Evaluation of optical techniques for characterising soil organic matter quality in agricultural soils

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ABSTRACT

Soil organic matter (SOM) is one of the main global carbon pools. It is a measure of soil quality as its presence increases carbon sequestration and improves physical and chemical soil properties. The determination and characterisation of humic substances gives essential information of the maturity and stresses of soils as well as of their health. However, the determination of the exact nature and molecular structure of these substances has been proven difficult. Several complex techniques exist to characterise SOM and mineralisation and humification processes. One of the more widely accepted for its accuracy is nuclear magnetic resonance (NMR) spectroscopy. Despite its efficacy, NMR needs significant economic resources, equipment, material and time. Proxy measures like the fluorescence index (FI), cold and hot-water extractable carbon (CWC and HWC) and SUVA-$_{254}$ have the potential to characterise SOM and, in combination, provide qualitative and quantitative data of SOM and its processes. Spanish and British agricultural cambisols were used to measure SOM quality and determine whether similarities were found between optical techniques and ^{1}H NMR results in these two regions with contrasting climatic conditions. High correlations ($p < 0.001$) were found between the specific aromatic fraction measured with ^{1}H NMR and SUVA-$_{254}$ (Rs = 0.95) and HWC (Rs = 0.90), which could be described using a linear model. A high correlation between FI and the aromatics fraction measured with ^{1}H NMR (Rs = −0.976) was also observed. In view of our results, optical measures have a potential, in combination, to predict the aromatic fraction of SOM without the need of expensive and time consuming techniques.

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1. Introduction

1.1. The importance of organic matter

Soil organic matter (SOM) is composed of organic residues that are originated from plant and animal remains and microbial

products at different stages of decomposition or humification (Hur et al., 2013). Additionally, it is one of the main global carbon pools, storing three times more carbon than living organisms or the atmosphere (Fischlin et al., 2007; Brevik, 2012). Aside from carbon sequestration, SOM is also a measure of soil quality because of the beneficial function it has on a variety of soil processes. For instance, it reduces erosion and, therefore, increases crop production by increasing the elasticity and resistance to deformation and compactability as well as porosity and water retention (Sellami et al., 2008; Paradelo and Barral, 2013). Increased water retention decreases potential runoffs by improving water infiltration in to soils and provides a store of water for plant uptake, buffering against moisture and rainfall fluctuations (Lal, 2004). This is of importance considering that the lack of water retention leads to a change in the hydrological patterns of agricultural areas and promotes the quantity and severity of floods and water-led erosion. Also, SOM leads to an increased vegetative cover, which ultimately reduces soil erosion (Cerdà, 1998, 2000; Novara et al., 2011; Zhao

et al., 2013). Carbon mineralisation is crucial in SOM dynamics and along with carbon input, determines how much carbon accumulates in soil and releases nutrients that are essential for plant growth. Factors that affect mineralisation are the size of labile carbon, environmental conditions and the local microbial community (Zhao et al., 2008; Li et al., 2013). SOM and soil assemblage; SOM decomposition and transport by organisms contribute to soil stabilisation and the improvement of soil structure (Brevik et al., 2015). Moreover, SOM quantity has been directly related to the preservation of soil aggregates, which in turn reduces soil erodibility (Novara et al., 2011). Also, the direct processing of SOM along with its decomposition contribute to the improvement of soil chemical properties and stability (Brevik et al., 2015). Therefore, optimal quantities of SOM improve structure, water retention, and nutrient holding capacity of soils, which has an effect in multiple aspects of the soil system. These are essential considering the wider context of Earth System, as SOM conservation techniques have been proven to improve the fertility of degraded soils of a wide variety of ecosystems that are the main resource of large communities of developing areas of our planet, as well as have an influence on biogeochemical cycles and climate change mitigation (Batjes, 2014; Saha et al., 2014; Srinivasarao et al., 2014).

1.2. SOM carbon fractions and their importance

SOM has been conceptualised as containing three pools, with different residence/turnover times (Trumbore, 2000). These pools are the active SOM (living biomass of microorganisms and partially decomposed residues; associated with 1 year turnover); the slow SOM (resistant plant material; associated to a turnover from years to centuries); and passive SOM (humic substances and inert organic matter), which has been traditionally associated with longer residence time (thousands of years) and more stability. Some authors consider that the inert organic matter should not be considered as part of the passive pool, but as a fourth pool (Trumbore, 1997; Ohno, 2002; Agren and Bosatta, 2002; Sparks, 2003; Bell and Lawrence, 2009; Dungait et al., 2012). Although the traditional view has been that decomposition led to complex molecules that were very stable as a result of their structure; it has recently been known that environmental conditions, organo-mineral associations and other processes influence more in SOM stability than structure, which only plays a secondary role. As a result of this new view, recent research has found that humic substances, which have always been considered high molecular mass polymers, could be simpler than originally thought (Kleber and Johnson, 2010; Schmidt et al., 2011). Still, their structure is on discussion and the separation of SOM into fractions with different turnovers remains a major challenge (Kleber, 2010; Schmidt et al., 2011; Schrumpf and Kaiser, 2015).

Non-humic substances are composed by microbial biomass, decomposable plant material (active SOM); and resistant plant material, mainly waxes, lignified tissues and polyphenols (slow SOM) (Dungait et al., 2012). Microbial biomass has been used for comparing natural and degraded ecosystems and as an early indicator of soil processes, fertility and health (García-Gil et al., 2000; Brevik, 2009; Chen et al., 2013).

1.3. Current SOM quality measurements. Challenges

Measures such as % organic matter measured by loss of ignition (LOI) are useful, popular and inexpensive methods to determine bulk SOM (Luke et al., 2009; Salehi et al., 2011). However, some studies have concluded that bulk SOM measurements cannot be used, on their own, as a representative indicator of carbon in soil due to their limitations (Koarashi et al., 2005; Salehi et al., 2011).

Humic substances have also been measured to determine soil quality, as their presence has been associated with a higher quality of soils as stated in Section 1.2. Their study is relevant in agricultural soils, as they increase crop yield and root dry weight, although this response is not fully understood (Rose et al., 2014). Therefore, the determination and characterisation of humic substances gives essential information of the maturity and stresses of soils as well as of their health.

Traditionally, alkali and acid abstraction methods have been used, to later interpret the chemistry of the extracted functional groups (Olk and Gregorich, 2006). Afterwards, these were combined with other complex techniques that enabled scientists to obtain new information on the structure and dynamic associations of humic substances (Sutton and Sposito, 2005; Schmidt et al., 2011). Despite these advances, SOM dynamics and cycling still have many questions to answer, with models differing in SOM fluxes results for the future, due to their sensitivity to SOM turnover time assumptions (Schmidt et al., 2011). There are a number of powerful but complex and expensive techniques that have been used for the study of soil fluxes (Helal et al., 2011). The economic resources needed, along with the time required to prepare the samples and conduct the analyses, make its use with a large number of samples difficult and delays experiments, while more work is still needed to accurately determine and define the molecular structures and linkages between the SOM components (Weishar et al., 2003; Helal et al., 2011 Helal et al., 2011).

Nuclear magnetic resonance (NMR) spectroscopy is a non-destructive technique that is valuable for the characterisation of SOM and humification processes, providing information on static and dynamic properties of molecules. This is due to its high performance to assess intermolecular interactions. The relationship between SOM, contaminants and metals can also be studied with NMR (Cardoza et al., 2004). Of the various variants that exist, ^{1}H NMR spectroscopy was used in this study. This technique analyses humic and fulvic acids dissolved in neutral or alkaline solutions to characterise the components of the substance, and gives a semi-quantitative notion of aromatic, aliphatic and carboxylic groups (Hemminga and Buurman, 1997). One of the main drawbacks of this technique is the quantity of economic resources that are necessary for its regular application in research laboratories/centres. This is due to the expensive deuterated solvents and NMR tubes, as well as the expensive equipment and significant sample preparation that are required (Weishar et al., 2003 Cardoza et al., 2004; MIT, 2008). Also, the technique is time consuming not only when measuring, but when interpreting 2-D or 3-D data resulting from it (Cardoza et al., 2004). Simpler methods for the characterisation of SOM are required.

1.4. Proxy measures. Opportunities to improve the ability to characterise SOM quality

Water extractable carbon is the most active component in the carbon cycle. Its quantity and biological nature is affected by the extraction temperature (Bu et al., 2010). Hot-water extractable carbon (HWC) contains simple compounds such as microorganisms, soluble carbohydrates and other compounds that account for the labile fraction of SOM (Ghani et al., 2003). HWC responds to land use changes in the short term and has been used to detect the effects of different land management practices and for determining the effects of soil amendments such as biochar or agricultural residues (Leifeld and Kogel-Knabner, 2005; Uchida et al., 2012; Alburquerque et al., 2014; Fernández-Romero et al., 2014). For these reasons, it has been proven useful to obtain information about soil quality (Ghani et al., 2003; Xue et al., 2013).

Fluorescence has become popular because of its potential to characterise SOM and study humic substances, as it is non-