2014) and soil texture (Segnini et al., 2014) and other chemical compositions affect the level of detection thus need signal correction to reduce the interference and improve estimation. By using LIBS the total carbon, organic carbon and inorganic carbon in soils of intact core without any pre-treatment can be discriminated in the 245–925 nm spectral range using LASSO and MRCE calibrations (Brickley et al., 2011). Unlike reflectance spectroscopy, the LIBS method can accurately determine soil bulk density and subsequently enable estimation of the SOC stock (Gehl, 2007). The LIBS can successfully estimate the humification degree (HD) of bulk organic matter in whole soil and its accuracy and precision are comparable to conventional methods such as electron spin resonance (ESR), nuclear magnetic resonance (NMR), and fluorescence spectroscopies (Ferreira et al., 2014; Senesi et al., 2018). However, further research is needed to mitigate limitations at the field level: soil structure, mineralogy, inorganic C (carbonates) content, moisture; and at the instrument level: plasma formation and interaction with the surroundings (Senesi et al., 2018). These issues must be dealt with order to ensure LIBS is widely accepted for SOC analysis.

### 5.3. Inelastic neutron scattering (INS)

INS is a non-destructive method of SOC determination unlike diffuse reflectance IR spectroscopy and LIBS, and requires very small samples (Gehl and Rice, 2007; Chatterjee et al., 2009). The INS system is based on inelastic neutron scattering of neutrons from SOC nuclei and measuring gamma rays' response by gamma ray spectroscopy (Wielopolski,

2011). Details regarding the methodology, operational guidelines, radiation safety, etc., are discussed elsewhere (Wielopolski et al., 2004; Wielopolski, 2011; Yakubova et al., 2014; Yakubova et al., 2017). It is suitable for both static and dynamic mode of scanning large areas, and scanning mode operation is possible due to rapid inelastic neutron scattering and gamma ray emission (Gehl and Rice, 2007). When comparing between the INS and the DC methods, Wielopolski (2011) reported a very good correlation for the combined results of three sites that suggest a possibility of a universal regression line for different regions with different soil types.

The most important advantage of the INS method is that it can be used in-situ, and examine large volumes of soil and up to a depth of 30 cm (Chatterjee et al., 2009). It can also be run in scanning mode that helps in determining the mean carbon content of a large area in a short time (Yakubova et al., 2017). The INS system does experience problems concerning gamma spectra peak identification in that some spectral peaks could be associated with the radio isotopes. These form due to interaction of neutrons (both fast and thermal) with the nuclei of soil samples and elements of the equipment (delay activation, DA). The natural background spectrum (called hot background) can be an issue (Kavetskiy et al., 2016).

While estimating the SOC, the double peak (due to interaction of neutrons with the nuclei of the elements in soil samples and parts of the equipment) should be accounted for during calculation. Interference by the non-targeted gamma rays should be removed by following the procedure as suggested by Yakubova et al. (2016). Concerns have been raised regarding the safe use of INS in the field (Izaurrealde et al., 2013) and low level of detection. For wider application of this technique, INS needs further improvement and specifically, this means system optimization, calibration in wider area and soil type and cheaper models to reduce errors.

## 6. Measurements of carbon sequestration by eddy covariance technique

The eddy covariance (EC) flux system can be used to measure, the net ecosystem exchange (NEE), net ecosystem production (NEP), carbon sequestration, and greenhouse gases measurement (Chapin et al., 2006). The EC method permits a direct measurement of  $\text{CO}_2$  exchange between the atmosphere and land area, which is considered to be one of the advanced and best ways to estimate: firstly, turbulent fluxes of  $\text{CO}_2$  (Burba et al., 2013; Wang et al., 2015); and secondly, carbon sequestration on land over time with reasonable accuracy (Baldocchi et al., 1996). The  $\text{CO}_2$  fixation takes place by photosynthesis which converts the solar energy into chemical energy. This is then used for the growth and development of plants and other living communities (Baldocchi, 2003).

Ecosystem respiration (RE) is a composite flux, comprising above-ground respiration (canopy respiration) by foliage and woody tissues, and belowground respiration (soil respiration) by roots (autotrophic soil respiration) and by soil organisms (heterotrophic soil respiration). Soil also plays a major role in ecosystem respiration by sequestering C in labile and non-labile pools and subsequent release as  $\text{CO}_2$ . Soil respiration depends on soil mineralogy, soil nutrient availability, soil temperature and moisture, litter quality or plant phenology that differs from site to site. The relative contribution of respiration to total fluxes affects ecosystem C-sequestration potentials (Alward et al., 1999). C-sequestration is altered according to different crop management practices such as mulching (Chatterjee et al., 2018), tillage and annual crops vs perennials (VandenBygaart et al., 2008), and integrated nutrient management (Nayak et al., 2012; Bhattacharyya et al., 2013; Shahid et al., 2017). Seasonal changes in crop growth occurring in response to management practices such as tillage, planting, harvesting and fallow period. Each activity affects net carbon fluxes, and the detection of such inter-seasonal and inter-annual soil organic carbon (SOC) change by destructive sampling requires a very large number of samples

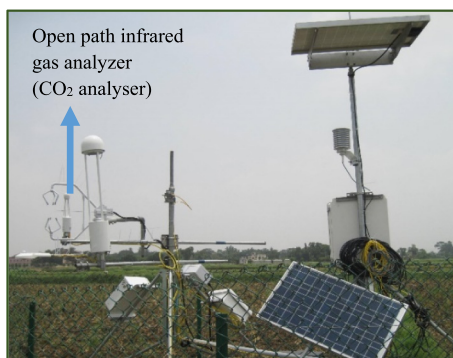


and a long period of time. However, recent technical advances have been made; for example, a micrometeorological technique like EC measurement is a practical (Wofsy et al., 1993) tool for measuring NEE over annual cycles and can evaluate several crop rotations (Taylor et al., 2013). Various aspects of flux measurement, flux partitioning and estimation of carbon budget, errors and uncertainties associated with measurement in carbon dynamics in the ecosystem are discussed in the following section.

### 6.1. Net ecosystem exchange measurement in agriculture

Croplands ecosystem is characterized by fast growth over a usually short growing period (Moureaux et al., 2006), and it can be modified periodically by a number of management practices. These include tillage, planting, applications of fertilizer, irrigation, herbicides, fungicides, insecticides and harvesting, etc. The latter activities are mainly influenced by type of crops, agroclimatic conditions and crop rotation. In addition to their impact on the NEE, CO<sub>2</sub> is emitted by agricultural tools or machinery, thus influencing CO<sub>2</sub> concentration and flux measurements. In order to monitor the changes, a flux measurement can be done in the subplots, in an effort to compare the management practices and quantify their impact on carbon fluxes and its budget (Eugster et al., 2010). To measure the fluxes' change over different management systems, a movable measuring eddy covariance system is a better option rather than a permanent installation.

A mobile or roving measurement system is often a less invasive solution. However, the eddy covariance system and other meteorological sensors could be fixed on aluminum mast tripod stands installed in the crop field after seeding. However, deep soil sensors could be installed before sowing without disturbing the field. Eddy covariance systems with different sensors have to be taken down during the growing season and before the harvesting commences, and reinstalled at the earliest opportunity (Chen and Hu, 2003). Management changes are projected to impact on carbon fluxes and carbon budget. On the issue of carbon mitigation, these practices have to be assessed in terms of whether carbon emissions are positive or negative. The technique for comparing agricultural practices by dividing a crop area with different management practices into subplots can be done using several eddy covariance masts (Pattey et al., 2006; Davis et al., 2010).



Open path eddy covariance system for measurement of turbulent flux.

Several studies have investigated different systems using the EC technique, such as: eddy covariance measurements over forests (Aubinet et al., 2012), grasslands (Wohlfahrt and Gu, 2015), agriculture crops (Moureaux et al., 2006), grazing pasture, wetlands (Laurila et al., 2012), and lakes (Vesala et al., 2012). Notably net CO<sub>2</sub> exchange between the crop and atmosphere have been evaluated, for example rice (Saito et al., 2005; Swain et al., 2018), wheat (Moureaux et al., 2008), soybean/maize (Verma et al., 2005) and potato (Anthoni et al., 2004), and overall carbon sequestration in soil during the crop cycle estimated.

Flux measurements using the EC method are not free from possible errors (Rannik et al., 2006; Wang et al., 2015). Systematic as well as random errors are associated with limited samplings of the eddy covariance measurements (Lenschow et al., 1994). A number of papers covering the errors and error estimations associated with eddy covariance have been published (Richardson, 2012; Vickers and Mahrt, 1997); several methods have emerged for estimating flux uncertainty (Finkelstein and Sims, 2001; Billesbach, 2011). These systematic errors arise from the instrument itself (acquisition frequency, sensor separation, etc.), aberrant environmental conditions (extreme events), complex data processing and long operational sequence. Finkelstein and Sims (2001) reported a sampling error of 25–30% when estimating trace gas. These rather large errors should be kept in mind in the flux data interpretation and analysis. Instrument calibration and averaging flux value in data processing can reduce the measurement error (Wang et al., 2015).

Representativeness errors are very noticeable at the grid scale (Chasmer et al., 2009; Raupach et al., 2005) and affected by the height, surface roughness and thermal regime associated with the heterogeneous structural and disturbance patterns of vegetation (Burba, 2001; Raupach et al., 2005; Chen et al., 2009; Chasmer et al., 2011). The typical agricultural field is relatively homogeneous in character with less spatial heterogeneity, this reduces uncertainty in flux estimation. However, heterogeneity is inevitable in hilly terrains, forests and fragmented landscapes that exist in some agro-ecosystems so this may exacerbate uncertainty. The uncertainties affecting eddy covariance estimates appeared to be lower than those associated with biomass sampling and resulting from crop heterogeneity (Aubinet et al., 2009). The successful and accurate assessment of NEE in a typical ecosystem depends on proper characterisation of the errors and associated factors and methods used to reduce these errors.

### 6.2. Partitioning of net ecosystem exchange

Net ecosystem exchange (NEE) measurements of CO<sub>2</sub> are now playing a vital role in the progress of climate change science (Baldocchi et al., 2001a; Baldocchi, 2008). Eddy co-variance measurements of NEE are widely used globally to assess the carbon sink and quantify the role of vegetation in controlling its magnitude and variability (Sarmiento and Wofsy, 1999; Baldocchi et al., 2001b). For assessing the processes which control NEE, EC data mostly depend on models that partition NEE into two components, i.e. gross primary productivity (GPP) and ecosystem respiration (RE) (Beer et al., 2010; Jung et al., 2011). Several measurement and modelling methodologies are used for partitioning NEE, each of which has its own advantages and disadvantages (Desai et al., 2008).

These 'flux partitioning' models (FPMs) used for filling in the gaps of missing data, permit estimates of CO<sub>2</sub> flux over long time periods (Falge et al., 2001). Hence, FPMs are important tools for completing the missing EC data, yet very few studies so far have critically examined how the choice of a given FPM affects the quantum of flux and its variability estimates in a given ecosystem. Proper partitioning of the measured NEE is required to have a better idea of the process that controls the NEE. During night-time, determination of fluxes becomes a source of uncertainty (Rannik et al., 2006) as emitted CO<sub>2</sub> is not captured by EC. However, this limitation can be overcome by respiration estimates under turbulent conditions using a regression (e.g. Aubinet et al., 1999) or other methods.

Similarly, day-time uncertainty in EC flux measurements has also been reported (e.g. Paw et al., 2000). These uncertainties lead to ambiguous estimates of GPP and RE (Hagen et al., 2006; Richardson et al., 2006). An algorithm for NEE partitioning was developed using hyperbolic light response curve fit to day-time data and addressing the temperature sensitivity of respiration and the VPD limitation of photosynthesis (Lasslop et al., 2010). The aim was to reduce the uncertainties based on day-time and night-time based estimates.

The GPP and RE are affected by inter-seasonal and inter-annual variation in structural traits such as plant height, leaf area index and functional traits, for instance change in N supply in the ecosystem which affects net as well as gross carbon fluxes (Richardson et al., 2007; van Dijk et al., 2005). In agriculture, both endogenous factors such as changes in crop and management practices, phenology (Shao et al., 2015; Knox et al., 2016; Dold et al., 2017) and exogenous factors such as burning crop residues, insect pest attacks and other disturbances can cause inter-seasonal/annual variations in flux. Climatic factors such as light, temperature and precipitation directly and indirectly through biotic effect (photosynthetic and respiratory responses to the climate) influence GPP and RE (Shao et al., 2015). Inter-annual variability of net and gross ecosystem carbon fluxes has recently been reviewed in detail (Baldocchi et al., 2018).

With respect to inter-seasonal variation of GPP and RE in a tropical low-land rice-growing scenario, GPP dominated RE during peak growth stages of rice and vice versa during the fallow period (Swain et al., 2018). GPP and RE control the variation of NEE, and GPP is a dominant control, especially if the variance of annual GPP is 20% larger than the variance of annual RE. For most land surfaces, the inter-annual variability of NEE is dominated by inter-annual variations of GPP, which is consistent with some regional and continental studies for Europe (Ciais et al., 2005; Luyssaert et al., 2007; Vetter et al., 2008), and Africa (Weber et al., 2009). Spatial variation of GPP and RE are also affected to different extents by temperature and precipitation; in Asian countries, GPP is determined mainly by temperature whereas RE by both (Chen et al., 2013).

### 6.3. Carbon budget

EC measures the net exchange of matter and energy between ecosystems and the atmosphere. Utilizing the EC technique, we can estimate the carbon flux, balance and budget of the carbon in the terrestrial ecosystem. The net carbon exchange of terrestrial ecosystem is the result of the difference between two larger fluxes, i.e. respiratory efflux at night-time and net photosynthetic uptake (balance between photosynthesis and respiration at day-time). Yet only a little negligence of night-time flux can lead to a large over-estimation of carbon sequestration in the long-term. Carbon sequestration rate on annual basis is usually determined on the basis of annual net ecosystem production (NEP). NEP (positive value indicates carbon sink and negative value is the source) is assumed to be equal to the annual net exchange of CO<sub>2</sub> with the atmosphere (integrated NEE), considering a very small carbon exchange is in a form other than CO<sub>2</sub> and by processes other than turbulent transport. The NEE results from two larger fluxes of opposite sign: CO<sub>2</sub> uptake by photosynthesis (GPP) and CO<sub>2</sub> released by ecosystem respiration (RE).

The partitioning of NEE is required so that both spatial and inter-annual carbon flux variabilities are better understood (Valentini et al., 2000; Xu and Baldocchi, 2004; Reichstein et al., 2005; Shi et al., 2012). For carbon budgeting, GPP, NPP and NEP are required to be estimated. Like in all other ecosystems, CO<sub>2</sub> exchange between a terrestrial ecosystem and atmosphere includes both CO<sub>2</sub> taken up by plants via photosynthesis and then released into the atmosphere through RE (Heimann and Reichstein, 2008). An imbalance would affect the CO<sub>2</sub> concentration in the atmosphere, which plays an important role in influencing global climate (Taneva and Gonzalez-Meler, 2011). Therefore, measurements of CO<sub>2</sub> flux are used to define whether an ecosystem is a net source or sink of CO<sub>2</sub> at different temporal scales. The NEE can be broken in either way. On one hand, the primary productivity rate (productivity of organic components from atmospheric CO<sub>2</sub>) of plants is related to the vegetation community type, which is driven by insolation duration, temperature, nutrient availability and hydrology (Frolking et al., 1998; Waddington et al., 1998; Griffis et al., 2000). On the other hand, ecosystem respiration is related to vegetation communities and it includes both

autotrophic respiration and the varying decomposability of organic matter substrates (Moore and Basiliko, 2006). However, ecosystem respirations are also affected by temperature, substrate composition and hydrology and so environmental variations may decide whether any agricultural system will behave as a CO<sub>2</sub> sink or source (Chimner and Cooper, 2003).

To understand the carbon budget of ecosystems, direct measurements of canopy CO<sub>2</sub> exchange on daily and annual scales are very useful. They provide data sets for the testing and parameterization of carbon balance models. For successful measurements, a multidisciplinary protocol needs to be developed with the assistance of micrometeorologists, eco-physiologists, bio-geochemists, modelers and experimentalists (Baldocchi et al., 1996). To estimate the NEE between the atmosphere and any terrestrial system, the balance between assimilation by photosynthesis and release from both dead and live organic matter is calculated. Net primary productivity is the rate of organic matter in plant tissues storage in excess of the respiratory utilization by the plants during the period of measurement. The NEE and NEP measurements do not include the non-CO<sub>2</sub> exchanges of carbon in their calculations. However, these carbon can be quantified using the EC method through appropriate gas analyzers such as those employed for methane and volatile organic compounds (VOCs) even though the later is lost in small amounts from crop land (Smith et al., 2010). Moreover, all carbon gains and losses that are not associated with turbulent fluxes, such as for instance, losses due to advection, removals by harvesting or applications of manure are often not included in carbon budgets at the ecosystem level. However, in the long-run, part of the annually accumulated NEP may be leached to ground water as dissolved (DOC), particulate organic (POC), dissolved inorganic carbon (DIC), escape to the atmosphere as microbially-produced methane (CH<sub>4</sub>) or transported from the system through pollen and seeds (Eugster, 2008). In an agricultural system, organic carbon can be moved due to the processes of fertilization and manure application, re-deposition from elsewhere in the form of sediments through the process of erosion, and deposition of DOC in water. Therefore, carbon losses and gains through non-CO<sub>2</sub> and non-respiratory pathways should be assessed and accounted for in the carbon budget (Fig. 3). For accurate assessment of carbon sequestration, a detailed spatio-temporal measurement of net biome productivity (NBP) is required (Davis et al., 2010; Tao et al., 2019).

One of the greatest difficulties in estimating the production of a particular ecological system is determining whether or not the system is in steady state, where inflows can balance the outflows of material and energy (Odum, 1971). In agricultural systems, the difficulty is even more pronounced since exogenous applications of fertilizers and irrigation, etc., are ubiquitous. Aboveground net primary production (ANPP) is relatively easy to estimate from repetitive harvest data, but below ground production is difficult to estimate and root harvests are inevitably incomplete. Usually the root: shoot ratio is used to convert ANPP to NPP, while non-consistent relationships between shoot and root production are widely reported (Mitchell et al., 1990).

Each year, part of the biomass produced is retained in the soil as litter and soil carbon pools, which decompose and contribute to heterotrophic respiration (Rh) and the process may continue for several years (Smith et al., 2010). The integrated net ecosystem carbon balance (NECB) over time and space equals the net biome production (NBP; Schulze and Heimann, 1998; Buchmann and Schulze, 1999; Chapin et al., 2006). Several researchers have used EC flux to estimate changes in carbon stock in agriculture (Davis et al., 2010; Schmidt et al., 2012; Swain et al., 2016) by measuring NBP. In their work on NBP, Swain et al. (2016) reported that the tropical low-land rice field acts as a sink, while Alberto et al. (2018) reported that a flooded rice-rice cropping system (862 kg C ha<sup>-1</sup> y<sup>-1</sup>) can sequester more SOC than rice-maize (293 kg C ha<sup>-1</sup> y<sup>-1</sup>) and rice-mung bean (684 kg C ha<sup>-1</sup> y<sup>-1</sup>).

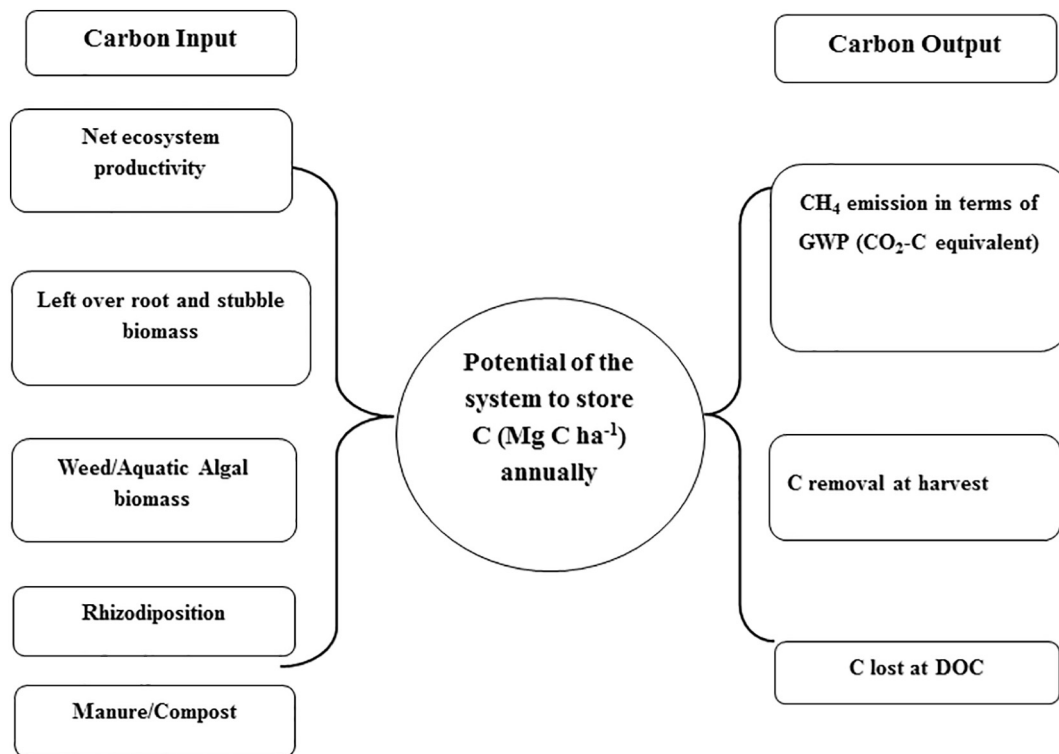


Fig. 3. Schematic diagrams of carbon balance taking all the source of input and output. (C: Carbon; DOC: Dissolved organic carbon; GWP: Global warming potential).

Using this system, Schmidt et al. (2012) found temperate winter wheat as a carbon source. However short-term estimation may not calculate accurately NBP when assessing the carbon sequestration. The estimation of carbon sequestration in agriculture using the EC method may lead to errors and uncertainty associated with turbulent flux estimation and carbon loss and gain associated with non-CO<sub>2</sub> and non-respiratory loss of carbon. Moreover, the carbon balance in the same crop in any given year will be different due to inter-annual variability. Therefore, for flux estimation we suggest using the long-term eddy covariance approach in specific agro-ecosystems using multiple flux towers for specific crop and management practices in sub-plots. This will help to reduce the uncertainty, understand inter-seasonal and inter-annual variations and trends, and distinguish it from random error. It requires investment and inter-institutional collaboration.

## 7. Emerging life cycle analysis (LCA) for measurement of C sequestration in soil

Life Cycle Assessment (LCA) is a widely used approach to assess and upscale the GHG emissions from agricultural field to broader horizon. This takes into account all the resource use in agriculture from all the sources. The changes in soil carbon storage however are not appropriately considered yet in LCA analysis (Zhang et al., 2010). The basic idea of not considering carbon sequestration in agricultural soil is that the sequestered carbon will be re-emitted into the atmosphere at a later date. Some climate models have shown that temporarily stored carbon when released back at a delayed date can increase the CO<sub>2</sub> concentration in the atmosphere and consequently increase the temperature at some time in future than without the temporary storage scenario (Korhonen et al., 2002; Kirschbaum, 2006). Therefore, current methodologies are not designed to assign any value to temporary carbon storage (Levasseur et al., 2012). The temporary storage of carbon is a contested subject and no consensus has been arrived at, specifically on how to account for soil carbon change in agricultural systems within the agricultural LCA framework (Goglio et al., 2015). However, some

researchers have attempted to include the soil carbon change in LCA using IPCC methodology and agroecosystem model (Kimming et al., 2011a; Goglio et al., 2015). The idea behind inclusion of soil carbon change in LCA is that, when carbon is stored in the soil for a certain period by removing it from the atmosphere, it decreases the cumulative radiative forcing temporarily, calculated over that time frame thus reduces the climate impacts (Levasseur et al., 2013). This process will buy time for negative emission technologies and knowledge to develop (Dornburg and Marland, 2008). Bio-energy with carbon capture and storage (BECCS) (Azar et al., 2010), direct air capture (Kumar et al., 2015), biochar and soil sequestration (Bolan et al., 2012; Sheng and Zhu, 2018; Zheng et al., 2018), enhanced weathering and ocean fertilization (Smith et al., 2016) are some negative emission technologies. Currently, some of these appear to be a bit far-fetched and futuristic, may substantially remove more CO<sub>2</sub> than that of anthropogenic emission in future (Rosen, 2018).

Irrespective of the debate on the role of soil carbon sequestration in reducing atmospheric CO<sub>2</sub>, it is clear that soil carbon plays a vital role in other ecosystem services and should be included in life cycle assessment. Soil carbon storage can be addressed either for delayed emissions impact category of LCA, or for the C footprinting (CF) framework (Brandão and i Canals, 2013; Guinée et al., 2006, 2009). Various methods that consider the temporary storage of soil carbon and relevant to land use change were reviewed by Brandão and i Canals (2013). Since carbon footprinting is a single impact category that considers only the global warming potential (GWP) (ISO, 2013), some researchers suggest looking at soil organic carbon sequestration as a separate impact category (Brandão et al., 2011).

Land use and land management changes affect soil carbon sequestration and greenhouse gas emissions. Management practices include crop selection, tillage, fertilizer, irrigation, crop residue and biomass burning (Petersen et al., 2013; Smith et al., 2012). With response to positive carbon build up management practices, the rate of SOC change diminishes over time until a steady state is attained, and SOC content at equilibrium is mainly affected by climate (Hutchinson et al., 2007;



Loubet et al., 2011; Virto et al., 2012). Land use change (LUC) refers to change in land cover upon anthropogenic intervention that is often divided into direct and indirect LUC (Planton, 2013). Consequential land use changes are mostly carried out using indirect LUC (Goglio et al., 2015) and attributional life cycle assessment for direct LUC (Schmidt, 2008). Land management changes sometimes result in a small variation of SOC, and a site-specific and site-dependent method can capture these variations (Vetter et al., 2008).

Although several studies have investigated carbon dynamics with respect to land use and management changes, no common standard procedure is available for SOC sequestration using agricultural LCA (Brandão and i Canals, 2013; Petersen et al., 2013; Arzoumanidis et al., 2014). Goglio et al. (2015) reviewed some methods used to account for soil carbon sequestration in agricultural LCA. The following subsection covers the selection of boundary line, appropriate methodology and data requirement so that soil carbon sequestration in life cycle inventory analysis in LCA can be assessed.

### 7.1. Boundary line selection

A boundary is an imaginary line temporally and spatially drawn around the system within which certain changes can be assessed. It is objective oriented and depends on the characteristics of the system. A spatial boundary must be selected so as to represent a depth and scale such that is site-specific, local, regional, national or global. With respect to depth, the simple IPCC tier 1 guideline (IPCC, 2006) takes top soil (0–30 cm) into consideration for assessing the changes in the soil's C stock, whereas the C-TOOL model (Petersen, 2010) uses a soil depth of 0–100 cm to capture a more precise estimate of the soil C sequestration. A compromise is made between LCA objectives, the system boundary and the accuracy and cost of assessment (Garrigues et al., 2012; ISO, 2006).

The temporal system boundary plays a crucial role in soil C dynamics, and every agricultural system reaches a soil C equilibrium after a number of years (Jenkinson, 1990). The rate of change is higher during initial years and thereafter, the gain or loss declines. The time required to attain a steady state with regard to an exogenous change in management practices varies from as short as 20 years (Hillier et al., 2012;

Broch et al., 2013) to as long as 30–100 years (Börjesson and Tufvesson, 2011; Tuomisto et al., 2012; Petersen et al., 2013). A 20-year time horizon is used in three EC Renewable Energy Directives (EU, 2009) and the IPCC's tier I approach (IPCC, 2006) for assessing soil C changes caused by LUC. In the context of soil and land management changes in agriculture where long-term data is rarely available, a smaller time horizon has been used to assess the soil carbon sequestration (Table 3).

### 7.2. Methods to account for soil C change in agricultural LCA

Along with spatial and temporal boundaries, the method used to account SOC change to a specific crop, other plants or crop management system is a key aspect in agricultural LCA that considers the soil carbon change. Various methods such as emission factors, simple carbon model, dynamic crop-climate-soil models and direct measurements are used to account soil carbon change with respect to change in land management (Goglio et al., 2015). All the four methods are used for site specific studies; however, the latter three are usually used for site dependent and site generic studies. Most of the reviewed site-specific assessments using crop-climate-soil models clearly indicate how SOC change was related to the production system. In contrast, most LCAs using tier I approach of IPCC based on global level data, used constant factors over time to arrive at a soil C change. Though the Tier II methods are developed from regional averaged data the constant factor methods still have limitations as follows: firstly, they cannot address temporal dynamics of soil C change; secondly, they disregard inter-annual variability due to variation in weather-induced; and thirdly, there is uncertainty whether the emission factors for land use and management changes are additive.

Of the many simple carbon models, C-TOOL, ICBM and Roth C (Table 3) have been tested in many countries (Kimming et al., 2011a, 2011b; Petersen et al., 2013; Knudsen et al., 2014). These models do not simulate crop production and hence they require C input to operate properly and consider soil, crop and climate characteristics in limited ways (Goglio et al., 2015). Dynamic crop-climate-soil models are process-based models that can address diverse management practices under varied climatic conditions and hence have advantages over the

**Table 3**  
Methods used in carbon sequestration assessment studies for land use change (LUC) and management change based on observations and models.

LCA method used	Key features	Time horizon	Agricultural system and crop	Crop management	Carbon storage (t C ha <sup>-1</sup> yr <sup>-1</sup> )	References
IPCC Tier I	Employ constant default factor for soil carbon change derived from an international body of studies	20	Annual crops	CT to NT Decrease fallow Increase perennials	0.23 ± 0.66 1.05 ± 0.72 1.87 ± 0.46	VandenBygaart et al., 2008
ICBM	Estimate long-term trends in SOC dynamics based on soil climate and management parameters	41	Wheat	–	2.3	Congreves et al., 2015
Roth C	Estimate turnover of organic carbon in aerobic soil based on soil type, temp, moisture and crop	24	Maize- wheat	Traditional tillage to conservation tillage	3.3 & 2.1 (measured and modeled)	Molina et al., 2017
C- Tool	Simulates soil C dynamics on the basis of soil characteristics, C inputs, and climate	20 100 200	Soybean	Conventional to organic	0.143 0.60 0.32	Petersen et al., 2013
CENTURY	Simulate long-term dynamics of carbon based on climatic parameters, SOM fractions and soil texture	30	Corn	Various tillage and residue management	–0.35–0.54 Phosphorus alone to phosphorus and nitrogen	Kwon et al., 2013
CropSyst	multi-year and multi-crop simulation model, was used to evaluate emissions and SOC change	30	Wheat	CT to NT	0.15	Zaher et al., 2013
The terrestrial ecosystem model (TEM)	Global scale model estimates carbon (C) fluxes interterrestrial ecosystems based on climate and ecological data	50	Corn, soybean, and wheat to Switchgrass and Miscanthus	Tillage and residue removal	0.67–0.95	Qin et al., 2012
Measurement	Site specific assessment	27	Rice-wheat	Different INM	0.23–0.62	Nayak et al., 2012

CT: Conventional tillage; NT: No tillage; INM: Integrated nutrient management; ICBM: Introductory Carbon Balance Model; Roth C: The Rothamsted carbon model; C- Tool: A simple tool for simulation of soil carbon turnover; CENTURY model: Soil Organic Matter Model Environment; CropSyst: Cropping Systems Simulation Model; The TEM: Terrestrial ecosystem model.

fixed emission factor and simple carbon models. Yet these models also require exhaustive data and expertise. For wider acceptance, these models need to be evaluated for their ability to predict SOC change in a shorter time scale and without site-specific calibration (Smith et al., 1997). Combining soil C dynamics within agricultural LCA using an attributional approach or consequential approach should depend on the assessment objectives of LCA (Anex and Lifset, 2014). However, investigating soil carbon sequestration using agricultural life cycle assessment is still a new approach and requires further research to develop a common, reliable and robust method.

## 8. Conclusions

In this paper we have discussed many aspects of sampling, bulk density correction, experimental methods, SOC determination techniques in laboratory, field and landscape contexts that will further improve soil carbon research. Many of the methods discussed have their own undisputed advantages but the development of international and national standards should also be investigated. The conventional dry/wet combustion method of SOC determination is the most widely used one and will continue to remain so in the foreseeable future despite its known limitations, particularly in developing and least developed countries. Future research should focus on SOC fractions and fractionation methodologies that explain their stability in soil and improve our understanding of short-term and long-term C sequestration in soil. Spectrometric techniques for sensing of SOC are rapidly developing. These techniques equipped with active gamma attenuation sensors coupled with proper calibration models will profoundly alter field measurements of SOC stock in the future but they still need to be inexpensive.

Estimation of SOC using current remote sensing techniques with aerial and satellite platforms is linked to problems of low accuracy and higher uncertainties. Imaging spectroscopy needs refinement with development of location-specific calibration and validation. At the landscape level, determination of SOC stock change using eddy covariance techniques require long-term studies and reduction of uncertainties associated with flux estimation and biomass sampling. Accounting soil carbon change using agricultural LCA method needs reliable SOC data in agricultural ecosystems, which can be achieved by using suitable modelling or measurement techniques. Continuous research that encourages investment in refining and developing SOC estimation techniques for furthering soil carbon and climate change science is highly recommended.

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