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Review paper

Some concepts of soil organic carbon characteristics and mineral interaction from a review of literature

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ABSTRACT

In the past decades, the molecular structure of soil organic carbon (SOC) has been regarded as a pivotal criterion for predicting organic carbon (OC) turnover in soils. However, newly emerging evidence indicates that molecular structure does not necessarily predetermine the persistence of OC in soils and that environmental factors (e.g., soil structure, availability of resources and diversity of microorganisms) exert an additional influence upon SOC turnover. Among these potential factors, adsorption to soil minerals and occlusion within soil aggregates have been universally demonstrated to shield SOC from decomposition. In this review, we identified the uncertainties involved in examining the turnover of specific SOC fractions (lignin, humic substances (HS), coal and black carbon (BC)) in soils. Moreover, we concluded that the role of minerals in SOC adsorption and stability depends on the mineralogy, chemical properties of SOC and soil conditions. Characterization of SOC chemical composition in different soil size fractions (e.g., sand, silt and clay) shows that different-sized minerals potentially protect different types of SOC. Aromatic C may be adsorbed to minerals in the coarse silt/sand fractions and preserved there, while fine-sized (fine silt and clay) minerals generally associate with microbial-derived SOC. Finally, by tabulating the data from the ^{13}C turnover time and ^{14}C ages of bulk SOC and specific SOC fractions (carbohydrate, lignin, aliphatic C, HS, and BC), we obtained further validation that molecular structure does not exclusively determine the turnover rate of OC in soils. Furthermore, the ^{13}C turnover time and ^{14}C age of SOC consistently increased with increasing soil depth, which may be partially attributed to the larger protective potential of SOC by minerals and the unfavorable conditions for biodegradation in the subsoils. Because the limitations of ^{13}C and ^{14}C-dating techniques have largely been neglected, they are emphatically discussed in this review. It is suggested that more geomorphic and spectroscopic evidence is paramount to further explore the mechanisms underlying the persistence of OC in soils.

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1. Introduction

Soil organic carbon (SOC) represents the largest pool of terrestrial C, with an average content of 2400 Pg to a soil depth of 2 m, which is 3.2 times the atmospheric pool and 4.4 times the biotic pool (Sparks, 2003). Due to the size of the SOC pool, even small changes in the global SOC stocks could significantly affect the concentrations of atmospheric CO_2 (Lal, 2004; Smith, 2008). It has been postulated that increasing SOC concentrations in the soils at depths of up to 2 m by 5–15% could decrease atmospheric CO_2 concentrations by 16–30% (Baldock, 2007). Therefore, understanding the mechanisms underlying the storage and stability of organic carbon (OC) in soils has drawn considerable attention.

The chemical characteristics of plant litter (e.g., the concentrations of nitrogen (N) or lignin) have been thought of as vital factors for determining initial decay rates, which has led to the idea that molecular structure alone could create ‘stable’ SOC (SOC whose molecular composition, concentration or both remain constant for extended periods of time) (Tenney and Waksman, 1929; Melillo et al., 1982). However, many studies have doubted the overriding importance of molecular structure in SOC persistence as advances in isotopic tracer techniques and various spectroscopic methods have been made (Mayer and Xing, 2001; Kleber et al., 2011; Basile-Doelsch et al., 2015). For instance, many authors found that the ‘stable’ C pool contains large amounts of structurally labile organic substances, such as polysaccharides and proteins (Gleixner et al., 2002; Kiem and Kögel-Knabner, 2003; Knicker, 2004). Moreover, these easily metabolizable polysaccharides showed old radiocarbon (^{14}C) ages. Several reports have indicated that organic coatings on mineral surfaces typically turnover slower than bulk C and are often depleted in aromatic structures and enriched in highly labile C (Wattel-Koekkoek et al., 2003; Kleber et al., 2005). Such observations reflect that the molecular structure of the input SOC cannot exclusively dominate the C cycling in soils (Marschner et al., 2008; Kleber, 2010). Therefore, other explanations have been proposed to explain the existence of old C (Baldock and Skjemstad, 2000; Lützow et al. (2006); Kögel-Knabner et al., 2008). Sollins et al. (1996) identified the three following mechanisms: (1) molecular characteristics of soil organic substances (‘recalcitrance’), (2) ‘low accessibility’ to microorganisms and enzymes, and (3) interactions with organic or inorganic materials. By contrast, Krull et al. (2003) suggested that the mechanisms should be divided into two categories, ‘biochemical recalcitrance’ and ‘physical protection’. Lützow et al. (2006) reviewed that all hypotheses fitted into three categories responsible for the delayed decomposition of SOC, namely ‘selective preservation’, ‘spatial inaccessibility’ and ‘interactions with surfaces and metal ions’. Although the mechanisms controlling SOC stability were summarized in a different way, the crucial role of association with soil minerals has been recognized by most researchers (Sørensen, 1969, 1972, 1975; Torn et al., 1997; Six et al., 2002; Chenu and Plante, 2006; Lützow et al., 2006; Wang et al., 2014; Throckmorton et al., 2015).

In this case, we conducted an extensive review of the international literature to provide an overview of the findings on the impacts of the molecular structures of OC and soil minerals on the stability of OC in soils. The three following principal issues were addressed: (1) SOC stability as defined according to molecular structure (2) the role of soil inorganic particles in SOC stability and its potential influence factors, and (3) SOC stability predicted by ^{13}C turnover time and ^{14}C age. In our review, changing information regarding the mechanisms for the persistence of four typical organic molecules with structural complexity (lignin, humic substances (HS), coal and black carbon (BC)) is presented, and ambiguous issues and potential lines of research for further examining the fates of these organics are suggested. In addition, possible factors that affect the potential of minerals to protect SOC from decomposition are discussed. We also summarize currently available data regarding the turnover of bulk SOC and specific OC fractions based on ^{13}C and ^{14}C techniques to reexamine whether molecular structures affect SOC stability. Finally, the uncertainties involved in ^{13}C turnover time and ^{14}C age, which are frequently but not critically used in most studies to predict OC turnover in soils, were also identified.

2. Soil organic carbon stability as defined according to molecular structure

OC in soils varies widely in composition, from newly deposited bits and pieces of biopolymers, to moderately aged HS, to well-aged coal, and naturally and anthropogenically altered BC (Senesi et al., 2009). Previously, some characteristics of chemical composition, such as alkyl-C or aromatic C content, were widely related to the decomposition rates of SOC (Melillo et al., 1982). One common hypothesis is that the decomposition rates of SOC can be predetermined by their molecular structures. The older ^{14}C ages of SOC with complex structures in soils have been considered to support this conclusion (Sollins et al., 1996). However, the old ^{14}C ages of SOC could be obtained using various processes independent of molecular structure that have recently been reviewed by Marín-Spiotta et al. (2014). To date, the increasing number of studies that challenge the dominant role of molecular structure in SOC cycling has gradually drawn greater attention (Kögel-Knabner et al., 2008; Berhe et al., 2012; Berhe and Kleber, 2013; Basile-Doelsch et al., 2015; Fang et al., 2015; O'Rourke et al., 2015). Particularly, readily biodegradable SOC (e.g., carbohydrates and proteins) has been recorded to persist for long periods of time in the soil (Berhe et al., 2012). Here, we briefly describe changes in our understanding of the roles of molecular structure in controlling the stability of typical SOC fractions (Table 1) and, more importantly, identify the ambiguous issues and/or possible lines of future research.

2.1. Lignin

Lignin is a major constituent of plant-synthesized compounds of terrestrial origin and represents nearly 30% of the C sequestered in plant materials annually (Senesi et al., 2009). It is a large insoluble, amorphous heteropolymer that consists of phenylpropane units, and contains no hydrolyzable bonds (Guillén et al., 2005). The involvement of lignin in the genesis of HS has been early popularized by Waksman (1936) and his colleagues. However, some

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