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Distinct bioenergetic signatures in particulate versus mineral-associated soil organic matter

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ABSTRACT

Physical and chemical stabilization, environmental conditions, and organic matter composition all play vital roles in determining the persistence of soil organic matter (SOM). Fundamentally, SOM stability depends on the balance of microbial bioenergetics between the input of energy needed to decompose it (i.e., activation energy; E_a) and the net energy gained (i.e., energy density; ED) from its decomposition. This relationship is complicated in soils by chemical and physical protection mechanisms, which require additional energies to overcome for decomposition to occur. In this study, we analyze the bioenergetics of soil density fractions, which vary in their degrees of organic matter-mineral association, and show that the relationship of ED and E_a has the ability to provide information about relative differences in SOM chemical composition and stability. Our results demonstrate distinct bioenergetic signatures between particulate, light (free and occluded) fractions versus mineral-associated, heavy fractions isolated from soil samples collected at two depths from a climosequence along an elevation gradient in the Sierra Nevada, California. While there were no significant differences in ED and E_a within each fraction across climates, the light fractions (LF) were characterized by larger ED and E_a values, whereas the heavy fractions (HF) were characterized by smaller ED and E_a values. Combined with CHN analyses, we conclude that SOM in HF pools is likely comprised of relatively simple organic compounds that have long turnover rates because of chemical association with soil minerals, whereas the LF pools are comprised of more chemically complex molecules with low chemical reactivity and high E_a.

1. Introduction

Soil organic matter (SOM) plays a crucial role in ecosystem functioning and global carbon sequestration, but the mechanisms of its stabilization remain insufficiently understood and constrained. SOM exists as a continuum of progressively decomposing organic compounds, from plant- and animal-derived large and energy-rich macromolecules, to small and energy-poor monomers (Lehmann and Kleber, 2015). Organic matter on this continuum can persist in soil for hundreds to thousands of years as a result of physical and chemical stabilization processes. Environmental and ecosystem conditions can play a critical role in SOM persistence by influencing oxygen availability, soil moisture, temperature, and microbial community composition (Schmidt et al., 2011), all of which affect the decomposition and stabilization of SOM. For example, climate and land management can affect aggregate formation and destruction, while temperature affects the processes of organic matter adsorption and desorption on mineral surfaces (Davidson and Janssens, 2006). However, while physical and chemical protection can extend the turnover times of SOM by decades to centuries, the composition of OM and its optimal decomposition pathways are also expected to change with soil and other environmental conditions (vegetation type, temperature, soil moisture) affecting the overall stability of SOM (Berhe and Kleber, 2013).

Multi-pool models and approaches are commonly implemented to describe the heterogeneity of SOM stability and decomposition kinetics. Physical soil fractionation techniques have been utilized to divide SOM into pools with differing composition, biological availability, and stability (Christensen, 1992) based on differences in particle size or density. Density fractionation is based on the observation that during SOM decomposition, portions of SOM become increasingly associated with mineral particles and thus occur in particles of higher density (Barrios et al., 1996). Three soil density fractions are typically recovered: the free light fraction (fLF) of partially decomposed plant materials and particulate OM not associated with soil minerals, the occluded light fraction (oLF) of particulate OM occluded within soil aggregates, and the heavy or dense fraction (HF) of organic matter complexed with soil

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minerals (Golchin et al., 1994). Radiocarbon analyses of these fractions from a variety of soils have shown that SOM in the lighter fractions is consistently younger, implying faster turnover times and reduced persistence compared to the heavier fraction (Berhe et al., 2012; Schrumpf and Kaiser, 2015; Sollins et al., 2006; Trumbore et al., 1996). However, the mechanisms imparting persistence within these fractions (e.g., molecular complexity, physical/chemical protection, or a combination of the two) are still poorly understood (Swanston et al., 2002). The greater stability of OM in HF is typically attributed to chemical bonds between organic functional groups and mineral surfaces that limit accessibility of the OM to decomposers, rather than to chemical recalcitrance (Dalal and Mayer, 1986; Golchin et al., 1995a; Golchin et al., 1995b; Skjemstad et al., 1986; Swanston et al., 2002). However, there is little data about OM cycling and composition in the mineral-complexed fraction (HF) of bulk soils (Christensen, 1992) because of low organic carbon concentrations and the influence of soil minerals on chemical and spectroscopic characterization of the OM (Schulten and Leinweber, 1999). Incubation studies using isolated soil density fractions have reported conflicting outcomes: suppression of microbial activity because of tungsten toxicity (Crow et al., 2007) or increased microbial activity because of the loss of soil structure (Franzluebbers, 1999; Sorensen, 1983; Swanston et al., 2002). This ambiguity and lack of data has limited our ability to interpret the dynamic behavior of individual fractions, and how these contribute to the dynamics of whole soil (Denef et al., 2010).

The aim of this study is to assess the role of climate and soil profile depth in SOM stabilization by quantifying the distribution of C in free particulate, occluded particulate, and mineral adsorbed physical fractions isolated from surface soils and subsoils sampled from a climosequence in the Southern Sierra Nevada, USA. We characterize and compare the stability of SOM in these fractions from a bioenergetics viewpoint, in which the stability of SOM depends on the balance of microbial bioenergetics between the input of energy from a microbial community needed to access and to decompose it (activation energy) and the net energy gained (energy density) from its decomposition (Rovira et al., 2008). Activation energy (E_a) and energy density (ED) were quantified using simultaneous differential scanning calorimetry (DSC) and evolved CO_2 gas analysis during ramped combustion. We expect that the LF will be composed of molecularly complex particulate organic matter (estimated by the H:C ratio), and hypothesize that: (1) the LF will exhibit greater ED and E_a than the HF and that (2) the ED and E_a of bulk soils will decrease with depth, because of the reduction of particulate OM inputs at depth. Similarly, we expect increased SOM decomposition rates at the warmer sites, particularly of the LF, and hypothesize that (3) the ED and E_a of bulk soils will decrease with increasing mean annual temperatures.

2. Materials and methods

2.1. Soils

Soils were collected February 2015 through June 2016 (Table 1) from three forested locations (Short Hair Creek, SH; Providence Creek, PVD; Soaproot Saddle, SPR) in the Sierra National Forest and one mixed forest/grassland site (San Joaquin Experimental Range, SJER) in the California central valley (Fig. 1) in conjunction with the Southern Sierra Critical Zone Observatory (SSCZO). The SSCZO is an elevation transect that extends from oak grassland at lower elevations, through mixed-conifer forest, to the red-fir transition at higher elevations. The transect extends from the rain-dominated California central valley, through the snow-dominated higher elevations of the Sierra Nevada, with precipitation increasing and mean annual temperatures decreasing eastward and with increasing elevation (Table 1). The soils are derived from granitic parent material throughout the transect. At each location, four soil pits were dug to the bedrock contact and soil genetic horizons (A, B, etc.) delineated. Surface soils (i.e., the first A-horizon) and subsoils (i.e., the first B-horizon) were utilized for this study. Average horizon thickness at each site and B-horizon depths are presented in Table 1. Within 24 h of collection, soils were air dried at room temperature, then sieved through a 2-mm wire mesh. Soil fractions > 2 mm were discarded. A portion of the bulk soil was ground to homogeneity using a ceramic mortar and pestle.

2.2. Density fractionation

Surface soils (i.e., the first A-horizon) and subsoils (i.e., the first B-horizon) were separated into three density fractions: free light fraction (fLF), occluded light fraction (oLF), and heavy fraction (HF), using 1.7 g/mL sodium polytungstate [SPT, $Na_6(H_2W_{12}O_{40})$] solution according to the methods of Berhe et al. (2012). Briefly, a 20 g soil sample (sieved but unground) was placed in a 250 mL centrifuge bottle with 75 mL of SPT, capped, then inverted gently by hand five times, left to settle undisturbed for 45 min, and centrifuged at 3500 rpm (2583 RCF) for 1 h. The fLF, was removed by aspirating floating material into a sidearm flask. This material was filtered on a 0.8 μm polycarbonate membrane filter (Whatman) and rinsed five times with deionized water, and the residue (fLF) dried for 24–48 h at 105 °C. The volume of the remaining soil mixture was adjusted to 75 mL with the SPT solution and mixed for 1 min using a desktop mixer (Ika RW 20 Digital Overhead Stirrer), sonicated (using a Branson Digital Sonifier 250) to attain a dispersion energy of 440 J/mL, and centrifuged at 3500 rpm (2583 RCF) for 1 h. The oLF fraction was recovered using the same process as fLF above. The final residual soil mixture (HF) was repeatedly (5 ×) washed with 150 mL deionized water and centrifuged for 20 min at 3500 rpm (2583 RCF) for the first two rinses and 4000 rpm (3315 RCF) for the final three (3315 RCF). This HF fraction was dried for 24–48 h at 105 °C and ground to homogeneity using mortar and pestle. Before calculating distribution of C in the free light, occluded light, or heavy fractions we assume that the recovered mass in the three fractions is equal to total mass.

2.3. Elemental and thermal analyses

Prior to thermal analysis, ground bulk soil samples and soil fractions were analyzed for carbon and nitrogen concentrations using a Costech elemental analyzer (EA), and for hydrogen concentrations using a Thermo thermoconversion elemental analyzer (TCEA). Detailed methods about SOM hydrogen analysis and pre-treatment can be found in Ruppenthal et al. (2015). The hydrogen to carbon ratio (H:C) is a measure of the relative aromicity or carbon saturation state of the SOM, with higher H:C ratios corresponding to more aromatic or unsaturated organic matter. The carbon to nitrogen ratio (C:N) is an approximate indicator of the quality or degradation state of SOM, such that larger values are associated with fresher SOM and plant material, whereas smaller values are associated with degraded soil materials (Baldock and Broos, 2011).

Thermal analyses were performed by ramped combustion using a Netzsch STA 449PC Jupiter simultaneous thermal analyzer equipped with an automatic sample carrier (ASC) and a type-S platinum/rhodium (Pt/PtRh) sample carrier (Netzsch–Gerätebau GmbH, Selb, Germany) at the University of Pennsylvania. Thermal analysis has been demonstrated to be highly reproducible on a variety of soil types (Plante et al., 2009), thus thermal analyses on individual samples were not replicated. Samples were weighed to contain 1 mg C and were heated from ambient temperature (25 °C) to 105 °C at 10 °C min^{-1} under an oxidizing atmosphere of 40 mL min^{-1} of CO_2-free synthetic air (20% O_2 and N_2 balance). Samples were held at 105 °C for 15 min to allow for equivalent drying/moisture equilibration, then heated at 10 °C min^{-1} to 800 °C. Evolved CO_2 was analyzed using a coupled LICOR LI-820 infrared gas analyzer. Differential scanning calorimetry (DSC) heat flux (the exothermic or endothermic energy flux from a sample, referenced to an empty Pt/Rh crucible), thermogravimetric (TG) mass loss, and