Options for Soil Organic Matter Fractionation in Tropical Soils

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Abstract
Soil organic matter (SOM) plays an important role in maintaining the productivity of tropical soils. An estimated 70% of the terrestrial C stocks that participate in the atmospheric C cycle are stored in soil organic matter. Since SOM exists in a wide diversity of forms with considerable variability in decomposition rates, fractions of SOM that reflect management effects deserve particular attention because they predict trends in soil productivity. Fractions that are more sensitiveto management and land-use changes than total C can serve as early indicators of potential decline in soil organic matter, soil productivity and net emissions of CO_2. Several fractions of SOM have been identified and characterized with varying sensitivities to changes in management and land-use. In this review, we examine the contemporary knowledge on the more common SOM fractions in tropical ecosystems.
Keywords:*Soil organic matter, fractionation, tropical soils, carbon sequestration*

I. Introduction

The importance of soil organic matter (SOM)in maintaining the productivity of tropical soils is now well recognized, and there have been extensive reviews covering this subject (eg.,Woomeret al., 1994; Lal, R., 2002). SOM holds the key to sustainable soil management and, therefore, the prevention or reversal of soil degradation. The identification of steps needed to understand and manage organic matter in tropical soils is a major challenge for soil science. SOM management practices in temperate and tropical climate zones differ. Much scientific attention has been focused on temperate zones rather than on the tropics, although degradation is most severe in tropical regions(Martiuset al., 2001). Existing knowledge about the management of organic matter in the tropics has found astonishingly little practical application.

The particular significance of soil organic matter for soil fertility lies on its influence on so many soil properties. Although the total organic matter in tropical soils rarely exceeds 5 % by soil weight, it is a key component of tropical agroecosystems, and variations in its abundance and nature have profound effects on many of the processes that occur in the system. A thorough understanding of soil organic matter is therefore essential for the development of more sustainable agroecosystems.

The role of soil organic matter in controlling the capacity of soil resources to sustain human societies at both local and global scales is also well established(Helfrichet al.,2006).Beyond its role in nutrient cycles, SOM has also come to be valued for its influence on a wide range of so-called ecosystem services. Theseinclude structure-related services such as water storage, availability and resistance to soil erosion, as well as the energy contributed to supporting the biomass and diversity of the soil biota and their actions(Swift et al.2004). With growing concern about atmospheric CO_2 levels, soil organic matter is known to be a major source and sink for atmospheric CO_2. An estimated 70% of the terrestrial carbon (C) stocks that participate in the atmospheric C cycle are stored in the soil organic matter(Olk and Gregorich,2006;).Therefore, the variation in organic matter concentration of a soil induced by a cropping system is a significant indicator of the sustainability of that cropping system.

Since SOM exists in a wide diversity of forms with considerable variability in decomposition rates, fractions that are more sensitive to land-use changes than the total SOM can serve as an early indicator of changes. Therefore, fractions of SOM that reflect management effect deserve particular attention because they predict trends in soil productivity and emission of CO_2 to the atmosphere(Lal, 2016). Once these fractions are accurately quantified, they are likely to show differences in susceptibility to management strategies aimed at improving soil properties and carbon sequestration. Consequently, several fractionation procedures capable of isolating functional SOM fractions have been proposed with varying successes and limitations.

Fractionation of SOM implies the separation of the total SOM into different parts that are thought to be functionally homogeneous with respect to physicochemical properties and turnover rate. The separation can be carried out by physical or chemical means: e.g. sieving, flotation, dispersion, or oxidation. The difference in

carbon content between fractions of an agricultural field and the corresponding native vegetation can yield information about the mechanisms of carbonsequestration(Six *et al*., 2002). Furthermore, fractions that are more sensitive to land-use changes than the total C can serve as an early indicator of changes(Six *et al*., 2002).

The quest continues to understand SOM contributions to soil productive capacity and sequestration of atmospheric CO_2. Successful efforts will identify consistently defined and derived SOM fractions that impart fundamental characteristics to soils. The main purpose of this article is to provide a review of the more common fractionation procedures of SOM, with particular reference to tropical soils, and identify the successes and challenges of the various fractions obtained with a view to supporting management practices aimed at improving organic matter storage in tropical agroecosystems.

Because SOM is largely comprised of carbon, most reports describe SOM in terms of its carbon content. Thus soil organic matter (SOM) and soil organic carbon (SOC) are frequently used interchangeably. Most studies use the content of total soil organic carbon (SOC) to quantify the stocks and changes in organic matter. This article will discuss soil organic matter (SOM) and soil organic carbon (SOC) as meaning the same thing.

II. Soil Organic Matter In Tropical Soils

The total mass of organic C stored in the soils of the world is 1576 Pg (1 petagram, Pg, is 10^{15} grams), of which approximately 32 % (or 506 Pg) is found in the tropics (Eswaran*et al*., 1993). Lack of suitable data, in terms of measured organic C and bulk density, is still a problem with respect to arriving at reliable estimates. This is particularly the case with Histosols, for which bulk density measurements are frequently lacking. Large areas of forest land in the tropics have been and are being cleared for agriculture and other purposes. Shifting cultivation and slash and burn agriculture are still practiced in many countries of the tropics and, with minimal or no soil conservation practices, soil erosion is rampant further complicating estimates of C stored in tropical soils.

Tropical soils generally have low inherent fertility, low base saturation and low phosphorus availability (Woomeret al, 1994; Bationo, 2004). In recent years, some authors have suggested that there are no major quantitative or qualitative differences between soil organic matter in temperate and tropical ecosystems (Woomeret al, 1994; Swift et al.,2004). But the physical and chemical similarities in the soil organic matter that develop in different ecosystems may be less important than the importance of soil organic matter in overcoming individual constraints to plant productivity within an ecosystem and the loss of total system C to the atmosphere (Woomeret al, 1994; Poeplau and Don, 2013). Some authors suggest that in tropical soils there is stronger metal complexation, a higher polymer nature, less importance of soil organic matter compared with the mineral fraction in aggregation effects, greater predominance of humic substance in cation retention and greater abundance of amino-acids and sugars than in temperate soils.

Contrary to widespread belief, the organic matter contents of tropical soils are not generally lower than those of temperate soils. In fact, they vary with vegetation (higher in forest than in savanna soils), climate (higher in mountain forests than lowland forests), soil texture (increasing with increasing clay and silt content of the soil), mineralogy (higher in volcanic soils due to the stabilizing effect of allophane on soil organic matter) and soil use (Schrothet al., 2003).

The transformation of tropical lands for agriculture exploits SOM, and in particular nutrient reserves. Once the soil is cultivated for agricultural production in the tropics, SOM is rapidly decomposed due to modifications in conditions such as aeration, temperature, and water content. This process of exploitation is accelerated by the necessity to increase agricultural production, largely through agricultural intensification, to overcome inadequate nutrition, and to cope with the limited reserves of arable land. This can affect many soil functions that are either directly or indirectly related to SOM, due to its capacity to retain water and nutrients. Yet in many tropical cropping systems, little or no agricultural residues are returned to the soil. This leads to a decline in soil organic matter which frequently results in lower productivity (Lal, R., 2002).

It is estimated that up to two thirds of Africa's original forest cover has been lost (Chapman *et al*., 2006), largely from conversion to agriculture (FAO, 2005). Extractive practices by subsistence farmers are estimated to have caused a loss of 60 to 80% of the original soil organic carbon in the tropics (Lal, 2016). The increasing demand for food can encourage farmers to reduce the length of fallow periods, cultivate continuously, overgraze fields, or remove much of the above-ground biomass through fuel collection or for building materials. Such practices can result in the reduction of SOM, water holding capacity, nutrients, as well as enhance soil erosion.

During a workshop organized by ZEF (*ZentrumfürEntwicklungsforschung)* to provide insight into the management of SOM in tropical soils (Martiuset al*.,* 2001), participants were asked to answer why, when and how should SOM be managed in tropical areas, and to review the needs for further research. The development of indicators and thresholds for SOM quantity and quality was considered top priority. These indicators should be reliable, easy-to-use and uniform, and should ideally be able to provide early warning signals to identify

stressed soils. The monitoring of SOM quantity and quality must be intensified, and this requires the development of suitable indicators. These indicators must be landscape- or soil-type specific. Thresholds must be identified, and monitoring criteria set.

Appropriate management of SOM in the tropics still requires considerable research into the regional differences and the variability of SOM quantity, quality and function; the importance of the quality of input material; the role of below-ground versus mulched organic matter (particularly the importance of roots and root exudates); the role of recalcitrant materials (e.g., charcoal) in building a stable SOM fraction in the long-term; and how to balance the need for stable forms against the need for short-term nutrient availability (Martiuset al., 2001).

Several management factors influence the rate of organic matter loss under cultivation in a manner that is often complex and difficult to predict. Most of the available data from trials in the West African moist savanna zone indicate that organic carbon contents of plots with fertilizer application are comparable to, or slightly higher than, those of unfertilized plots (Schrothet al., 2003). Measures that increase the amount of plant biomass above and below ground and its rate of accumulation tend to improve the organic matter balance by increasing carbon inputs to the soil and may also reduce erosion of otherwise incompletely covered soils, especially during the early part of the cropping season.

CONSTITUENTS OF SOIL ORGANIC MATTER

An understanding of the various constituents of soil organic matter is essential for effective management of organic matter in soils. Organic matter in soil is present as carbohydrates, soil enzymes, microbial biomass, nitrogenous compounds, fats, waxes and resins, organic phosphorus and sulfur compounds, and a wide range of unidentified, highly decomposed matter that is generally classified as humic substances. The exact composition of humic substances is a subject of controversy. Organic carbon is also present as charcoal arising from cyclic burning of vegetation(Skjemstadet al., 1996) and in the litter layer on the soil surface. Few data are available on the carbon content of the litter layer and its contribution to total organic carbon is ignored in most studies.

Evidence suggests that a significant proportion of soil organic carbon is physically protected from decomposition by clay minerals and within aggregates (Skjemstadet al. 1996). Much of this organic carbon is thought to comprise a pool with intermediate residence time (e.g., 10 - 50 years), but which may decompose much faster upon soil disturbance. More active organic carbon, representing microbial biomass, cycles the most rapidly and makes up only 3 - 5% of the total soil organic carbon. At the other extreme is very old material, which is not subject to rapid change due to soil management (Lutzowet al., 2007).

Among numerous protective mechanisms (Figure 1) are physical, chemical, biological, and ecological (Lal, 2016). Physical mechanisms include encapsulation within stable micro aggregates (Lutzowet al., 2007), formation of organo–mineral complexes, and transfer deep into the subsoil away from the zone of natural and anthropogenic perturbations. Formation of organo–mineral complexes can store SOC for millennia.
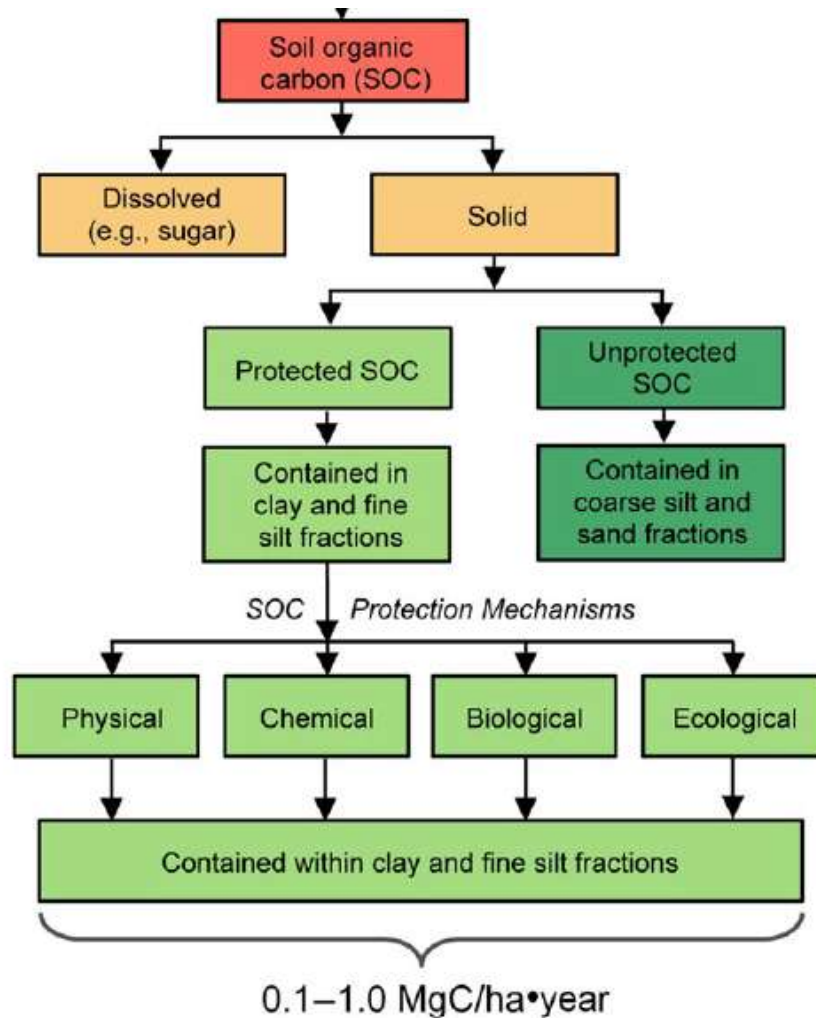
Figure 1: Types of organic and inorganic carbon pools in soil. The numerical values listed on the last line are ranges of sequestration of organic carbon in diverse soils and ecoregions(Lal, 2016).

Chemical protection involves formation of some recalcitrant compounds, including aromatic and double-bond hydrocarbons and some hydrophobic substances that coat stable aggregates. Biological mechanisms include some microbial exudates that repel other organisms, transfer of SOC into biologically non-preferred soil spaces and substrate-driven biological rate limitations (Ekschmittet al. 2008).

A more recent perspective suggests that the persistence of soil organic carbon is primarily not a molecular property, but an ecosystem property(Schmidt et al., 2011). This perspective is based on observations that molecules predicted to persist in soils (such as lignins or plant lipids) have been shown to turn over more rapidly than the bulk of the organic matter (Figure 2). Furthermore, other potentially labile compounds, such as sugars, can persist not for weeks but for decades.
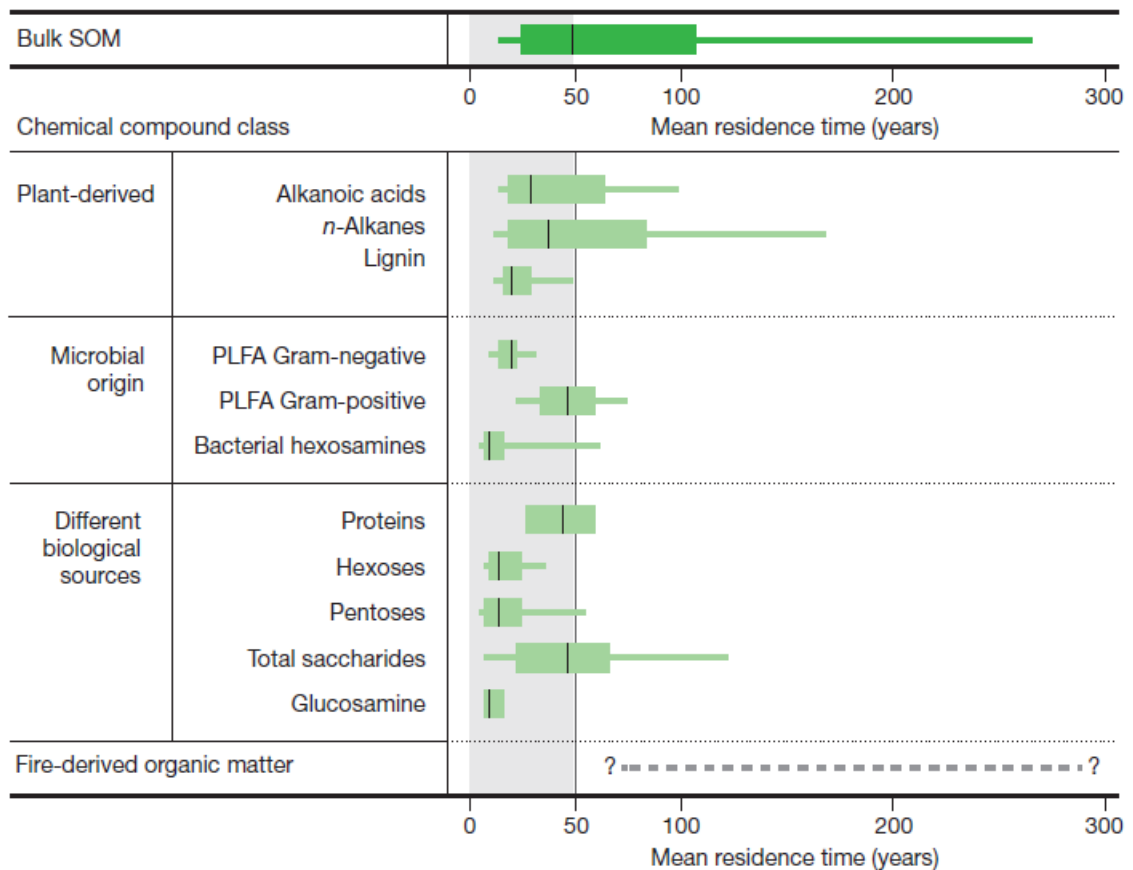
Figure 2: Mean residence time for specific organic components(Schmidt *et al.*, 2011)

In essence, Schmidtet al. (2011) argued that molecular structure does not control long-term decomposition of soil organic matter (SOM). Even components that appear chemically labile, including proteins and saccharides of plant and microbial origin, instead seem to turn over at rates similar to those of bulk SOM,that is, on the order of years or even decades.

Schmidt et al*; (*2011) further suggest that the molecular structure of plant inputs and organic matter has a secondary role in determining carbon residence times over decades to millennia, and that carbon stability instead mainly depends on its biotic and abiotic environment (Figure 3). They argued that the persistence of organic matter in soil is largely due to complex interactions between organic matter and its environment, such as the interdependence of compound chemistry, reactive mineral surfaces, climate, water availability, soil acidity, soil redox state and the presence of potential degraders in the immediate microenvironment. Rather than describing organic matter by decay rate, pool, stability or level of 'recalcitrance'—as if these were properties of the compounds themselves—organic matter should be described by quantifiable environmental characteristics governing stabilization, such as solubility, molecular size and functionalization
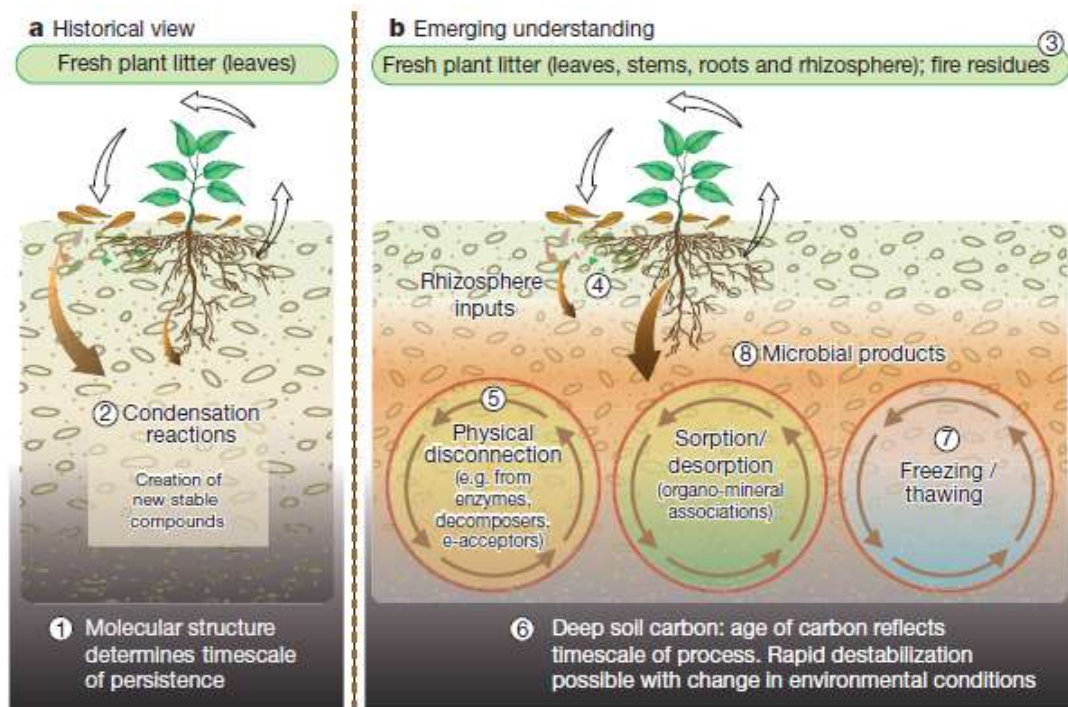
Figure 3: The historical view as compared to the emerging view(Schmidt et al., 2011)

The emerging understanding (Figure 3) is that the molecular structure of organic material does not necessarily determine its stability in soil. Rather, SOM cycling is governed by multiple processes shaped by environmental conditions (such as physical heterogeneity). Soil organic matter also includes well characterized chemical compounds that can be synthesized by micro-organisms or can arise directly from, or from modifications of similar compounds in the original debris. Thus, variations in environmental conditions provide a physically heterogeneous environment for the stabilization (biochemical) and protection (physical) of SOM and account for the variations in the persistence of SOM in different ecosystems.

III. Physical Fractionation Of Soil Organic Matter

Soil organic matter (SOM) consists of various functional pools that are stabilized by specific mechanisms and have certain turnover rates. A number of approaches have been proposed to separate soil organic matter into various physical fractions based on aggregate-size, particle density or a combination of both. Physical fractionation methods are based on the premise that the association of soil particles and their spatial arrangement play a key role in SOM dynamics, because bioaccessibility is a prerequisite for decomposition (Lutzowet al., 2007). Physical fractionation procedures are considered less destructive than chemical fractionation procedures of soil organic matter, and have yielded useful information on the nature and dynamics of the soil organic matter pool (egLutzowet al., 2007;Helfrichet al., 2006). The results obtained from physical soil fractions are anticipated to relate directly to the structure and function of SOM in situ. Physical fractionation involves the application of various degrees of disaggregating treatments (dry and wet sieving, slaking), dispersion (ultrasonic vibration in water), density separation and sedimentation.Comprehensive reviews on the use of physical fractionation in soil organic matter studies can be found in Wander (2004), Helfrichet al. (2006),andLutzowet al. (2007).

Particle size fractionation:

Particle sizefractionationinvolves complete dispersion of a soil so that its primary organo-mineral complexes are released. This fractionation technique relies on the concept that SOM associated with particles of different sizes differs in its structure and function (Lutzowet al., 2007). Besides differences in SOM contents, the chemical composition of SOM changed with particle size: results from ^{13}C CPMAS NMR spectroscopy (Cross Polarization Magic Angle Spin Nuclear Magnetic Resonance spectroscopy) and CuO oxidation showed that plant derived carbohydrates and lignin contribute to SOM in the sand-sized fractions, while the clay-sized fraction was dominated by products of the microbial synthesis, which corroborates the hypothesis that the degree of decomposition increases with decreasing particle size (Baldocket al., 1992). Further, a general trend of increasing apparent C turnover times with decreasing particle size was observed(Helfrichet al.,2006).

In general, fractionation by particle sizes provides a rough differentiation between young (active) and older (intermediate and passive) SOM. Slower C turnover rates in clay fractions compared to the sand fraction were explained by a combined action of all three process groups of SOM stabilization: the chemical change in SOM quality, an increase in spatial inaccessibility (e.g. due to microaggregation) and the adsorption of SOM on mineral surfaces. For this reason, the particle size fractions are not homogeneous in terms of their turnover time and cannot be equivalent to model pools.

Particulate organic matter plays a significant role in the fertility of soils, particularly tropical soils, and is important in understanding changes in soil fertility of tropical soils and has the potential for use as an indicator of soil quality. It is composed primarily of plant residues (Christensen, 1992) including partially decomposed root fragments and has an average C/N ratio of about 16. Amara *et al* (2016) used light fraction and particulate organic matter to study the effect of land use change in a tropical soil. They observed that the largest decline was in the light fraction carbon (16.46%)., followed by the particulate organic carbon (15.82%), total organic carbon (14.63%) and the silt+clay fraction (5.83%). The least decline occurring in the silt+clay fraction indicates that organic matter is better protected in silt+clay fraction. The results showed that there are greater losses of particulate organic carbon (17.24%), light fractions (18%) and total organic carbon (16.21) than from the silt+clay fraction (7.34) when the land use is changed from secondary forest to arable cropping.

Aggregate fractions

Aggregate fractionation of soil organic matter is used to isolate different aggregate size classes from a soil. It is based on the separation of free SOM and protected SOM that is occluded in secondary organo–mineral assemblages of different sizes. The different aggregate fractions aim to isolate active from intermediate and passive SOM pools (separation of free SOM from SOM occluded by macro- and microaggregate and SOM in clay microstructures, respectively). Aggregate fractions are obtained by dry or wet sieving and slaking.

Kamara et al (2007) used the dry sieving method to study the dynamics of soil carbon in aggregate-size fractions (250–2000 μm, 53–250 μm, and 53 μm) on a tropical toposequence. They showed that organic carbon distribution in aggregate-size fractions decreased with decreasing aggregate-size and is a function of the amount of soil contained in the aggregate size fraction.

Because water is considered to be the main agent for aggregate breakdown(Baldock et al., 1992), most studies refer to water-stable aggregation. Up to 90% of SOM in surface soils were found to be associated with aggregates. In soils where SOM is the main agent for soil aggregation, aggregates were found to break down hierarchically(Tisdall and Oades, 1982) where soil macroaggregates (> 250 μm) were generally richer in SOM than microaggregates (< 250 μm) (John et al., 2005). Decreasing C/N ratios with decreasing aggregate size suggest an increasing degree of decomposition with decreasing aggregate size (John et al., 2005).Earlier, Angers and Recous (1997) traced C and N deriving from $^{13}C^{15}N$-labelled wheat straw and found a redistribution of the ^{13}C from macro- to microaggregates with time, indicating the progressive incorporation of C from the larger to the finer aggregate fractions. This is further corroborated by findings of several studies that the apparent C turnover time increases from several decades in macroaggregates to several centuries in microaggregates (John et al., 2005).

Density fractionation

Density fractionation is applied to isolate SOM that is not firmly associated with soil minerals (light fraction) from organo–mineral complexes (heavy fraction). The intention of density fractionation is to achieve active, intermediate and passive OM pools.

Physical fractionation of soil organic matter based on particle density allows the separation of light organic matter within specific classes from the heavier density mineral particles. Several approaches using liquids of different densities have been proposed to separate the light fraction organic matter from the heavier organo-mineral fraction. Since the density of soil minerals is usually greater than 2.0 Mg m^{-3} compared with most organic materials with densities of about 1.5 Mg m^{-3}, heavy liquids with densities approximately 2 Mg m^{-3}can be used to separate the light fraction from the heavy mineral component.

Because it allows the creation of heavy liquids of various densities (between 1.0 and 3.1 Mg m^{-3}), the preferred density agent in recent times is sodium polytungstate ($Na_6H_2W_{12}O_{40}$) (Six et al., 2002). Organic matter without strong interaction with the soil mineral matrix, which generally consists of particulate plant residues, belongs to the light fraction with a density < 1.6–2.0 Mg m^{-3}. When this particulate organic matter (POM) exists free in the soil, it turns over within years(Christensen, 1992; John et al., 2005) while POM occluded in aggregates was found to turn over more slowly(John et al., 2005). This slower turnover can result from differences in recalcitrance and/or spatial inaccessibility. Organic matter strongly associated with soil minerals belong to the heavy fraction, because it is most often characterized by a density > 1.6–2.0 Mg m^{-3}.

Due to its short turnover time and to correlations between SOC in the light fraction and soil respiration rates (Lützow et al., 2007), the light fraction seems to accurately represent the active SOM pool. An exception

are soils with high black carbon contents, because black carbon has turnover times up to several thousands of years and thus likely belongs to the stable SOM pool, but is mainly associated with the light fraction due to few interactions with soil minerals. The passive pool is too heterogeneous to be represented by the heavy fraction(Lützowet al., 2007). However, density fractionation of soil organic matter has not been very successful in tropical soils(John *et al.*, 2005), probably due to the similarity in densities between organic matter complexes with sesquioxides and other soil colloids.

IV. Chemical Fractions Of Soil Organic Matter
Fractionation of humic substances

The fractionation scheme proposed byOden (1919, as cited by Hayes and Swift, 1978) appears to have been the earliest and most widely used fractionation of soil organic matter. This fractionation scheme is based on differences in solubilities of organic constituents in acid and alkali. The technique involves extraction with an alkaline reagent, separation of the alkaline extract from the residue, and then acidification of the extract. This procedure gives rise to three gross fractions, Humic acid (HA), Fulvic acid (FA) and Humin. This has been a common technique used to separate and examine soil organic matter and has been the basis of many studies*(eg*Schnitzer1991; Nguyenet al., 2004). The chemical properties of HA and FA have been studied extensively. This fractionation scheme has provided useful guide in interpretation of organic matter dynamics. For example, the HA:FA ratios have been used as indicators of the degree of humification in a soil. Higher HA:FA ratios found in surface soils of most environments are believed to reflect more intense humification as a result of greater biological activity (Anderson and Coleman, 1985). The ratio of the optical densities or absorbance of dilute aqueous solutions of HA and FA at 465 and 665 nm (E4/E6 ratio) has been used to indicate the degree of condensation of the aromatic carbon network, with a low ratio indicative of relatively high degree of condensation of aromatic humic constituents(Chen *et al.,* 1977). Conversely, a high E4/E6 ratio reflects a low degree of aromatic condensation and infers the presence of relatively large proportions of aliphatic structures.

The major problem with this fractionation scheme has been the choice of a suitable solvent for extracting organic matter from soils. The ideal extractant should remove practically all organic matter from soil without altering its physical and chemical properties. The use of dilute aqueous solutions of NaOH as SOM extractant has been proposed byArchard (1786, as cited by Schnitzer and Schuppli, 1989), and has gained considerable applications. Other reagents that have been widely used for the extraction of organic matter in soil include dilute solutions of neutral salts such as $Na_4P_2O_7$.

Treatments using oxidizing agents (H_2O_2, $Na_2S_2O_8$, NaOCl) have been suggested to mimic biodegradation to the extent that treatments preferentially remove SOM in weak association with the mineral matrix with a prevailing modern isotopic signature from various soils and subsequently cause the relative enrichment of older, ^{14}C-depleted SOM components(Planteet al., 2004) more intimately associated with mineral surfaces. Results of several studies on the size and stability of oxidation-resistant SOC vary greatly. WhereasEusterhues*et al.* (2005) found the proportion of H_2O_2-resistant SOC to increase with soil depth and hence with C depletion, Plante*et al.* (2004) found no correlation between oxidation-resistant SOM and C depletion in the clay fraction of a silt loam derived from a cultivation chronosequence. Furthermore, mean ^{14}C ages of oxidation-resistant SOM reported in the literature vary extensively(Eusterhues*et al.*, 2005).

Labile fraction oxidized with potassium permanganate (KMnO₄)

Recent insights into SOM assert that virtually all soil organic compounds can be decomposed in the soil regardless of intrinsic molecular recalcitrant(Lehman and Kleber, 2015). Small changes in SOC resulting from changes in soil management are often difficult to measure, but can have pronounced effects on soil behavior and microbial processes. It may take many years for contrasting soil management practices to cause measurable differences in SOC(Planteet al., 2004). Changes in small but relatively labile fractions of SOC may provide an early indication of soil degradation or improvement in response to management practices. The labile fractions of soil C are the most readily decomposable as opposed to the non-labile carbon, which belongs to a highly recalcitrant or passive C pool that is only very slowly altered by microbial activities. The labile fraction of soil organic carbon represents the active C pool, and can serve as sensitive indicator of changes in management-induced soil quality.

Solutions of potassium permanganate (KMnO₄) have been used extensively for the oxidation of organic compounds, the rates and extents of oxidation of the different substrates governed by their chemical composition. The need to investigate the products formed by the use of different concentrations of permanganate over varying conditions of time had been felt over the years. For instance, studies with less than the theoretical amounts of permanganate required for complete oxidation could reveal the quantity of readily oxidisable components. Some attempts to carry out studies in this direction had been undertaken bySavage and

Stevenson (1961), which however, were based on the use of strong oxidizers for investigation into the chemical structures of humic compounds.

In later years, Loginow et al.(1987) developed a method of fractionating soil organic matter based on susceptibility to oxidation by $KMnO_4$. In its original form, the degree of oxidation with three different concentrations of $KMnO_4$ was used, in conjunction with the total carbon concentration of the soil to obtain four fractions of soil organic carbon based on their ease of oxidation. Although the technique cannot be used to obtain the organic fractions *in substantio,* work done by Lefroy et al. (1993) has shown the technique to be useful for monitoring small, short-term changes in soil organic matter, characterization of organic matter of various soils, and evaluation of qualitative changes occurring under the influence of organic and mineral fertilization. The method is based on the supposition that the oxidative action of potassium permanganate on soil organic carbon is comparable to that of enzymes produced by soil microorganisms. The procedure involves reacting the soil organic matter with an excess of three different concentrations of $KMnO_4$. As some classes of organic compounds are oxidized, the permanganate is reduced and the reduced permanganate, which is equivalent to the amount of carbon oxidized, is measured by spectrophotometry. The lower the concentration of $KMnO_4$ required for oxidation of a certain class of compounds, the more labile that organic component. Using this procedure, Loginow et al. (1987) obtained four fractions with 3 different concentrations of permanganate.

After detailed experimentation, Blair et al. (1995) proposed the use of one concentration of $KMnO_4$ solution, 333 mM, to determine the labile component of soil organic matter. The un-oxidised fraction, refered to as the non-labile carbon, is calculated from the total carbon concentration. By comparing the labile and non-labile carbon of a cropped soil relative to a native or reference soil, Blair et al.(1995) developed a carbon management index as an indicator of organic matter status of soil. The $KMnO_4$ oxidation procedure of Blair et al. (1995) has been employed in several studies(Conteh et al, 1998;Conteh and Blair., 1998). Shang and Tiessen (1997) showed that oxidation by $KMnO_4$ was able to predict the proportion of labile carbon which indicated a decrease in organic matter stability after cultivation.

To date, most research on $KMnO_4$-reactive soil C has used the 333 mM $KMnO_4$ method of Blair et al. (1995) to oxidize a fraction of soil C considered active or labile. Blair *et al*. (2001) report that this reagent appears to react with a relatively labile pool of soil C, and that changes in soil management often influence 333 mM $KMnO_4$-reactive soil C more markedly than they do total SOC. Significant correlations have been reported between 333 mM $KMnO_4$-reactive C and several soil chemical and physical properties(Blair et al., 1995).

There are some indirect analyses showing that SOM that can be oxidized with $KMnO_4$ may represent an active fraction. A comparison of cropped and uncropped soils in New South Wales has shown a more intensive decline of the $KMnO_4$-oxidizable SOC compared to the resistant fraction in cropped soils (Blair*et al*., 1995). Likewise, there are reports that any soil management activity that increases SOM contents or decreases the intensity of soil disturbance increases the amount of $KMnO_4$-oxidizable OC (Blair et al., 1995; Conteh*et al*., 1997). In arable Kenyan soils,Murage et al. (2007) showed that $KMnO_4$-oxidizable SOC relates well to POM-C and to MBC and that all parameters were significantly larger in productive soils than in unproductive ones.

This active C method is rapid, inexpensive and can be modified for use in the field, and in low-cost fee-for-service soil testing for commercial growers(Idowu et al., 2008). Weil et al. (2003) showed that $KMnO_4$-oxidizable SOC was related to most measures of soil microbial activity, including Microbial Biomass Carbon (MBC), soluble carbohydrate C, and total SOC. Other studies have found significantly positive relationships between $KMnO_4$-oxidizable SOC and microbial biomass, phospholipid fatty acids and particulate organic carbon (POC) (Culman et al., 2012).

Permanganate oxidizable C was more strongly related to heavier and smaller POC fractions than lighter and larger POC fractions, indicating that it reflects a more processed, stabilized pool of labile soil C. This suggests that $KMnO_4$-oxidizable SOC may be well suited to track management practices that promote soil C sequestration, making it a particularly useful indicator for soil quality research. Permanganate oxidizable C appears to be equally capable as POC, MBC, and SOC in detecting differences in soils due to management or environmental factors (Conteh et al., 1999).

The sensitivity of this method and the relative ease of measurement suggest that $KMnO_4$-oxidizable SOC can be used to routinely evaluate biologically active soil C. Permanganate-oxidizable C is a promising and affordable active organic matter test currently being implemented in soil health frameworks (Idowu et al., 2008).

In a comparison of $KMnO_4$-oxidizable SOC and other more established measures of active organic matter, Culman et al. (2012) found that $KMnO_4$-oxidizable SOC was closely related with smaller and heavier particulate organic C fractions, indicating that $KMnO_4$-oxidizable SOC reflects a relatively processed or stabilized pool of active soil C. Their work also showed $KMnO_4$-oxidizable SOC is more sensitive to changes in management than other soil C fractions, which suggests that $KMnO_4$-oxidizable SOC can be a useful metric for rapidly tracking management-induced changes in SOM.

Overall, $KMnO_4$-oxidizable SOC and mineralizable C were either the first or second best predictor in 21 out of 28 comparisons (Culman et al., 2012), indicating that both of these measurements are capable of

predicting agronomic performance relative to other soil C fractions. Consistent with the results presented here,Stine and Weil (2002) reported significant relationships between $KMnO_4$-oxidizable SOC and crop productivity (r^2 = 0.58 and 0.74 for corn aboveground biomass and grain yield, respectively). Likewise,Culmanet al., 2012reported a significant relationship (r^2 = 0.89) between mineralizable C and crop productivity (in particular rice and wheat). Furthermore, $KMnO_4$-oxidizable SOC better reflected conservation-oriented practices that are expected to promote accumulation or stabilization of organic matter (long-term C sequestration), whereas mineralizable C better reflected practices that are expected to promote organic matter mineralization (short-term nutrient availability). Consistent with findings by others, both mineralizable C and $KMnO_4$-oxidizable SOC in our study also appeared to predict crop productivity better than other soil C fractions such as total SOC. If used in combination, $KMnO_4$-oxidizable SOC and mineralizable C can play complementary roles by providing a framework for evaluating the relative dynamics of organic matter stabilization and mineralization functions in agroecosystems.

V. Conclusion

Monitoring the quantity of soil organic matter still relies on measurement of the total quantity of organic matter in soils. It is now clear that total organic carbon measurements alone have not provided much information against the background of diverse components of soil organic matter. The complex nature of organic matter in soil coupled with its association with the mineral matrix has led to the development of a wide range of approaches for its estimation. Recent advances in soil organic matter methodologies such as solid-state ^{13}C NMR spectroscopy, pyrolysis mass spectrometry, uv-photooxidation, and infrared spectroscopic techniques have contributed significantly towards understanding the nature of organic carbon in soils.Such techniques however, are not readily accessible for monitoring purposes. Total organic carbon measurements such as the loss-on-ignition, dichromate oxidation, and dry combustion techniques have been widely employed for monitoring soil organic matter changes. A drawback with the use of total organic carbon measurements alone is that soil organic matter changes are gradual and short-term changes in organic carbon may be difficult to detect against a high background level. This article has presented some useful fractionation procedures that have been usedfor monitoring short term changes in soil organic matter.

Despite numerous approaches to improve and combine fractionation methods, a major remaining problem is that most procedures are not specific enough with regard to stabilization mechanisms. Therefore, most available fractionation methods do not yield homogeneous or functional SOM pools. Especially the conceptual passive pool, which is stabilized by various mechanisms, is still difficult to characterize. All efforts to isolate this pool so far have yielded SOM fractions that are still heterogeneous in terms of turnover times and reveal no causal relationships to stabilization mechanisms (Strosser, 2010).

In summary, combinations of physical and chemical fractionation methods yield fractions that are still heterogeneous and are not able to fully differentiate SOM stabilized by specific mechanisms. Thus, the fractions do not characterize functional SOM pools. Still, these methodologies can provide valuable information for the understanding of different stabilization mechanisms in specific soil horizons and soil types.

References

[1]. Amara, Denis M. K., Sahr A. Koroma, Philip J. Kamanda, Augustine M. Kamara, Daniel H. Saidu. 2016. Effects of land use on Soil Organic Carbon fractions in soils of Njala Landscape in Sierra Leone. International Journal of Environment, Agriculture and Biotechnology (IJEAB) Vol-1, Issue 4, Nov - Dec-. DOI: 10.22161/ijeab/1.4.5

[2]. Anderson, D. W., and Coleman, D. C. (1985). The dynamics of organic matter in grassland soils. *Journal of Soil and Water Conservation* 40, 211-216. http://www.jswconline.org/content/40/2/211.full.pdf+html

[3]. Angers, D.A. &Recous, S. 1997. Decomposition of wheat straw and rye residues as affected by particle size. *Plant & Soil* 189, 197–203. DOI:10.1023/A:1004207219678

[4]. Baldock, J.A., Oades, J.M., Waters, A.G., Peng, X. Vassallo, A.M. & Wilson, M.A. 1992. Aspects of the chemical structure of soil organic materials revealed by solid-state 13C NMR spectroscopy. *Biogeochemistry* 16, 1–42. DOI:10.1007/BF02402261

[5]. Bationo, A. 2004. Managing Nutrient Cycles to Sustain Soil Fertility in Sub-Saharan Africa. *Academy Science Publishers (ASP) in association with the Tropical Soil Biology and Fertility Institute of CIAT.* http://hdl.handle.net/10919/65475

[6]. Blair G.J., Lefroy R.D.B. and Lisle L. 1995. Soil carbon fractions based on their degree of oxidation and the development of a carbon management index for agricultural Systems. Aust. J. Agric. Res. 46: 1459–1466. (https://doi.org/10.1071/AR9951459)

[7]. Blair, G.J., R. Lefroy, A. Whitbread, N. Blair, and A. Conteh. 2001. The development of the KMnO4 oxidation technique to determine labile carbon in soil and its use in a carbon management index. In R. Lal, J. Kimble, R. Follet, and B. Stewart (eds.). Assessment Methods for Soil Carbon. Lewis Publishers, Boca Raton, FL. p. 323±337.

[8]. Chapman, C.A., Lawes, M.J., Eeley, H.A.C., 2006. What hope for African primate diversity? African Journal of Ecology 44, 116–133. https://doi.org/10.1111/j.1365-2028.2006.00636.x

[9]. Chen, Y., Senesi, N., and Schnitzer, M. (1977). Information provided on humic substances by E4/E6 ratios. *Soil Science Society of America Journal* **41,** 352-358. doi:10.2136/sssaj1977.03615995004100020037x

[10]. Christensen, B.T. 1992. Physical fractionation of soil and organic matter in primary particle size and density separates. *Advances in Soil Science* 20, CRC-Lewis-Publishers, Boca Raton, pp. 1–90. *Soil Science* **33,** 141-63. https://doi.org/10.1046/j.1365-2389.2001.00417.x

[11]. Conteh A. and Blair G.J. 1998. The distribution and relative losses of soil organic carbon fractions in aggregate size fractions from cracking clay soils (Vertisols) under cotton production. Aust. J. Soil Res. 36: 257–271. (https://doi.org/10.1071/S97073)

[12]. Conteh A., Blair G.J. and Rochester I.J. 1998. Soil organic fractions in a Vertisol under irrigated cotton production as affected by burning and incorporating cotton stubble. Aust. J. Soil Res. 36: 655–667. (https://doi.org/10.1071/S97117)

[13]. Conteh, A.,Blair, G.J., Lefroy, R., and Whitbread, A. (1999). Labile organic carbon determined by permanganate oxidation and its relationships to other measurements of soil organic carbon. *Humic Substances in the Environment* **1**, 3-15.

[14]. Craswell, E.T., and Lefroy, R.D.B. 2001. The role and function of organic matter in tropical soils. Nutrient Cycling in Agroecosystems 61: 7–18, 2001

[15]. Culman, S.W., Snapp, S.S., Freeman, M.A., et al. 2012. Permanganate Oxidizable Carbon Reflects a Processed Soil Fraction that is Sensitive to Management. Soil Sci. Soc. Am. J. 76:494–504. doi:10.2136/sssaj2011.0286

[16]. Ekschmitt, K., E. Kandeler, C. Poll, A. Brune, F. Buscot, M. Friedrich, et al. 2008. Soil-carbon preservation through habitat constraints and biological limitations on decomposer activity. J. Plant Nutr. Soil Sci. 171:27–35. https://doi.org/10.1002/jpln.200700051

[17]. Eswaran, H., Berg, E. van den, and Reich, P. 1993. Organic Carbon in Soils of the World. Soil Sci. Soc. Am. J. 57:192-194 (1993).

[18]. Eusterhues, K., Rumpel, C. &Kögel-Knabner, I. 2005. Stabilization of soil organic matter isolated via oxidative degradation. *Organic Geochemistry* 36, 1567–1575. https://doi.org/10.1016/j.orggeochem.2005.06.010

[19]. FAO, 2005. Global Forest Resources Assessment 2005: 15 Key Findings. Food and Agricultural Organization of the United Nations, Rome, Italy. http://www.fao.org/3/a-i4808e.pdf

[20]. Hayes, M. H. B., and Swift, R. S. (1978). The chemistry of soil organic colloids. In *The Chemistry of Soil Constituents.'* (Eds. Greeland, D. J., and Hayes, M. H. B.) pp.179-320. (John Wiley:Chichester).

[21]. Hefrich M. 2007. Composition and stability of organic matter fractions in soils under different land use regimes. Doktors der Naturwissenschaften (Dr. rer. nat.) imFachbereichNaturwissenschaften der Universität Kassel. January 2007. https://d-nb.info/984696407/34

[22]. Helfrich, M, B. Ludwig, R. Mikutta, A. Dreves and H. Fless. 2006. Are chemical fractionation methods able to isolate stable soil organic matter pools? Geophysical Research Abstracts, Vol. 8, 06912, 2006 SRef-ID: 1607-7962/gra/EGU06-A-06912

[23]. Idowu, O.J., H.M. Es, G.S. Abawi, D.W. Wolfe, J.I. Ball, B.K. Gugino, B.N. Moebius, R.R. Schindelbeck, and A.V. Bilgili. 2008. Farmer-oriented assessment of soil quality using fi eld, laboratory, and VNIR spectroscopy methods. Plant and Soil 307: 243–253. doi:10.1007/s11104-007-9521-0

[24]. John, B., Yamashita, T., Ludwig, B. &Flessa, H. 2005. Storage of organic carbon in aggregate and density fractions of silty soils under different types of land use. Geoderma 128, 63–79. https://doi.org/10.1016/j.geoderma.2004.12.013

[25]. Kamara, A., Rhodes, E. R. and Sawyerr, P. A. 2007. Organic Carbon Dynamics along a Toposequence in a Peri-urban Site, Communications in Soil Science and Plant Analysis, 38:17, 2371 – 2379. DOI: 10.1080/00103620701588502

[26]. Lal, R. 2016. Soil health and carbon management. *Food and Energy Security* 2016; 5(4): 212–222. doi:10.1002/fes3.96

[27]. Lal, R., 2002. Soil carbon dynamics in cropland and rangeland. Environmental Pollution, 116: 353-362. https://doi.org/10.1016/S0269-7491(01)00211-1

[28]. Lefroy, R. D. B., Blair, G. J., and Strong, W. M. (1993). Changes in soil organic matter with cropping as measured by organic carbon fractions and natural isotope abundance. *Plant and Soil* 1551156, 399-402. https://www.jstor.org/stable/42939345

[29]. Lehmann, J., Kleber, M., 2015. The contentious nature of soil organic matter. Nature 528, 60. DOI:10.1038/nature16069. https://www.nature.com/articles/nature16069

[30]. Loginow, W., Wisniewski, W., Gonet, S. S. and Ciescinska, B. (1987). Fractionation of organic carbon based on susceptibility to oxidation. *Polish Journal of Soil Science* 20, 47-52. https://eurekamag.com/research/005/483/005483804.php

[31]. Lutzow, M.v., Kogel-Knabner, I., Ekschmitt, K., Flessa, H., Guggenberger, G., Matzner, E., and Marschner, B. 2007. SOM fractionation methods: Relevance to functional pools and to stabilization mechanisms. Soil Biology and Biochemistry 39 (2007) 2183–2207

[32]. Martius, C., Tiessen, H., and Vlek, P.L.G. 2001. The management of organic matter in tropical soils: what are the priorities? Nutrient Cycling in Agroecosystems 61: 1–6, 2001

[33]. Murage EW, Voroney P, Beyaert RP. 2007. Turnover of carbon in the free light fraction with and without charcoal as determined using the ^{13}C natural abundance method. Geoderma. 2007;138:133-43. doi:10.1016/j.geoderma.2006.11.002

[34]. Nguyen BaoVe, D. C. Olk, and K. G. Cassman. 2004. Characterization of Humic Acid Fractions Improves Estimates of Nitrogen Mineralization Kinetics for Lowland Rice Soils. Soil Sci. Soc. Am. J. 68:1266–1277. DOI:10.2136/sssaj2004.1266

[35]. Olk, D.C., Gregorich, E.G., 2006. Overview of the symposium proceedings,"Meaningful pools in determining soil carbon and nitrogen dynamics". Soil Sci. Soc. Am. J. 70, 967–974. https://pdfs.semanticscholar.org/2d98/a3385fbe1b85d0539622229a0959c7691da8.pdf

[36]. Plante, A.F., Chenu, C., Balabane, M., Mariotti, A. &Righi, D. 2004. Peroxide oxidation of clay-associated organic matter in a cultivation chronosequence. *European Journal of Soil Science* 55, 471–478. https://doi.org/10.1111/j.1365-2389.2004.00626.x

[37]. Poeplau, C., Don, A., 2013. Sensitivity of soil organic carbon stocks and fractions to different land-use changes across Europe. Geoderma 192, 189–201. https://doi.org/10.1016/j.geoderma.2012.08.003

[38]. Savage, S. M., and Stevenson, F. J. (1961). Behaviour of soil humic acids towards oxidation by hydrogen peroxide. *Soil Science Society of America Proceedings* 25, 35-39. doi:10.2136/sssaj1961.03615995002500010x

[39]. Schmidt, M.W.I, Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kogel-Knabner, I., Lehmann, J., Manning, D.A.C., Nannipieri, P., Rasse, D.P., Weiner, S., and Trumbore, S.E. 2011. Persistence of soil organic matter as an ecosystem property. Nature vol 478. doi:10.1038/nature10386

[40]. Schnitzer, M. (1991). Soil organic matter-the next 75 years. *Soil Science* **151**, 41-58. dx.doi.org/doi:10.1097/00010694-199101000-00008

[41]. Schnitzer, M., and Schuppli, P. (1989). Method for the sequential extraction of organic matter from soils and soil fractions. *Soil Science Society of America Journal* **53**, 1418-1424. doi:10.2136/sssaj1989.03615995005300050019x

[42]. Schroth, G., Vanlauwe, B., and Lehmann, J. 2003. Soil Organic Matter. . In, '*Trees, Crops and Soil Fertility'* (eds. G. Schroth and .L. Sinclair). CAB International 2003.

[43]. Shang, C., and H. Tiessen. 1997. Organic matter lability in a tropical oxisol: Evidence from shift ing cultivation, chemical oxidation, particle size, density, and magnetic fractionations. Soil Sci. 162: 795–807. doi:10.1097/00010694-199711000-00004

[44]. Six, J., Callewaert, P., Lenders, S., De Gryze, S., Morris, S.J., Gregorich, E.G., Paul, E.A., Paustian, K., 2002. Measuring and understanding carbon storage in afforested soils by physical fractionation. Soil Sci. Soc. Am. J. 66, 1981–1987. doi:10.2136/sssaj2002.1981.

[45]. Skjemstad, J. 0., Clarke, P., Taylor, J. A., Oades, J. M., and McClure, S. G. (1996). The chemistry and nature of protected carbon in soil. *Australian Journal of Soil Research* **34**, 251- 271. https://doi.org/10.1071/SR9960251

[46].   Stine, M.A., and R.R. Weil. 2002. The relationship between soil quality and crop productivity across three tillage systems in south central Honduras. Am. J. Altern. Agric. 17:2–8. DOI:10.1079/AJAA20011

[47].   Strosser, E. 2010. Methods for determination of labile soil organic matter: An overview. J Agrobiol 27(2): 49–60, 2010. DOI 10.2478/s10146-009-0008-x

[48].   Swift, M.J., Izac, A.M.N., van Noordwijk, M. Swift, M.J., Izac, A.M.N. & van Noordwijk, M. 2004. Biodiversity and ecosystem services in agricultural landscapes-are we asking the right questions? *Agriculture Ecosystems and Environment,* 104, 113–134. https://doi.org/10.1016/j.agee.2004.01.013

[49].   Tisdall, *J.* M., and Oades, J. M. (1982). Organic matter and water-stable aggregates in soils. *Journal of Soil Science* 33, 141-63. https://doi.org/10.1111/j.1365-2389.1982.tb01755.x

[50].   Wander, M.M. 2004. SOM fractions and their relevance to soil function. In: F. Magdoff and R.R. Weil, editors, Soil organic matter in sustainable agriculture. CRC Press, Boca Raton, FL. p. 67–102. doi:10.1201/9780203496374.ch3

[51].   Weil, R.R., K.R. Islam, M.A. Stine, J.B. Gruver, and S.E. Samson-Liebig. 2003. Estimating active carbon for soil quality assessment: A simplified method for laboratory and fi eld use. Am. J. of Alt. Agric. 18: 3–17. doi:10.1079/AJAA2003003

[52].   Woomer P.L., Martin A., Albrecht A., Resch D.V.S. and Scharpenseel H.W. 1994. The importance and management of soil organic matter in the tropics. In: Woomer P.L. and Swift M.J. (eds), The Biological Management of Soil Fertility. John Wiley and Sons, Chichester, pp. 47–80. http://horizon.documentation.ird.fr/exl-doc/pleins_textes/pleins_textes_7/b_fdi_55-56/010021562.pdf