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Chemical and mineral control of soil carbon turnover in abandoned tropical pastures

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Abstract

We investigated changes in soil carbon (C) cycling with reforestation across a long-term, replicated chronosequence of tropical secondary forests regrowing on abandoned pastures. We applied CP MAS ^{13}C NMR spectroscopy and radiocarbon modeling to soil density fractions from the top 10 cm to track changes in C chemistry and turnover during secondary forest establishment on former pastures. Our results showed that inter-aggregate, unattached, particulate organic C (free light fraction) and particulate C located inside soil aggregates (occluded light fraction) represent distinct soil C pools with different chemical composition and turnover rates. The signal intensity of the O-alkyl region, primarily representing carbohydrates, decreased, and alkyl C, attributed to recalcitrant waxy compounds and microbially resynthesized lipids, increased from plant litter to soil organic matter and with incorporation into soil aggregates. The alkyl/O-alkyl ratio, a common index of humification, was higher in the occluded than in the free light fraction. Greater variability in the chemical makeup of the occluded light fraction suggests that it represents material in varied stages of decomposition. Mean residence times (^{14}C-based) of the free light fraction were significantly shorter (4 ± 1 years) than for the heavy fraction. We report two scenarios for the occluded light fraction, one fast-cycling in which the occluded and free light fractions have similar turnover rates, and one slow-cycling, in which the occluded light fraction resembles the heavy fraction. Mean residence times of the occluded light fraction and heavy fraction in active pastures and 10-year old secondary forests in the earliest stage of succession were longer than in older secondary forests and primary forests. This is likely due to a preferential loss of physically unprotected C of more labile composition in the pastures and in the youngest successional forests, resulting in an increase in the dominance of slow-cycling C pools. Soil carbon turnover rates of the mineral-associated C in secondary forests recovering from abandoned pasture resembled those of primary forests in as little as 20 years of succession.

Keywords: Soil organic matter; Density fractionation; Radiocarbon; CP MAS ^{13}C NMR spectroscopy; Reforestation; Land-use change

1. Introduction

Tropical and subtropical forests have the greatest potential to sequester and conserve large amounts of C relative to other forest biomes, as reported by the Third Assessment Report of the Intergovernmental Panel of Climate Change (Metz et al., 2001). Over half of this C sequestration potential could be achieved by slowing deforestation and by allowing for forest regeneration on abandoned agricultural and pasture lands (Brown et al., 1996). Reforestation and afforestation in the tropics result in high rates of C uptake in biomass (Watson et al., 2000). Less is known about the potential for C storage in soil organic matter (SOM), which is also an important contributor to soil fertility (Tiessen et al., 1994; Silver et al., 2000). As the largest terrestrial reservoir of C, soils may exert a strong influence on atmospheric CO_2 concentrations as C sources or sinks (Post et al., 1982; Eswaran et al., 1993; Batjes and Sombroek, 1997).

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Biochemical and physical stabilization of SOM are important mechanisms of soil C sequestration (Paul, 1984; Oades, 1988; Sollins et al., 1996; Krull et al., 2003; Mikutta et al., 2006). Biochemical processes include recalcitrant litter chemistries that slow down or inhibit microbial degradation (Scholes et al., 1997), and chemical transformations during humification and other oxidative reactions that lead to the synthesis of new compounds that are more resistant to decay than their precursors (Kögel-Knabner, 1993). In this paper, humification refers to the suite of chemical changes in organic matter resulting from the processes of microbially driven decomposition. Physical protection of C occurs though sorption to mineral and organic surfaces, reactions with Fe and Al oxides to form insoluble complexes, and occlusion inside soil aggregates (Hassink, 1997; Kaiser and Guggenberger, 2000; Baldock and Skjemstad, 2000; Balesdent et al., 2000; Six et al., 2002; Kalbitz et al., 2005). Other factors that affect SOM formation and decomposition include temperature, pH, and the availability of nutrients, O_2, and water (Fog, 1988; Zech et al., 1997; Scholes et al., 1997; Giardina et al., 2004; Swanston et al., 2004), as well as microbial community composition and enzyme availability (Schimel, 2001).

Modeling and experimental studies of SOM decomposition and the effects of cultivation on soil C have provided evidence for at least three distinct pools turning over on different time scales (Jenkinson and Rayner, 1977; Parton et al., 1987; Trumbore, 1993; Townsend et al., 1997): (1) an active or labile pool (one to five years), (2) a slow or intermediate pool (decades), and (3) a passive pool (centuries to millennia). Several approaches have been developed to reconcile these modeled C pools with operational, identifiable pools in soils (e.g., Greenland and Ford, 1964; Trumbore and Zheng, 1996; Christensen, 1996; Falloon and Smith, 2000; Wander, 2004; Ellerbrock and Kaiser, 2005; Kleber et al., 2005; Paul et al., 2006; Zimmerman et al., 2006). Physical fractionation separates SOM by particle-size, -aggregate-size, or density, without chemical modifications (Elliott and Cambardella, 1991; Golchin et al., 1994a,b; Baisden et al., 2002a). Methods that couple density fractionation with physical disruption of aggregates are useful for separating SOM fractions based on location in the soil matrix and degree of association with minerals (Golchin et al., 1995; Christensen, 2001; Swanston et al., 2005).

Recent applications of solid-state cross polarization magic angle spinning (CP MAS) ^{13}C nuclear magnetic resonance (NMR) spectroscopy to soils have increased our understanding of the chemical structure of SOM (Golchin et al., 1995; Kögel-Knabner, 1997, 2000; Preston 2001). ^{13}C NMR provides a first approximation of the relative abundance of organic C functional groups, which can be used as indicators for different compounds. The relative distributions of these broad C categories in SOM vary with decay and microbial processing (Baldock et al., 1992; Golchin et al., 1994b). Further information on specific types of compounds can be gained from ^{13}C NMR spectra by applying a molecular mixing model (Baldock et al., 2004). These techniques, coupled with physical fractionation and radiocarbon (^{14}C) modeling can provide a powerful assessment of the nature and turnover of soil C pools.

Little is known about long-term changes in tropical soil C with reforestation, particularly beyond the first two decades (Silver et al., 2000). Our research takes advantage of a historical trend in post-agricultural natural reforestation in Puerto Rico (Grau et al., 2003) to study long-term soil C dynamics. We used variable-amplitude (VA) CP MAS ^{13}C NMR and ^{14}C-based modeling of soil C turnover times to investigate changes in chemistry and stability of soil density fractions. The transitions from pasture grasses to forest trees, and from early to late successional species allowed us to study how changes in plant cover and litter chemistry affect soil C. We hypothesized that soil C pools, especially the fraction associated with aggregates, would turn over more rapidly in the active pastures compared to primary forests. Conversion of forest to pasture is often associated with a decrease in the amount of C associated with larger-sized aggregates and with their destabilization due to cattle disturbance and combustion during the slash-and-burn clearing process (Garcia-Oliva et al., 1999). We also hypothesized that concentrations of chemically recalcitrant compounds in SOM would increase due to aboveground changes in litter recalcitrance from forage pasture grasses to woody forest species. Plants produce lipids, such as waxes, cutin, suberin, and terpenoids, that are resistant to oxidation and consumption, as protection against herbivory and parasitism (Gleixner et al., 2001). The production of these and other plant secondary compounds is hypothesized to increase during tropical forest succession (Coley and Barone, 1996). We expected that differences in litter chemistry would result in increased soil C turnover time, not only between pastures and forests, but also with increasing forest age. We compared two approaches used to assess litter chemistry, solid-state ^{13}C NMR of whole litter and the more traditional proximate C fraction analysis (Preston et al., 2000).

2. Methods

2.1. Study sites

Our study sites were located between 580 and 700 m above sea level in the subtropical wet forest life zone (Ewel and Whitmore, 1973) in the Sierra de Cayey in southeastern Puerto Rico (18°01′ N, 66°05′ W). The dominant soil type is classified as very-fine, mixed, isothermic Inceptic Hapludox in the Los Guineos series (USDA soil map, Lugo-López et al., 1995). Soils are very deep, well-drained and from sandstone parent material. Mean annual temperature is estimated at 25 °C with little interannual variation and mean annual precipitation is 2000 mm (Daly et al., 2003; SERCC, 2006). The land-use chronosequence included three replicate sites each of primary forests, pastures, and secondary forests re-growing on pastures abandoned 10, 30, 60 and 80 years ago, and two replicate forests on pastures abandoned 20 years ago (Marín-Spiotta et al., 2007). Land-use history was identified by use of a time-sequence of aerial photographs and interviews with local landowners. The potential forest vegetation types in the region are lower montane wet evergreen forest, tall cloud forest, and palm breaks (Helmer et al., 2002). Primary forest sites were remnant forest fragments that had not been under pasture cover for at least the last century. Dominant pasture forage species included *Axonopus compressus*, *Panicum laxum* and *Sporobolus jacquemontii* (Sánchez-de León et al., 2003). Pasture sites were actively grazed at the time of sampling.