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 the 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

Table 1
Historical views and recent findings about the correlations between molecular structure and persistence of soil organic carbon (SOC) (Kiem and Kögel-Knabner, 2003; Kleber, 2010; Keith et al., 2011; Berhe et al., 2012; Dungait et al., 2012; Marín-Spiotta et al., 2014).

Compound	Historical views	Recent findings
Carbohydrate	Carbohydrates and proteins are usually considered rapidly metabolized due to their labile molecules	Carbohydrates and proteins are preserved in soils through association with inorganic soil particles
Lignin	Lignin persists in soils because of its non-hydrolyzable C−O−C and C−C bonds and the abundance of aromatic structures	Under favorable conditions, lignin can be mineralized within a relatively short period
Lipid	Lipids have a higher resistance to microbial degradation owing to their a polar chemistry	With a plenty of oxygen and a way to bridge between substrate and decomposer, lipid is by no means able to resist decomposition
Humic substance (HS)	Persistence of humic acids results from complex, aromatic structures	Other environmental variables may control the degradation of HS
Black carbon (BC)	With highly condensed aromatic structures, BC can persist in soils with an exceedingly long time, up to millennia	The persistence of BC is a function of environmental conditions and is much more labile than previously reported

investigators (Kononova, 1961; Orlov et al., 1975) had clearly refuted Waksman's ligno-protein theory. They suggested that lignin could be decomposed or altered in soils by microorganisms, which is in line with little lignin found in soils (Rumpel et al., 2002; Kiem and Kögel-Knabner, 2003; Thevenot et al., 2010; Dungait et al., 2012). Despite of the low abundance of unmodified lignin in soils, some litter studies still interestingly showed the lignin and lignin to N ratio effects on decomposition rates of plant residues. For example, Yanni et al. (2011) reported that plant lignin is good predictor of CO_2 production and N mineralization potential. Talbot et al. (2012) highlighted that litter decay rates are correlated with the initial value of lignin: N or that of lignin: cellulose of the litter, which suggests that interactions between lignin and more labile compounds are important controls over litter decomposition. Similarly, Zhou et al. (2008) showed that initial C/N and N/P ratios are demonstrated to be important factors regulating litter decomposition rate. With respect to the effect of lignin on decomposition, Austin and Ballaré (2010) clearly concluded that lignin has a dual role affecting litter decomposition, which depends on the dominant driver (biotic or abiotic) controlling C turnover.

The lignin contents in litter and soils are mainly measured by alkaline CuO-oxidation. However, due to the interactions of lignin-derived phenol with minerals (Kaiser et al., 2004), CuO-oxidation method potentially involves profound uncertainties to measure lignin-derived phenols in mineral matrixes, which has been described by Hernes et al. (2013). These authors tested the potential irreversible binding of lignin extracted from 3 types of plant litter (blue oak, foothill pine, and annual grasses) to 5 minerals (ferrihydrite, goethite, kaolinite, illite, and montmorillonite) using the CuO oxidation technique and observed that up to 56% of sorbed lignin-derived phenols could not be extracted from the minerals. Based on this research, CuO oxidation can only capture a fraction of lignin-phenols compounds in mineral soils. In addition, most observations on the amounts of aromatic components in mineral soils rely on cross polarization magic angle spinning ^{13}C nuclear magnetic resonance spectroscopy (CP-MAS ^{13}C NMR), an approach that is relatively insensitive to aromatic compounds (Ernst et al., 1987) unless careful pretreatments, such as demineralization techniques, are taken to remove paramagnetic minerals that are tightly associated with organics (Schmidt et al., 1997). However, demineralization of mineral soil samples by hydrofluoric acid (HF) results in the loss of any mineral-bound soluble SOC (Hernes et al., 2013), and may not be beneficial for tracking lignin-derived phenols that may bind strongly to mineral phases and have solubility of several hundred mg/L (Hernes et al., 2007). The limitations within these analytical methods would, to some extent, obscure the exact storage and turnover of lignin-derived phenols in mineral soils and litter.

2.2. Humic substances

Relying on simple extraction with alkalis and acids, HS were obtained from soils as 'humic acid (HA), fulvic acid (FA) and humin (HM) by soil chemists (Olk and Gregorich, 2006). HM is assumed to contain large, complex macromolecules that persist for decades and is equated to the most stable SOC fraction (Dungait et al., 2012). However, these fractions are operationally defined and may be chemically and physically different from the actual organic materials that occur in the soil (Berhe et al., 2012). In fact, rather than forming a macromolecular complex, HSs have been considered as molecular associations of small biomolecules bound through intermolecular interactions (Piccolo, 2001). Hydrophobic interactions and hydrogen bonds are major mechanisms that are responsible for the formation of HS with a large molecular size (Piccolo, 2001). Hence, environmental variables that can affect the formation of hydrophobic interactions and hydrogen bonds may change the steric-chemical arrangement of HS and alter the structural stability of HS. For example, when simple organic molecules penetrate large hydrophobically bonded associations of HS, the structural stability of HS can be disrupted (Piccolo et al., 1996). Thus, the structural stability of HS is relative rather than absolute. Besides, other controls (e.g., mineral and fire) may influence the persistence of HS. For example, strong binding of HA to clay particles and the persistence of HA due to sorption were reported by Senesi et al. (2009). Several authors documented that the oxidation of BC may be one of mechanisms of HA formation and that such HAs are referred to as pyrogenic HAs in areas with a high incidence of fire and, subsequently, high oxidation rates (e.g., volcanic soils) (Haumaier and Zech, 1995). The aromatic C within pyrogenic HAs can be derived from BC, whose aromatic structure is highly condensed, and thus predictably, pyrogenic and non-pyrogenic HAs vary regarding molecular structure, potentially leading to that different mechanisms dominate their stability in soils. Currently, few researchers have carefully considered the origins of HAs (pyrogenic or non-pyrogenic HAs) when studying the persistence of HAs in soils.

2.3. Coal

Coal is a combustible sedimentary rock formed by lithification of plant debris, and mainly contains C, oxygen (O), sulfur (S), and N and various trace elements, which vary in abundance depending on the specific conditions of coal beds (Crowell, 2000; Smith et al., 2013). The specific formation process of coal has been elegantly reviewed (Abraham and Royo, 1973; Ussiri et al., 2014). According to the standard classification by American Society of Testing Materials (ASTM), coal can be divided into four classes: anthracite

(hard coal), bituminous, subbituminous coal and lignite (brown coal) according to the decrease of rank (Smith et al., 2013). As the rank increases, the aromaticity and hydrophobicity of coal gradually increase probably owing to the gradual elimination of polar groups (e.g., OH- and COOH-) during coalification (Krevelen, 1993). However, there exist significant variations in properties amongst coals of the same rank, caused by differences in the assemblage of plant constituents that formed from the original peat-forming vegetation and other factors (e.g., geological settings, age and coalification history) (Given, 1984; Ussiri et al., 2014).

Mine soils are the soils formed on landscapes altered by surface mining activities (Ussiri and Lal, 2005). Some regions in the world can be rich in this type of soil due to a large number of mining activities. Coal makes up a large percentage of SOC in mine soils formed from reclamation of surface mining of coal (Ussiri and Lal, 2005; Shrestha and Lal, 2006). For instance, lignite-C accounted for 25–99% of the total SOC in rehabilitated and reforested mine soils in Lusatia mining district (Rumpel et al., 1999). Schmidt et al. (1996) reported that coal accounted for 80% of the OC in the surface soils of cultivated Mollisol contaminated by brown coal emissions from a briquette factory. Thus, when the mine soils are to be managed for the reduction in CO_2 emission into the atmosphere, it could be particularly interesting to know the turnover of coal-derived OC in mine soils. Compared to recent OC, OC in coal is relatively inert to microbial degradation and highly resistant to thermal and chemical oxidation (Rumpel et al., 2000; Schmidt et al., 2000; Ussiri et al., 2014). The resistance of coal to decomposition may be a result of their predominantly aromatic structure formed during the coalification process and the inaccessibility of the small pores in the coal matrix to microorganisms (Cohen and Gabriele, 1982). However, the degree of resistance of coal is rank-dependent (Ussiri et al., 2014). In general, coals of lower rank (e.g., lignite) are more effectively decomposed by microorganisms. It has been identified that lignite could be decomposed not only in the early stages of mine soils, but also in the older stages where recent OC accumulated (Rumpel and Kögel-Knabner, 2002). The difference in ability to resist decomposition is likely brought about by the different degree of aromaticity and hydrophobicity and other factors. In general, the contents of volatile matter and O in coals follow in the order of anthracite < bituminous coal < subbituminous coal ≤ lignite (Spokas, 2010). Both volatile matter and O have been considered to exert an impact on short-term microbial activity (Clough et al., 2010; Spokas, 2010). For example, Reiss (1992) noted that the volatile matter plus O contents were the principal factors positively influencing the intensity of microbial decomposition of coal. Guillén (2002) recorded that some portions of the volatile organics can be utilized by the soil microbial community as a food source. Based on these, in addition to the relatively low aromaticity and hydrophobicity, the high contents of volatile matter and O may also contribute to the decomposition of lignite by microorganism.

Mine soils, as complex matrices, may also include mineral protected organic compounds (Kleber et al., 2014). As identified by Vassilev and Vassileva (1996), there is a variety of minerals in coals, such as clay minerals, carbonates, oxides, and silicates. The presence of manganese oxides, carbonates, and other protective mineral phases can reduce the efficiency of OC removal from soils by chemical reagents (Ussiri et al., 2014). Furthermore, lignite may be enriched in mineral horizons. Rumpel et al. (2003) showed that lignite accounted for 80–93% of the total C in the top mineral horizon of the age-chronosequence series of mine soils ranging from 11 to 32 years old at Lusatian mining district. As summarized by Huang et al. (2014), lignite contained surface reactive functional groups such as hydroxyl groups, the carboxyl groups, the methoxyl groups and carbonyl groups. These reactive functional groups could

offer lignite opportunities to interact with minerals, in turn, influencing its decomposition in soils. In addition, lignites from different origins may have different OC quality, and weathering processes can also considerably affect chemical functions of lignite from outcrop or mine overburden soils (Clouard et al., 2014). This variability in chemical functions may therefore modulate the interactions of such fossil C with minerals. As a result, it is necessary to conduct the study on the impact of minerals on the stability of lignites from different origins or suffering from different degree of weathering. However, few studies evaluate the effects of mineralogical properties of coal itself and soil on the resistance of coal-derived OC to biological or chemical decomposition.

2.4. Black carbon

BC, the solid residue from incomplete combustion, is increasingly being added to soils or sediments due to natural vegetation fires, anthropogenic pollution, and strategies for C sequestration ("biochar") (Preston and Schmidt, 2006; Keiluweit et al., 2010). Despite differences in analytical methodologies, current estimates of the amount of natural BC range from 10 to 45% in prairie and agricultural soils (Schmidt et al., 1999), 10–60% in forest soils (Ponomarenko and Anderson, 2001), and 3–15% in ocean sediments (Gustafsson and Gschwend, 1998). Due to its highly condensed structure, BC has been reported as the least bioavailable component of SOC (Marín-Spiotta et al., 2014). Nevertheless, the stability of BC in soils has recently been suggested to be exaggerated, which was illustrated by Jaffé et al. (2013), who showed that dissolved BC can contribute up to 10% of riverine dissolved OC (DOC) flux. In the meantime, observational evidence for decomposing BC has continuously emerged. For instance, BC deposited approximately 6000 years ago appears as a highly aromatic core surrounded by a highly functionalized outer layer surface where microbial degradation has occurred (Lehmann et al., 2005). Hofrichter et al. (1997) suggested that the degradation of BC could be caused by the physical breakdown of the BC structure, which could be initiated by fungal hyphae entering microscopic cracks and crevices. This physical breakdown of BC would allow extracellular enzymes (e.g., Mn-peroxidase, lignin-peroxidase and laccase) the opportunity to attack the surface region of BC (Willmann and Fakoussa, 1997; Czimczik and Masiello, 2007). Moreover, Hamer et al. (2004) concluded that, with the addition of glucose, BC mineralization would be enhanced to some extent. These findings imply that the decomposition of BC occurs and could be accelerated by the extra supply of fresh substrates.

The contradictions in the persistence of BC in soils potentially resulted from the different formation conditions of BC, such as, heterogeneity of the starting materials (e.g., biomass and fossil fuel), pyrolysis conditions (Liang et al., 2008; Wang et al., 2015) and other environmental variables (e.g., climate, soil aggregation, mineralogy and biological activity) (Masiello, 2004), as well as the use of different methods to assess decay rates. It is well established that the degree of condensation of aromatic C in anthropogenic BC (biochars) varies depending on the biomass feedstock and pyrolysis/charring temperature (Keiluweit et al., 2010). Consequently, the resulting biochars may be mineralized at different rates. Singh et al. (2012) conducted a long-term (5 years) incubation study under controlled conditions using 11 biochars produced from 5 C_3 biomass feedstocks (eucalyptus saligna wood, leaves, papermill sludge, poultry litter, and cow manure) at 400 °C and/or 550 °C. Their data showed that the C in manure-based biochars was mineralized faster than that in plant-based biochars at the same temperature. Nguyen and Lehmann (2009) mentioned that the higher levels of mineral nutrients in the manure-derived biochars could cause defects in the core of the biochar C structures, reducing the degree of

directly linked organic structures and the stability of biochars. Soot, another typical type of BC, is a secondary combustion product of fossil fuel (e.g., coal) under pyrolysis conditions (without O) at temperatures above 700 °C. Its atomic H/C ratios of <0.3 were determined (Senesi et al., 2009), which are in accordance with highly condensed aromatic network suggested by Sergides et al. (1987). Due to its highly condensed structure, soot can survive under harsh thermal and chemical oxidation (Skjemstad et al., 2002) and even would remain in soils for thousands of years (Major et al., 2010).

Considering anthropogenic BC and the BC generated from natural wildfires or lava flow, the long-term persistence of BC in soils may be also affected by interactions with minerals. By investigating the distribution of BC in soil density fractions, Glaser et al. (2000) found that a large portion of BC was embedded within iron and aluminum oxide plaques on mineral surfaces. Qian and Chen (2014) examined the interactions of aluminum with BC and oxidized BC and observed that carboxylic functional groups on BC surfaces could serve as binding sites for Al^{3+}. Furthermore, an increasing number of authors suggested energetically strong adsorption mechanisms between the aromatic π-systems of organic compounds and the sorption sites at the mineral surfaces (Keiluweit and Kleber, 2009). Moreover, SOC and soil BC abundances are usually correlated (Czimczik and Masiello, 2007; Vasilyeva et al., 2011), which indicates that BC is preserved through processes that are similar to those that preserve native SOC, whose persistence partially results from sorption to minerals (Krull et al., 2003). Consequently, it is possible that binding with soil minerals is one mechanism that can be used to extend the period of BC remaining in soils, while several questions regarding the interaction mechanisms of BC with minerals are largely elusive but significant. For example, a few studies indicated that "BC-mineral interactions may stabilize partially oxidized BC in soil" (Hilscher and Knicker, 2011; Keith et al., 2011; Singh et al., 2012). However, it is unclear if this suggests that the oxidative functional groups of BC offer sorption sites for minerals. If this is the case, because BC generated under high heating temperatures (>700 °C) generally exhibits highly condensed aromatic structures and very low polarity (Lützow et al., 2006; Keiluweit et al., 2010), the stability of this fraction of BC would benefit little from adsorption to minerals and may be governed by its own molecular structures unless it remains in soils for a certain period and is oxidized. In natural soil ecosystems, the presence of BC at different oxidation stages is expected, which could differ with structural properties (e.g., polarity, aromaticity and aliphaticity) and association with different types of mineral.

Although some issues remain partially known, the aforementioned arguments show that molecular structure does not exclusively predetermine the persistence of SOC in soils. A comprehensive analysis by Lützow et al. (2006) shows that the roles of molecular structures in SOC are only important during early decomposition and in active surface soils, which has also been supported by other reports (Six et al., 2002; Rovira and Vallejo, 2007). Then, the following fundamental conundrum was articulated: what other factors would additionally regulate the persistence of SOC? Gathering a new generation of research on this topic, the role of soil inorganic particles in protecting SOC from decomposition has been widely accepted (Sørensen, 1969, 1972, 1975; Marín-Spiotta et al., 2014; Throckmorton et al., 2015).

3. The role of inorganic particles in soil organic carbon stability

The positive influence of soil inorganic particles on the stability of OC in soils can be achieved by organic-mineral sorption or physical isolation of SOC within aggregates. Previously, exhaustive
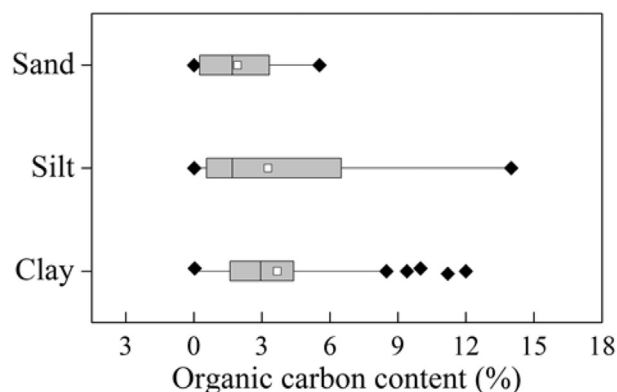
Fig. 1. The amount of soil organic carbon (SOC) associated with clay or silt or sand in different soils with different textures. Data points: thin horizontal lines, 10th and 90th percentiles; box, 25th and 75th percentiles; central vertical line, median; central square, mean; black points, outliers beyond the 10th/90th percentiles. The data in this figure are presented in Table S1.

studies have been conducted to quantify the amount, composition and dynamics of OC preserved by minerals or aggregates (Chenu and Plante, 2006; Mastrolonardo et al., 2015; Rumpel et al., 2015). The classification of organic-mineral interactions and entrapment within aggregates has been proposed by different authors in different ways. For example, several researchers consider the formation of organo-mineral complexes to be physical protection (Krull et al., 2003), while others use chemical or biochemical protection to represent the same mechanisms (Six et al., 2002). Here we avoided classifying organic-mineral interactions or entrapment within aggregates into physical, chemical or biochemical protection mechanisms in the following discussion.

3.1. Adsorption of soil organic carbon to minerals and potential influence factors

The much lower mineralization of mineral-associated OC relative to free OC has been frequently reported in the literature, highlighting the potential importance of minerals on the stability of OC in soils (Aoyama et al., 1999; Six et al., 2002; Kleber et al., 2005; Chenu and Plante, 2006; Kang and Xing, 2008; Bol et al., 2009). It has become increasingly clear that the sorption of minerals around SOC can shield SOC from microbial attack by placing a physical barrier between SOC and the decomposer (Kleber et al., 2005; Rasmussen et al., 2005; Wissing et al., 2014). Based on the concept that soil mineral particles of different size vary with mineralogical composition and are associated with SOC in their specific patterns, particle size fractions can be used to identify the amounts and composition of SOC preserved by minerals (Christensen, 1992). In this review, the data of the amount of SOC associated with clay or silt or sand in different soils with different textures were tabulated in Table S1 and presented in Fig. 1. It is found that the contents of OC associated with clay, silt and sand ranged from 0.042 to 12%, 0.012–14%, and 0.010–5.54%, with averages of 3.68%, 3.27% and 1.93%, respectively. The relatively higher OC concentrations present in the clay fractions are generally considered to result from the larger surface area (SSA) of clay minerals (Kennedy et al., 2002). In addition, the SSA of mineral phases is considered a promising indicator of the potential of soil (Kiem and Kögel-Knabner, 2002) and marine sediments (Mayer, 1994) for C storage. However, multiple lines of emerging evidence suggest that SSA does not control the amount of OC preserved by minerals (Krull et al., 2003; Kleber et al., 2004; Knicker, 2004; Kögel-Knabner et al., 2008; Hanke et al., 2014). Particularly, SOC

is not evenly distributed over the available mineral surface (Kahle et al., 2003). In fact, several observations showed (Krull et al., 2003) that mineralogy exerts an additional effect on the content of SOC preserved by minerals. For instance, the reports by Kahle et al. (2003) and Kleber et al. (2004) showed that the higher Fe oxide densities in the coarse-clay versus fine-clay fractions corresponded well to higher OC loading in the coarse-versus fine-clay fractions, which implied that reactive surface sites affect the ability of minerals to preserve OC.

3.1.1. Reactive surfaces sites of minerals

The reactive surfaces sites are different among the three typical types of minerals (1:1 versus 2:1-layer-typed phyllosilicates versus Fe/Al oxides), which offer diverse adsorbing possibilities for SOC. In general, smectites have larger SSAs and higher cation exchange capacities (CEC) than kaolinites (Greenland, 1971), which partially accounts for that higher SOC contents had been detected in smectites (Greenland, 1971; Six et al., 2002). Apart from the differences in SOC load, the chemical composition of OC associated with kaolinite is different from that of smectite-bound OC. However, information regarding the chemistry of smectite- and kaolinite-bound SOC is often conflicting. For instance, kaolinite-bound OC was observed to contain greater concentrations of polysaccharides than smectite-associated OC, which is rich in many types of aromatic compounds (Wattel-Koekkoek et al., 2001). By comparison, Feng et al. (2005) suggested that the kaolinite surface prefers higher-molecular-weight components compared with the smectite surface. The revealing OC-clay interactions may be difficult because the existence of the clay particles is very sensitive to the environmental conditions (e.g., soil-available moisture and weathering degree) (Singer, 1980; Velde, 1992; Khormali and Abtahi, 2003). Extensive literature on the turnover rates of bound-OC by kaolinite and smectite has also been addressed. Several researchers (Balesdent et al., 1988; Theng et al., 1992; Wattel-Koekkoek et al., 2003) have consistently proposed that smectite-associated SOC generally has a lower turnover rate than kaolinite-associated SOC. For instance, Wattel-Koekkoek et al. (2003) reported that the OC associated with smectite and kaolinite in natural savanna systems had different turnover rates, with averages of 1000 and 360 years (^{14}C age), respectively. However, their investigated samples originated from 7 different countries with different local climates and vegetations. To eliminate the geographical effect, Wattel-Koekkoek and Buurman (2004) focused on samples from one region and observed that kaolinite-bound SOC did not differ significantly from smectite-bound SOC.

Fe/Al oxides are another type of minerals and provide most of the reactive surface sites onto which OC can be adsorbed. These oxides occur in many acidic soils and are characterized by surfaces that are inhabited by single coordinated hydroxyl groups (Kögel-Knabner et al., 2008). Currently, large amounts of experimental data indicate that Fe/Al oxides can serve as an efficient 'rusty sink' for SOC (Mikutta et al., 2006), which is best illustrated by the positive correlation between the Fe/Al oxides content and OC content in the bulk samples and the particle size fractions of various soils (Kaiser and Guggenberger, 2000). Moreover, Fe/Al oxides are suggested to be stronger stabilizers for SOC than smectites and kaolinites in most acid soils (Chorover and Amistadi, 2001). For instance, once Fe oxides are removed, clay fractions have weaker SOC adsorption in acid soils (Kaiser and Guggenberger, 2000). Thus, the extent by which acidic soils can inhibit SOC decomposition is assumed to depend on the Fe/Al oxide content. The significance of Fe/Al oxides in the persistence of SOC has partly been attributed to their physiochemical properties: (1) such minerals provide dense hydroxyl sites that allow organic acids to be strongly and efficiently adsorbed by mineral surfaces to form

associations via co-precipitation (Lalonde et al., 2012) or ligand exchange, which has been proposed as one of the energetically strongest associations between SOC and mineral surfaces (Eusterhues et al., 2005; Kleber et al., 2005; Mikutta et al., 2006; Kang and Xing, 2007, 2008), (2) micropores (<2 nm) and small mesopores (2–10 nm) of Fe/Al oxides can offer extra sorptive sites for SOC and increase reactivity (Kaiser and Guggenberger, 2003). However, crystalline Fe/Al oxides display smaller SSA and have lower hydroxyl site densities than poorly crystalline Fe/Al oxides (Bracewell et al., 1970). As a result, poorly crystalline Fe/Al oxides are better predictors of stable SOC content in acid soils than crystalline Fe/Al oxides. Moreover, poorly crystalline Fe/Al oxides were reported to be particularly rich in acid subsoils (Kleber et al., 2005). According to these, it is reasonable that the capacity of a given mineral matrix for shielding OC in acid subsoils against biological attack could be expressed as a function of the poorly crystalline Fe/Al oxide content in the soil, which has already been demonstrated in the subsoil horizons of temperate forest and grassland soils in the USA (Torn et al., 1997; Rasmussen et al., 2005) and Germany (Spielvogel et al., 2008). However, it should bear in minds that Fe oxides may be short lived in soils. For example, when soils become water saturated, the microorganisms that normally use oxygen as the terminal electron acceptor for OC oxidation will change over to other electron acceptors such as Fe and Mn (Stumm and Sulzberger, 1992). This may result in the reductive dissolution of Fe oxides, followed by a release of associated substances (Davranche and Bollinger, 2000), including SOC (Grybos et al., 2009). Nonetheless, the actual processes have not yet been studied in detail.

3.1.2. The properties of soil organic carbon

Apart from the types of minerals, the sorption of OC to minerals also depends on the properties of SOC (Berhe et al., 2012). Spielvogel et al. (2008) indicated that the composition of OC that is readily adsorbed by clay minerals may be distinct. Detecting the chemical composition of SOC in particle size fractions may help identify which categories of organic compounds would be preserved by minerals in given soil size factions. Table 2, which contains the solid-state ^{13}C-NMR structural parameters of the OC in the four investigated soils, shows the high percentages of alkyl C and O/N-alkyl C throughout the soil profiles. However, aromatic C and carbonyl C are of minor importance. The contributions of aromatic C to SOC decreased as the particle size decreased, which corresponded with the distributions of the two typical aromatic compounds (BC and lignin) in the soil size fractions. The maximum BC concentration was found in the coarse silt and sand fractions of soils in Russia (Rodionov et al., 2006) and North America (Glaser and Amelung, 2003). Similarly, the highest proportions of lignin were observed in the coarse sand fractions, and the lignin concentrations gradually decreased as the particle size decreased (Kiem and Kögel-Knabner, 2003; Trumbore, 2009). The distribution of aromatic C across the particle size fractions strongly indicated that aromatic C may be connected to minerals in the coarse silt and sand and preserved. In comparison, alkyl and O-alkyl C were enriched in fine silt and clay. The contributions of alkyl C increased from the 200–2000 μm fraction to the <20 μm fractions, and the contributions of O/N-alkyl C increased from the 2–20 μm fractions to the <2 μm fractions (Table 2). This pattern is displayed in the topsoil and subsoil (Table 2). As demonstrated by the hexose-to-pentose ratios, the alkyl C and O/N–alkyl C in the coarse and fine fractions are mainly composed of plant materials (Lorenz et al., 2004) and microbial products (Kanazawa and Filip, 1986; Monrozier et al., 1991), respectively. In addition, aromatic structures, which are mainly plant-/fire-derived and are rarely produced as secondary metabolic products in soils, have been observed to be depleted in clay fractions. Considering all of this information, the

Table 2
Distribution of chemical composition of organic carbon (OC) in different soil particle size.

Soil classification	Soil depth (cm)	Fractions (μm)	Distribution of signal intensity (% total signal intensity)				References
			Alkyl C (0—45 ppm)	O/N-alkyl (45—110 ppm)	Aromatic C (110—160 ppm)	Carboxyl & Carbonyl C (160—220 ppm)	
Haplic Podzol	10—12	200—2000	20	53	17	10	Rumpel et al. (2004)
		20—200	35	36	15	14	Rumpel et al. (2004)
		2—20	43	34	11	12	Rumpel et al. (2004)
	12—30	200—2000	25	40	20	15	Rumpel et al. (2004)
		20—200	32	40	13	15	Rumpel et al. (2004)
		2—20	34	37	12	18	Rumpel et al. (2004)
		<2	33	40	9	18	Rumpel et al. (2004)
Stagnic Luvisol	0—8	200—2000	25	48	21	6	Schöning and Kögel-Knabner, (2006)
		2—20	27	44	18	11	Schöning and Kögel-Knabner, (2006)
		<2	29	53	9	9	Schöning and Kögel-Knabner, (2006)
	8—31	200—2000	28	48	17	7	Schöning and Kögel-Knabner, (2006)
		2—20	42	34	5	8	Schöning and Kögel-Knabner, (2006)
		<2	38	46	7	9	Schöning and Kögel-Knabner, (2006)
	31—58	200—2000	26	42	23	9	Schöning and Kögel-Knabner, (2006)
		2—20	35	43	11	10	Schöning and Kögel-Knabner, (2006)
		<2	33	48	9	10	Schöning and Kögel-Knabner, (2006)
Dystric Cambisol	0—6	200—2000	24	49	18	9	Schöning and Kögel-Knabner, (2006)
		2—20	36	39	13	11	Schöning and Kögel-Knabner, (2006)
		<2	31	43	13	13	Schöning and Kögel-Knabner, (2006)
	6—44	200—2000	14	52	26	8	Schöning and Kögel-Knabner, (2006)
		2—20	45	30	18	8	Schöning and Kögel-Knabner, (2006)
		<2	45	34	11	10	Schöning and Kögel-Knabner, (2006)
	0—8	200—2000	27	47	19	7	Schöning and Kögel-Knabner, (2006)
		2—20	31	40	16	13	Schöning and Kögel-Knabner, (2006)
		<2	27	51	11	11	Schöning and Kögel-Knabner, (2006)
	8—19	200—2000	48	28	17	7	Schöning and Kögel-Knabner, (2006)
		2—20	45	29	17	10	Schöning and Kögel-Knabner, (2006)
		<2	36	44	9	11	Schöning and Kögel-Knabner, (2006)
	19—35	200—2000	27	43	16	13	Schöning and Kögel-Knabner, (2006)
		2—20	30	43	18	9	Schöning and Kögel-Knabner, (2006)
		<2	26	46	13	15	Schöning and Kögel-Knabner, (2006)
	0—5	200—2000	30	41	19	10	Rumpel et al. (2004)
		20—200	36	38	17	9	Rumpel et al. (2004)
		2—20	45	34	12	9	Rumpel et al. (2004)
		<2	37	42	9	12	Rumpel et al. (2004)
Andosol	0—10	2—20	16	39	26	19	Baldock et al. (1992)
		<2	21	47	16	16	Baldock et al. (1992)

microbial biomass may represent the organic compounds that are prone to be associated with fine-sized (fine silt and clay) minerals, which has been indicated in previous studies (Grandy and Neff, 2008; Kögel-Knabner et al., 2008; Lalonde et al., 2012). Jenkinson (1977) and Sørensen (1983) have observed that soils of high clay content generally have larger amounts of microbial biomass than sandy soils. Bol et al. (2009) observed that plant-derived signals were only found in the particulate organic matter that forms a minor C fraction in the clay minerals. Spielvogel et al. (2008) reported that the microbial sugars in the clay fractions of the subsoil horizons were associated with poorly crystalline Fe oxides but not for plant-derived lignin. The relative enrichment of microbial-derived compounds in fine-sized minerals may be explained by the small size of microorganisms and the structural properties of

microbial-derived SOC (e.g., more N or higher $\delta^{15}N$ values of microbial-derived SOC compared with plant-derived compounds) (Almendros et al., 2000; Baumann et al., 2009). Because microorganisms are small, they often surround themselves with fine particles. Inevitably, these microorganisms degrade organics and subsequently excrete microbial metabolic products. The organics produced from degradation will increasingly accumulate in these particles. Moreover, microbial-derived compounds may dramatically and stably bind with fine minerals, especially clay minerals (Gianfreda et al., 1992; Calabi-Floody et al., 2012). As early as 1960s, Sørensen (1972) clearly showed that clays protect SOC with N compounds being more protected than carbohydrates. Moreover, Amato and Ladd (1992) identified that the adsorption of organisms to the surface of clay mineral is an important factor in determining the survival of the soil microorganism. A review by Kögel-Knabner et al. (2008) proposed that microbial-derived compounds can act as so-called "conditioning films" to promote mineral–organic associations. Previously, some microorganisms, such as mycelial fungi, were reported to secrete a broad range of surface-active organics that exhibit discrete hydrophilic and hydrophobic domains. The abilities of these organics to bind either hydrophilic or hydrophobic surfaces would allow for sorption across a range of mineral surfaces (Wösten, 2001; Sollins et al., 2006). The fixed SOC on the mineral is broadly segregated into two categories, namely, OC that is intimately and directly associated with minerals (internal mineral-bound OC) and OC that is indirectly fixed on mineral surfaces by associating with internal mineral-bound OC (external mineral-bound OC) (Wang and Xing, 2005; Kleber et al., 2007). The SOC in the internal layer is highly resistant to decomposition (Wang and Xing, 2005). Because of the amphoteric surface, microbial-derived organics are more likely to form internal mineral-bound OC and resist decomposition.

3.1.3. Soil conditions

The soil conditions would influence the stock of OC associated with the minerals, which could be reflected by the observation that the extent of surface loading in acid soils depends on pH (Mayer and Xing, 2001). Differences in the soil's hydrologic conditions, for example, can induce shifts of both soil pH and redox conditions, which result in the alteration of the reactive soil minerals, such as Fe/Al oxides (Berhe and Kleber, 2013). The chemical reactivity of pedogenic oxides is largely determined by the site density of the hydroxyl groups on their surfaces and their pH-dependent charge status (Parfitt, 1976). Increases in pH above their point of zero charge (typically between 7.5 and 9 for many Fe and Al oxides) results in more negative charged surfaces, while decreases in pH can protonate surface hydroxyls and render oxides more attractive towards negatively charged soil organic compounds (Berhe and Kleber, 2013). Furthermore, the decreasing ionic strength is observed to increase the amount of SOC desorbed from three mineral soil horizons (Evans et al., 1988). The work with marine sediments showed that the simple desorption of organic molecules is sufficient for increasing the rates of degradation by 30–40 fold (Keil et al., 1994). Hence, an improved understanding of the environmental factors affecting SOC desorption from soil particles is needed to avoid soil degradation.

3.2. Occlusion of soil organic carbon within aggregates

Based on particle size, aggregates can be roughly divided into two categories: macroaggregates (>250 μm) and microaggregates (<250 μm) (Sollins et al., 1996). Aggregates not only physically shield SOC from microbial and enzymatic attack (Six et al., 2002; Krull et al., 2003) but also affect microbial community structure, and limit oxygen diffusion and regulate nutrient cycling (Sollins

et al., 1996; Baldock and Skjemstad, 2000; Lützow et al., 2006; Sollins et al., 2006). Consequently, an enormous amount of research has been conducted regarding SOC entrapped in aggregates (Christensen, 2001; Denef et al., 2004; Six et al., 2004; Peth et al., 2014; Six and Paustian, 2014; Chaplot and Cooper, 2015). According to previous studies, the following four broad distinctions between macroaggregates and microaggregates can be summarized: (1) macroaggregates often contain more SOC than microaggregates (Puget et al., 1995; Six et al., 2000); (2) the degree of decomposition increases with the decreasing aggregate size, as demonstrated by a decrease in the C/N ratio from about 20 to 8 as the aggregate size decreases (Aoyama et al., 1999; Gregorich et al., 2003); (3) the size of the soil aggregates is generally inversely proportional to the amount of energy needed to disrupt them (Stewart et al., 2007); and (4) the turnover time elevates with decreasing aggregate size (Puget et al., 2000; Six et al., 2002; John et al., 2005). However, until now, no exact explanation has been available to explain why SOC associated with microaggregates is generally preserved for a longer periods than one with macroaggregates. Moreover, most studies to date have primarily concentrated in 50–250 μm microaggregates (Six et al., 2002), and the smaller microaggregates have been paid little attention. Yet, the significant role of nanometer- to micrometer-sized microaggregates in SOC retention in soils is identified by Chenu and Plante (2006), who clearly identified that <2 μm microaggregates are the sites of protection of OC from decomposition by entrapment and adsorption to minerals. Thus it is possible that silt and even clay-sized aggregates can also protect SOC from decomposition (Chenu et al., 2001; Chenu and Plante, 2006).

Previously, it was suggested that the protection of SOC by aggregation is a function of the bonding strength of OC to clay mineral surfaces (Krull et al., 2003). Studies conducted by Franzluebbers and Arshad (1996) and Boix-Fayos et al. (2001) showed that the water stability of microaggregates is positively correlated with clay and Al- and Fe-oxide contents. Moreover, because mineral-SOC complexes can be combined with other inorganic and/or organic materials to form aggregates, SOC that is protected by adsorption to minerals would be further occluded by aggregation. Consequently, these two mechanisms, namely, sorption to minerals and occlusion within aggregates, co-operate or interact. However, the relative importance of these two mechanisms remains largely unclear. Although approaches combining physical-fractionation procedures with chemical treatments have been adopted to isolate SOC preserved only by a given mechanism (Christensen, 1992; Aoyama et al., 1999), these procedures have not been standardized. The standardization of isolation approaches would lay the foundation for directly comparing results from different laboratories and could help determining the precise drawbacks of different isolation methods.

4. Soil organic carbon stability predicated by turnover time and radiocarbon ages

Turnover time and ^{14}C age are helpful parameters for identifying crucial mechanisms for the persistence of SOC (Bol et al., 1996; Paul et al., 2001; Burke et al., 2003; Mendez-Millan et al., 2014; Menichetti et al., 2015). According to the study by Torn et al. (2009), the turnover time of SOC is defined as the time it would take for a SOC reservoir to be completely depleted if no further inputs of C or soil particles occurred. Most often, the turnover time of SOC is determined by isotopic analyses, including the natural abundance of the ^{13}C labeling tracer approach. This isotopic approach is a commonly used method that considers the differences in photosynthetic CO_2 fixation between C_3 and C_4 plants, which have distinctive $\delta^{13}C$ values. When the vegetations in an area change from C_3 to C_4 plants

(or from C₄ to C₃), the rate of change of the δ^{13}C values in SOC will provide a turnover time for SOC (Dignac et al., 2005; Chenu et al., 2014). The experimental periods investigated using this method generally include a year or a few years. Thus, the method does provide a suitable method for probing the decomposition of readily biodegradable organic molecules in soils or for quantifying the dynamics of the SOC pool over a short-term scale (Trumbore, 2009). However, the method is not suitable for evaluating the dynamics of SOC with a very slow decomposition rate, such as HS and BC. Furthermore, turnover time calculation includes a non-negligible uncertainty that depends on the assumptions made (investigated soil systems are in equilibrium or at steady state, i.e., when C inputs match the C outputs of one pool and there is no change in C stock from year to year). Using the steady-state assumption for C stocks and the constant rate of plant C input, the equations used to calculate turnover time can be greatly simplified (Torn et al., 2009; Kögel-Knabner and Kleber, 2012). However, the balance assumption is difficult to make for sites where input or output rates have changed as a result of natural and anthropogenic disturbance (Clapp et al., 2005; Horwath, 2007; Kögel-Knabner and Kleber, 2012; Chenu, 2015), which was demonstrated by Neff et al. (2009), who calculated the turnover time in soil fractions from a sequence of semiarid sites that underwent woody vegetation expansion between 50 and 325 years ago. In their studied sites, C inputs to the fractions varied as a function of time. They further used the simple non-steady state model to quantify the dynamics of SOC, and observed that the turnover time of the light fractions

covered a large range (spanning 237–613 years with an estimate of 433 ± 61 years). This estimate of turnover time is much longer than many previous estimates (Connin et al., 1997) in which the turnover time of the sites undergoing shrub expansion were obtained simply by assuming steady state conditions. Nonetheless, as the study by Neff et al. (2009) reports, in which non-steady state models parameterized by estimating litter input rates were developed (Torn et al., 2013), the turnover times for SOC calculated by these models would probably vary with the estimated input rates (Baisden and Canessa, 2013). Fortunately, the ^{14}C-dating technique can quantify the ^{14}C age (which is also expressed in the term "mean residence time (MRT)" of steady state soil) of organics in soil systems under steady or non-steady state conditions (Wang et al., 1996; Trumbore, 2009). However, this technique also involves potential uncertainties. For example, Stubbins et al. (2012) suggested that recent inputs of C from fossil energy sources add C that is free of ^{14}C. If this C is incorporated into the global soil C cycle, the age of the OC in the soils assessed by using ^{14}C analysis could be overestimated. Moreover, it must be considered that the estimation of OC turnover via the gradual replacement of one isotopic label with another inherently assumes that any substance, which can no longer be found analytically, has been decomposed. Although the assumption is correct when bulk SOC is analyzed, it only provides apparent turnover times and ages when specific compounds, like lignin monomers, are analyzed. This is caused by the fact that decomposition processes could alter the lignin molecule in such a way that the analytical approaches no longer detect the typical lignin monomers (Heim and Schmidt, 2007). With the present method, it is difficult to discern between lignin that has been altered in such a way and lignin that has been completely mineralized to CO_2. Therefore, the obtained ^{13}C turnover times and ^{14}C age refer to the unaltered lignin molecules and provide a minimum turnover of lignin in soils (Heim and Schmidt, 2007). The ^{13}C turnover times and ^{14}C age of the modified lignin-derived C in soils may be substantially longer.

Despite the above mentioned limitations, we collected a large set of published data of ^{13}C turnover time and ^{14}C age of the bulk SOC and the specific organic compounds, including carbohydrates, lignin, aliphatic C, HS and BC, to compare their dynamics in soils and understand their turnover (Fig. 2 and Tables S2 and S3). As illustrated in Fig. 2 and Tables S2 and S3, the averages of ^{13}C turnover time and ^{14}C age for bulk SOC were 179.44 and 2347.90 years, respectively. Paul et al. (2001) compared the data obtained using ^{13}C and ^{14}C on the same site, and showed the curvilinear regression:

$$^{14}\text{C MRT} = 176(^{13}\text{C MRT})^{0.54}.$$

In this review, the predicted ^{14}C age (2901.50) based on this equation was generally similar to the actual value. Lignin, which should persist in soils expected from its molecular complexity, appears to turnover faster than the bulk SOC when considering the ^{13}C turnover time and ^{14}C age. Despite their chemically labile structure, carbohydrates from plant and microbial origins exhibit ^{13}C turnover times that are similar to aliphatic C and greater than lignin (Fig. 2A). These data demonstrate that the persistence of SOC cannot be solely determined by molecular structure, which corresponds with earlier circumstantial evidence that lignin is not part of the refractory C pool (Kiem and Kögel-Knabner, 2003; Lützow et al., 2006; Berhe et al., 2012). Interestingly, carbohydrates with long ^{13}C turnover times have always been detected in organo-mineral fractions (Bol et al., 1996; Gleixner et al., 2002; Burke et al., 2003; Derrien et al., 2006; Kramer and Gleixner, 2006), which reflects the potential of minerals for protecting SOC from decomposition. Fig. 2B reveals that aliphatic C and BC exhibit much larger ^{14}C ages
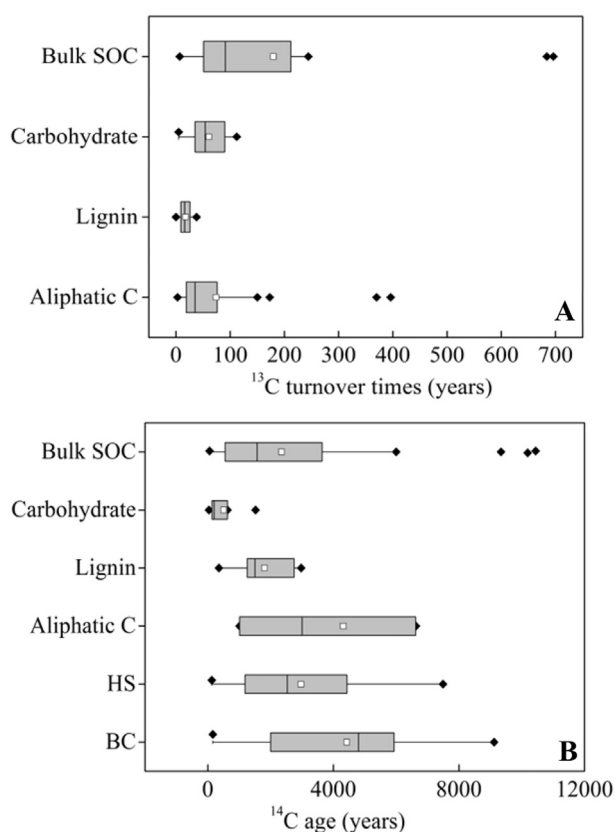
Fig. 2. The turnover time of bulk soil organic carbon (SOC) and specific SOC fractions estimated by natural abundance stable carbon isotope (^{13}C) analysis (A); the ^{14}C age of bulk SOC and specific SOC fractions estimated by ^{14}C-dating technique (B). Data points: thin horizontal lines, 10th and 90th percentiles; box, 25th and 75th percentiles; central vertical line, median; central square, mean; black points, outliers beyond the 10th/90th percentiles. The data in this figure are showed in Table S2 and S3.
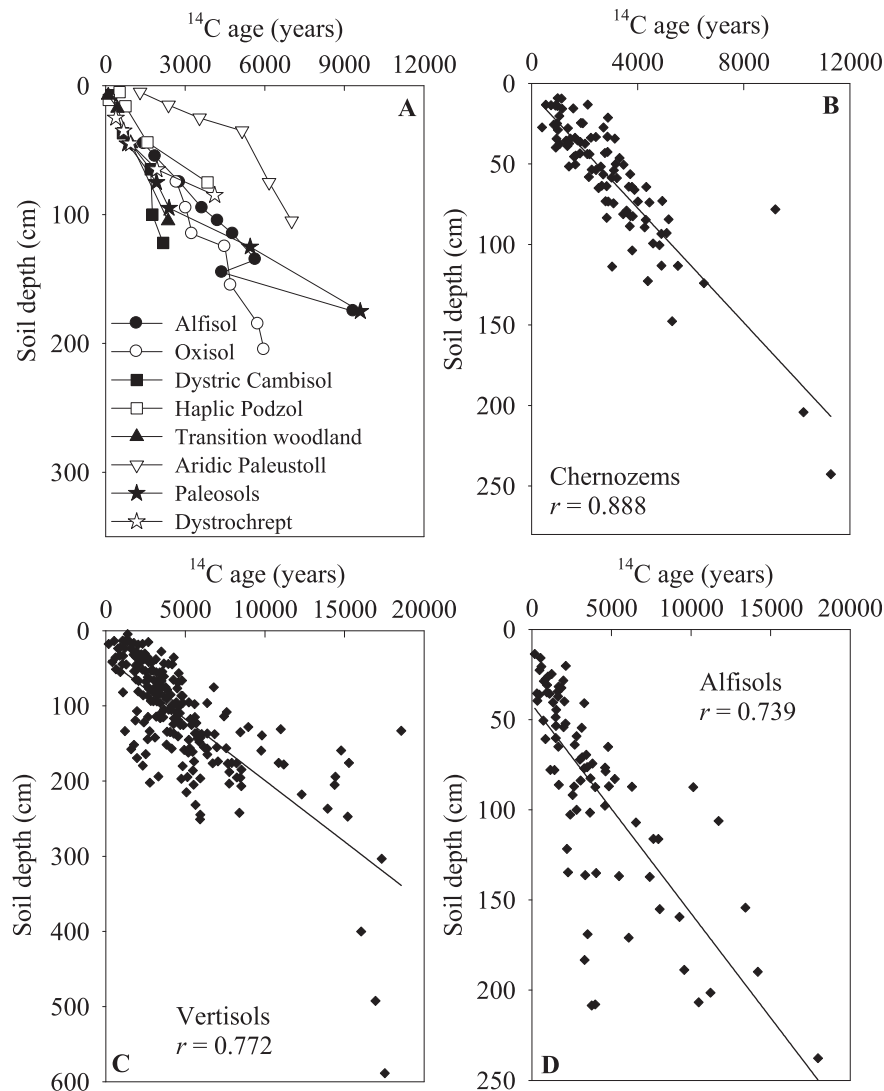
Fig. 3. The change of ^{14}C age of soil organic carbon (SOC) with soil depth. The data in Figure A were compiled from seven studies (Goh and Molloy, 1978; O'brien and Stout, 1978; Paul et al., 1997; Boutton et al., 1998; Pessenda et al., 2001; Rumpel et al., 2002; Budge et al., 2011); the data in Figure B, C and D were cited from the study by Scharpenseel (1972).

than bulk SOC. However, this result does not necessarily suggest that aliphatic C and BC are prime candidates for intrinsically recalcitrant materials in soils because the relative contributions of organic-mineral interactions are not clear (Lehmann et al., 2009). In addition, the ^{13}C turnover times and ^{14}C ages of the bulk SOC and specific compounds significantly varied with soil type (Tables S2 and S3). This may result from the unique environmental and climatic conditions in the different soils, including soil temperature, rainfall and vegetation composition. When considering the same soil type, the ^{14}C age of bulk SOC consistently increases with increasing depth (Fig. 3A), consistent with the report by Scharpenseel (1972) who found the positive relationship between ^{14}C age and soil depth of several soils types (e.g., Vertisols, Chernozems and Alfisols) (Fig. 3C and D); however, the reasons for this increase are not completely understood. The increasing ^{14}C age of SOC with depth may be partially caused by the following two mechanisms:

1) as mentioned above, the SOC fixed on the mineral could be broadly segregated into two categories, namely internal and external mineral-bound OC (Wang and Xing, 2005; Kleber et al.,

2007). Internally bound SOC in the minerals is highly resistant to decomposition (Wang and Xing, 2005), while SOC on external mineral layers may be preferentially removed with oxidation treatment (Mikutta et al., 2006); thus, the long-term protection of organic materials by sorptive interactions is limited to the organic molecules directly bound to the mineral surface. Therefore, the degree of saturation of such protective sites on the mineral surfaces should influence the preservation potential of newly added C to the soil. Because of the concentrations of clay minerals are greatest in the subsoil (Rumpel and Kögel-Knabner, 2011), the subsoil's protective capacity is less likely to be saturated and, therefore, would display a greater potential for protecting SOC from decomposition.

2) organo-mineral associations could be disrupted under variable environmental conditions (Golchin et al., 1994; Baldock and Skjemstad, 2000), and the released SOC could be utilized by microorganisms again. The absence of disruption due to cultivation in subsoils would facilitate the stabilization of organo-mineral associations. Moreover, deeper soil horizons correspond to different decomposition environments. Compared with topsoils, subsoils with a relatively small C supply are

unfavorable for microbial growth, therefore, SOC in subsoils may more likely show longer turnover time.

Unfortunately, current analytical techniques cannot clearly identify which mechanisms are critical. Schulze et al. (2009) suggested that, as with Podzolic soils, the larger protective potential of SOC by minerals in deeper horizons may explain the increased turnover time with increasing soil depth. In addition, Budge et al. (2011) demonstrated that the low temperatures in alpine environments are likely a major cause for the slow turnover rate observed in subsoils. Therefore, the relative role of these mechanisms should be specific to soil type. Additionally, most studies have focused on surface soils (0–30 cm), which only contain 10–30% of the total C in the soil (Jobbágy and Jackson, 2000), and the SOC in deeper soil horizons has not been fully understood.

5. Future research

As indicated throughout the review, some critical knowledge is still lacking. We suggest that the following changes in studies of SOC dynamics would help fill knowledge gaps and better examine SOC dynamics:

1. The effects of mineralogical properties of coal itself and soils on the resistance of coal-derived OC to biological and/or chemical decomposition should be further evaluated.
2. The turnover of pyrogenic HAs in soils, whose aromatic C is partially derived from BC, may differ from that of non-pyrogenic HAs. We suggest that the future research on HA stability should consider its origin.
3. A growing body of circumstantial evidence indicates that association with minerals is one of the mechanisms for the persistence of BC produced under wildfires in soils. However, direct investigations of the relationships between mineralogy and the chemistry of natural BC remain limited.
4. Although Fe oxides can strongly adsorb SOC in acidic soils, it should be noted that oxides can be very short lived and release organic colloids very quickly. The relevant process should be carefully explored.
5. Based on the chemical composition of SOC detected in the soil size fractions from different soil types, the microbial products may be prone to associating with clay minerals. The experimental demonstration of this hypothesis will have far-reaching implications for understanding SOC cycling in soils.
6. Nanometer- to micrometer- sized microaggregates also provide the sites in which SOC can be physically preserved, and should be given more attention.
7. As highlighted in the review, the roles of molecular structure and minerals in SOC stability may be obscured by contrasting climates, mineral types, or land use. Thus, it will be useful to explore the mechanisms responsible for the persistence of SOC by using chemical and/or physical extraction of SOC fractions from a same soil.
8. The SOC in the deep soil horizons has not been fully understood, which was underlined by Rumpel and Kögel-Knabner (2011), who pointed out that several issues regarding deep SOC are unclear, including: 1) the relative importance and controlling factors of deep SOC sources, 2) the contributions of microbial versus plant-derived SOC, and 3) the C fluxes from deep horizons related to C input and output. Little knowledge of SOC in subsoils has, to some extent, made the complete elucidation of the mechanisms underlying the persistence of deep SOC with much difficulty. Accordingly, in addition to a specific soil type, additional research of SOC in subsoils is necessary to gain a clear understanding of the mechanisms controlling deep SOC dynamics.
9. The simultaneous operation of several mechanisms results in an unclear understanding of SOC sequestration. To isolate SOC preserved by a given mechanism, many techniques combining physical-fractionation procedures (e.g., particle-size separation, aggregation and density fractionations) with chemical treatments should be further developed.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.soilbio.2015.11.023.

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