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The effect of composition on stability (^{14}C activity) of soil organic matter fractions from the albic and black soils

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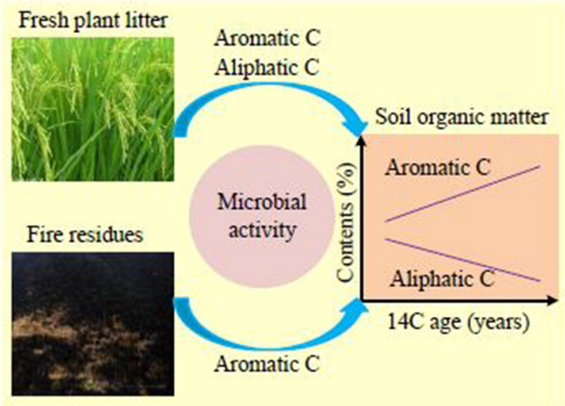
HIGHLIGHTS

- The effect of composition on stability of SOM fractions (SOMs) was examined.
- There was a potential link between thermal and biological stability of SOMs.
- Fire-derived aromatic C was likely more stable than microbial-derived aliphatic C.
- Chemical composition could be related to Δ^{14}C values of SOMs from a same source.

GRAPHICAL ABSTRACT



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ABSTRACT

The importance of the composition of soil organic matter (SOM) for carbon (C) cycling is still under debate. Here a single soil source was used to examine the specific influence of its composition on stability (^{14}C activity) of SOM fractions while constraining other influential C turnover factors such as mineral, climate and plant input. The following SOM fractions were isolated from two soil samples: four humic acids, two humins, non-hydrolyzable carbon, and the demineralized fraction. We examined the isotope ratios of SOM fractions in relation to composition (such as aliphatic and aromatic C content) using solid state ^{13}C nuclear magnetic resonance (NMR) and thermal analysis. The Δ^{14}C values of the fractions isolated from both an albic soil (SOMs-A) and a black soil (SOMs-B) correlated negatively with their peak temperature of decomposition and the temperature where half of the total heat of reaction was evolved, implying a potential link between thermal and biogeochemical stability of SOM fractions. Aryl C contents of SOMs-A determined using ^{13}C NMR varied inversely with δ^{15}N values and directly with δ^{13}C values, suggesting that part of aryl C of SOMs-A might be fire-derived. The Δ^{14}C values of SOMs-A correlated positively with aliphatic C content and negatively with aromatic C content. We therefore concluded that fire-derived aromatic C in SOMs-A appeared to be more stable than microbially-derived aliphatic C. The greater decomposition of SOMs-B fractions weakened the relationship of their Δ^{14}C values with alkyl and aryl C contents.

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Hence, the role of the composition of SOM fractions in regulating stability might be dependent on the source of specific C forms and their stage of decomposition.

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1. Introduction

Soil organic matter (SOM) is essential to many ecosystem services, such as fertility, resistance to erosion, immobilization and transport of nutrients and anthropogenic chemicals; it is particularly important in C sequestration and climate mitigation in recent years (Schmidt et al., 2011). Globally, the SOM pool to 1 m depth is estimated at 1580 Pg C (probable range 1200–1600 Pg C; Post et al. 1990), compared with the vegetation and atmospheric pools of 610 and 750 Pg C, respectively (Lal, 2004; Rodeghiero et al., 2009). The release of CO_2 to the atmosphere by way of SOM mineralization is one order of magnitude larger than anthropogenic emissions (Lal, 2008; Schlesinger and Bernhardt, 2013). The impact has led to substantial attention being paid to the persistence of SOM and has resulted in the development of a number of soil C cycling models to predict SOM persistence (Jenkinson et al., 1991; Parton et al., 1987; Six et al., 2002). The most widely applied SOM simulation models (e.g. Century and RothC) divided soil C into pools with varying intrinsic decomposition rate (Khalaf et al., 2014; Kleber et al., 2011). The models rely on biochemical recalcitrance as a major sequestration mechanism by assuming that SOM components are resistant to decomposition mainly as a consequence of their composition (Khalaf et al., 2014). Biochemical recalcitrance is usually associated with complex aromatic structures or long alkyl chains (Kleber et al., 2011), while components like carbohydrates are assumed to be readily bioavailable (Feng et al., 2008). Thus, strategies for enhancing the C sink in soil suggest the enhancement of the inputs of biochemically recalcitrant material (such as black carbon, the charred remains of biomass with a predominance of aromatic structures) to augment the stable SOM stock (Lehmann, 2007).

However, recent research challenges the recalcitrance concept (Dungait et al., 2012; Kleber et al., 2011; Schmidt et al., 2011). In particular, old and stable SOM has been reported to be not necessarily related to complex components, based on the data from three different soils (Kleber et al., 2011). Studies of the turnover of SOM from a wide range of soils are helpful for a comprehensive understanding of C dynamics considering the abundant soil types over the world. However, different sample sites may differ in mineralogy, pedogenesis, climate, vegetation, depth, OM type and content, and other environmental factors. Studies have shown that these factors greatly influenced decomposition pathways and stability of SOM in part via changing its composition (Craine et al., 2010; Eusterhues et al., 2007; Lützow et al., 2006; Mikutta et al., 2009), as result, the role of SOM composition in C persistence is likely ignored. Therefore, by extraction of SOM fractions from the same soil, the influence of the above factors on the correlation of SOM stabilization and composition should be eliminated as much as possible. Thus, we isolated a series of SOM fractions from a single mineral soil using the humic substances (HS) fractionation scheme developed by Kononova (1966); their $\Delta^{14}C$ values were also determined to represent the stability of SOM fractions. We hypothesize that the composition can be related to the stability (^{14}C activity) of SOM fractions isolated from the same source.

The long standing questions regarding composition of SOM could likely be answered when several characterization methods are used in tandem to gain insights into C preservation and accumulation (Simpson and Simpson, 2012). Stable isotope (^{13}C and ^{15}N) and radioactive isotope (^{14}C) analysis can provide information about the cycling, processing and stability of SOM, and ^{13}C solid state nuclear magnetic resonance (NMR) can allow close examination of SOM. Isotopic techniques and NMR are widely applied to the study of SOM dynamics and composition (Kang and Xing, 2005; Kayler et al., 2011; Khalaf et al., 2014). Analysis of isotopic signatures along with chemical functional groups may therefore yield important information about SOM turnover. However, the abundances of ^{15}N, ^{13}C and ^{14}C have rarely been related to NMR data from SOM fractions. Furthermore, thermal analysis could provide an addition to the understanding of SOM composition and stability (Kleber et al., 2011; Peltre et al., 2013). In this study, relationships between biogeochemical stability and thermal stability of SOM fractions were also examined.

We hypothesize that 1) the recalcitrant structure can be related to the stability (^{14}C activity) of SOM fractions isolated from a same source; 2) there might be a potential link between thermal and biogeochemical stability of SOM fractions. To test the hypotheses, SOM functional characteristics were examined using a series of humic acids (HAs), humins (HMs), non-hydrolyzable carbons (NHCs), and the demineralized fraction (DM) isolated from a single soil. Specifically, we obtained isotope ratios ($\delta^{15}N$, $\delta^{13}C$ and $\Delta^{14}C$) and composition using ^{13}C NMR analysis of the fractions along with their thermal stability determined from thermal analysis.

2. Material and methods

2.1. SOM fractions

Albic (A) and black (B) soil samples (0–20 cm) were collected after harvest (in October) from a farming area (46°58′ N, 132°53′ E) on the Sanjiang Plain, northeast China (Sun et al., 2013). The plain is a marshy low one, formed mainly by the alluvial confluence of the Songhua, Heilongjiang and Ussuri rivers. The region is characterized by a temperate continental monsoon. Its mean annual temperature is 2.1 °C, mean annual precipitation is 525 mm (80% during June to September) and the average frost-free period is 130 d. The site has been under consecutive rice (C_3 vegetation) cropping for decades, with one harvest per year, and annual straw burning after harvesting. No crop is grown during the winter. Microbial processing is slow in the rice paddy lands as a consequence of the cool and anaerobic conditions (Ouyang et al., 2013). The A soil is widely distributed in this area. It is characterized by three distinct layers of texture: a mollic epipedon, an albic E horizon, and a thick argillic horizon, good for water holding but poor for air flux. The pH was slightly acidic (5.7 in distilled water). Quartz and hydrous mica were major minerals in the albic soil. The B soil had a clay loam texture and was slightly acidic (pH 6.2 in distilled water). Minerals in the black soil were mainly quartz and montmorillonite. The A and B bulk soil samples stored 2.7% and 4.4% organic carbon (OC), respectively (Table 1). The N contents of A and B bulk soils were 0.13% and 0.30%, respectively (Table 1). The relatively more acidic context and slightly lower N content of the A soil may limit the microbial activity (Kramer et al., 2003; Ouyang et al., 2013), implying that the SOM fractions from the A and B soil might have different stages of degradation. This could lead to their difference in the composition, which in turn, might affect the correlations between the composition and the stability of SOM fractions. SOM fractions including HAs, HMs, NHCs, and DM of A and B soils were isolated (Supporting Information, Fig. S1) and are referred to as SOMs-A and SOMs-B, respectively. Specifically, HA1 was obtained from mixing the 7 extractions with 0.1 M $Na_4P_2O_7$ from the bulk soils; then HA2 was extracted 5 times with 0.1 M NaOH. HA1 and HA2 were further de-ashed with HCl/HF (0.1/0.3 M) to get the de-ashed HA samples. The bulk soils were also demineralized with 1 M HCl and 10% (*v*/*v*) HF to get the DM fractions. The NHC was extracted from the DM fraction using a HCl/HF/CF_3CO_2H (TFA) method described elsewhere (Gélinas et al., 2001). Using 0.1 M NaOH, HA3 and HA4 were isolated from the DM and the NHC fraction, respectively. The residue after HA2 extraction was demineralized to provide the HM1

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