

An Overview of Methods Used In Assessing the Dynamics of Organic Matter in Soils

Abdul R Conteh

Principal Research Officer (Soils), Njala Agricultural Research Centre (NARC), Sierra Leone Agricultural Research Institute (SLARI), PMB 1313, Freetown, Sierra Leone.

Abstract

The organic matter content of a soil is a key indicator of a sustainable soil management system because of its influence on the physical, chemical and biological health of a soil. Management of soil organic matter requires appropriate methods to characterize and quantify the status of organic matter under different management practices. A wide range of approaches has been adopted for the determination of organic matter in soils. Some of these approaches include loss-on-ignition, dry combustion, wet oxidation, spectroscopic methods and isotopic methods. This article examines each of these methods highlighting their shortcomings.

Date of Submission: 02-08-2020

Date of Acceptance: 17-08-2020

I. Introduction

The achievement of both financial and ecological sustainability is a major goal in the utilization and management of soils for crop production. To achieve these goals, soil quality must be maintained at a level which ensures that none of the following soil related factors are allowed to restrict crop growth and function; aeration, water supply, nutrient supply, temperature, and hardness. However, many soils on which crops are typically grown are prone to some of these growth limiting factors. This inevitably leads to reductions in yields and farm income. In the longer term, a reduction in soil quality reduces the land value, and this, combined with shorter term reductions in yields and income, provides agricultural stakeholders with strong incentives to avoid or reverse adverse soil conditions.

The soil problems outlined above can be mostly alleviated through efficient management of the organic matter content in the soil. The soil organic matter content is a key indicator of a sustainable cropping system because of its influence on the physical, chemical and biological health of a soil. The importance of organic matter to soil fertility and sustainable crop production is now well recognized and there have been extensive reviews covering the role of organic matter in soils (Mathers et al., 2000; Syers and Craswell, 1995). 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 agricultural soils rarely exceeds 5% by soil weight, it is a key component of any ecosystem, and variations in its abundance and nature have profound effects on many of the processes that occur in the system.

Soil organic matter adds structure, stability and permeability to soils high in clay (Syers and Craswell, 1995). For all soils, it is a source of nutrients through its decomposition or through its contribution to the soil's cation exchange capacity. Soil compaction and many other soil problems are mainly due to soil organic matter losses. Soil organic matter protects against heavy metal and salt toxicities, it detoxifies pesticides and prevents their leaching down the soil profile. In acid soils, organic matter has been reported to be a potential factor in improving the efficiency of soil and fertilizer phosphorus utilization by reducing phosphorus fixation (Syers and Craswell, 1995). With growing concern about atmospheric CO₂ levels, soil organic matter is a significant source and sink for atmospheric CO₂ (Mathers et al., 2000). Plants use atmospheric CO₂ to synthesize the structural tissues that form the majority of organic matter in terrestrial ecosystems (Figure: 1). This is the basis for the formation of soil organic matter. Plants release litter from roots and leaves into and onto the soil. In addition they exude sugars, organic acids, and other low molecular weight compounds into the rhizosphere (Gleixner, 2013).

Therefore, the variation in organic matter content of a soil induced by a land-use system is a significant indicator of the sustainability of that land-use system.

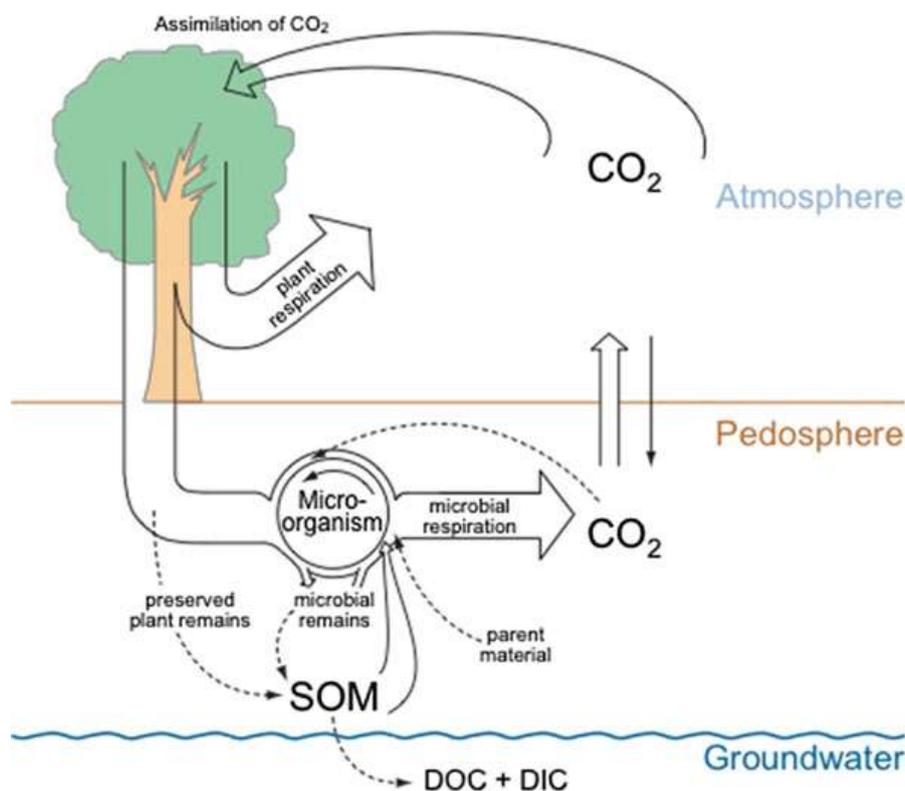


Figure 1: Soil organic matter formation and carbon cycling in soil. Source: Gleixner, 2013

Management of soil organic matter requires appropriate methods to characterize and quantify the status of organic matter under different management practices. A wide range of approaches has been adopted for the determination of organic matter in soils and some earlier reviews can be found in Nelson and Sommers (1982), and Stevenson and Elliott (1989). The purpose of this article is to provide an overview of some of the most common methods used for organic matter analysis.

II. Loss-On-Ignition

This was one of the earliest methods of determining the organic matter content of soils. The procedures involved in this method are essentially gravimetric in which the organic matter content of pre-weighed soil is supposedly destroyed by ignition and the loss in weight used as a measure of the organic matter content. Ignition can be carried out either at low temperatures (350 - 400°C) or at high temperatures (800 - 900°C). Inadequacies of this approach have been ascribed (Nelson and Sommers, 1982) to the lack of discrimination between loss of organic matter and loss of mineral matter such as carbon dioxide from carbonates and water and hydroxyl groups from clay.

Proponents of this method such as Spain et al. (1982) and Donkin (1991) have argued that ignition carried out at temperatures below 450°C can give estimates of organic matter that are sufficiently accurate for most purposes. Ball (1964) examined the loss-on ignition procedure for over one hundred soils having a wide range of organic matter content and obtained significant correlations with the dichromate method of Tinsley (1950). Davies (1974) found that the presence of carbonates in soil does not affect its loss-on-ignition value at 430°C and concluded that the gravimetric estimation of soil organic matter is generally applicable to both calcareous and non-calcareous soils provided that the furnace temperature is controlled between 375 and 450°C. Davies (1974) mentioned an exception in soils having gibbsite in their clay fraction because of previous reports that gibbsite loses substantial amounts (approximately 35 %) of water at around 300°C. Ben-Dor and Banin (1989) also obtained significant linear correlations ($r = 0.97$) between organic matter determined by the loss-on-ignition procedure and organic carbon determined by the method of Walkley and Black (1934) in soils from the arid region of Israel (Figure 2).

Spain et al. (1982) compared the organic matter values determined by the Walkley-Black procedure and the loss-on ignition for 766 surface soil samples representing 21 soil groups in Australia and found a close relationship between the two measurements. They found that the Walkley-Black values range from 0.1 to 14 % and the loss-on-ignition from 0.8 to 36 %. Generally, most studies utilizing the loss-on ignition method in estimating organic matter content reported satisfactory results. It is however still unclear as to what extent this method is applicable to soils from a wide range of ecosystems.

III. Dry Combustion Techniques

In dry combustion techniques, a sample is combusted in a furnace at elevated temperatures to convert all carbon-containing compounds to carbon dioxide (CO₂) which is subsequently measured to give an indication of organic carbon content. The evolved CO₂ can be measured by a wide range of procedures which include gravimetric, titrimetric, volumetric, and spectrophotometric and gas chromatographic techniques. This method has a limitation that samples containing significant quantities of carbon in the form of carbonates and elemental carbon will give an overestimate of organic carbon contents (Nelson and Sommers, 1982). This limitation can be minimized by treating the samples with dilute acid before combustion to remove all carbon existing in the form of carbonates. Alternatively, inorganic carbon can be measured separately and subtracted from the total carbon measurements to give an estimate of soil organic carbon content. A detailed description of various dry combustion procedures can be found in Nelson and Sommers (1982). In recent times, there has been an increase in the number of studies that determine organic carbon status using continuous-flow analyzers (Santiet *al.*, 2006).

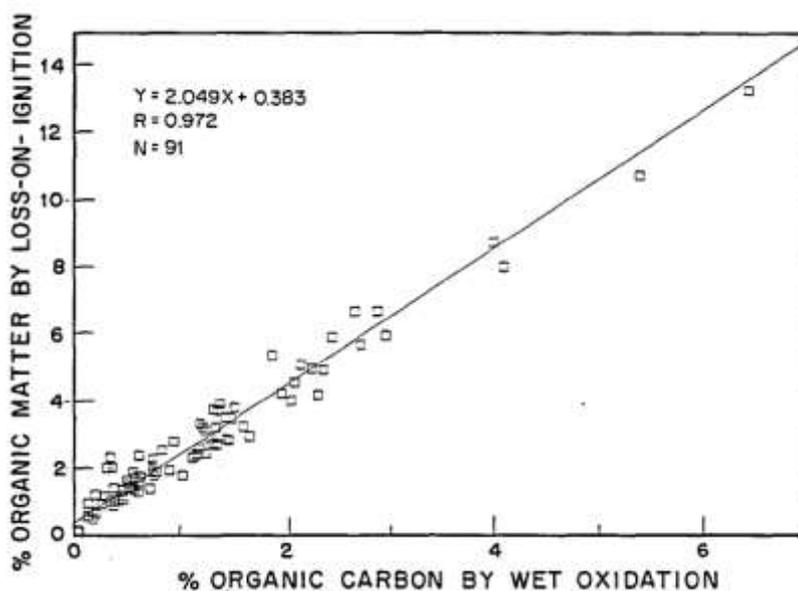


Figure 2: Organic matter content (loss-on-ignition) versus organic carbon content (dichromate wet-oxidation) of 91 Israeli aridic and semiarid soils. Source: Ben-Dor and Banin (1989)

One of the best known continuous-flow analyzers is the Automatic Carbon and Nitrogen Analyzer by Mass Spectrometry or ANCA-MS (Barrie, 1991). This instrument is usually used for the automated analysis of ¹⁵N and ¹³C in plant and soil samples but can also determine % N and % C on weighed samples. Samples containing up to 5 mg C are placed in tin capsules and dropped into a heated silica combustion tube (>1000°C) containing Cr₂O₃ granules as oxidation catalyst. A pulse of pure oxygen is introduced into the He gas stream which flows continuously through the combustion tube.

The timing of the O₂ pulse and the tin capsule introduction is so arranged that flash combustion of the sample occurs (Figure 4). The combustion products are then swept through a heated (~600°C) reduction furnace containing copper wire in which NO is reduced to N₂. Water vapour is then removed by passage through a moisture trap containing magnesium perchlorate, after which the remaining combustion products, N₂ and CO₂, are separated on a chromatographic column. Percentage C is determined as CO₂ using a thermal conductivity detector placed between the moisture trap and the mass spectrometer.

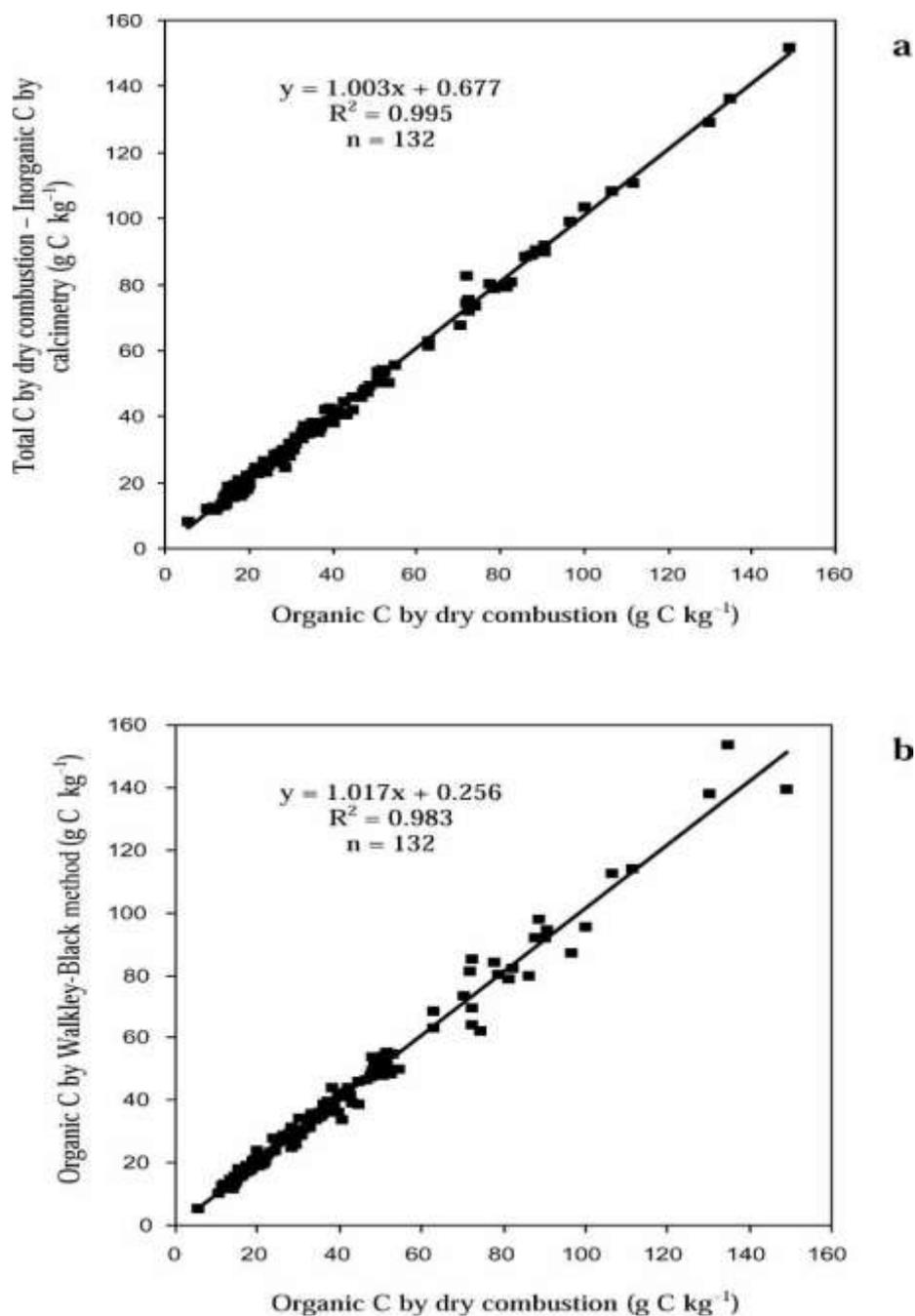


Figure 3: Plot of linear regressions for organic C measured in the soils of Pianosa Island by dry combustion after removal of inorganic C by excess acid as a function of (a) organic C as difference between the total C determined by dry combustion and the inorganic C determined by a volumetric calcimeter or (b) organic C determined by the Walkley-Black method with a CF of 1.30. Source: Santiet al., 2006.

Although modern dry combustion instruments are capable of handling large numbers of samples with minimal variability due to operator error, they are often very costly and cannot be afforded by most analytical laboratories.

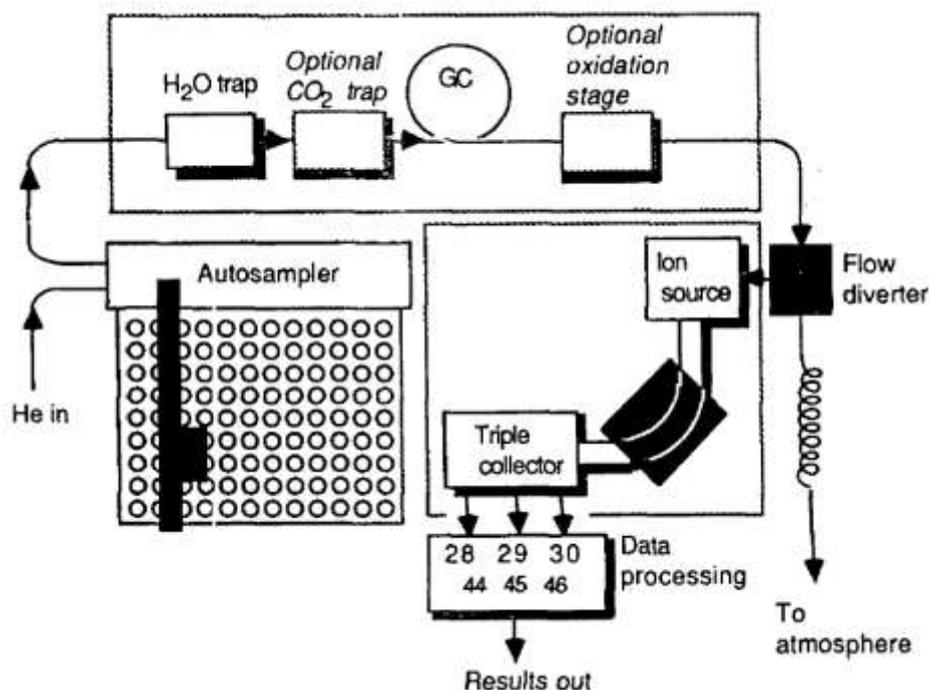
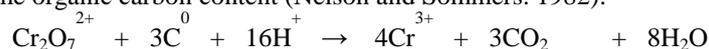


Figure 4: Schematic of an Automatic Carbon and Nitrogen Analyzer by Dry Combustion. Source: Barrie, 1991.

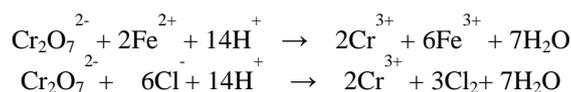
IV. Wet Oxidation Techniques

Several oxidizing agents have been employed for the determination of organic carbon in soil, the most common of which has been the dichromate oxidation proposed by Schollenberger(1927)and modified by Walkley and Black (1934). The fundamental principle of the method is that allorganic carbon is oxidized by the dichromate under acid conditions, and the amount of dichromateconsumed, or Cr^{3+} released, or CO_2 evolved, gives an indication of the organic carbon content (Nelson and Sommers. 1982):

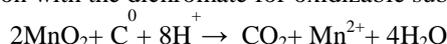


This method has been employed in so many studies that a complete review of its applicationsis beyond the scope of this review. The procedure has been the basis of routine organic carbon determinations in most soil laboratories. The various modifications of this method that have been proposed abound in the literature. Despite its wide usage, dichromate procedures are subject to certain limitations. Several studies have shown that recovery of organic carbon is rarely complete and varies considerably between soils (Nelson and Sommers, 1982). In addition to the incomplete recovery of organic carbon, several substances present in soil can interfere with the determination of oxidizablecarbon, notably chlorides, iron (II) and higher oxides of manganese leading to incorrect values for organic carbon because of the participation of these ions in redox reactions involving chromic acid mixtures.

For example,



Therefore, the presence of these ions in soils in significant amounts can result in higher values of organic carbon. The presence of higher oxides of manganese (MnO_2) can result in underestimation of organic carbon values because of competition with the dichromate for oxidizable substances. For example,



In addition to the aforementioned limitations, the assumption that all organic carbon in soil exists in a valence state of zero may not be appropriate. There has been no study to evaluate this assumption.

V. Physical Fractionation

The use of physical fractions in organic matter studies has received considerable attention and has been the basis of several studies on soil organic matter turnover (eg Camberdella and Elliott, 1994). Physical fractionation of soil organic matter is considered by several workers to be less destructive, and the results obtained from physical soil fractions are believed to relate more directly to the structure and function of soil organic matter *in situ* (Golchinet al., 1995). Two basic methods of physical fractionation of soil have been reported; particle-size fractionation and particle density fractionation.

Physical fractionation of soil according to particle size has been used extensively to study soil organic matter and the methods have proven to be useful in revealing differences in the structural and dynamic properties of organic matter from different soils. Methods used for particle-size fractionation have extended from dry sieving, which may retain macro-aggregates in the mm size range, to crushing of soil in mills and the use of chemical extractants to achieve complete dispersion (Ladd et al., 1993). The most common method used to obtain a high degree of disruption of the soil structure prior to physical fractionation is ultrasonication (Christensen, 2001). The use of sonication prior to physical fractionation has the potential problem of creating redistribution of organic matter among the various size fractions (Camberdella and Elliott, 1994). Although differences observed in the distribution of organic matter and particle-size fractions have been used to reveal differences in organic matter turnover under various management practices, such differences may also arise as a result of differences in methodology (Christensen, 2001).

Physical fractionation of soil organic matter has also been carried out on the basis of particle density. Such fractionation allows the physical separation of organic matter found within a specific size class from the heavier density mineral particles. Separations based on density have been used for two main purposes in soil organic matter studies; to separate the 'light fraction' (free or non-complexed soil organic matter) consisting largely of undecomposed residue and their partial decomposition products, and to separate organo-mineral associations, usually in aggregates (Golchinet al., 1995). Fractions separated on the basis of particle density have yielded useful information on the extent of association of organic and inorganic materials in soils, as well as some mineralogical characterization of the fraction components. Generally, soil samples ground no finer than 0.2 mm are suspended in solutions of known density and centrifuged to separate the materials with greater and lower density than the solution. The light fraction obtained by the use of solutions with densities less than 1.6 Mg/m³ consists largely of unaltered or partially degraded plant materials and charcoal (Skjemstad et al., 1996). It has also been shown that the rate of loss of carbon from a number of fractions separated from vertisols decreased with increasing density and time of cultivation (Skjemstad and Dalal, 1987).

VI. Fractionation Of Humic Substances

The fractionation scheme proposed by Oden (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 Schnitzer et al., 1981; Schnitzer and Schuppli, 1989). The chemical properties of HA and FA have been studied extensively. HA is believed to be the most biologically resistant fraction of soil organic matter, with a core of strongly condensed aromatic structures surrounded by aliphatic side-chain components. FA appears to be composed mainly of microbial metabolites and younger material not highly associated with the mineral fraction, although all material, young and old, can be part of the FA. This fractionation scheme has provided useful guide in interpretation of organic matter dynamics. For example, the C:N:P ratios of HA and FA fractions have been used to assess the origin and turnover of nutrients in soil organic matter from different depths and zones (Schoenau and Bettany, 1987). The HA:FA ratios have also been used as indicators of the degree of humification in 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 (Chenet 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. This difficulty arises from the varying properties of the many organic compounds present in soils and the ability of these compounds to be bound, in varying degrees, to each other and complexed with inorganic components. 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 by Archard (1786, as cited by Schnitzer and Schuppli, 1989), and has gained considerable applications. The major concerns with the use of NaOH are the creation of artifacts in the extracted organic matter due to hydrolysis and auto-oxidation (Stevenson, 1982) and the arbitrary nature of these separation into HA and FA fractions. Other reagents that have been widely used for the extraction of organic matter in soil include dilute solutions of neutral salts such as $\text{Na}_4\text{P}_2\text{O}_7$.

Little is known as to whether and to what extent soil organic matter extracted by dilute NaOH solution differs from that removed by dilute $\text{Na}_4\text{P}_2\text{O}_7$ solution (Schnitzer and Schuppli, 1989). Problems with hydrolysis and auto-oxidation appear to be at least partly overcome by extracting under an atmosphere of N_2 (Anderson and Schoenau, 1993) although Tanet et al. (1991) found no difference between organic matter extracted under air and under N_2 .

Despite the popularity of this fractionation scheme, the fractions obtained are not conceptual pools but procedurally defined fractions with limited utility in studies of SOM dynamics (Stevenson and Elliott, 1989).

VII. Isotopic Techniques

Soil organic matter has also been studied extensively using both stable and radioactive isotopes of carbon. The type of isotopic measurements performed usually depends on the type of information required and the objectives of the study. The use of isotopes is reported to provide precise quantification of changes in SOM during decomposition (Gregorich et al, 2016). The most common isotopic techniques used are ^{14}C -labelling and ^{13}C natural abundance. Generally, ^{14}C -labelling is used to study short-term dynamics of SOM, and the ^{13}C natural abundance is used to characterize the long-term status.

^{14}C -labelling

The application of ^{14}C in studies of SOM seems to have been first brought to the attention of soil chemists by Binger et al. (1953). Since then ^{14}C has been used in so many aspects of SOM research that a complete review of its applications is beyond the scope of this presentation. The use of ^{14}C as a label has been made possible because of its radioactive nature, a β -emitter with a half-life of 5730 years. The use of ^{14}C -labelled substrates has been found necessary to trace the fate of added organic matter in various soil constituents.

Substrates labeled with ^{14}C have ranged from simple compounds, such as glucose and amino acids, to complex compounds, such as proteins and cellulose, to plant leaves and roots. With the addition of ^{14}C -labelled substrates to the soil, information has been obtained on the amount and rate of mineralization of the substrate.

This approach has been used by many researchers to examine the distribution of labeled carbohydrates among size fractions from soils incubated with ^{14}C -labelled glucose (28 days), rye-grass (1 year) and straw (4 years). Despite the popularity of ^{14}C -labelling techniques in SOM studies, erroneous conclusions may be drawn if the decay rates of the ^{14}C -labelled components of plant materials differ from those of the unlabeled components (Voroney et al., 1993). Also, producing artificially and uniformly labelled plant material remains difficult and requires sophisticated equipment.

^{13}C Natural abundance

Carbon has two stable naturally occurring isotopes, ^{12}C and ^{13}C . The isotope ^{12}C makes up approximately 98% of the carbon in nature while ^{13}C makes up approximately 1%. The ratio of these two stable isotopes ($^{13}\text{C}/^{12}\text{C}$) is affected by differences in photosynthetic pathways in plants. As a result, plants have been classified into C3, C4 and CAM based on photosynthetic pathway. The $^{13}\text{C}/^{12}\text{C}$ ratio is often measured relative to a standard and expressed as $\delta^{13}\text{C}$. Plants with a C4 pathway have a higher $^{13}\text{C}/^{12}\text{C}$ ratio ($\delta^{13}\text{C}$ of approximately -12 to -21%) than C3 plants ($\delta^{13}\text{C} < -21\%$). Detailed reviews on the mechanistic causes of variations in the carbon isotope ratios in plant materials are given by Boutton (1996). The use of ^{13}C natural abundance as a tracer in SOM studies is based on the fact that the ^{13}C content of SOM corresponds closely to the ^{13}C content of the plant material from which it is derived and that there is negligible fractionation of ^{13}C during the decomposition of plant material in soil (Gregorich et al., 2006). Therefore, the incorporation of C3 plant material into a soil that previously carried C4 vegetation will lead to a corresponding change in the $\delta^{13}\text{C}$ value of the soil. This approach has been used to study SOM dynamics and plant residue carbon in particle-size fractions in temperate and tropical soils. Using this method, researchers have studied the changes in SOM as a result of cropping, the dynamics of SOM in particle-size fractions of forested and cultivated oxisols, and used it to quantify maize root-derived soil organic carbon. Some extensive reviews on the use of ^{13}C natural abundance in SOM studies have been presented by Boutton (1996). A major source of error in the use of this technique is the changes in the isotopic composition of SOM during decomposition which in turn may be due to differences in $\delta^{13}\text{C}$ between degradable and recalcitrant SOM.

VIII. Spectroscopic Techniques

A wide range of spectroscopic techniques have been employed in understanding the nature and dynamics of organic matter in soils. The use of such techniques has made it possible to identify different compounds present in soil organic matter based on functional groups. Such techniques are known to be non-abrasive and therefore can provide detailed information on the nature of soil organic materials *in situ*. The most common spectroscopic techniques employed in studies of SOM are solid-state ^{13}C NMR (Nuclear Magnetic Resonance) spectroscopy and pyrolysis-mass spectrometry. These will be covered in this review. Other spectroscopic techniques include Infrared spectroscopy and electron spin resonance spectroscopy.

Solid-state ^{13}C NMR Spectroscopy

The application of NMR spectroscopy to SOM studies appears to have first been carried out by Barton and Schnitzer (1963) in their studies on ^1H NMR of a methylated humic acid. Since then, many studies on the application of ^{13}C NMR spectroscopy to SOM studies have been conducted. Useful reviews regarding the principles and applications of NMR spectroscopy in the study of SOM can be found elsewhere (Ivanova and Randall, 2003; Chukovet al., 2018; Mathers et al., 2000; Preston, 2015).

^{13}C NMR spectroscopy is widely accepted as being one of the most powerful forms of spectroscopy for structural elucidation of complex biomolecules. It offers the possibility of quantification which should allow the relative amounts of carbon in different chemical environments to be determined (Mathers et al., 2000). The great strength of NMR in SOM research is its unique ability to provide information on very complex materials, such as those characterized by low solubility, irregular structures, and strong physical or chemical links to each other or to mineral matter (Preston, 2015). The information provided by NMR spectroscopy can also aid in choosing appropriate methods for conventional chemical analysis, for example, for individual lipids, sugars, or amino acids (Golchinet et al., 1995). Initially, the low sensitivity of the ^{13}C nucleus meant that carbon values above 2% were generally required to obtain spectra with an acceptable signal-to noise ratio (Skjemstad et al., 1996).

However, the development of Fourier-transform (FT) techniques for data acquisition, and CPMAS (Cross-Polarisation Magic-Angle Spinning) methods have further improved the sensitivity of solid-state ^{13}C NMR spectroscopy. Also, Skjemstad et al. (1996) showed that the treatment of a soil sample with a solution of 2% and 10% HF, respectively, can remove mineral matter without significantly affecting the organic component, thereby improving the ^{13}C NMR spectra obtained.

The technique of CPMAS ^{13}C NMR has been applied to a wide range of studies in understanding the processes of SOM decomposition and has produced voluminous information (eg Smernik, 2005; Ivanova and Randall, 2003; Chukovet al., 2018). Probably the most important discovery from ^{13}C NMR spectroscopy is that soil organic matter, in general, contains significant quantities of aliphatic macromolecules which are not carbohydrates, proteins, or low molecular weight waxes. These compounds are often referred to as polymethylene or paraffinic structures.

Other important findings from the application of ^{13}C NMR showed that phenolic carbon is not as dominant a structural feature of soil organic matter as previously thought, and that labile substances such as carbohydrates are only a transitory component of soil organic matter. Using this technique, it has been shown that the most noticeable change in the initial stages of decomposition is a decrease in the ratio of o-alkyl to alkyl C (Mathers et al., 2000). This change is often associated with the loss of the most easily metabolizable carbohydrates and an accumulation of alkyl carbon. The technique has also been used in understanding the structure and dynamics of organic matter in size and density fractions of soils (Golchinet et al., 1995).

Although the use of ^{13}C NMR has produced useful information on SOM studies, the method requires the presence of more carbon than many agricultural soils contain and the results can be obscured by the presence of paramagnetic Fe^{3+} ions (Arshad et al., 1988). Also, in studies of SOM, signals in ^{13}C NMR spectra tend to be broad and overlap. As such, only information on carbon types (eg aliphatic, aromatic, carbonyl etc) can be derived from these spectra. Furthermore, the high cost associated with the equipment required for such analysis makes it of remote accessibility for most soil laboratories.

Pyrolysis-Mass Spectrometry

The technique of pyrolysis-mass spectrometry (Py-MS), as applied to soil organic matter studies, appears to have been pioneered by Schulten et al. (1987). In this technique, the sample is pyrolysed directly under vacuum in the ion source of a mass spectrometer during which weaker bonds in organic compounds are broken by a pulse of thermal energy and the volatile compounds are identified by mass spectrometry. Based on the identified products, the nature of the original macromolecule is inferred. The ratios of the different products obtained give an indication of the degree of humification. Extensive reviews regarding the origin, principles and applications of this technique in SOM studies have been published in recent years (Saiz-Jimenez, 1996).

Pyrolysis-Mass Spectrometry has been applied extensively in the investigation of complex biomaterials, humic substances and forest soils ranging widely in organic matter contents (Schulten et al., 1987). Further improvements in the technique, which include Curie-point Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS), Pyrolysis-Field Ionization Mass Spectrometry (Py-FIMS), and Pyrolysis-Field Desorption Mass Spectrometry (Py-FDMS) have enabled the characterization of molecular subunits of SOM. These techniques are described in detail in Schnitzer and Schulten (1995).

Despite the wealth of information provided by the technique of pyrolysis-mass spectrometry, Saiz-Jimenez (1996) cautioned that pyrolysis data of humic substances are not correctly interpreted, and misunderstandings often occur in pyrolysis papers. The technique can cause drastic modifications of the original building blocks which can lead to incorrect conclusions. The technique considers pyrolysis products as building blocks of the macromolecules from which they were derived. Other studies have failed to confirm this. For example, Derenne and Quenea (2014) found that pyrolysis of plant and soil polysaccharides results in complex pyrolysates containing a wide variety of volatile, relatively low molecular weight compounds. Pyrolysis of cellulose was found to produce carbonyl compounds, mainly aldehydes and ketones of different chain lengths. Based on these results, there is a tendency to conclude that cellulose is a polymer made up of all those compounds identified. Cellulose, however, is known to be a polymer of glucopyranose units linked by β -1,4 linkages, but no such units were found in cellulose pyrolysis products.

These, and many other observations, have shown that interpretations of the chemical nature of biomacromolecules, in the light of information provided by pyrolysis, data is a difficult task.

IX. Oxidation By Potassium Permanganate (KMnO_4)

Solutions of potassium permanganate (KMnO_4) 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 (Hayes and Swift, 1978). An extensive literature dealing with the oxidation of organic compounds by permanganate is given by Stewart (1965). It was Piret et al. (1957, as cited by Hayes and Swift, 1978) who first brought to the attention of soil chemists the usefulness of KMnO_4 solutions in oxidizing soil organic matter when they showed that oxidation of peat by KMnO_4 yielded 12 to 22% of aromatic polycyclic acids. More recently, extensive work in understanding the chemistry of soil organic matter had utilized the oxidizing power of KMnO_4 (Schnitzer and Desjardins, 1964). Most of the work, however, was concerned with identification of the oxidation products of humic and fulvic acids.

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 oxidizable components. Some attempts to carry out studies in this direction had been undertaken by Schnitzer and Desjardins (1964), which however, were based on the use of strong oxidizers for investigation into the chemical structures of humic compounds.

In relatively recent 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 Conteh et al. (1998, 1999) 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 three different concentrations of permanganate.

After detailed experimentation, Blairet 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-oxidized fraction, referred 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, Blairet 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 recent studies (eg Weil et al., 2003; Jensen et al., 2018). Shang and Tiessen (1997) and Conteh and Blair (1998) 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. Conteh et al (1999) showed that

the labile carbon determined by KMnO_4 oxidation procedure gave very good correlations with other measurements of labile carbon in soil.

X. Conclusion

Maintenance of soil organic matter is key to sustainable soil management. This however must be accompanied by reliable methods that can monitor the quality and quantity of soil organic matter in the short and long term. This review has clearly shown that this is not as simple as it sounds. Much work has been accomplished and demonstrated with spectroscopic methods in understanding the nature of soil organic matter, especially the use of ^{13}C NMR spectroscopy and Pyrolysis. These techniques have contributed immensely to the current understanding of soil organic matter. Their use is however lagging in the tropical world, where soil organic matter is of major importance. The use of radioisotopes has provided much information in tracking the decomposition of organic matter in soils. Physical and chemical fractionation procedures have also contributed immensely in isolating the labile component of soil organic matter. Much work remains in ensuring that these techniques become global in their usage.

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Abdul R Conteh. "An Overview of Methods Used In Assessing the Dynamics of Organic Matter in Soils." *IOSR Journal of Agriculture and Veterinary Science (IOSR-JAVS)*, 13(8), 2020, pp. 01-11.