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Accumulation of aliphatic compounds in soil with increasing mean annual temperature

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ABSTRACT

Chemical recalcitrance of biomolecules, physical protection by soil minerals and spatial inaccessibility to decomposer organisms are hypothesized to be primary controls on soil organic matter (SOM) turnover. Previous studies have observed increased sequestration of plant derived aliphatic compounds in experimentally warmed soils but did not identify the mechanisms for this enhanced preservation. To further test the role of environmental conditions in the preservation of aliphatic carbon, we analyzed native soils along a bicontinental, longitudinal, mean annual temperature (MAT) gradient to examine relationships between SOM composition, soil physical properties and temperature. Using biomarker analysis by gas chromatography–mass spectrometry and solid state ^{13}C nuclear magnetic resonance to characterize SOM, we observed that the concentration of aliphatic compounds derived from the waxes and cuticles of plant leaves increased with MAT. We did not observe any significant correlations between aliphatic SOM and clay mineral content which suggests that their inherent chemical recalcitrance is responsible for their persistence in soils. Other SOM components were not correlated with MAT, indicating that temperature alone does not control the overall preservation and biodegradation of soil carbon. As such, other environmental factors (e.g., microbial community structure and activity, litter quality and quantity, mineral surfaces, soil moisture content and antioxidant capacity) also play a role in the selective preservation or accumulation of various SOM components. However, our study shows that the accumulation of aliphatic SOM components is highly correlated to MAT.

1. Introduction

Climate change is predicted to increase the world's average temperature by 0.3–4.8 °C over the next 60–80 years (Collins et al., 2013). Warmer temperatures will likely alter plant species distribution (Walther et al., 2002) and increase vegetation productivity and litterfall (Liu et al., 2004). The response of different SOM components to rising temperature has been examined (Feng and Simpson, 2008; Feng et al., 2008; Haddix et al., 2011), however the mechanisms for stabilization and preservation in soils with a changing climate are still uncertain and further examination is an important step towards elucidating controls on SOM turnover in a changing world (Kirschbaum, 2006; Trumbore and Czimczik, 2008; von Lützow and Kögel-Knabner, 2009). The processes leading to SOM stabilization have been hypothesized to include: (1) selective preservation of chemically recalcitrant compounds, (2) spatial inaccessibility to decomposer organisms, (3) organic matter interactions with minerals, (4) the antioxidant activity of certain compounds and (5) water level fluctuations (Baldock and Skjemstad, 2000; Kögel-Knabner et al., 2008a; Marschner et al., 2008; Abbott et al., 2013; Schlichting et al., 2013). The temperature sensitivity of SOM decomposition can be described by kinetic theory and environmental constraints such as physical and chemical protection of organic matter, drought, flooding and freezing (Davidson and Janssens, 2006; Conant et al., 2011). Recently, it has been suggested that molecular structure alone does not control SOM stability and that this process should be viewed as an ecosystem property controlled by several environmental factors such as the presence of reactive mineral surfaces, climate, water availability, soil acidity, soil redox state and soil microbial community (Schmidt et al., 2011). Nonetheless, specific SOM components are believed to persist in soils due to their chemical recalcitrance which may be an inherent property of their molecular structure

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(e.g., aliphatic chains in lipids; Lorenz et al., 2007). Aliphatic molecules are abundant in the cuticles of plant leaves (9–25% of leaf carbon) and in the suberin of roots (8–12% of root carbon; Kolattukudy, 1980; Lorenz et al., 2007) and may comprise as much as 40% of the organic carbon in forest soils (Kögel-Knabner et al., 1992). These aliphatic compounds are believed to be relatively stable (Baldock et al., 1992; Riederer et al., 1993) and have been observed to accumulate in various types of soils (Nierop, 1998; von Lützow et al., 2006; Lorenz et al., 2007; Feng et al., 2008). Cuticle derived aliphatic compounds have also been shown to interact with mineral surfaces through selective sorption of polymethylene carbon (Feng et al., 2005), which may provide physical protection against microbial attack (Baldock and Skjemstad, 2000). In addition, cuticle derived compounds have been observed to accumulate with soil warming. For example, Feng et al. (2008) observed that after 14 months of soil warming, the concentration of cutin derived compounds originating from the waxy coatings of leaves, increased significantly, and this was attributed to both increased litter inputs and selective biodegradation of other SOM constituents at elevated temperatures. The mechanism for the stabilization of these aliphatic structures is still unknown. Thus, it is important to study the fate of plant derived aliphatic compounds in soils to better understand SOM turnover patterns at elevated temperatures.

To test the role of temperature as a control of SOM molecular composition, we analyzed soils collected along a mean annual temperature (MAT) gradient (Table 1) using several molecular marker (biomarker) analyses and solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The bicontinental, longitudinal MAT gradient spans from Indian Head, Saskatchewan to Rondônia, Brazil and represents a MAT range from 2–25.6 °C. We used a set of biomarkers to help elucidate the relationship between temperature and the persistence of SOM compounds of differing stability. The targeted biomarkers include: free lipids (of plant and microbial origin), ester bound lipids (from cutin and suberin biopolymers) and ether bound, lignin derived phenols. These SOM components have different chemical structures and have shown different stabilities and decomposition patterns in response to temperature (Feng and Simpson, 2008; Feng et al., 2008). For example, free lipids including long chain aliphatic compounds and plant steroids, were found to decompose faster at higher temperatures in a soil incubation study (Feng and Simpson, 2008). In addition, suberin is believed to be more resistant to biodegradation than cutin because it has a high content of phenolic units and is embedded in bark and root tissues (Riederer et al., 1993). However, the aliphatic components of suberin have been reported to degrade faster than those derived from cutin in a soil incubation study although no clear degradation trend was observed with increasing incubation temperature (Feng and Simpson, 2008). In fact, cutin derived aliphatic structures have been shown to accumulate in experimentally warmed soils (Feng et al., 2008). Finally, the decomposition of lignin in soils has been reported to increase with increasing temperature (Feng and Simpson, 2008; Feng et al., 2008). The combination of biomarker and NMR techniques has been applied successfully to directly examine the responses of SOM to soil warming (Feng et al., 2008). These techniques are highly complementary and provide detailed information on the source and degradation state of specific compounds (biomarkers) and the overall SOM structure (Simpson et al., 2008).

2. Material and methods

2.1. Soil collection and site characteristics

Soil samples were collected from six locations along a MAT gradient: Indian Head, Saskatchewan; Mandan, North Dakota; Akron, Colorado; Vernon, Texas; Alajuela, Costa Rica; Rondônia, Brazil (Table 1). The MAT ranges from 2 °C in Saskatchewan to 25.6 °C in Brazil. The mean annual precipitation (MAP) ranges from 402 mm in North Dakota to 2700 mm in Costa Rica. The temperate samples were collected from native grassland sites while the samples from Costa Rica and Brazil were collected from native forest sites. Surface litter and aboveground vegetation were cleared away prior to sampling and all samples were collected from 0–20 cm. Three field replicates were collected at each site and combined into one composite sample for laboratory analysis. Because of the low error obtained on the organic carbon analysis of the field replicates (Table S1), these were combined into one composite sample. After sampling, the soils were air dried, passed through a 2 mm sieve, ground with a mortar and pestle and stored at room temperature. Soil pH was measured using a 1:2 ratio of soil to deionized water (Thomas, 1993) with an Accumet® Basic AB15 pH meter (Fisher Scientific).

2.2. Soil organic matter analyses

Sequential chemical extractions (solvent extraction, base hydrolysis and cupric(II) oxide oxidation) were conducted in triplicate on the soil samples to analyze the free lipids, bound lipids and lignin derived phenols, respectively (Otto and Simpson, 2005, 2006a, 2006b). The soils (~15 g) were extracted in triplicate by sonication for 15 min with 30 ml CH_2Cl_2, CH_2Cl_2:CH_3OH (1:1 v:v) and CH_3OH. The combined solvent extracts were filtered through glass fiber filters (Whatman GF/A and GF/F), concentrated by rotary evaporation and dried under a N_2 stream in 2 ml glass vials. The soil residues were subjected to base hydrolysis to yield ester linked lipids (Goñi and Hedges, 1990; Otto and Simpson, 2006a). The air dried soil residues (0.1–2 g) were heated at 100 °C for 3 h in Teflon lined

Table 1
Sample characteristics including geographical location, soil type classification, sand, silt and clay content (%), mean annual temperature (MAT, °C), mean annual precipitation (MAP, mm), dominant vegetation, soil pH, total organic carbon (%) and total nitrogen (%).

Location	Latitude	Longitude	Soil type	Sand (%)	Silt (%)	Clay (%)	MAT (°C)	MAP (mm)	Vegetation	pH	C (%)	N (%)
Indian Head, Saskatchewan	50°53′N	103°52′W	Udic Borroll	28.6	21.1	50.2	2	427	Grassland, mostly cool season grasses	7.40	3.7	0.4
Mandan, North Dakota	46°77′N	100°92′W	Typic Argiboroll	25.5	46.3	28.3	5	402	Warm mixed grass prairie	6.58	3.2	0.3
Akron, Colorado	40°15′N	103°15′W	Aridic Paleustoll	36.1	40.9	23.0	9.2	420	Grassland, mostly C_4 grasses	7.00	1.2	0.1
Vernon, Texas	33°94′N	99°40′W	Typic Paleustoll	17.5	51.6	30.9	17	665	Grassland, mix of C_3 and C_4 grasses	7.47	1.1	0.1
Alajuela, Costa Rica	N/A	N/A	Hydric Melanudand	68.2	23.1	8.7	20	2700	Tropical forest, mostly C_3 species	5.22	20.0	1.7
Rondônia, Brazil	10°17′N	62°82′W	Paleudult & Kandiuldult	59.8	10.0	30.1	25.6	2200	Tropical forest, mostly C_3 species	4.33	1.1	0.1

Table information taken from Haddix et al. (2011) and references therein.