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Biochemical changes across a carbon saturation gradient: Lignin, cutin, and suberin decomposition and stabilization in fractionated carbon pools

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ABSTRACT

Soils that exhibit soil organic carbon (SOC) saturation provide an opportunity to examine mechanisms of C storage in soils with increasingly limited C-stabilization potential. A manure rate experiment in Lethbridge, Alberta, in which SOC responded asymptotically to long-term manure C additions, allowed us to assess changes in SOC biochemical composition in response to soil C saturation. By quantifying the cupric oxide oxidation products of lignin, cutin, and suberin in fractionated SOC pools that are characterized by chemical (i.e., mineral-associated), physical (i.e., microaggregate-associated), or no protection (i.e., free particulate organic matter), we evaluated the interaction between C saturation and the biochemical characteristics of SOC.

We tested the specific responses of soil fraction lignin, cutin, and suberin to C saturation level by using the bulk soil to approximate C-input composition across manure input treatments. Carbon-normalized lignin (lignin-VSC/OC) in the chemically protected fractions did not differ, while in the non-protected and physically protected soil fractions, it decreased with C saturation level. Neither the stabilization of cutin and suberin, nor the lignin:cutin + suberin ratio, differed in any of the measured soil fractions in response to C saturation level.

These results indicate that with C saturation and decreased C stabilization potential, lignin, cutin, or suberin were not preferentially stabilized or depleted in mineral protected soil C pools. The lack of evidence for biochemical preference in mineral associations with C saturation supports the existence of an outer kinetic zone of organomineral associations, in which partitioning of organic compounds, rather than sorption, controls mineral SOC accumulation at high SOC loadings. Furthermore, despite theories of inherent lignin recalcitrance, depleted lignin concentrations with C saturation in the non-protected and aggregate protected fractions indicate that lignin was, in this study, preferentially decomposed when not protected by association with mineral phases in the soil. In conclusion, C-input quantity, and not quality, combined with physical and chemical protection mechanisms that govern long-term C storage, appeared to control C saturation and stabilization at this site.

1. Introduction

The maximum C stabilization potential of a soil limits the effectiveness of soil organic carbon (SOC) storage (Six et al., 2002; Stewart et al., 2007; West and Six, 2007). Long-term field studies demonstrate that increased C-input or C-input proxies, such as bulk soil C content or elevated CO_2, do not produce a concomitant increase in SOC for whole soils or mineral and aggregate soil fractions (Kool et al., 2007; Chung et al., 2008; Gulde et al., 2008; Stewart et al., 2008). The observed asymptotic C response under equilibrium conditions has been termed “soil C saturation”, a premise that infers that inherent limits to soil C stabilization affect the rate, duration, and permanence of SOC (Six et al., 2002; Stewart et al., 2007; West and Six, 2007). Although process-defined biogeochemical models, such as DayCENT, Century, and EPIC, model linear equilibrium SOC responses to C-input (Parton et al., 1987; Schimel et al., 1994; Izaurralde et al., 2006), C saturation models better fit soils with high SOC stocks or high input levels (Stewart et al., 2007; West and Six, 2007). Inclusion of a saturation parameter in biogeochemical models would, therefore, improve estimates of the rate and duration, as well as the total potential of C

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stabilization in terrestrial soils (Hassink and Whitmore, 1997; West and Six, 2007).

The role of SOC biochemical composition in C saturation and stabilization processes remains unclear, but could inform our understanding of SOC models. It has been suggested that biochemical composition of inputs, i.e., residue quality, can affect C accumulation through the addition of recalcitrant macromolecules coupled with the availability of N substrate (Melillo et al., 1982; Vanlauwe et al., 1996; Trinsoutrot et al., 2000). Current SOC models implicitly incorporate these theories of biochemical C protection by correlating C stabilization in slower turning over pools to residue quality (i.e., lignin:N ratios) (Parton et al., 1987; Palm et al., 2001). The preferential sorption of specific compounds to soil minerals offers another mechanism to explain how SOC biochemical composition can affect SOC stabilization. Preferential sorption could result from ligand exchange reactions that favor complexation of carboxyl and phenolic groups at mineral surfaces (Guggenberger and Kaiser, 2003). Furthermore, the organomineral association of specific molecules can be affected by the dominance of hydrophilic or hydrophobic interactions with distance from the mineral surface (Kleber et al., 2007). Alternatively, SOC stabilization can be independent of SOC biochemical composition, as common decomposition processes can override biochemical input controls (Grandy and Neff, 2008; Crow et al., 2009; Fierer et al., 2009) or common reactions with mineral surfaces can attenuate biochemical differences (Grandy et al., 2008).

Lignin, a structural plant biopolymer dominated by aromatic moieties, and cutin and suberin, waxy biopolymers in roots and leaf cuticles that are dominated by aliphatic moieties, have been considered important contributors to stable SOC pools due to innate biochemical recalcitrance (Kögel-Knabner et al., 1992; Stevenson, 1994; Kögel-Knabner, 2002; Krull et al., 2003; Lorenz et al., 2007). More recent studies contradict the innate biochemical recalcitrance of lignin in soils and suggest that its importance in stable SOC pools is overstated (Thevenot et al., 2010). Lignin was found to cycle faster than total SOC in ^{13}C tracer experiments (Dignac et al., 2005; Rasse et al., 2006; Heim and Schmidt, 2007a), had shorter residence times than proteins based on pyrolysis isotope ratio mass spectrometry measurements (Gleixner et al., 1999), and did not accumulate in the refractory SOC pool of C-depleted soils (Kiem and Kögel-Knabner, 2003).

The enrichment of cutin and suberin in the free particulate organic matter (POM) fraction of soils converted from grasslands to woodlands suggests that the recalcitrance of cutin and suberin contributes to the accumulation of refractory POM-C (Filley et al., 2008). The preservation of cutin and suberin in soils has been attributed to the biochemical recalcitrance of alkyl C in SOM (Lorenz et al., 2007). Furthermore, cutin + suberin-derived aliphatic waxes exhibit even greater inherent recalcitrance than lignin, as evidenced by their relative enrichment with depth and decreasing particle size (Riederer et al., 1993; Nierop and Verstraten, 2003; Rumpel et al., 2004; Lorenz et al., 2007), and the greater turnover of lignin relative to cutin + suberin (Feng and Simpson, 2007).

The interaction of specific biomolecules with mineral protection of SOC is also contradictory. Kaiser and Guggenberger (2000) found that lignin in hydrophobic dissolved organic matter (DOM) fractions sorbed to goethite in preference to alkyl and carbonyl C. Mikutta et al. (2006) observed that most stable lignin occurred in mineral fractions, but that lignin had a quantitatively small contribution to mineral-associated SOC. NMR spectroscopy found greater mineral protection of aliphatic structures in mineral fractions, which suggests greater preservation of compounds such as cutin and suberin relative to lignin (Feng et al., 2005). Other studies suggest that favorable conformational changes and amphiphilicity of proteinaceous compounds leads to preferential mineral protection of microbially-derived, rather than plant-derived C, at mineral surfaces (Omoike and Chorover, 2006; Sollins et al., 2006; Kleber et al., 2007).

Studies on the selective preservation of SOC biochemical components, such as lignin, cutin, and suberin, are often limited to the bulk soil or particle size separates, and, therefore, do not address the effects of specific C protection mechanisms on SOC biochemical composition. To date, this study is the first we know of to additionally look at lignin, cutin, and suberin in aggregated versus non-aggregated mineral and POM fractions, as well as to observe the effects of C saturation on the stabilization of these compounds. To accomplish this, soil C pools were fractionated after the conceptual model of Six et al. (2002) to isolate measurable pools corresponding to C protection mechanisms. We isolated primarily chemical protection in the silt + clay fraction (SC); primarily physical protection in the microaggregate-associated POM fraction (iPOM); combined physical and chemical protection in the macroaggregated silt + clay fraction (Magg-SC); and innate biochemical protection in the non-protected POM fraction (cPOM) (Fig. 1). By measuring the cupric oxide oxidation products of lignin, cutin, and suberin in these fractions, we aimed to better constrain the role of chemical, physical, and innate biochemical protection mechanisms in the preservation of SOC.

We utilized a C saturation gradient, established by long-term manure additions in Lethbridge, Alberta (Gulde et al., 2008), to address the overall hypothesis that SOC preservation in all fractions is compound-specific and that this specificity will amplify with increased C saturation. Specifically, we expected the progressively limited protective capacity for mineral adsorption with increasing C saturation (Hassink, 1997; Six et al., 2002, 2004) to limit the preservation of plant-derived lignin, cutin, and suberin in the

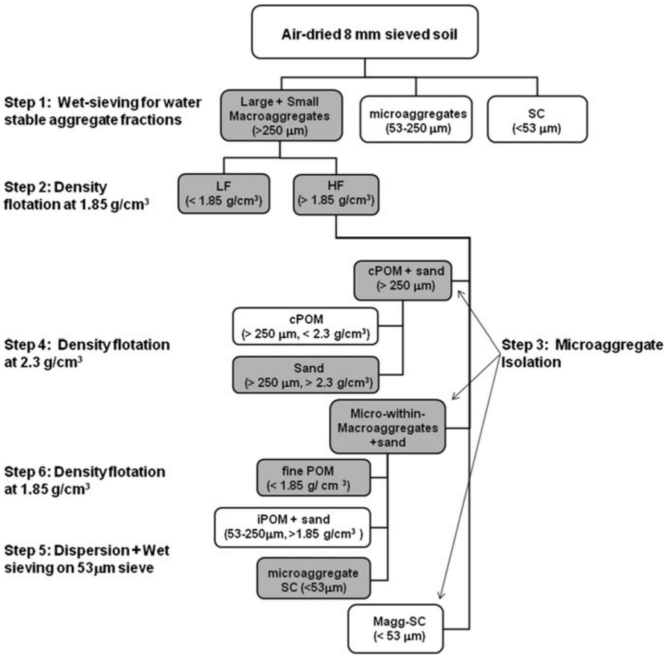

Fig. 1. The physical and density fractionation scheme modified from Gulde et al. (2008), which isolated functional SOC pools utilized in this study. The easily dispersed silt + clay (SC) was directly utilized; whereas, the coarse particulate organic matter (cPOM), the micro-within macroaggregate protected intra-aggregate particulate organic matter (iPOM), and the macroaggregated silt + clay (Magg-SC) were bulked by fractional proportion of large and small macroaggregates. After Six et al. (2002), these functional pools model chemically-protected SOC in the SC, physically + chemically-protected SOC in the Magg-SC, physically-protected SOC in the iPOM, and non-protected SOC in the cPOM. Shaded fractions were not utilized in this study.