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Large fluxes and rapid turnover of mineral-associated carbon across topographic gradients in a humid tropical forest: insights from paired ^{14}C analysis

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Abstract

It has been proposed that the large soil carbon (C) stocks of humid tropical forests result predominantly from C stabilization by reactive minerals, whereas oxygen (O₂) limitation of decomposition has received much less attention. We examined the importance of these factors in explaining patterns of C stocks and turnover in the Luquillo Experimental Forest, Puerto Rico, using radiocarbon (¹⁴C) measurements of contemporary and archived samples. Samples from ridge, slope, and valley positions spanned three soil orders (Ultisol, Oxisol, Inceptisol) representative of humid tropical forests, and differed in texture, reactive metal content, O₂ availability, and root biomass. Mineral-associated C comprised the large majority (87 ± 2%, *n* = 30) of total soil C. Turnover of most mineral-associated C (74 ± 4%) was rapid (9 to 29 years, mean and SE 20 ± 2 years) in 25 of 30 soil samples across surface horizons (0–10 and 10–20 cm depths) and all topographic positions, independent of variation in reactive metal concentrations and clay content. Passive C with centennial – millennial turnover was much less abundant (26%), even at 10–20 cm depths. Carbon turnover times and concentrations significantly increased with concentrations of reduced iron (Fe(II)) across all samples, suggesting that O₂ availability may have limited the decomposition of mineral associated C over decadal scales. Steady-state inputs of mineral-associated C were similar among the three topographic positions, and could represent 10–30% of annual litterfall production (estimated by doubling aboveground litterfall). Observed trends in mineral-associated Δ¹⁴C over time could not be fit using the single pool model used in many other studies, which generated contradictory relationships between turnover and Δ¹⁴C as compared with a more realistic constrained two-pool model. The large C fluxes in surface and near-surface soils implied by our data suggest that other studies using single-pool Δ¹⁴C models of mineral-associated C dynamics, unconstrained by multiple time points, may have systematically underestimated C turnover.

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1 Introduction

Humid tropical forest soils represent a large terrestrial C reservoir (~ 500 Pg; Jobbagy and Jackson, 2000) with the potential to exert important feedbacks on global climate change, yet much remains unknown about the biogeochemical mechanisms underlying their C dynamics. Patterns and controls on plant litter decomposition in tropical ecosystems have been well documented in recent years (e.g. Cusack et al., 2009; Powers et al., 2009), but the turnover dynamics of soil organic C have received less attention (Trumbore et al., 1995; Torn et al., 1997; Telles et al., 2003; Marin-Spiotta et al., 2008; Giardina et al., 2014). The majority of organic matter (56–95 %) in humid tropical forests spanning a broad range of soil types has been shown to be associated with mineral particles (Trumbore et al., 1995; de Camargo et al., 1999; Telles et al., 2003; Marin-Spiotta et al., 2009; Cusack et al., 2011; Giardina et al., 2014). Previous work used radiocarbon (^{14}C) modeling to demonstrate that turnover times of mineral-associated C pools can vary by several orders of magnitude – from decades to millennia – within and among humid tropical soils (Trumbore et al., 1995; Torn et al., 1997; Telles et al., 2003). Nevertheless, relatively few studies have described the dynamics of mineral-associated C turnover in natural humid tropical forests, particularly in relation to proposed biogeochemical mechanisms of C stabilization. Constraining the turnover times of surface soil C pools and their biogeochemical drivers in humid tropical soils remains an important research challenge given their intimate couplings with plant productivity and potentially rapid responses to climate change.

Much of the recent work on soil organic matter stabilization has focused on the importance of reactive metals and short range-order minerals in protecting C via sorption and precipitation. Accordingly, concentrations of iron (Fe) and aluminum (Al) in various soil extractions often correlate strongly with spatial variation in soil C stocks (Torn et al., 1997; Baldock and Skjemstad, 2000; Powers and Schlesinger, 2002; Kleber et al., 2005; Kramer et al., 2012). Positive relationships between reactive Fe and Al and C stocks of mineral soils appear robust across a broad range of ecosystems, although

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there have been fewer tests of their impacts on C turnover rates. This distinction is important, because positive relationships between reactive metals and C stocks do not provide information regarding the dynamics of these C pools or the temporal scale of stabilization. Carbon turnover rates increased strongly with short range-order mineral content across gradients of precipitation and soil age in allophane-rich tropical Andisols (Torn et al., 1997; Giardina et al., 2014), and increased with reactive Al content across a sequence of temperate Mollisols, Alfisols, and Inceptisols (Masiello et al., 2004). However, the relative impact of reactive Fe and Al on mineral-associated C turnover has received less attention in highly weathered soils (Ultisols, Oxisols) that are commonly prevalent in humid tropical forests at a global scale. Similarly, the content and composition of silicate clay minerals are likely to contribute to soil C stabilization in many tropical ecosystems (Feller and Beare, 1997), although their impact on C turnover times in these soils remains unclear.

In addition to reactive metals and minerals, oxygen (O_2) availability and redox dynamics can also influence C dynamics in humid ecosystems where anaerobic microsites are especially prevalent in surface soils. All else being equal, rates of organic matter decomposition typically decline under sustained anaerobic conditions (Ponnamperuma, 1972). However, recent work has demonstrated high spatial and temporal variation in O_2 availability in surface soils of humid tropical forests, and the concomitant importance of anaerobic metabolic processes such as dissimilatory Fe reduction in maintaining high rates of soil respiration (Silver et al., 1999; Schuur et al., 2001; Dubinsky et al., 2010; Liptzin et al., 2011; Hall et al., 2013). Soil C stocks increased with decreasing redox potential across a Hawaiian rainfall gradient even as net primary productivity declined, suggesting that reducing conditions constrained decomposition and promoted organic matter accumulation at the landscape scale (Schuur et al., 2001). At smaller spatial scales ranging from topographic catenas to soil microsites, variation in O_2 availability and reducing conditions could potentially have similar impacts on soil C cycling.

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Radiocarbon analysis is a powerful method for modeling turnover times of slow-cycling C pools, such as those associated with mineral surfaces, which are generally thought to exhibit turnover times of many decades to millennia. However, a paucity of replicated ^{14}C measurements in many studies has typically prevented statistical examination of relationships between turnover times and proposed C stabilization mechanisms. Furthermore, many previous ^{14}C studies have used turnover models assuming that operationally-defined organic matter pools (separated by physical or chemical fractionation) have homogeneous turnover rates. Yet, it has been demonstrated that operationally-defined C fractions (e.g. free, aggregate-occluded, and mineral-associated) seldom represent pools with uniform turnover, and the inclusion of multiple pools with distinct turnover times *within* measured fractions is often necessary to generate realistic model results (Trumbore et al., 1995; von Lützow et al., 2007; Baisden et al., 2013; Torn et al., 2013). Using multiple ^{14}C measurements over time provides a valuable method for constraining the turnover of multiple pools within a single measured fraction (Trumbore et al., 1996; Koarashi et al., 2012; Baisden et al., 2013), particularly in humid tropical ecosystems (Telles et al., 2003).

Here, we assessed the relative importance of several proposed C stabilization mechanisms (reactive metal content, soil texture, and proxies for reducing conditions) in explaining patterns of mineral-associated C concentrations, stocks, and turnover, using ^{14}C measurements and modeling of density-fractionated samples. We intensively sampled soils across a topographic catena spanning three soil orders (an Ultisol, Oxisol, and Inceptisol) typical of humid tropical forest ecosystems (McDowell et al., 2012). Samples represented a range of soil geochemical characteristics and O_2 dynamics in close spatial proximity (tens of m) (Silver et al., 1999). Our sampling strategy captured relatively large differences in soil biogeochemical characteristics while controlling for temperature, a potentially critical influence on the turnover of decadal-cycling C (Townsend et al., 1995). To provide a more rigorous interpretation of our contemporary soil ^{14}C data, we constrained models of C turnover with ^{14}C measurements from archived (1988) samples from the same site. Finally, to illustrate

the importance of considering multiple pools and ^{14}C timepoints for fitting C turnover models to data, we compared modeled turnover times of mineral-associated C between a simple one-pool model commonly used in the current literature, and a two-pool model constrained by historical data.

2 Methods

2.1 Site description

We sampled ridge, slope, and valley topographic positions along a hillslope catena in the Bisley Watershed of the Luquillo Experimental Forest, Puerto Rico, an NSF-funded Long Term Ecological Research and Critical Zone Observatory site. Our sites (250 m a.s.l., 18.3157° N, 65.7487° W) support a lower montane tabonuco (*Dacryodes excelsa*) forest with a mean annual temperature of 23°C. Annual precipitation averaged 3800 mm yr⁻¹ and varied between 2600 and 5800 mm yr⁻¹ from 1989–2011 (Scatena et al., unpublished data); see McDowell et al. (2012) for a detailed site description. Soils formed from volcanoclastic sedimentary rocks derived from andesitic to basaltic material, and catena positions represent three different orders in the USDA taxonomy (Soil Survey Staff, 2002). Ridges are dominantly Ultisols (Typic Haplohumults), slopes are Oxisols (Inceptic and Aquic Hapludox), and valleys are Inceptisols (Typic Epiaquepts). Catena positions differed in surface soil O₂ concentrations, measured at 10 cm depth over several years (Silver et al., 1999). Mean O₂ concentrations decreased from ridges to slopes to riparian valleys (19, 16, and 10% O₂, respectively), with increasing temporal variability such that valley soils frequently experienced low O₂ (≤ 3%). Anaerobic microsites are present in all topographic positions, indicated by periodic methane emissions (Silver et al., 1999). Given that Fe oxides represent the most abundant anaerobic terminal electron acceptor in these soils (Hall et al., 2013) we used measurements of Fe(II) to provide an index of reducing conditions at the scale of individual soil samples. We acknowledge that soil Fe(II) concentrations constitute

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a one-time measurement in a dynamic redox environment, but indices of O₂ availability and other redox reactions tended to vary consistently with Fe(II) concentrations among plots and over time (Hall et al., 2013).

2.2 Soil sampling and analysis

5 We dug a soil pit in each catena position to establish relationships between soil depth and horizons. Mineral soil A horizons spanned depths of 0–10, 0–9, and 0–10 cm in the ridge, slope, and valley, whereas B1 horizons were at depths of 10–22, 9–25, and 10–20 cm, respectively. Visual inspection of soil cores showed that A horizon depths were reasonably consistent among samples, but total soil depth varied among plots and
10 occasionally did not exceed 20 cm in the riparian valley (due to the sporadic presence of buried boulders). We thus sampled soils at depths of 0–10 and 10–20 cm, which contain the large majority of roots and organic matter in this ecosystem (Silver and Vogt, 1993).

We established five 0.25 m² plots in each topographic position (ridge, slope, and valley) for a total of 15 plots in the same field sites previously examined by Silver et al. (1999). Plots were randomly placed within 5–10 m intervals along a 50 m linear transect. On the slope position, the slopes of individual plots varied between 25 and 40°. Surface organic horizons were usually sparse, and any O horizon material was removed prior to coring. In each plot and depth increment (total $n = 30$), we
20 collected a total of four replicate 6 cm diameter soil cores. Two cores from each plot were sampled in July 2011 to determine bulk density and fine root biomass, and two additional cores were sampled in February 2012 for C density fractionation and chemical analysis.

The cores for chemical analyses were immediately homogenized in the field, and separate subsamples extracted in 0.5 M hydrochloric acid (HCl) and 0.2 M sodium citrate/0.05 M ascorbic acid solutions within 1–2 min of sampling. The low pH of the HCl extraction inhibits oxidation of Fe(II). Soil subsamples (3 g dry mass equivalent) were immersed in a 1 : 10 ratio with HCl, vortexed, shaken for 1 h, and filtered

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to 0.22 μm . Concentrations of Fe(II) were measured using a colorimetric ferrozine assay and corrected for Fe(III) interference (Viollier et al., 2000). We used Fe(II) concentrations as an index of reducing conditions at the scale of soil samples, given that Fe reduction represents the dominant anaerobic respiratory process in this system (Dubinsky et al., 2010), and that Fe(II) readily oxidizes in the presence of O_2 . Separate subsamples were extracted in the field with sodium citrate/ascorbate solution (Reyes and Torrent, 1997) to provide an estimate of reactive Fe oxides (Fe_{ca}) and associated Al (Al_{ca}) in short range-order minerals and organic fractions. Short range-order Fe and organo-Fe complexes are analytically indistinguishable in chemical extractions, with nano-scale Fe (oxy)hydroxides often dominating (Thompson et al., 2011); thus we subsequently refer to Fe_{ca} as “reactive.” Aluminum is not redox active in soils but frequently substitutes in Fe minerals, and various Al (oxy)hydroxide species and monomeric Al also associate with organic compounds. In the absence of detailed Al speciation data, we similarly refer to Al_{ca} as “reactive.” Soil subsamples (1.5 g dry mass equivalent) were immersed in a 1 : 30 ratio with citrate/ascorbate solution, vortexed, shaken for 18 h, and centrifuged for 10 min at 1500 rcf.

Field extractions likely yield the most representative patterns of reactive metal abundance due to rapid crystallization of short range-order minerals upon drying, but we also extracted oven-dried (105 $^{\circ}\text{C}$) and ground heavy density fractions (described below) with acid ammonium oxalate solution in the dark at pH 3 to allow comparison with previous studies (e.g. Kleber et al., 2005). Drying soils leads to mineral crystallization, thus decreasing extractable metal concentrations. However, oxalate extraction of moist samples with high Fe(II) is undesirable and can promote catalytic extraction of crystalline Fe oxides (Phillips et al., 1993). Subsamples (0.5 g) were extracted for two hours in 30 mL of ammonium oxalate solution. For all of the above extractions, concentrations of Fe and Al were analyzed in triplicate using an inductively coupled plasma optical emission spectrometer (ICP-OES; Perkin Elmer Optima 5300 DV, Waltham, Massachusetts). Total Fe measured colorimetrically in HCl extractions agreed within 1 % of ICP-OES measurements. Soil pH was measured in 1 : 2 slurries of

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soil and deionized water. Additional subsamples of field-moist soil from each plot were analyzed for particle size by the hydrometer method (Gee and Bauder, 1986). Samples (50 g dry mass equivalent) were passed through a 2 mm sieve and immersed for 16 h in sodium hexametaphosphate solution (50 g L^{-1}) to chemically disperse aggregates, which were then physically dispersed in an electric mixer. We measured changes in soil suspension density over 24 h to calculate clay, sand, and silt fractions.

We assayed the two remaining replicate 6 cm diameter cores from each plot and depth increment for fine root biomass and bulk density, respectively. Fine roots (< 2 mm diameter) were separated from soil by wet sieving and separated into live and dead fractions based on visual observations of turgor and tensile strength. Roots were thoroughly washed in deionized water and dried at 65°C . To determine bulk density from the intact cores, we carefully removed any coarse roots and rocks (which were rare) after cleaning them to retain all soil. We estimated the volume of coarse roots > 5 mm using a cylindrical approximation, and measured the volumetric water displacement of rocks with diameter > 2 mm; these corrections minimally affected our bulk density measurements (mean relative change of 2%). Soils were dried at 105°C to constant mass, and bulk density was calculated as dry soil mass divided by coarse root and rock-corrected sample volume.

2.3 Soil density fractionation

We separated soil organic matter from each plot/depth increment ($n = 30$) into three fractions based on density and occlusion: (1) a free light fraction consisting of low-density ($< 1.85 \text{ g cm}^{-3}$) organic matter not contained within aggregates, (2) an occluded light fraction, comprising low-density organic matter released from aggregates following sonication, and (3) a heavy fraction with density $> 1.85 \text{ g cm}^{-3}$ associated with soil minerals. Soil cores for density fractionation were stored at field moisture in sealed polyethylene bags at 4°C and analyzed within 6 months of collection. We used the same protocol to fractionate four air-dried archived samples (0–10 cm increment) that were collected in 1988 from nearby slope and riparian

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valley plots representative of the plots sampled in 2012 (Silver et al., 1994). The samples from 1988 served as a benchmark for a two-pool ^{14}C model, and were not intended to describe ecosystem-scale or temporal patterns in the C content of density fractions. The fractionation assay followed Swanston et al. (2005) as modified for Fer-rich soils (Marin-Spiotta et al., 2008). We passed samples (20 g dry mass equivalent) through a 4.75 mm sieve to remove coarse litter fragments while maintaining aggregate structure. The free light fraction was separated by flotation after immersing soils in sodium polytungstate at a density of 1.85 g cm^{-3} . The occluded light fraction was similarly obtained after mixing and sonicating soils to disrupt aggregates, with a total energy input of 200 J mL^{-1} . The heavy fraction consisted of the remaining mineral-associated organic matter. Mass recovery of density fractions from 2012 samples measured $100 \pm 1\%$ (mean \pm SE) of the initial soil mass; mass recovery greater than 100% may reflect residual sorption of a small amount of sodium polytungstate or heterogeneous soil moisture content of the moist soil samples. Recovery measured $95.0 \pm 0.3\%$ for the air-dried 1988 soils. Masses of free and occluded light fractions may differ between the air-dried 1988 samples and field-moist 2012 samples due to the notable effects of air-drying on aggregate structure, but variation in sample moisture during fractionation is less likely to impact the partitioning of C between particulate C and mineral-associated fractions. Oven-dried (105°C) density fractions were analyzed in duplicate for C concentrations and $\delta^{13}\text{C}$ isotopic ratios relative to V-PDB on a Vario Micro elemental analyzer in-line with an Isoprime 100 isotope ratio mass spectrometer (Elementar, Hanau, Germany).

2.4 Radiocarbon measurements and modelling

We measured radiocarbon content of the 30 heavy fraction samples from 2012 and the four samples from 1988 on the Van de Graaff FN accelerator mass spectrometer at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory, Livermore CA. Heavy C fractions were subsampled into quartz tubes which were evacuated, flame-sealed, and combusted in the presence of copper oxide and silver.

Resulting CO₂ was reduced to graphite on iron powder in the presence of H₂ at 570 °C. Corrections were applied for mass-dependent fractionation using measured δ¹³C, for sample preparation background using ¹⁴C-free coal, and for ¹⁴C decay since 1950. We report final radiocarbon values in Δ¹⁴C notation with an average precision of 3‰ (Stuiver and Polach, 1977).

We modeled the turnover time of mineral-associated C using a time-dependent steady-state difference equation model of soil Δ¹⁴C dynamics in conjunction with Δ¹⁴C of atmospheric CO₂ (Trumbore, 1993; Torn et al., 2009). We assumed that Δ¹⁴C of a soil organic matter pool in a given year is a function of soil Δ¹⁴C from the previous year minus losses from decomposition and radioactive decay, plus additions of recently-fixed CO₂ with atmospheric Δ¹⁴C, represented by the following equation:

$$F'_{\text{soil pool},t} = kF'_{\text{atm},t} + F'_{\text{soil pool},t-1}(1 - k_{\text{soil pool}} - \lambda) \quad (1)$$

Here, F' equals $\Delta^{14}\text{C}/1000 + 1$ at time t , k is the decomposition rate constant, and λ is the radioactive decay constant; the subscripts atm and soil pool indicate the atmosphere and an arbitrary soil C pool, respectively. We used a time series of atmospheric $\Delta^{14}\text{CO}_2$ measurements from 1511 to 1950 (Stuiver et al., 1998) and 1950–2009 (Hua et al., 2013) for atmospheric zone 2, which includes Puerto Rico, and assumed a 5‰ annual decline in atmospheric $\Delta^{14}\text{C}$ from 2010 to 2012 (Fig. 1). This model implies first-order decay such that the inverse of the modeled decomposition rate constant represents the mean turnover time of a soil C pool. The modeled turnover time of a soil C pool represents a maximum estimate given that plant C does not always enter the soil during the same year that it is fixed via photosynthesis; thus, turnover times represent the residence time of C in the plant/soil system. The model also assumes that mineral-associated C pools are at steady state, an assumption supported by annual soil C measurements in nearby plots over a decade that included multiple hurricanes (Teh et al., 2009), and similarities in forest above-ground biomass since the late 1980's (Heartsill Scalley et al., 2010).

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A single-pool model for the mineral-associated (heavy) C fraction could not reproduce the observed temporal trend of $\Delta^{14}\text{C}$ between 1988 and 2012. Therefore, we assumed that the mineral-associated C fraction was the sum of two pools that cycled over different timescales: a slow pool with decadal turnover, and a passive pool with centennial to millennial turnover (Trumbore et al., 1995; Telles et al., 2003; Baisden et al., 2013).

$$F'_{\text{heavy},t} = P_{\text{slow}}F'_{\text{slow},t} + (1 - P_{\text{slow}})F'_{\text{passive},t} \quad (2)$$

Here, P_{slow} represents the proportion of mineral-associated C in the slow pool. Incorporating two separate pools of organic matter in the dense fraction was necessary to fit decomposition rate constants to the observed $\Delta^{14}\text{C}$ values in 2012 and 1988, and is consistent with long-term observations of soil organic matter dynamics constrained by frequent $\Delta^{14}\text{C}$ measurements (Baisden et al., 2013). The passive C fraction contains negligible modern ^{14}C and acts to dilute the modern ^{14}C signal of the faster-cycling slow C pool.

Thus, our model had three free parameters: turnover times of the slow and passive pools, and the proportion of mineral-associated C in the slow pool. We estimated two of the three parameters, the proportion of slow pool C and its turnover time, with our data (soil $\Delta^{14}\text{C}$ from 1988 and 2012). For the third parameter, turnover time of the passive pool, we assumed a liberal range of values (100–1000 years), and assessed impacts on the other parameters by randomly selecting values from a uniform distribution. Previous studies have assumed passive C turnover times of several hundred to 100 000 years (Trumbore et al., 1995; Telles et al., 2003; Baisden et al., 2013). However, empirically determining passive C ages is difficult. Radiocarbon analysis of C remaining after acid hydrolysis has been used to define passive C age, yet even hydrolysis residue may contain bomb ^{14}C , indicative of faster turnover times (Telles et al., 2003). Here, we assumed a relatively faster distribution of passive turnover times because these allow for realistic increases in model uncertainty. For example, allowing passive C turnover to increase from 1000 to 100 000 years in our

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models had very little effect on mean slow pool turnover (< 0.2 year), but substantially *decreased* the variance by decreasing the overall proportion of model runs that had shorter turnover times of the passive pool, given that shorter turnover times have more leverage on model results.

To infer temporal trends in $\Delta^{14}\text{C}$, previous studies have used representative samples collected at locations within 100 m of one another (Trumbore et al., 1996), and over even greater distances when similarities in ecosystem state factors could be maintained (Baisden et al., 2013). However, soils display fine-scale spatial heterogeneity that can potentially complicate the assessment of temporal trends, even when samples are collected in close spatial proximity. The differences in $\Delta^{14}\text{C}$ that we observed among 2012 samples over fine spatial scales (meters to tens of meters) thus precluded *absolute* comparisons between individual samples from 1988 and 2012, as 1988 sampling locations could not be located to that degree of resolution. To assess the impacts of fine-scale spatial variation in $\Delta^{14}\text{C}$ on model outcomes, we varied the values of 1988 $\Delta^{14}\text{C}$ in the model by sampling from a normal distribution defined by the observed values (mean and standard deviation of $\Delta^{14}\text{C} = 186 \pm 10\text{‰}$), and excluding the extreme 5% of the distribution to ensure model convergence. Thus, we generated 1000 distinct sets of parameters (passive pool turnover time and the resulting passive $\Delta^{14}\text{C}$ in 1988 and 2012, and total mineral-associated $\Delta^{14}\text{C}$ in 1988) to evaluate impacts on modeled slow pool C abundance and turnover. We acknowledge that fitting each of the 2012 samples to the same distribution of $\Delta^{14}\text{C}$ in 1988 is imperfect, as $\Delta^{14}\text{C}$ in 1988 and 2012 are likely correlated. However, the Monte Carlo approach employed here allowed us to assess the importance of variation in assumed 1988 $\Delta^{14}\text{C}$ on modeled turnover times. Varying the assumed 1988 $\Delta^{14}\text{C}$ had relatively minor impacts on modeled slow pool turnover, affecting turnover times by an average of four years (Table S1 in the Supplement).

For each 2012 soil sample and randomly generated parameter set, we calculated the turnover time and proportion of slow-cycling C with Eqs. (1) and (2), adjusting k_{slow} and P_{slow} until modeled $\Delta^{14}\text{C}$ matched measured $\Delta^{14}\text{C}$ in 1988 and 2012. Five

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2012 samples had $\Delta^{14}\text{C}$ less than the 2012 atmosphere; therefore, slow pool turnover times for these samples could not be realistically constrained using the bomb- ^{14}C enriched 1988 samples (Fig. 1). We made the simplifying assumption that variation in the proportion of slow vs. passive C was primarily responsible for the lower $\Delta^{14}\text{C}$ of these samples, and that slow pool turnover times were of similar magnitude as the other samples. To estimate proportions of slow vs. passive cycling C in these five samples, we randomly selected 1000 slow pool turnover times from the previously modeled distribution (19 ± 3.9 years) in addition to the other randomly selected parameters described above. Then, we solved for P_{slow} without constraining the model to 1988 data. All modeling was conducted with R version 3.0.2, and free parameters were fit using the “optim” function with the Nelder–Mead method. After estimating k_{slow} and P_{slow} , we calculated annual C inputs to the slow pool under steady state by dividing slow pool C stocks by turnover times. This calculation involves a ratio of two modeled parameters ($P_{\text{slow}}/k_{\text{slow}}$) with known variances; thus, we used a Taylor Series approximation to estimate the standard deviation of slow pool C inputs. Standard errors reported below include the sum of modeling variation and spatial variation.

2.5 Statistical analysis

We assessed relationships between biogeochemical variables and C cycling among individual samples and catena positions using linear mixed effects models fit with the lme function in R (Pinheiro et al., 2014). Interactions among topographic positions and depths were assessed by assigning a distinct factor level to each position/depth combination, with post-hoc comparisons using the Tukey method. To assess topographic variation in C from 0 to 20 cm, C was summed by depth increment for each plot. In addition, we fit linear mixed effects models for mineral-associated C concentrations and stocks in individual samples. Potential predictor variables included $\Delta^{14}\text{C}$ and the other measured biogeochemical variables described above. We normalized predictor variables by mean and standard deviation to allow comparison

of their relative importance (analogous to Pearson's r). Models included plots as potential random effects to account for any correlation between depth increments in a given plot. We selected the optimal random effect structure by comparing the Akaike Information Criterion (AIC) of saturated models fit using restricted maximum likelihood.

5 Including random effects did not improve fit, so we proceeded with multiple regression. We selected fixed effects on models fit using maximum likelihood using backwards selection and AIC with a correction for small sample size, and reported models with similar goodness of fit.

3 Results

10 3.1 Topographic patterns in soil C and biogeochemical variables

Mineral-associated C comprised the dominant C fraction across all topographic positions, representing 90 ± 1 , 89 ± 1 , and $80 \pm 4\%$ of total soil C in the ridge, slope, and valley soils, respectively (Table 1, Fig. 2, Table S1). Mineral-associated C content (soil mass basis) in ridge 0–10 cm soils was 1.45 times greater ($p < 0.01$) than slopes and valleys (Fig. 2, Table 1). Mineral associated C content was also greater in surface (0–10 cm) than subsurface (10–20 cm) soils on ridges and slopes, but did not differ by depth in valleys. Free light C content was similar among topographic positions. Valleys had significantly more occluded light C when considering both depth increments together, measuring 3.6 times the occluded light C on ridge and slope soils (Fig. 2; $p < 0.05$). Carbon concentrations of the individual fractions generally showed similar trends with topography and depth as soil mass-based C content (Table 1). Heavy fraction C concentrations were greatest in ridge surface soils, and occluded light C concentrations were greatest in valley soils. Heavy fraction C content was lower in the four 1988 samples than in many of the 2012 samples (Table S2), but replication was
25 insufficient to assess any temporal changes.

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Paralleling the topographic patterns in mineral-associated C, most measured biogeochemical indicators varied strongly and significantly across the catena (Tables 2 and S3). Ridges supported the highest fine root biomass, which declined in the slopes and valleys. Soil pH was significantly more acidic (4.6 ± 0.0) in the ridge and slope samples than in the valleys (5.2 ± 0.1 ; $p < 0.0001$), regardless of depth increment. Clay content was consistently high in ridge and slope samples ($41 \pm 3\%$) and significantly lower in the valley soils ($23 \pm 2\%$; $p < 0.0001$). Conversely, sand content was low in ridge and slope samples but was 2–3 times greater in the valley soils, and silt content was similar across topographic positions. Clay content increased and silt declined with depth in the ridge soils, while texture did not vary significantly with depth in the other topographic positions.

Reactive Fe and Al showed distinct patterns among topographic positions and depths that varied by chemical extraction (Table 2). Concentrations of Fe and Al extracted in the field by citrate-ascorbate solution (Fe_{ca} and Al_{ca}) were significantly (more than two-fold) greater in ridge than in slope or valley surface soils. Oxalate extractions of dried soil heavy fractions yielded significantly greater Al in ridge surface soils than most other positions/depths, but Fe_{ox} varied little among samples. Concentrations of Fe_{ox} and Fe(II) were the only measured biogeochemical variables that did not vary by topographic position. Fe(II) concentrations were variable and consistently measurable, indicative of the ubiquitous presence of reducing microsites across the plots.

Mineral-associated C stocks varied almost three-fold among samples, between 1230 – 3030 g C m^{-2} (mean 2150 ± 100) in each 10 cm depth increment (Tables 1 and S1). Summing the two 10 cm depth increments in each plot yielded mineral-associated C stocks of 3310 – 6630 g C m^{-2} (mean 5010 ± 290) to 20 cm depth. Despite the large and significant differences in C concentrations, mass based C content, and reactive Fe and Al across the catena, mineral-associated C stocks were statistically similar among the topographic positions (Fig. 2) due to co-variation in bulk density. Bulk density was significantly lower in ridge 0–10 cm soils than all other positions, whereas mineral-associated C concentrations and mass based C content were greatest in these

samples ($p < 0.01$; Fig. 2, Table 1). Mass-based mineral-associated C content and bulk density also negatively co-varied at the scale of individual samples ($R^2 = 0.49$, $p < 0.0001$).

Of the density fractions measured, only the occluded light fraction C stocks differed by topographic position; these were significantly greater in valleys when considering both depth increments together ($p < 0.05$). Total soil C stocks (sum of all three fractions in each depth increment) did not significantly differ among positions in either depth increment. Similarly, total C stocks summed to 20 cm in each plot (g C m^{-2}) did not differ significantly, although valleys tended to be greatest (5558 ± 511), ridges intermediate (5112 ± 337), and slopes lowest (4370 ± 579 ; Table 1).

3.2 Patterns in $\Delta^{14}\text{C}$, turnover and C inputs

The four soil samples from 1988 were enriched in ^{14}C relative to the 2012 samples, reflecting a dominance of C with decadal turnover in the 0–10 cm depth increment (Fig. 1a and b, Tables 3 and S2). Figure 1 shows temporal trends in modeled $\Delta^{14}\text{C}$ for three representative 2012 samples. Radiocarbon content in the 2012 mineral-associated C fractions exceeded the 2012 atmosphere for most samples (25 of 30; Fig. 4, Table S2), reflecting the dominance of bomb C inputs over the preceding decades. Radiocarbon content tended to be greatest in valley 10–20 cm and lowest in slope 10–20 cm soils, but differences were not significant across catena positions and depths, with the exception of slope and valley 10–20 cm samples (Table 3). Five slope and ridge samples had lower $\Delta^{14}\text{C}$ than the 2012 atmosphere ($< 30\%$), indicating dominance of slower cycling C pools (centennial – millennial; Fig. 1c) where turnover could not be constrained using the bomb ^{14}C -enriched surface soil samples from 1988 (Fig. 1c). Figure 1 shows that in samples dominated by decadal-cycling C, larger $\Delta^{14}\text{C}$ values in 2012 correspond with longer turnover times, whereas for samples dominated by centennial-cycling C, smaller $\Delta^{14}\text{C}$ values in 2012 imply longer turnover times.

Mean modeled turnover times of the slow pool of mineral-associated C varied between 9 and 29 years, with an overall mean and SE of 20 ± 2 years ($n = 25$) among

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samples where $\Delta^{14}\text{C}$ exceeded the 2012 atmosphere (Fig. 1; Table S2). Sensitivity analyses showed that varying turnover times of the passive mineral-associated C pool and sample $\Delta^{14}\text{C}$ in 1988 had relatively little impact on slow pool size and turnover times. The combined impact of varying passive C turnover between 100 and 1000 years and varying 1988 $\Delta^{14}\text{C}$ over 1000 model runs generated standard deviations in slow pool turnover times between 3 and 6 years (mean 4.0 ± 0.1) for individual samples (Table S1). Slow pool turnover times and relative abundance did not differ significantly among topographic positions or depth, although the modeled percentage of slow pool C was smallest in the slope 10–20 cm soils, corresponding with lowest sample $\Delta^{14}\text{C}$ (Table 3).

Slow pool C greatly exceeded passive C in most (25 of 30) samples, accounting for $74 \pm 4\%$ of the mineral-associated fraction (Table 3). Variation in model parameters had little impact on the size of the mineral-associated slow C pool; standard deviations of the percentage of slow pool C varied between 3 and 10% for individual soil samples (mean $5.0 \pm 0.4\%$). However, inputs of C to the slow pool required to maintain steady-state C stocks in each 10 cm depth increment varied more than five-fold among samples (between 27 and $153 \text{ gC m}^{-2} \text{ yr}^{-1}$) with an overall mean and SE of $82 \pm 11 \text{ gC m}^{-2} \text{ yr}^{-1}$ (Table 3; Table S1). When summed over both depths, slow pool C inputs tended to be greatest on ridges, intermediate in valleys, and lowest on slopes, measuring 191 ± 30 , 166 ± 21 , $138 \pm 24 \text{ gC m}^{-2} \text{ yr}^{-1}$; these differences were not statistically significant.

The slow pool of our constrained two-pool model and the simple one-pool model of mineral-associated C turnover implied contradictory relationships (of opposite sign) between C turnover times and $\Delta^{14}\text{C}$ (Fig. 3). Slow pool turnover time increased with $\Delta^{14}\text{C}$, whereas the overall turnover times of a single pool model decreased with $\Delta^{14}\text{C}$.

3.3 Statistical models of C concentrations, stocks, and turnover

Mineral-associated C concentrations (mass basis) decreased with depth, increased with Al_{ca} , Fe(II), and Al_{ox} concentrations, and showed no relationship with $\Delta^{14}C$ or modeled slow pool turnover times (Table 4). Excluding depth as a potential variable in model selection yielded a model with similar explanatory power that included live fine root biomass. Both models explained the majority of spatial variation in mineral-associated C concentrations, with R^2 values of 0.88 and 0.73, respectively. Two similar models of mineral-associated C stocks included (a) $\Delta^{14}C$ and Al_{ox} , or (b) Fe(II) and depth, and explained less variation than models of C concentrations ($R^2 = 0.46$ and 0.43 respectively, Table 4). The optimal model for $\Delta^{14}C$ and the slow pool turnover time of the mineral-associated C fraction included only one variable: $\Delta^{14}C$ increased with log-transformed Fe(II) concentrations ($R^2 = 0.35$, $p < 0.001$; Table 4, Fig. 4), as did slow pool turnover times ($R^2 = 0.25$, $p < 0.05$; Table 4).

4 Discussion

We examined relationships between soil C content, turnover of mineral-associated C, and a suite of soil biogeochemical variables thought to affect C storage across topographic zones representing three different soil orders characteristic of humid tropical forests. Samples differed greatly in their concentrations of reactive Fe and Al, reducing conditions (as measured by Fe(II) concentrations), and live fine roots – drivers that have been proposed to control soil C dynamics within and among ecosystems (Torn et al., 1997; Schuur et al., 2001; Powers and Schlesinger, 2002; Kleber et al., 2005). While we found strong relationships between several of these biogeochemical indices and mineral-associated C concentrations, they explained less variation in mineral-associated C stocks and turnover, which were surprisingly consistent across these disparate soils. Thus, despite the demonstrable differences in biogeochemical characteristics among topographic positions, our results implied that

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these soils received similar annual inputs of C to a slow-cycling mineral-associated C pool.

4.1 Patterns of mineral-associated C concentrations and stocks

The mineral-associated “heavy” fraction comprised the vast majority of soil C in this ecosystem, similar to findings from other humid tropical forests (Trumbore, 1993; Marin-Spiotta et al., 2009; Cusack et al., 2011), and contrasting with many temperate forests where low-density C fractions are often significant in mineral soils (von Lützow et al., 2007). We could explain a large majority of the variation in mineral-associated C concentrations across the catena with a small suite of biogeochemical drivers: concentrations of reactive Al, Fe(II), and depth, a factor that could largely be explained by live fine root biomass. These models of C concentrations are consistent with previous work documenting strong and widespread relationships between reactive metals, short range-order minerals and C content across disparate soils (e.g. Baldock and Skjemstad, 2000; Kleber et al., 2005; Kramer et al., 2012). However, models also reflected the likely importance of reducing microsites, as indicated by Fe(II). Reduced iron accumulation is reflective of O₂ limitation, which can decrease decomposition rates by inhibiting oxidative enzymes and decreasing the ATP yield of respiration. Iron reduction can also release DOC into the soil solution and increase its bioavailability (Thompson et al., 2006), although the positive relationship shown here between Fe(II) and mineral-associated C content and turnover times suggests that any inhibitory effects of anaerobiosis on organic matter decomposition may predominate in these soils over decadal timescales. Reduced Fe is potentially vulnerable to leaching, although O₂ heterogeneity promotes Fe oxidation and precipitation in close proximity to anaerobic microsites (Hall et al., 2013), leading to the maintenance of large pools of short range-order Fe in this system as indicated by the soil extraction data. Depth was another effective surrogate for mineral-associated C, which could largely be explained by increased live fine root biomass in 0–10 cm samples. Substituting live fine roots for depth only slightly decreased model predictive power, suggesting the influence of

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root C inputs or other covariate(s) related to live fine root biomass in increasing mineral-associated C content. Standardized regression coefficients indicated that each of these variables (reactive Al, Fe(II), and live fine roots) was similarly important in explaining spatial variation in C concentrations. Clay content showed no relationship with soil C, suggesting that hydrous oxides and metals were more important in stabilizing C than silicates in these soils, which are dominated by relatively less-reactive kaolinite.

The measured biogeochemical variables were less effective in explaining patterns of surface soil C stocks than C concentrations among these samples. This may have been partially due to a strong inverse relationship between soil mass-based C concentrations and bulk density that has been widely documented in other soils (Saini, 1966). Translocation of surface C to deeper (and denser) un-sampled horizons could also contribute to this discrepancy.

4.2 Patterns of mineral-associated C turnover

4.2.1 Comparisons with previous studies in tropical forests

Despite the importance of tropical forest soils to the global C cycle, few studies have rigorously constrained the turnover rates of organic matter pools associated with mineral surfaces, which represent the bulk of soil C in these ecosystems. Numerous studies have exploited tropical land-use conversions characterized by shifts from C3 to C4 vegetation and concomitant changes in C isotopes to examine C turnover, yet these investigations cannot separate effects of disturbance and species change from background C dynamics (Ehleringer et al., 2000). Our results demonstrated consistently rapid turnover of the mineral-associated slow C pool (9–29 years, mean 19 years), which represented a large majority of mineral-associated C in most samples. We note that modeled C turnover times represent conservative upper estimates, given that multiple-year lags between C fixation and C inputs would imply more rapid decomposition rates. These estimates are remarkably consistent with ¹⁴C-derived turnover estimates by Trumbore et al. (1995) from Oxisols in seasonally dry Amazonian

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forests, where the slow pool of dense organic matter turned over on timescales of 10–30 years. Our estimates of slow pool C turnover are also similar to several Hawaiian ecosystems (Townsend et al., 1995; Torn et al., 2005), but faster than those modeled in an Amazonian Oxisol in Manaus, where most C (70 %) turned over on timescales of 70 years at 10 cm depth (Telles et al., 2003).

4.2.2 Trends in C turnover with depth

Notably, we generally found similar $\Delta^{14}\text{C}$ and turnover rates in surface (0–10 cm) and subsurface (10–20 cm) depths (corresponding with A and B horizons, respectively) across all catena positions. This finding contrasts with steep declines in decomposition rates frequently observed in relatively shallow B horizons in other ecosystems (Trumbore et al., 1995; Gaudinski et al., 2000; Telles et al., 2003; Torn et al., 2013). Inputs of surface litter and root biomass are typically thought to be lower in B horizons, but C redistribution by anecic earthworms and other soil fauna likely provides an important source of C inputs to the subsoil, as these organisms are extremely abundant in many humid tropical forests (Gonzalez et al., 2006). Dissolved organic C (DOC) represents another likely source of C to subsurface soils, and concentrations are very low ($\sim 2 \text{ mg L}^{-1}$) at A/B horizon boundaries at this site (Hall et al., 2013), indicative of high sorption capacity. Intriguingly, five of the 30 samples had $\Delta^{14}\text{C}$ lower than the 2012 atmosphere, and also tended to have lower C concentrations. These samples may reflect recent fine-scale redistribution of surface soil and exposure of deeper soil horizons following disturbances such as small treefall gaps (scale of m^2), which are common in this forest (Scatena and Lugo, 1995). Overall, our findings of high $\Delta^{14}\text{C}$ and relatively fast turnover across the two depths sampled here suggests that both surface and shallow subsurface mineral-associated organic matter may respond more rapidly to environmental change than was previously thought (de Camargo et al., 1999).

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4.2.3 Impacts of biogeochemical drivers on C turnover

The overall similarities in turnover times across topographic positions despite large differences in concentrations of reactive Al, Fe, and clay content suggest that spatial variation in mineral-organic interactions may have less impact on C turnover rates in these highly weathered soils (Ultisols, Oxisols, and Inceptisols) than in allophanerich Andisols, where short range-order minerals were a dominant predictor of $\Delta^{14}\text{C}$ (Torn et al., 1997). Herold et al. (2014) similarly found a positive relationship between reactive metals and C content, but not $\Delta^{14}\text{C}$, in German Luvisols and Stagnosols. Thus, strong positive relationships between soil C concentrations and the reactive Al content measured in soil extractions may reflect the importance of metal-organic associations in transient C accumulation rather than long-term C stabilization in this ecosystem. Concentrations of Fe(II) indicative of microbial Fe reduction were the only variable significantly correlated with $\Delta^{14}\text{C}$ and turnover times. Although Fe(II) concentrations vary over time in this ecosystem in response to microsite-scale biogeochemical processes, nearby plots tended to maintain differences and rank order in reducing conditions (Hall et al., 2013), likely as a function of microtopography (i.e. concave vs. convex surfaces over scales of tens of cm). Thus, the nearly four orders of magnitude of variation in Fe(II) concentrations that we observed among plots likely reflects, to at least some extent, constitutive differences in reducing conditions. The positive relationship between Fe(II) and $\Delta^{14}\text{C}$ may suggest that microsite O_2 limitation affects slow-pool C turnover, possibly due to the inhibition of oxidative enzymes and/or decreased energy yield of decomposition, as discussed above. The trend towards greater $\Delta^{14}\text{C}$ (implying longer turnover) in 10–20 cm horizons of the valley soils, which experience the lowest bulk soil O_2 availability, is also supportive of this hypothesis. We found no significant differences in mineral-associated C turnover and stocks across ridge, slope, and valley positions despite variation in bulk soil O_2 measured previously (Silver et al., 1999). Differences between bulk soil O_2 and Fe(II) concentrations are by no means surprising, as they reflect different spatial scales of redox heterogeneity (macropore O_2 content vs.

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soil microsites) that have long been known to exist in soils (Sexstone et al., 1985). The pattern of significantly greater occluded light C content in valley soils, however, may imply that consistently lower bulk soil O₂ availability might promote the accumulation of this fraction. Berhe et al. (2012) found a similar pattern of light-fraction C accumulation in a poorly-drained valley in a Mediterranean shrub/grassland.

4.2.4 Steady-state mineral-associated C inputs

Another implication of the relatively rapid turnover of the slow cycling C pool and the uniform C stocks across the catena is the substantial C input to the mineral-associated fraction required to maintain steady state. Aboveground litterfall NPP averages approximately 900 g biomass m⁻² yr⁻¹ in this forest (Scatena et al., 1996), implying that root NPP is likely of similar magnitude (Malhi et al., 2011). Assuming a C concentration of 50 % in above- and belowground litter inputs, this implies that roughly 900 g C m⁻² yr⁻¹ are delivered to the soil via leaf and root litter. Modeled turnover times of the mineral-associated slow pool imply C inputs of 78–249 g C m⁻² yr⁻¹ (mean = 165 g C m⁻² yr⁻¹) from 0 to 20 cm in each plot. Inputs of C to the mineral-associated slow pool thus represent a substantial C flux of approximately 10–30 % of annual litter inputs in this forest. These are likely conservative estimates given that inputs to the mineral-associated slow fraction C below 20 cm depth may also be important, especially in ridges and valleys where the 0–10 and 10–20 cm horizons did not differ in $\Delta^{14}\text{C}$ or C stocks.

4.2.5 Erosion/deposition impacts on $\Delta^{14}\text{C}$

Erosion and deposition also represent potentially important fluxes of C in these soils over pedogenic timescales given their steep slopes and high precipitation, but erosion is unlikely to have an overriding impact on interpretations of decadal C turnover times in our sites. Other studies have shown $\Delta^{14}\text{C}$ enrichment in toeslope positions corresponding with recent C inputs from upslope erosion (Berhe et al., 2012; Berhe and

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Kleber, 2013). In these studies, relatively small inputs of modern C had a large impact on soil $\Delta^{14}\text{C}$ and inferred turnover times due to the predominance of pre-modern ^{14}C in these soils. In our study ecosystem, however, rapid cycling of the mineral-associated slow C pool led to significant bomb ^{14}C enrichment in all samples, regardless of year sampled or topographic position. In this context, realistic inputs of C from erosion would have negligible impact on mineral-associated $\Delta^{14}\text{C}$, given that erosive transport in this site is relatively minor in comparison with biological C fluxes over annual to decadal timescales. Lateral surface fluxes of fine litter and soil on slopes averaged 5 ± 4 and $9 \pm 6 \text{ g m}^{-2} \text{ yr}^{-1}$ (masses of litter and soil, respectively) in sites located near our plots (Larsen et al., 1999). Even if erosion were ten-fold greater at our site, the C fluxes would be negligible in comparison with litter inputs to the mineral-associated slow pool. We acknowledge that large episodic landslides impacting $> 100 \text{ m}^2$ can occur in this forest (Scatena and Lugo, 1995), although there is no evidence of major landslides at this site over the preceding decades. The low clay content of the riparian valley soils relative to ridges and slopes suggests that clay removal by irregular flood events exceeds clay deposition over pedogenic timescales. Thus, large-scale geomorphic processes such as landslides and floods shape this forest landscape over scales of centuries to millennia, but their impact on C dynamics of the mineral-associated slow pool has likely been minor at this particular site over at least the last several decades.

4.3 Implications for soil ^{14}C turnover modeling

The presence of archived soil samples was critical for constraining our models of mineral-associated C turnover, yet relatively few historical datasets have been analyzed for ^{14}C . We are aware of only one such study conducted in humid tropical soils (Telles et al., 2003), although this approach has been applied more frequently in temperate soils (Trumbore et al., 1996; Koarashi et al., 2012; Baisden et al., 2013). Radiocarbon analysis of archived 1988 samples revealed that we could not model the mineral-associated C fraction as a uniform pool with a single turnover time. Although the heterogeneous nature of mineral-associated C and the implications for modeling were

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noted almost two decades ago (Trumbore et al., 1995), many recent studies have continued to model the turnover of physically-separated mineral-associated C fractions as uniform pools (Crow et al., 2007; Marin-Spiotta et al., 2008; Leifeld and Fuhrer, 2009; Meyer et al., 2012; McFarlane et al., 2013; Herold et al., 2014). Other studies

have further separated mineral-associated C by additional density fractions or chemical treatment (Telles et al., 2003; Sollins et al., 2009; Giardina et al., 2014), but it appears likely that these fractions also contain mixtures of faster and slower-cycling pools that complicate interpretation of the single mean residence times provided in these studies. For example, we found that modeling the mineral-associated C fraction as a pool with uniform turnover time, vs. slow and passive pools with turnover times of decades and centuries – millennia, respectively, yielded contradictory relationships between $\Delta^{14}\text{C}$ and modeled mean residence times. The two-pool model was more ecologically meaningful and corresponded well with previous ^{14}C soil C turnover models constrained by multiple data points (Baisden et al., 2013), whereas the single pool model could not capture observed changes in $\Delta^{14}\text{C}$ between 1988 and 2012. Importantly, the single pool model reversed the *sign* of the relationship between $\Delta^{14}\text{C}$ and turnover time, because the slow pool constituted the majority of mineral-associated C. In a single pool model, Eq. (1) yielded turnover times of either 67–150 or 6–15 years. Mass balance constraints on C inputs imply that only the longer turnover times are plausible, a conclusion supported by weighted mean turnover times from the two-pool model. However, the single-pool model would imply a *negative* relationship between $\Delta^{14}\text{C}$ and overall turnover time. This interpretation contradicts the constrained two-pool model, which showed a *positive* relationship between soil $\Delta^{14}\text{C}$ and turnover time of the slow fraction, the dominant C pool, despite the fact that these two models had similar overall turnover times. Phrased differently, for a single-pool model we would expect shorter overall turnover times to correspond with greater bomb ^{14}C in 2012, whereas for a two-pool model, shorter turnover times for the slow pool correspond with less bomb ^{14}C in 2012. Thus, single pool turnover models based on mineral-associated

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$\Delta^{14}\text{C}$ can lead to misleading interpretations of turnover times and their relationship to $\Delta^{14}\text{C}$.

If other ecosystems are characterized by similarly rapid rates of mineral-associated C cycling, we suspect that single-pool models of mineral-associated $\Delta^{14}\text{C}$ should be treated with caution. For example, single-pool models of dense fraction $\Delta^{14}\text{C}$ in temperate soils often imply mean turnover times of hundreds of years (Leifeld and Fuhrer, 2009; Meyer et al., 2012; McFarlane et al., 2013; Herold et al., 2014). However, repeated $\Delta^{14}\text{C}$ measurements in New Zealand Andisols and Alfisols showed much more rapid turnover (9–17 years) of a pool that represents 73–85 % of total C (Baisden et al., 2013). These findings are consistent with our present data, and suggest that decadal turnover of the majority of mineral-associated C may be more prevalent across ecosystems than previously thought, with important implications for interpreting published data. For example, Leifeld and Fuhrer (2009) argued that differences in the $\Delta^{14}\text{C}$ of silt and clay-associated organic matter among two alpine grasslands could not be attributed to differences in management over decadal scales because of the long mean turnover times of these fractions (200–800) implied by single-pool models. Acknowledging the presence of decadal-cycling mineral-associated C pools challenges these and similar interpretations.

5 Conclusions

Overall, we found that dynamics of mineral-associated soil C pools were remarkably similar across biogeochemically distinct soils spanning three taxonomic orders and two surface soil depths in a humid tropical forest, with 74 % of this C decomposing after approximately 20 years. Our results highlight the importance of dynamics of the mineral-associated slow pool in mediating surface soil responses to global change. Our data indicate that soil depths of at least 20 cm can be dominated by mineral-associated C with decadal rather than centennial/millennial turnover times, and that large differences in soil biogeochemical properties such as texture, pH, reactive

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metal content, root biomass, and bulk soil O₂ do not necessarily have discernable impacts on decadal turnover rates. However, an index of reducing conditions (Fe(II) concentrations) at the scale of individual soil samples provided the best single predictor of $\Delta^{14}\text{C}$, slow-pool turnover, and C stocks, suggesting the influence of microsite redox conditions on C dynamics in these upland soils.

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Table 1. Mean (SE) concentrations and stocks of soil C by density fraction, topographic position, and depth; $n = 5$ for each position/depth combination. Total C represents the sum of all density fractions. Means with different letters are significantly different ($p < 0.05$).

Position	Depth (cm)	(mgC g ⁻¹ fraction)			(mg g ⁻¹ soil)			Bulk density (g cm ⁻³)	(g m ⁻²)			Total C
		Free light fraction	Occluded light fraction	Heavy fraction	Free light C	Occluded light C	Mineral- associated	Free light C	Occluded light C	Mineral- associated C		
Ridge	0–10	384 (10)	333 (13) bc	49 (2) a	3.7 (0.8)	2.7 (0.3)	47.7 (1.9) c	0.51 (0.02) a	195 (45)	137 (13)	2429 (157)	2762 (187)
	10–20	347 (34)	249 (24) ab	32 (3) b	1.3 (0.4)	1.3 (0.3)	31.6 (2.6) ab	0.68 (0.05) b	88 (22)	86 (19)	2177 (277)	2350 (299)
Slope	0–10	357 (22)	333 (29) bc	33 (3) b	2.4 (0.5)	2.6 (1.0)	32.9 (3.3) b	0.69 (0.06) b	142 (30)	161 (67)	2214 (154)	2517 (232)
	10–20	316 (41)	193 (40) a	22 (5) b	1.5 (0.9)	0.9 (0.3)	21.8 (5.1) a	0.79 (0.03) b	111 (59)	67 (24)	1675 (295)	1852 (361)
Valley	0–10	325 (28)	376 (10) c	34 (2) b	4.4 (2.0)	4.7 (1.8)	32.7 (2.4) ab	0.71 (0.03) b	311 (149)	341 (130)	2347 (231)	3000 (233)
	10–20	291 (28)	382 (20) c	27 (2) b	2.6 (0.7)	3.8 (0.8)	26.1 (2.1) ab	0.78 (0.05) b	212 (59)	310 (71)	2037 (214)	2558 (313)

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Table 2. Soil characteristics (mean \pm SE) by topographic position and horizon, $n = 5$ for each position/depth combination. Means with different letters are significantly different. Fe_{ox} and Al_{ox} denote ammonium oxalate extractions on air-dried samples, Fe_{ca} and Al_{ca} were measured in citrate/ascorbate extractions of field-moist samples immediately after sampling, and $\text{Fe(II)}_{\text{HCl}}$ was field-extracted in 0.5 M HCl.

Position	Depth (cm)	pH	$\text{Fe(II)}_{\text{HCl}}$ (mg g^{-1})					Clay	Silt (%)	Sand	Live fine roots (g m^{-2})
			Fe_{ox}	Fe_{ca}	$\text{Fe(II)}_{\text{HCl}}$	Al_{ox}	Al_{ca}				
Ridge	0–10	4.51 (0.03)a	8.9 (0.8)	25.9 (1.7) c	0.31 (0.05)	2.4 (0.3) b	9.9 (0.8) b	38 (4) a	51 (4) a	11 (2) a	250 (60) b
	10–20	4.64 (0.04)a	7.6 (0.6)	24.0 (1.7) bc	0.13 (0.01)	1.9 (0.2) ab	8.1 (0.7) b	49 (4) b	43 (5) b	8 (1) a	140 (30) ab
Slope	0–10	4.68 (0.06)a	8.6 (1.0)	16.4 (2.2) ab	0.90 (0.07)	1.5 (0.1) a	4.1 (0.7) a	37 (6) abc	53 (5) ab	10 (2) a	150 (40) ab
	10–20	4.75 (0.07)a	7.3 (2.0)	13.7 (2.8) a	2.18 (2.13)	1.6 (0.1) a	3.4 (0.8) a	39 (3) ab	49 (5) ab	13 (2) ab	80 (20) a
Valley	0–10	5.23 (0.16)b	7.4 (0.4)	9.9 (1.2) a	0.44 (0.19)	1.6 (0.1) a	2.2 (0.4) a	23 (2) c	51 (5) ab	26 (6) bc	80 (20) a
	10–20	5.23 (0.15)b	8.3 (0.3)	9.5 (1.4) a	0.83 (0.27)	1.8 (0.2) ab	2.0 (0.5) a	23 (3) c	45 (4) ab	31 (6) c	60 (20) a

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Table 3. Mean (SE) $\Delta^{14}\text{C}$, modeled turnover of the mineral-associated slow C pools, and the percent contributions of the slow pool and passive pools to mineral associated C by topographic position; $n = 5$ for each position/depth combination except where indicated (see Sect. 2.4 for details on modeling). Slow pool C inputs were estimated by the quotient of the slow pool C stock and its mean turnover time.

Position	Depth (cm)	Mineral-associated $\Delta^{14}\text{C}$ (‰)	Slow pool turnover time (years)	Percent slow pool	Percent passive pool	C input to slow pool (g m^{-2})
Ridge	0–10	81 (4) ab	19 (3), $n = 5$	76 (3)	24	94 (12)
	10–20	64 (11) ab	17 (5), $n = 4$	70 (5)	30	97 (27)
Slope	0–10	74 (14) ab	21 (5), $n = 4$	72 (5)	28	78 (12)
	10–20	40 (14) a	16 (6), $n = 2$	57 (8)	43	60 (22)
Valley	0–10	81 (5.0) ab	20 (1), $n = 5$	76 (4)	24	91 (12)
	10–20	86 (3.0) b	21 (1), $n = 5$	77 (4)	23	75 (11)

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Table 4. Linear models of C concentrations, stocks, and slow pool turnover. Normalized model coefficients (SE) are analogous to Pearson's r . See Table 2 for variable descriptions. Models A and B represent different models with similar AICc.

C concentrations		
Model A	Depth	−0.90 (0.14)
	Al _{ca}	0.51 (0.09)
	Fe(II)	0.35 (0.07)
	Al _{ox}	0.22 (0.09)
	R^2	0.88
Model B	Al _{ca}	0.41 (0.16)
	Fe(II)	0.35 (0.11)
	Live fine roots	0.27 (0.14)
	Al _{ox}	0.25 (0.13)
	R^2	0.73
C stocks		
Model A	$\Delta^{14}\text{C}$	0.53 (0.14)
	Al _{ox}	0.36 (0.14)
	R^2	0.46
Model B	Fe(II)	0.58 (0.15)
	Depth	−0.53 (0.29)
	R^2	0.43
$\Delta^{14}\text{C}$		
	Fe(II)	0.59 (0.15)
	R^2	0.35
Slow pool turnover		
	Fe(II)	0.47 (0.18)
	R^2	0.25

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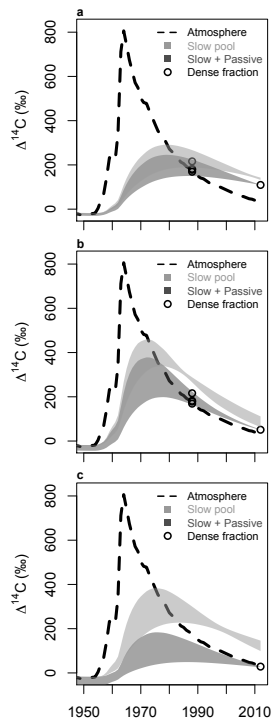


Figure 1. Modeled soil $\Delta^{14}\text{C}$ over time for the slow pool (light grey shading) and the slow + passive pools (dark grey shading) of mineral-associated C. The dashed line shows atmospheric $\Delta^{14}\text{C}$ for zone 2 of the Northern Hemisphere. Shaded regions represent 95% confidence intervals for $\Delta^{14}\text{C}$ of a given soil sample calculated using Monte Carlo methods that varied 1988 $\Delta^{14}\text{C}$ and turnover time of passive C. Panels (a) and (b) show trends for individual samples where 2012 $\Delta^{14}\text{C}$ = 109.4 and 51.0‰, respectively in 2012, along with four samples from 1988. Panel (c) shows trends for a sample where 2012 $\Delta^{14}\text{C}$ = 28.5‰; this and four other samples with $\Delta^{14}\text{C}$ less than the 2012 atmosphere could not be realistically constrained by 1988 surface soil $\Delta^{14}\text{C}$ (see Sect. 2.4).

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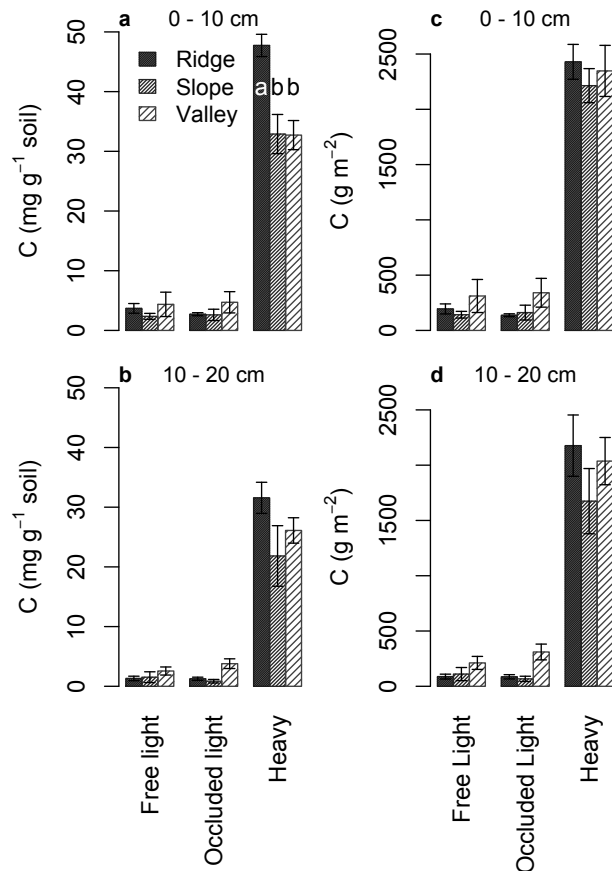


Figure 2. Carbon concentrations and stocks (mean \pm SE, $n = 5$ for each bar) by density fraction, catena position, and depth increment. Means with different letters are significantly different. Occluded light fractions were greatest in valleys when compared across positions irrespective of depth.

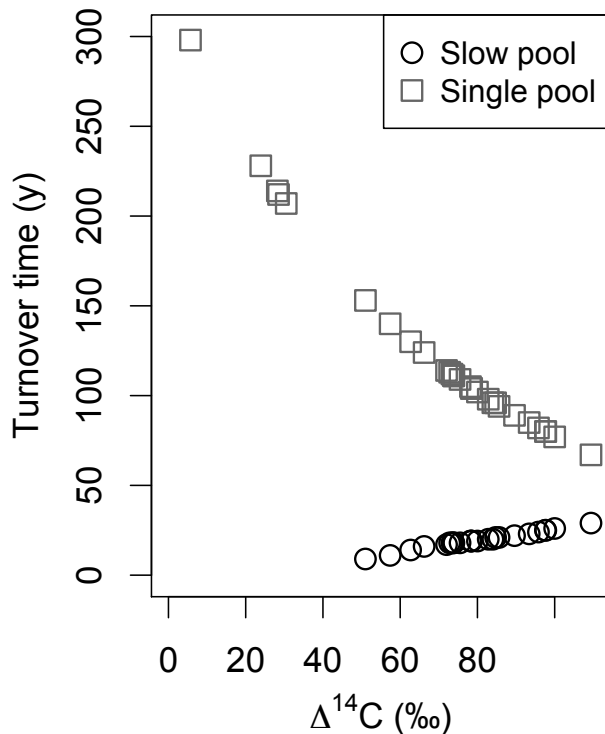


Figure 3. Relationships between $\Delta^{14}\text{C}$ of the mineral-associated fraction and modeled turnover time. Circles represent the slow mineral-associated pool, which comprised most ($71 \pm 3\%$) of total mineral associated C. Squares represent a single-pool model of mineral associated C, which has commonly been employed in other studies but could not be fit to both our 1988 and 2012 samples.

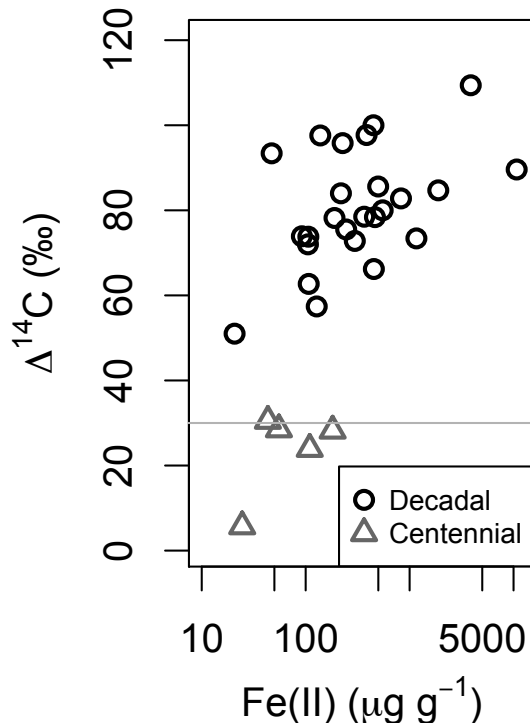


Figure 4. Soil $\Delta^{14}\text{C}$ vs. Fe(II) concentrations measured in 0.5 M HCl extractions conducted in the field ($R^2 = 0.35$, $p < 0.001$). Reduced Fe was the best single correlate of $\Delta^{14}\text{C}$ and slow pool turnover times; Fe(II) correlated positively with turnover times. Circles indicate samples with a majority of C in the decadal-cycling slow pool, triangles indicate samples dominated by passive C of centennial to millennial age. The relationship between $\Delta^{14}\text{C}$ and C turnover was qualitatively different between these groups of samples; increased $\Delta^{14}\text{C}$ implied longer turnover times for the circles, and smaller $\Delta^{14}\text{C}$ implied longer turnover for the triangles. The grey horizontal line indicates the approximate $\Delta^{14}\text{C}$ of the 2012 atmosphere in the Northern Hemisphere zone 2.