Title

SOIL CARBON STOCKS NOT LINKED TO ABOVEGROUND LITTER INPUT AND CHEMISTRY OF OLD-GROWTH FOREST AND ADJACENT PRAIRIE

Authors

McFarlane, Karis J

Mambelli, Stefania

Porras, Rachel C

et al.

Publication Date

2024

DOI

10.1017/rdc.2024.5

Radiocarbon, Vol 00, Nr 00, 2024, p 1–18 DOI:10.1017/RDC.2024.5
Selected Papers from the 24th Radiocarbon and 10th Radiocarbon & Archaeology International Conferences, Zurich, Switzerland, 11–16 Sept. 2022

SOIL CARBON STOCKS NOT LINKED TO ABOVEGROUND LITTER INPUT AND CHEMISTRY OF OLD-GROWTH FOREST AND ADJACENT PRAIRIE

Karis J McFarlane[1]* • Stefania Mambelli[2] • Rachel C Porras[3] • Daniel B Wiedemeier[4,5] • Michael W I Schmidt[4] • Todd E Dawson[2] • Margaret S Torn[3]

[1]Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, 7000 East Ave, Livermore, CA, 94551, USA
[2]Department of Integrated Biology, University of California-Berkeley, 30040 Valley Life Sciences Building, Berkeley, CA, 94720, USA
[3]Earth Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA, 94720, USA
[4]Department of Geography, University of Zurich, Winterthurerstrasse 190, 8057 Zürich, Switzerland
[5]Currently at Center of Dental Medicine, University of Zurich, Plattenstrasse 11, 8032 Zürich, Switzerland

ABSTRACT. The long-standing assumption that aboveground plant litter inputs have a substantial influence on soil organic carbon storage (SOC) and dynamics has been challenged by a new paradigm for SOC formation and persistence. We tested the importance of plant litter chemistry on SOC storage, distribution, composition, and age by comparing two highly contrasting ecosystems: an old-growth coast redwood (*Sequoia sempervirens*) forest, with highly aromatic litter, and an adjacent coastal prairie, with more easily decomposed litter. We hypothesized that if plant litter chemistry was the primary driver, redwood would store more and older SOC that was less microbially processed than prairie. Total soil carbon stocks to 110 cm depth were higher in prairie (35 kg C m^{-2}) than redwood (28 kg C m^{-2}). Radiocarbon values indicated shorter SOC residence times in redwood than prairie throughout the profile. Higher amounts of pyrogenic carbon and a higher degree of microbial processing of SOC appear to be instrumental for soil carbon storage and persistence in prairie, while differences in fine-root carbon inputs likely contribute to younger SOC in redwood. We conclude that at these sites fire residues, root inputs, and soil properties influence soil carbon dynamics to a greater degree than the properties of aboveground litter.

KEYWORDS: ^{13}C-NMR spectroscopy, density fractionation, grassland, radiocarbon, soil carbon, soil organic matter.

INTRODUCTION

Old-growth coast redwood (*Sequoia sempervirens*) are among the world's largest trees, capable of living over 2000 years because of their shade tolerance, resistance to fungi, and resilience to fire and flood (Sawyer et al. 2000). Old-growth redwoods are highly productive, with increasing wood production with age (Sillett et al. 2010), large amounts of aboveground litterfall (Pillers and Stuart 1993), and large accumulations of detrital material (Busing and Fujimori 2005) because their highly aromatic tissues are resistant to decomposition (Anderson et al. 1968). Redwood tissues are particularly rich in complex lipid compounds such as terpenes (Hall and Langenheim 1986) and the polyphenolic compounds lignin and tannin (Hergert 1992). Despite the importance of these forests for C storage in aboveground biomass, little is known about belowground C storage and cycling in these ecosystems. Furthermore, throughout much of the redwood range, redwood forest is interspersed with coastal prairie, providing a striking contrast to old-growth redwood forest in terms of plant stature, productivity, and tissue chemistry. This creates a unique opportunity to investigate the effects of litter input chemistry on soil carbon storage and persistence.

*Corresponding author. Email: kjmcfarlane@llnl.gov

The effect of litter chemistry, particularly lignin and nitrogen content, on litter decomposition is well documented (Zhang et al. 2008; Cusack et al. 2009; Prescott 2010) and incorporated into ecosystem and land surface models (Bonan et al. 2013; Ricciuto et al. 2021). High amounts of aromatics, particularly polyphenols, decrease initial decomposition rates and form secondary metabolite complexes that further inhibit decomposition (Horner et al. 1988; Hättenschwiler and Vitousek 2000). In contrast, litter from grasses and other prairie plants are comparatively depleted in aromatics but rich in polysaccharides and N compared to forest litters, characteristics that result in high decomposition rates (Osono et al. 2013; Zhang et al. 2013). Different plant tissues within a plant also decompose at different rates, with aboveground tissues generally decomposing faster than roots (Bird and Torn 2006; Ziter and MacDougall 2012), likely because aboveground tissues tend to have more water-soluble carbohydrates and cellulose (Cusack et al. 2009). Additionally, fine roots decompose more quickly than coarse roots (Wang et al. 2014) and decomposition of root litter slows with depth (Hicks Pries et al. 2018). Furthermore, higher soil organic carbon (SOC) storage in sites with higher litter polyphenols (Northup et al. 1998) and hydrophobic lipid (Ostertag et al. 2008) contents has been observed.

However, the importance of chemical recalcitrance of plant litter inputs to soil carbon storage and persistence is challenged by a growing body of research emphasizing the importance of root inputs over aboveground inputs, pyrogenic (fire-derived) carbon (PyC), microbial processing of organic matter, physical disconnection, and organo-mineral associations (Schmidt et al. 2011; Lehmann and Kleber 2015). For example, studies have demonstrated that compounds identified as resistent to decay decompose, in some cases more rapidly than bulk organic matter or other labile compounds such as sugars (Amelung et al. 2008). In turn, isotopic labeling experiments showed that pure glucose persisted longer than wheat straw (Vorony et al. 1989) and proteins had lower turnover than bulk soil C (Miltner et al. 2009).

Many factors influence soil C storage and cycling, including climate (Post et al. 1982) and soil physical and chemical properties such as texture (Jobbágy and Jackson 2000) and mineralogy (Torn et al. 1997). Physical protection by soil aggregates can also increase soil organic matter (SOM) storage, particularly in grasslands and prairies (Ewing et al. 2006; Pérès et al. 2013) where aggregation is attributed to dense root systems (Young et al. 1998). Grasslands and prairies also tend to have considerable amounts of PyC, because of high fire frequencies (Schmidt and Noack 2000; Glaser and Amelung 2003). Pyrogenic C consists primarily of aromatic compounds (Schmidt and Noack 2000) with slower initial decay rates than most direct plant inputs. Thus, differences in litter chemistry, C allocation above- and belowground, root morphology, PyC inputs, and soil properties may contribute to differences in SOC storage and dynamics between forests and prairies.

We assessed the importance of the type of C inputs on soil C storage and cycling in an old-growth coast redwood stand and an adjacent coastal prairie. Since climate and parent material are also major controls of SOC storage and dynamics, we conducted our comparison at one location where these ecosystem properties were shared between the two vegetation types. We hypothesized that if the chemistry of plant litter inputs was the primary control on SOC storage and dynamics, the redwood forest would store more SOC that was less microbially processed than the prairie, that SOC would be older on average under old-growth redwood, and that differences in SOC would be more pronounced near the surface where plant litter inputs are concentrated. We also tested the relationship between light density fraction molecular composition and ^{14}C values to see if there were differences in these relationships between redwood forest and prairie. Specifically, we hypothesized that older fractions would show evidence of being more microbially processed than younger fractions in prairie and that this relationship would be stronger in prairie than in redwood.

METHODS

Study Site

This study was conducted at Prairie Creek Redwoods State Park in northwestern California (Table S1). The region has a Mediterranean climate. Local mean annual precipitation is 1709 mm and mean annual temperature is 11°C (Western Regional Climate Center 2010). The redwood forest and prairie sampling locations were 550 m apart on soils derived from alluvial deposits. The redwood grove is dominated by old-growth coast redwood, while perennial grasses dominate the prairie. The prairie results from waterlogged conditions in winter followed by rapid drying in spring and summer, which favors dry season dormant grasses and herbs (Veirs 1987). The prairie was extensively grazed from approximately 1885 until the park was established in 1923 and grazing by wild elk continues.

Both sites were subject to fires historically. The fire history for the coast redwood range is complex, and the importance of the intentional use of fire by indigenous peoples is becoming increasingly appreciated frequent, low intensity fire intervals were used by the indigenous peoples to keep villages and resources safe from wildfire; open trading routes; maintain prairie habitat for elk and deer grazing; and sustain habitat for plants vital for food, medicine, and basket-making supplies (Noss 1999; Huntsinger and McCaffrey 2007; Anderson 2013). These fires would have burned surface litter, burned much of the aboveground biomass in the prairie, and killed tree seedlings and shrubs, maintaining prairie patches and preventing the establishment of trees that might otherwise have out-competed redwood, such as Douglas fir (*Psuedotsuga menziesii*). Based on dating of fire scars on redwood trees in Prairie Creek Redwoods State Park, the fire intervals from the early 18th century (pre-fire suppression) to mid-20th century were 6–8 years (Brown and Swetnam 1994). The prairie was subject to light-severity prescribed fires between 1983 and 2005 (Stassia Samuels, personal communication, 2011). More specific fire histories, with regards to both intensity and frequency, are not available for our specific sampling locations.

Field Sampling and Sample Processing

Belowground samples were collected in July 2009 from 5 equally spaced plots along a 50 m sampling transect in prairie and 7 randomly selected plots within a 0.2 ha area in redwood. More plots were used in redwood because we expected greater spatial variability there. O horizon samples and standing biomass from prairie plots were collected in a 0.0625 m^2 quadrat. Aboveground litterfall was collected in redwood using eight 0.135 m^2 litter traps placed near our soil sampling plots. O horizon and litter samples were dried, weighed, and ground for chemical analysis.

We were not able to attain permits to dig soil pits in this ecologically and culturally significant park, so mineral soils and roots were sampled using a hammer-driven 7.5 cm diameter corer. One core was sampled from each plot in 10 cm increments to 30 cm and in 20 cm increments from 30 to 110 cm depth. At both sites, a gravelly layer was encountered at 110 cm. Bulk density and soil C and N concentrations were determined for all depths and plots. Three cores from each site were selected for further analysis.

Fine roots (< 2 mm diameter) were hand-picked using a combination of dry and wet sieving and sorted into < 0.25 mm, 0.25–0.50 mm, and 0.50–2.0 mm diameter size classes. Coarse roots were sorted for chemical analyses into 2–5 mm and > 5 mm (redwood only). Redwood roots < 0.25 mm in diameter were virtually non-existent. Roots were thoroughly cleaned with tap water, dried, and weighed. A subset of roots was ground for chemical analysis.

Sieved soil samples from 0–10 cm and 50–70 cm depths were fractionated into free light (fLF), occluded light (oLF), and dense (DF) density fractions sodium polytungstate (SPT-0, TC Tungsten Compounds) adjusted to a density of 1.65 g cm^{-3} using the procedure described in detail in McFarlane et al. 2013. The fLF is comprised of free particulate organic matter, oLF contains light-density organic matter occluded in aggregates, and DF includes mineral-associated organic matter. During soil density fractionation, some C and N are dissolved in SPT solution or during water rinses and is lost from the solid sample. The reported proportions of bulk soil C and N in different fractions are based on total C and N recovered following density fractionation (< 9% of bulk soil C and < 4% of bulk soil N were lost in this procedure).

Chemical and Isotopic Analysis

Plant material, litter, soil, and soil fraction C and N concentrations were measured on dry, ground samples using a Carlo Erba Elantech elemental analyzer at UC Berkeley. Soil texture was measured using the micropipette method (Miller and Miller 1987; Burt et al. 1993). Bulk soil pH was measured in water and 0.01M $CaCl_2$ (Thomas 1996). Soil and soil fractions were analyzed for ^{14}C on the Van de Graaff FN accelerator mass spectrometer (AMS) at the Center for AMS at Lawrence Livermore National Laboratory. Samples were prepared for ^{14}C measurement as described in Vogel et al. (1984). Aliquots of CO_2 were analyzed for ^{13}C at the Department of Geological Sciences Stable Isotope Laboratory, University of California Davis (GVI Optima Stable Isotope Ratio Mass Spectrometer). Measured ^{13}C values were used to correct for mass-dependent fractionation of ^{14}C, and $\delta^{13}C$ is reported relative to V-PDB. Radiocarbon values are reported in $\Delta^{14}C$ notation, had an average AMS precision of 3‰, and were corrected for ^{14}C decay since 1950 and the year of measurement, 2011 (Stuiver and Polach 1977).

The amount of PyC in a subset of samples was determined by analyzing benzene polycarboxylic acids (BPCA) molecular markers by high-performance liquid chromatography at the University of Zurich (Wiedemeier et al. 2013). We present PyC results "as measured" without the use of a conversion factor and should therefore be considered low-end estimates of total PyC contents. They provide a conservative and very robust basis to compare PyC contents in our study soils as was shown for diverse environmental materials (Hammes et al. 2008; Wiedemeier et al. 2013).

Molecular Characterization of Plant Tissues, Litter, and Light Density Fractions

We assessed differences in the molecular composition of above and belowground biomass and light-density fractions in redwood and prairie using solid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR), which can be applied to a wide range of organic materials without relying on extensive chemical extraction procedures and used to assess differences between the chemistry of different organic materials or transformations in the chemical composition of organic matter during decomposition (Nelson and Baldock 2005). The chemical structure of aboveground litter and biomass, roots, and light density fractions was characterized by variable amplitude cross-polarization magic-angle spinning (VACPMAS) ^{13}C NMR

https://doi.org/10.1017/RDC.2024.5 Published online by Cambridge University Press

spectroscopy at the Pacific Northwest National Laboratory (Agilent/Varian VNMRS solid-state 300 MHz spectrometer and 5 mm HXY Chemagnetics MAS probe). We selected all light fractions from 0–10 cm (n = 3 cores) and 2 samples each of redwood needles, wood, and bark; prairie grass and mixed aboveground biomass; each of the fine root classes at each site; and light fractions from 50–70 cm from each site. Useful ^{13}C-NMR spectra for dense fractions could not be attained because low C concentrations and interference from the iron present in the soil minerals resulted in low C signal strength, a common challenge for organic matter characterization of mineral-rich soil samples (Kögel-Knabner 2000; Yeasmin et al. 2020). 80–100 mg of sample was packed into 5 mm zirconia rotors using Kel-F spacers and a vespel drive tip. Samples were spun at 10 kHz to reduce interference due to spinning side bands. The VACP pulse program was optimized using hexamethylbenzene and glycine to achieve maximum intensity for all peaks. The contact time for samples was 1 ms, the proton 90 was 3 μs, the decoupling power was 62.5 kHz for 25 ms, and the recycle delay was 1–2 seconds. The number of scans for litters was 3000 and for light fractions was about 12000. Examples of representative spectra are provided in Figure S1. Spectra were digitally processed using MNova NMR software (Mestrelab Research SL, Spain) to integrate peak areas in the following chemical shift regions: 0–45 ppm (alkyl), 45–110 ppm (O-alkyl), 110–165 ppm (aromatic), 165–210 ppm (carbonyl). Integrated spectral areas were normalized to the total signal intensity for each spectrum.

Sample “aliphaticity” (A/O-a), defined as the ratio alkyl to O-alkyl (C peak area in the region 0–45 ppm/C peak area in the region 45–110 ppm), was used to infer the degree of microbial processing in soils where a higher ratio indicates higher processing (Baldock et al. 1997). This approach assumes that as decomposition progresses (1) carbohydrates are degraded resulting in a decrease in the concentration of O-alkyl C, and (2) the metabolic products of decomposers (including lipids and long-chain aliphatic compounds) accumulate resulting in an increase in the concentration of alkyl C (Baldock et al. 1990; Baldock and Preston 1995; Baldock et al. 1997; Webster et al. 2000). Sample aromaticity (AR) was defined as the ratio of aromatic to alkyl plus O-alkyl and aromatic (C peak area in the region 110–165 ppm/C peak areas in the region 0–165 ppm) where a higher ratio indicates higher aromaticity (Kögel-Knabner 1997). A “combined” index (CI) was defined as the ratio of alkyl and aromatic to O-alkyl (C peak area in the region 0–45 plus 110–165 ppm/C peak areas in the region 45–110 ppm) (Baldock and Preston 1995; Baldock et al. 1997). Alkyl and aromatic C are considered less preferred C substrates; thus, we interpreted litter A/O-a, CI and AR as indices of substrate quality for microbes as well as the extent of microbial processing of SOM fractions (Baldock and Preston 1995).

We measured a significant amount of PyC at our sites, especially at depth (Figure 2d in Results section). The presence of char in the 110–165 ppm region affects the interpretation of CI and AR as indexes of the extent of decomposition. Therefore, we controlled for the influence of char in CI and AR by subtracting the percentage of signal intensity from char according to Baldock et al. (2004) (64.9% from 110-145 ppm and 17.5% from 145–165 ppm). These char-corrected indexes are presented as CI* and AR*.

^{13}C NMR spectroscopy does not provide a quantitative measure of the molecular composition of organic materials, so we applied a molecular mixing model (MMM) for terrestrial soils (Baldock et al. 2004) to infer the molecular structure of our samples based on spectral intensities. We used a 5-component model (carbohydrate, lignin, lipid, protein, and carbonyl) for the litter samples and a 6-component model (5-component model plus char) for soil fractions. This model iteratively determines the linear combination of components that best fit the integrated regions of the NMR spectra constrained with the molar N:C ratio for each sample.

Data Analysis

Results are reported as means followed by standard errors. Statistical tests were performed in R 3.6.1 and effects were considered significant at $\alpha = 0.05$. Depth, ecosystem, root size, and density fraction effects were tested by analysis of variance (ANOVA) with repeated measures for depth accounted for using mixed-effect models with the nlme package (Pinheiro et al. 2019; R Core Team 2019) and interaction effects were investigated using Phia (De Rosario-Martinez 2015). ^{13}C NMR results were compared by site and litter/fraction type using Type III ANOVA to account for imbalanced design with regards to the numbers of tissue types analyzed. Modest heterogeneities in variances for aromatic signal intensity, combined index, carbohydrate content, and char content were improved with a log transformation. Post hoc comparisons were performed using a Tukey adjustment with the Multcomp package (Hothorn et al. 2008). Relationships between soil density fraction molecular composition and ^{14}C values were investigated using correlation analysis and linear regression.

RESULTS AND DISCUSSION

Aboveground Biomass, Litter, and Fine Root Biomass

Aboveground biomass in our coast redwood forest was previously reported as 428 kg m^{-2} (Sillett and Van Pelt 2007). Annual litterfall in redwood consisted mainly of needles (81 ± 2% by mass) and was similar in dry mass to standing aboveground biomass in prairie at the time of sampling, which was mostly grasses (97 ± 3% by mass) and dead or senesced material (91± 1% by mass). Total C and N mass, as indicators of inputs to the soil, were similar between plant types, but redwood aboveground litter had higher C concentration, lower N concentration, and higher C:N ratio than prairie (Table 1). Total fine root biomass to 110 cm, an indicator of belowground C inputs, was more than double in redwood than in prairie and fine-root C and N stocks were similarly higher in redwood than prairie. Redwood roots tended to be larger diameter and declined less strongly with depth than prairie roots (Figure S2). Like aboveground plant tissues, redwood roots had lower N concentration and higher C:N ratio than prairie roots (Table 1).

Aromaticity and combined (aliphatic plus aromatic) indices were higher in litter and tissues from redwood than prairie (Figure 1), reflecting a higher abundance of aromatics and lipids and lower abundance of carbohydrates (Figure S3). The molecular mixing model (MMM) indicated that carbohydrates and lignin were the most prominent litter compounds (Figure S3). Also estimated by the MMM, carbohydrates were 73 ± 1% of observed C in prairie litters, but only 58 ± 2% in redwood litters, while lignin was nearly double in redwood (34 ± 1%) than prairie (18 ± 1%). Protein and lipid content did not differ between sites and no carbonyl C was detectable in litters by the MMM.

These results confirm that litters and plant tissues in redwood are more aromatic and depleted in N compared to those in prairie. A global synthesis found the rate of litter decomposition decreased with increasing C:N ratio and was higher in grasslands than in coniferous forests (Zhang et al. 2008). As redwood litter contains particularly high amounts of lignin and tannin

https://doi.org/10.1017/RDC.2024.5 Published online by Cambridge University Press

Table 1 Aboveground litter and fine root mass and general chemistry characteristics in Coast Redwood Forest and Coastal Prairie. Values are means with standard errors in parentheses. Different letters indicate statistically significant differences between plant litter or biomass types within a column. N = 6 for redwood and n = 3 for prairie.

Site	Litter type	Dry mass (g m^{-2})	C (%)	N (%)	C:N ratio	C mass (g m^{-2})	N mass (g m^{-2})
Aboveground							
Redwood	Annual aboveground litterfall	780 (57)^{a}	48.8 (0.2)^{a}	0.58 (0.02)^{a}	90 (2)^{a}	380 (28)^{a}	8.1 (0.4)^{a}
Prairie	Standing aboveground biomass	1041 (81)^{a}	44.1 (0.1)^{b}	0.79 (0.03)^{b}	56 (2)^{b}	459 (35)^{a}	4.5 (0.3)^{a}
Belowground							
Redwood	Fine root biomass to 110 cm	1794 (274)^{b}	35.9 (1.2)^{c}	1.1 (0.0)^{c}	63 (4)^{c}	776 (115)^{b}	18 (3)^{b}
Prairie	Fine root biomass to 110 cm	775 (251)^{a}	36.8 (0.3)^{c}	2.3 (0.1)^{b}	44 (0.2)^{b}	334 (94)^{a}	5 (1)^{a}

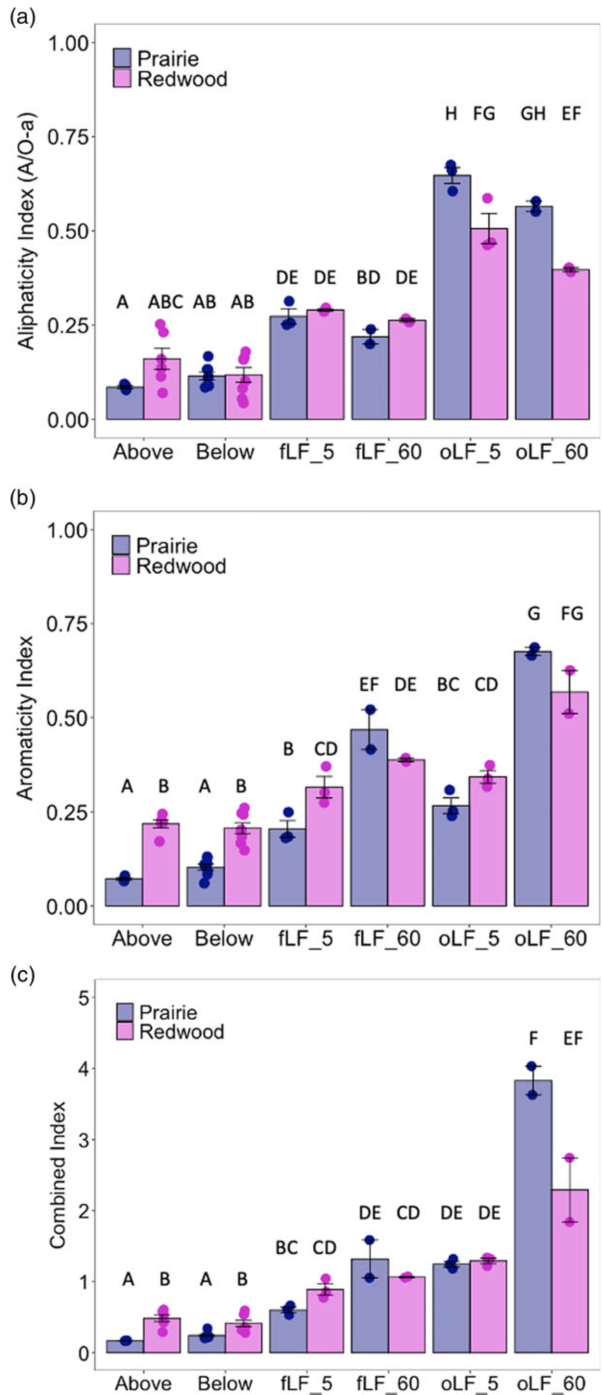

Figure 1 (a) Aliphaticity, (b) Aromaticity, and (c) Combined Indices calculated from ^{13}C-NMR spectroscopy. For fractions, numbers after the underscore signify the middle of the depth increment. Letters indicate statistically significant differences at $\alpha = 0.05$ among organic matter fraction (aboveground litter and biomass, "Above"; belowground biomass "Below"; free light fractions, fLF; and occluded light fractions, oLF) and vegetation cover (Prairie and Redwood) as there was a significant interaction between organic matter fraction and vegetation cover. Values are means ± standard error and n ranges from 2 to 8 as samples were pooled into the categories shown.

https://doi.org/10.1017/RDC.2024.5 Published online by Cambridge University Press

that slow decomposition, plant inputs likely decompose more slowly in the redwood forest than prairie, which should facilitate the accumulation of soil organic matter that has undergone relatively little decomposition and microbial processing.

Bulk Soils

Contrary to expectations, total soil C stock to 110 cm was lower in redwood (28 ± 1 kg C m^{-2}) than prairie (35 ± 1 kg C m^{-2}), as was N stock (Figure 2a–b, $p < 0.01$). Redwood mineral soils had lower C and N concentrations in the top 30 cm (Figure S5a–b, $p < 0.01$) and layer-specific stocks were higher in prairie only in the top 50 cm—soil C and N concentrations and stocks converged at depth. Redwood mineral soils had higher C:N ratios than prairie throughout the profile, consistent with higher C:N ratios in redwood litters (Figure 2c, $p < 0.01$).

At both sites, $\delta^{13}C$ values increased and $\Delta^{14}C$ values decreased with depth (Figure 2e–f), indicating a presence of older, and possibly more decomposed, carbon at depth (Garten 2006). Bulk soil $\delta^{13}C$ and $\Delta^{14}C$ values were higher in redwood than prairie throughout the profile (Figure 2e–f, $p < 0.05$). Only redwood forest floor and 0–10 cm mineral soils had $\Delta^{14}C$ values higher than 0‰, indicating the presence of ^{14}C associated with atmospheric weapons testing. Therefore, the difference in $\Delta^{14}C$ values between sites indicates the presence of younger C throughout the soil profile in redwood than prairie. This is consistent with recent comparisons of forests and grasslands, which have found $\Delta^{14}C$ of soil organic carbon to be less depleted in forests than grasslands (Heckman et al. 2020; Moreland et al. 2021).

Pyrogenic C constituted a larger amount (Figure S5d) and percentage of total C in prairie than redwood ($p < 0.01$). This percentage increased slightly with depth at both sites (Figure 2d). At least 20% of the difference in total mineral-soil C stocks can be attributed to higher PyC stocks in prairie. With the commonly used multiplier of 2.27 to convert the conservative BPCA measurements to more realistic PyC content (Schneider et al. 2011), PyC explains at least 40% of this difference. Larger amounts of PyC in prairie may also contribute to older soil C in prairie than redwood as fire-derived C has been found to be among the oldest and most chemically refractory components of soil organic matter, though its fate in soils depends on conditions during formation as well as physical and chemical interactions with organic matter and minerals (Preston and Schmidt 2006; Czimczik and Masiello 2007; Eckmeier et al. 2010; Schmidt et al. 2011; Cusack et al. 2012).

Despite their proximity, there were some differences in soil characteristics between the redwood and prairie that could influence soil C storage and age. Specifically, pH of shallow soil (0–30 cm) was slightly higher in redwood than prairie (Figure S6a–b), redwood soils had higher sand contents throughout the profile, and deep prairie soils (below 50 cm) had higher clay content than redwood (Figure S6c–d). While these differences in pH are likely too small to impact soil carbon storage, chemistry, and persistence, a tendency for soil C to be higher in finer textured soils is well documented in the literature (Homann et al. 2007; McFarlane et al. 2010; Slessarev et al. 2020) and this difference in soil texture may partly explain our observation of more and older soil C in prairie than redwood. For our sites, however, differences in soil texture between sites were most pronounced below 50 cm where soil C stocks were similar.

Alternatively, the presence of younger soil C in redwood may result from a higher rate of recently fixed C inputs in redwood, particularly to deep soils. There is growing evidence that belowground C inputs through root turnover and rhizosphere deposition are more important C

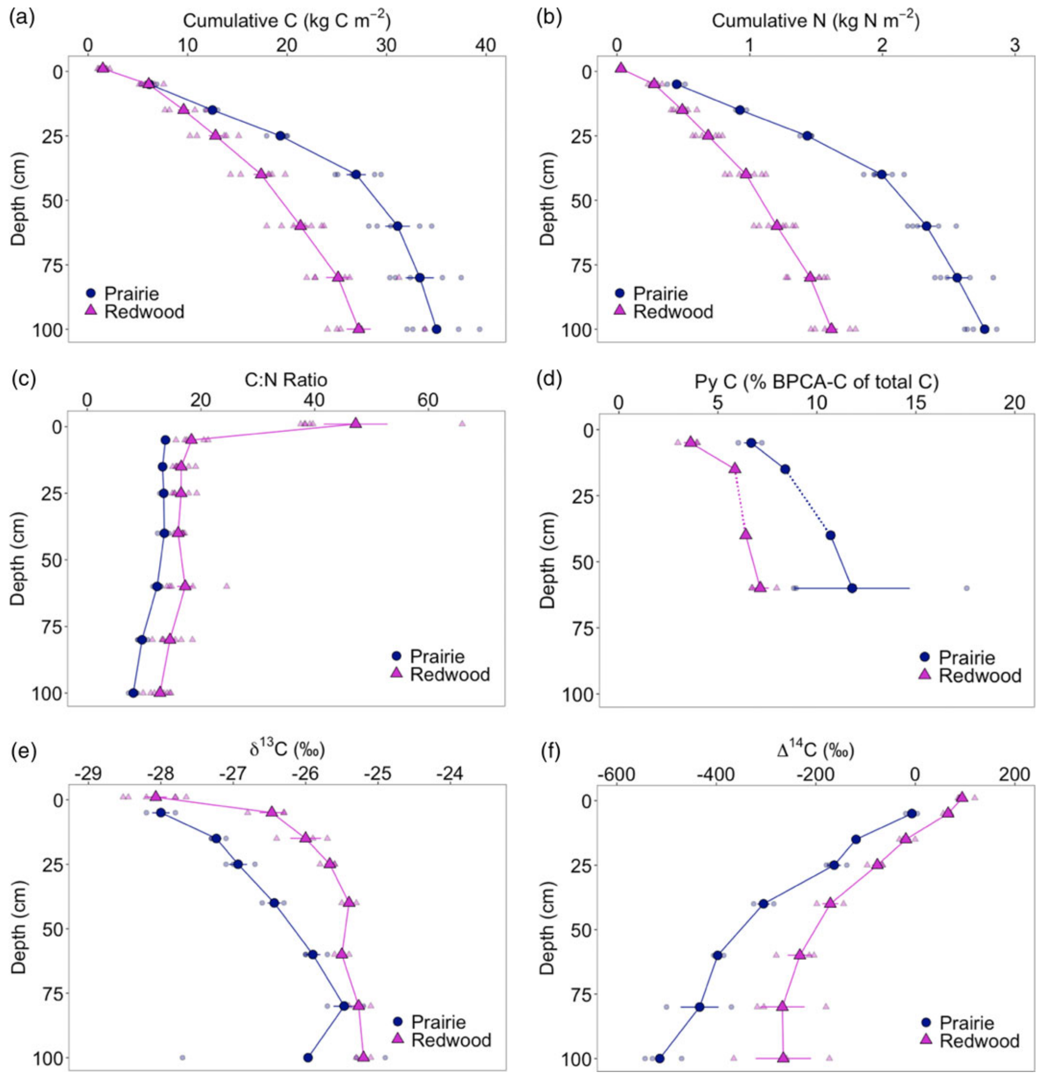

Figure 2 Bulk soil characteristics by middle increment depth for Coastal Redwood Forest and Coastal Prairie. Data are means ± 1 SE. n = 7 for Redwood and 5 for Prairie and 7 for (a) Cumulative C stock, (b) Cumulative N stock, and (c) C:N Ratio. For (d) Py C measured as BPCA, n = 3 for 0–10 cm and 50–70 cm and n = 1 for 10–20 cm and 30–50 cm for each site. Cumulative C stock. N = 3 for both sites for (e) δ ^{13}C and (f) Δ ^{14}C. Depths > 0 cm are for the forest floor (O-horizon), which was only present in redwood forest.

sources to soils than aboveground litter (Schmidt et al. 2011). We did not quantify belowground input rates, but redwood fine-root biomass to 110 cm depth was more than double that in prairie, and below 50 cm depth redwood had nearly 10 times the fine-root density of prairie. The few direct comparisons of belowground litter production between paired prairie and forest suggest that forests have higher root turnover (Pärtel and Wilson 2002), higher root productivity and belowground C inputs (Zhang et al. 2013), and that belowground inputs occur deeper in the soil profile in forest than in prairie (Steinaker and Wilson 2005).

Soil Fractions

Larger bulk soil C and N stocks in prairie than redwood were attributed to larger DF stocks in prairie ($p < 0.01$), as DF contained most of the soil C (71–91%) and N (84–95%, Figure S7). Light fraction C and N stocks were similar between vegetation types, but there was a shift in the proportion of C distributed across light fractions in the surface; fLF contained a larger portion of soil C and N in prairie (17 ± 1% of C and 12 ± 1% of N) while oLF contained a larger proportion of soil C and N in redwood (21 ± 6% of C and 10 ± 3% of N).

Nitrogen concentrations were higher in prairie than redwood for all fractions, though this difference was more pronounced in the surface and in oLF (Table 2). Light fraction C:N ratios were lower in prairie than redwood ($p < 0.01$), but DF had similar C:N ratios between sites. Like bulk soil, fraction $\delta^{13}C$ values became more enriched with depth and were more enriched in redwood than prairie at the surface (Table 2). Regardless of depth, $\delta^{13}C$ values were more enriched in DF than in light fractions, possibly reflecting differences in the molecular chemistry between fractions or a greater degree of microbial processing in the mineral-associated fraction. These results suggest that light fractions in redwood may be less microbially processed than those in prairie.

Except for redwood fLF, fraction $\Delta^{14}C$ values declined with depth (Table 2). This lack of change in $\Delta^{14}C$ values with depth for fLF in redwood may results from higher rates of recently fixed root-C inputs to deep soils in redwood, as described above, while fresh plant inputs may be more limited to near-surface soils in prairie. Significant two-way interactions between depth and site and depth and fraction showed that (1) in the top 10 cm, $\Delta^{14}C$ values were similar amongst fractions and sites, and (2) at 50–70 cm depth, $\Delta^{14}C$ values were highest for fLF and lowest for oLF and were higher in redwood than prairie at depth ($p < 0.01$).

Carbohydrates and aromatics were the most prominent compounds in light fractions (Figure S3). In general, aliphaticity, aromaticity, and combined indices were highest in oLF and lowest in biomass and litters (Figure 1). Char-corrected decomposition indices (AR* and CI*) followed similar patterns to the indices that included char (Figure 1 and Figure S8). Light fractions tended to be enriched in alkyl, aromatic, and carbonyl C and depleted in O-alkyl C compared to biomass and litters (Figure S3). The molecular mixing model indicated that light fractions tended to be depleted in carbohydrates and enriched in lipids and proteins compared to biomass and litters (Figure S4). These shifts in the molecular composition from litter to fLF and oLF are consistent with expected changes as organic matter decomposes.

Deep light fractions tended to have higher aromaticity and combined indices than surface fractions because of lower Alkyl C and higher aromatic C than surface light fractions (Figure S3). Char content, derived from the molecular mixing model, increased with depth for oLF at both sites from an average of 17 ± 2% to 60 ± 6% and for fLF in prairie (Figure S8). At 50–70 cm depth, char accounted for most (94 ± 9%) of the aromatic C in the oLF, but a considerable amount of char (37 ± 14% of total C) was also present in prairie fLF. Char-corrected aromaticity also increased with depth (Figure S8).

Molecular composition of light fractions did not differ greatly between redwood and prairie, with a few key exceptions. The molecular mixing model suggested that lignin content was about double in redwood than prairie and that protein content was higher in surface fractions from prairie than redwood (Figure S4). Deep oLF from prairie appeared to be more decomposed than that from redwood as it had higher decomposition indices (aliphaticity, char-corrected

https://doi.org/10.1017/RDC.2024.5 Published online by Cambridge University Press

Table 2 Soil fraction C and N concentration and isotopes for 0–10 and 50–70 cm depths. Values are means with standard errors in parentheses, n = 3. Different letters indicate statistically significant differences among fractions, sites, and depths within a column.

Site	Depth (cm)	Fraction	C (%)	N (%)	C:N ratio	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)
Redwood	0–10	fLF	34.0 (1.9)[ab]	1.0 (0.1)[ab]	35.6 (1.7)[a]	–27.0 (0.3)[ab]	44 (15)[a]
		oLF	35.9 (1.2)[ac]	1.1 (0.0)[bc]	32.6 (1.7)[a]	–27.5 (0.2)[a]	25 (13)[a]
		DF	5.1 (0.4)[de]	0.4 (0.0)[e]	13.5 (0.4)[b]	–25.3 (0.3)[c]	82 (7)[a]
	50–70	fLF	32.7 (1.2)[ab]	0.7 (0.0)[f]	49.0 (3.8)[c]	–27.4 (0.1)[a]	–67 (43)[ab]
		oLF	38.4 (2.8)[bc]	0.8 (0.0)[af]	46.9 (2.5)[c]	–26.3 (0.0)[b]	–302 (94)[cd]
		DF	1.5 (0.1)[de]	0.1 (0.0)[d]	13.2 (0.4)[b]	–24.9 (0.1)[c]	–218 (40)[bd]
Prairie	0–10	fLF	23.1 (0.6)[f]	1.3 (0.0)[c]	18.4 (0.6)[b]	–28.7 (0.2)[d]	63 (9)[a]
		oLF	36.8 (0.3)[ac]	2.3 (0.1)[g]	16.3 (0.7)[b]	–28.7 (0.1)[d]	31 (6)[a]
		DF	8.9 (0.7)[e]	0.7 (0.1)[ad]	12.2 (0.1)[b]	–27.6 (0.2)[a]	–2 (11)[ae]
	50–70	fLF	32.1 (1.6)[ac]	0.9 (0.1)[bf]	36.0 (4.3)[a]	–27.3 (0.2)[ae]	–197 (98)[bed]
		oLF	40.8 (1.7)[c]	1.1 (0.1)[bc]	37.5 (0.9)[a]	–26.5 (0.0)[be]	–505 (31)[c]
		DF	1.4 (0.2)[d]	0.1 (0.0)[de]	11.3 (0.6)[b]	–25.3 (0.1)[c]	–344 (20)[cd]

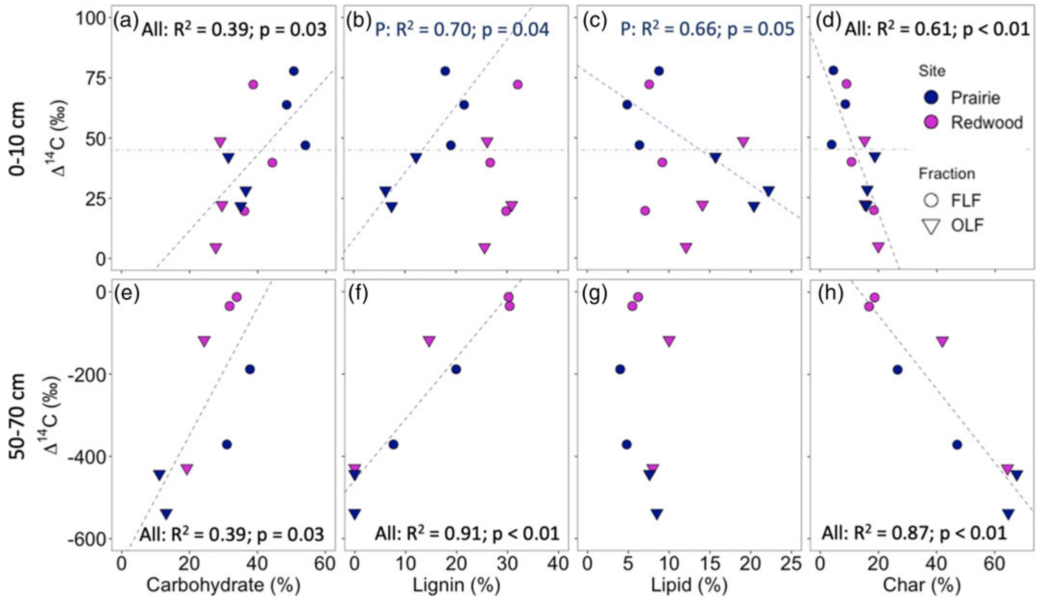

Figure 3 Light density fraction ^{14}C and molecular composition for 0–10 cm (top) and 50–70 cm (bottom) depths. A reference line is provided for the approximate atmospheric ^{14}C value in 2009, the year of sampling (gray horizontal dash-dotted line). Regression lines, R^2, and p values are provided for regressions with $p < 0.05$. Dashed lines show statistically significant linear regressions for all points (black, denoted "All") or prairie only (blue, denoted "P").

aromaticity, combined, and char-corrected combined indices), lower lignin content, and higher carbohydrate content.

Relationships between SOM Chemistry and ^{14}C Values

We found that light fractions with higher ^{14}C values (indicating a younger C average age) had higher carbohydrate content (Figure 3). Fractions with higher ^{14}C values also had higher lignin content regardless of depth in prairie but only at 50–70 cm depth in redwood. The presence of more carbohydrate and more lignin in younger soil fractions suggests the presence of relatively recent plant C inputs and that these compounds, including lignin, are not retained as organic matter decomposes even *in situ.* In contrast, fractions with lower ^{14}C values had higher char content (Figure 3) and combination indices, though the relationship between older C and higher aromaticity was only significant for deep soils (Figure 4). This further demonstrates that PyC helps to explain the presence of older C in prairie than redwood.

We hypothesized that relationships between SOC molecular composition and age would be weaker in redwood than prairie. We found that some relationships between molecular composition and age were consistent across sites, but that overall, there were more significant relationships in prairie than redwood. The most striking difference was that fractions with lower ^{14}C values (older C) also had higher lipid content and higher aliphaticity in prairie only (Figure 4), suggesting an accumulation of lipids in these fractions over time. These results support an indirect role of litter chemical structure in soil carbon formation, wherein plant inputs are processed by microbes and microbial processing promotes SOC persistence (Mambelli et al. 2011; Cotrufo et al. 2013; Gleixner 2013; Olagoke et al. 2022). Fast degrading

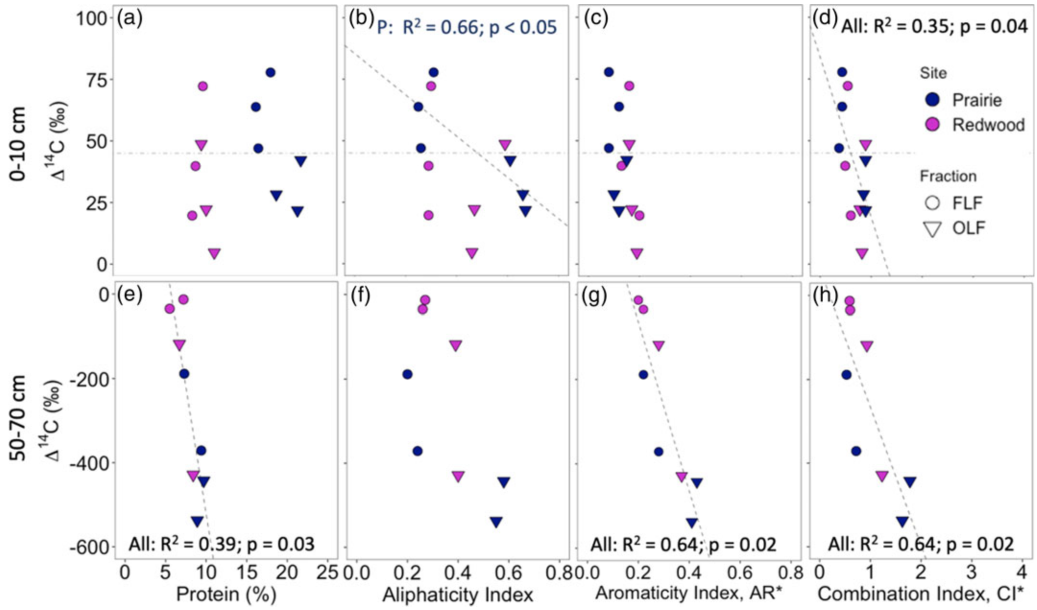

Figure 4 Light density fraction ^{14}C and molecular composition or indices for 0–10 cm (top) and 50–70 cm (bottom) depths. A reference line is provided for the approximate atmospheric ^{14}C value in 2009, the year of sampling (gray horizontal dash-dotted line). Regression lines, R^2, and p values are provided for regressions with $p < 0.05$. Dashed lines show statistically significant linear regressions for all points (black, denoted "All") or prairie only (blue, denoted "P").

litter may be transformed more efficiently into SOC by soil microbes (Manzoni et al. 2012; Bradford et al. 2013; Kallenbach et al. 2015), resulting in greater accumulation of microbial products compared to less labile litter (Cotrufo et al. 2013). This transformation of plant-derived substrates to microbial products appears to be key for the persistence of soil C especially in grasslands (Kallenbach et al. 2016; Angst et al. 2021). However, we did not identify the source (plant or microbial) of lipids in our study and research addressing this hypothesis in complex natural systems is sparse.

CONCLUSION

We compared the storage, age, and molecular characterization of SOC in old-growth coast redwood forest and adjacent prairie. These systems have highly contrasting amounts, types, and chemistry of plant litter inputs, allowing us to assess the role of plant litter in driving soil carbon storage and persistence in sites selected to minimize differences in climate and soil characteristics. As expected, redwood forest plant litters included more aromatic compounds, less nitrogen, and less carbohydrates than prairie litters. Despite having more easily degradable plant litter, prairie stored more and older soil C than redwood. Our observation of smaller soil carbon stocks and higher $\Delta^{14}C$ values in bulk soils and density fractions in redwood forest than prairie, implies the presence of more recently fixed, faster cycling C in redwood soils and/or longer residence time of soil carbon in prairie soils. Greater amounts of fire residues account for up to 40% of the larger soil carbon stocks, and likely contribute to longer soil C residence times, in prairie than redwood. Greater physicochemical protection of SOC may contribute to larger stocks and older soil carbon in prairie than redwood as most soil C was found in mineral-associated fractions and we found evidence for an increase in lipid content in older prairie light density fractions. Litter chemistry may indirectly influence soil carbon dynamics in redwood forest and prairie, but litter recalcitrance does not drive soil carbon storage and persistence in these ecosystems. Instead, differences in root inputs with depth, the amount of fire-residue, and microbial processing likely contribute to differences in soil carbon storage and age between old-growth redwood forest and coastal prairie.

ACKNOWLEDGMENTS

We thank Alex Morales for help during field collection; Lynn Murphy, Kai Orans, Abe Rohilla and Paloma Cuartero for help with laboratory and fieldwork, and Cristina Castanha and Melissa Payton for assistance in the laboratory. We also thank Stassia Samuels and Leonel Arguello at the Redwood National and State Parks for information on site history and Joe Seney at the Natural Resources Conservation Service for help with soil surveys and classification. We acknowledge the traditional, ancestral, unceded territory of the Yurok First Nations, on which this research was conducted and thank members of the community as well as park staff for observing field sampling.

This work was supported in part by the Director, Office of Science, Office of Biological and Environmental Research, Climate and Environmental Science Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 to Lawrence Berkeley National Laboratory as part of the Terrestrial Ecosystem Science Program. A part of this work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 (LLNL-JRNL- 843128) and was supported by the LLNL Postdoctoral Research Program and Laboratory Development (21-ERD-021). Save-the-Redwoods League provided additional funding to S. Mambelli.

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2024.5

REFERENCES

Amelung W, Brodowski S, Sandhage-Hofmann A, Bol R. 2008. Chapter 6: combining biomarker with stable isotope analyses for assessing the transformation and turnover of soil organic matter. Advances in Agronomy 100:155–250.

Anderson AB, Riffer R, Wong A. 1968. Chemistry of the genus sequoia—VI: on the cyclitols present in heartwood of sequoia sempervirens. Phytochemistry 7(10):1867–1870.

Anderson MK. 2013. Tending the wild: Native American knowledege and the managment of California's natural resources. Berkeley: University of California Press.

Angst G, Mueller KE, Nierop KGJ, Simpson MJ. 2021. Plant- or microbial-derived? A review on the molecular composition of stabilized soil organic matter. Soil Biology and Biochemistry 156:108189.

Baldock J, Oades J, Vassallo A, Wilson M. 1990. Solid-state cp/mas ^{13}C nmr analysis of bacterial and fungal cultures isolated from a soil incubated with glucose. Soil Research 28(2): 213–225.

Baldock J, Preston C. 1995. Chemistry of carbon decomposition processes in forests as revealed by solid-state carbon-13 nuclear magnetic resonance. Carbon Forms and Functions in Forest Soils 89–117.

Baldock JA, Masiello CA, Gélinas Y, Hedges JI. 2004. Cycling and composition of organic matter in terrestrial and marine ecosystems. Marine Chemistry 92(1):39–64.

Baldock JA, Oades JM, Nelson PN, Skene TM, Golchin A, Clarke P. 1997. Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy. Soil Research 35(5):1061–1084.

Bird JA, Torn MS. 2006. Fine roots vs. Needles: A comparison of ^{13}C and ^{15}N dynamics in a ponderosa pine forest soil. Biogeochemistry. 79:361–382.

Bonan GB, Hartman MD, Parton WJ, Wieder WR. 2013. Evaluating litter decomposition in earth system models with long-term litterbag experiments: An example using the community land model version 4 (clm4). Global Change Biology 19(3):957–974.

Bradford MA, Keiser AD, Davies CA, Mersmann CA, Strickland MS. 2013. Empirical evidence that soil carbon formation from plant inputs is positively related to microbial growth. Biogeochemistry 113(1):271–281.

Brown PM, Swetnam TW. 1994. A cross-dated fire history from coast redwood near Redwood National Park, California. Canadian Journal of Forest Research 24(1):21–31.

Burt R, Reinsch T, Miller W. 1993. A micro-pipette method for water dispersible clay. Communications in Soil Science and Plant Analysis 24:2531–2544.

Busing RT, Fujimori T. 2005. Biomass, production and woody detritus in an old coast redwood (sequoia sempervirens) forest. Plant Ecology 177(2):177–188.

Orick prairie, california (046498) 2010. Desert Research Institute; [accessed]. https://wrcc.dri.edu/cgi-bin/cliMAIN.pl?ca6498.

Cotrufo MF, Wallenstein MD, Boot CM, Denef K, Paul E. 2013. The microbial efficiency-matrix stabilization (mems) framework integrates plant litter decomposition with soil organic matter stabilization: Do labile plant inputs form stable soil organic matter? Global Change Biology 19(4):988–995.

Cusack DF, Chadwick OA, Hockaday WC, Vitousek PM. 2012. Mineralogical controls on soil black carbon preservation. Global Biogeochemical Cycles 26(2):GB2019.

Cusack DF, Chou WW, Yang WH, Harmon ME, Silver WL, The Lidet T. 2009. Controls on long-term root and leaf litter decomposition in neotropical forests. Global Change Biology 15(5):1339–1355.

Czimczik CI, Masiello CA. 2007. Controls on black carbon storage in soils. Global Biogeochemical Cycles 21(3):GB3005.

De Rosario-Martinez H. 2015. Phia: Post-hoc interaction analysis.

Eckmeier E, Egli M, Schmidt MWI, Schlumpf N, Nötzlic M, Minikus-Stary N, Hagedorn F. 2010. Preservation of fire-derived carbon compounds and sorptive stabilisation promote the accumulation of organic matter in black soils of the southern alps. Geoderma 159:147–155.

Ewing SA, Sanderman J, Baisden WT, Wang Y, Amundson R. 2006. Role of large-scale soil structure in organic carbon turnover: Evidence from california grassland soils. Journal of Geophysical Research: Biogeosciences 111(G3): G03012.

Garten CT. 2006. Relationships among forest soil C isotopic composition, partitioning, and turnover times. Canadian Journal of Forest Research 36(9):2157–2167.

Glaser B, Amelung W. 2003. Pyrogenic carbon in native grassland soils along a climosequence in north america. Global Biogeochemical Cycles 17(2):1064.

Gleixner G. 2013. Soil organic matter dynamics: A biological perspective derived from the use of compound-specific isotopes studies. Ecological Research 28(5):683–695.

Hall GD, Langenheim JH. 1986. Temporal changes in the leaf monoterpenes of sequoia sempervirens. Biochemical Systematics and Ecology 14(1): 61–69.

Hammes K, Torn MS, Lapenas AG, Schmidt MWI. 2008. Centennial black carbon turnover observed in a russian steppe soil. Biogeosciences 5(5): 1339–1350.

Hättenschwiler S, Vitousek PM. 2000. The role of polyphenols in terrestrial ecosystem nutrient cycling. Trends in Ecology & Evolution (personal edition) 15(6):238–243.

Heckman KA, Nave LE, Bowman M, Gallo A, Hatten JA, Matosziuk LM, Possinger AR, SanClements M, Strahm BD, Weiglein TL et al. 2020. Divergent controls on carbon concentration and persistence between forests and grasslands of the conterminous us. Biogeochemistry.

Hergert HL. 1992. The nature of non-proanthocyanidin units in “condensed tannins” from conifer wood and bark. In: Hemingway RW, Laks PE, editors. Plant polyphenols: dynthesis, properties, significance. Boston, MA: Springer US. p. 385–409.

Hicks Pries CE, Sulman BN, West C, O’Neill C, Poppleton E, Porras RC, Castanha C, Zhu B, Wiedemeier DB, Torn MS. 2018. Root litter decomposition slows with soil depth. Soil Biology and Biochemistry 125:103–114.

Homann P, Kapchinske J, Boyce A. 2007. Relations of mineral-soil C and N to climate and texture: regional differences within the conterminous USA. Biogeochemistry 85(3):303–316.

Horner JD, Gosz JR, Cates RG. 1988. Carbon-based plant secondary metabolites in decomposition in terrestrial ecosystems. The American Naturalist 132(6):869–883.

Hothorn T, Bretz F, Westfall P. 2008. Simultaneous inference in general parametric models. Biom J. 50(3):346–363.

Huntsinger L, McCaffrey S. 2007. A forest for the trees: forest management and the yurok environment, 1850 to 1994. American Indian Culture and Research Journal 19(4):155–192.
Jobbágy EG, Jackson RB. 2000. The vertical distribution of soil organic carbon and its relation to climate and vegetation. Ecological Applications 10(2):423–436.
Kallenbach CM, Frey SD, Grandy AS. 2016. Direct evidence for microbial-derived soil organic matter formation and its ecophysiological controls. Nature Communications 7:13630.
Kallenbach CM, Grandy AS, Frey SD, Diefendorf AF. 2015. Microbial physiology and necromass regulate agricultural soil carbon accumulation. Soil Biology and Biochemistry 91:279–290.
Kögel-Knabner I. 1997. ^{13}C and ^{15}N nmr spectroscopy as a tool in soil organic matter studies. Geoderma 80(3):243–270.
Kögel-Knabner I. 2000. Analytical approaches for characterizing soil organic matter. Organic Geochemistry 31(7):609–625.
Lehmann J, Kleber M. 2015. The contentious nature of soil organic matter. Nature 528(7580):60–68.
Mambelli S, Bird JA, Gleixner G, Dawson TE, Torn MS. 2011. Relative contribution of foliar and fine root pine litter to the molecular composition of soil organic matter after in situ degradation. Organic Geochemistry 42(9):1099–1108.
Manzoni S, Taylor P, Richter A, Porporato A, Ågren GI. 2012. Environmental and stoichiometric controls on microbial carbon-use efficiency in soils. New Phytologist 196(1):79–91.
McFarlane KJ, Schoenholtz SH, Powers RF, Perakis SS. 2010. Soil organic matter stability in intensively managed ponderosa pine stands in california. Soil Science Society of America Journal 74(3):979–992.
McFarlane KJ, Torn MS, Hanson PJ, Porras RC, Swanston CW, Callaham MA, Guilderson TP. 2013. Comparison of soil organic matter dynamics at five temperate deciduous forests with physical fractionation and radiocarbon measurements. Biogeochemistry 112(1–3): 457–476.
Miller W, Miller D. 1987. A micropipette method for soil mechanical analysis. Communications in Soil Science and Plant Analysis 18:1–15.
Miltner A, Kindler R, Knicker H, Richnow H-H, Kästner M. 2009. Fate of microbial biomass-derived amino acids in soil and their contribution to soil organic matter. Organic Geochemistry 40(9):978–985.
Moreland K, Tian ZY, Berhe AA, McFarlane KJ, Hartsough P, Hart SC, Bales R, O'Geen AT. 2021. Deep in the sierra nevada critical zone: Saprock represents a large terrestrial organic carbon stock. Environmental Research Letters 16(12):124059.
Nelson PN, Baldock JA. 2005. Estimating the molecular composition of a diverse range of natural organic materials from solid-state ^{13}C NMR and elemental analyses. Biogeochemistry. 72(1):1–34.
Northup R, Dahlgren R, McColl J. 1998. Polyphenols as regulators of plant-litter-soil interactions in northern california's pygmy forest: a positive feedback? Biogeochemistry 42(1–2):189–220.
Noss RF. 1999. The redwood forest: history, ecology, and conservation of the coast redwoods. Island Press.
Olagoke FK, Bettermann A, Nguyen PTB, Redmile-Gordon M, Babin D, Smalla K, Nesme J, Sørensen SJ, Kalbitz K, Vogel C. 2022. Importance of substrate quality and clay content on microbial extracellular polymeric substances production and aggregate stability in soils. Biology and Fertility of Soils 58(4):435–457.
Osono T, Azuma J-i, Hirose D. 2013. Plant species effect on the decomposition and chemical changes of leaf litter in grassland and pine and oak forest soils. Plant and Soil 376(1–2):411–421.
Ostertag R, Marín-Spiotta E, Silver WL, Schulten J. 2008. Litterfall and decomposition in relation to soil carbon pools along a secondary forest chronosequence in puerto rico. Ecosystems 11:701–714.
Pärtel M, Wilson SD. 2002. Root dynamics and spatial pattern in prairie and forest. Ecology 83(5):1199–1203.
Pérès G, Cluzeau D, Menasseri S, Soussana JF, Bessler H, Engels C, Habekost M, Gleixner G, Weigelt A, Weisser WW et al. 2013. Mechanisms linking plant community properties to soil aggregate stability in an experimental grassland plant diversity gradient. Plant and Soil 373(1–2):285–299.
Pillers MD, Stuart JD. 1993. Leaf-litter accretion and decomposition in interior and coastal old-growth redwood stands. Canadian Journal of Forest Research 23(3):552–557.
Pinheiro J, Bates D, DebRoy S, Sarkar D, R Core Team. 2019. Nlme: linear and nonlinear mixed effects models.
Post WM, Emanuel WR, Zinke PJ, Stagenberger AG. 1982. Soil carbon pools and world life zones. Nature 298:156–159.
Prescott C. 2010. Litter decomposition: What controls it and how can we alter it to sequester more carbon in forest soils? Biogeochemistry 101(1–3):133–149.
Preston CM, Schmidt MWI. 2006. Black (pyrogenic) carbon: A synthesis of current knowledge and uncertainties with special consideration of boreal regions. Biogeosciences 3(4):397–420.
R Core Team. 2019. R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing.
Ricciuto DM, Yang X, Wang D, Thornton PE. 2021. The impacts of model structure, parameter uncertainty and experimental design on earth

system model simulations of litter bag decomposition experiments. Biogeosciences Discuss 2021:1–36.

Sawyer JO, Sillett SC, Popenoe JH, LaBanca A, Sholars T, Largent DL, Euphrat F, Noss RF, Van Pelt R. 2000. Characteristics of redwood forests. In: Noss RF, editor. The redwood forest: History, ecology and conservation of the coast redwoods. Washington, D.C.: Island Press. p. 39–79.

Schmidt MWI, Noack AG. 2000. Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. Global Biogeochemical Cycles 14(3):777–793.

Schmidt MWI, Torn MS, Abiven S, Dittmar T, Guggenberger G, Janssens IA, Kleber M, Kogel-Knabner I, Lehmann J, Manning DAC et al. 2011. Persistence of soil organic matter as an ecosystem property. Nature 478(7367):49–56.

Schneider MPW, Smittenberg RH, Dittmar T, Schmidt MWI. 2011. Comparison of gas with liquid chromatography for the determination of benzenepolycarboxylic acids as molecular tracers of black carbon. Organic Geochemistry 42(3):275–282.

Sillett SC, Van Pelt R. 2007. Trunk reiteration promotes ephiphytes and water storage in an old-growth redwood forest canopy. Ecological Monographs 77(3):335–359.

Sillett SC, Van Pelt R, Koch GW, Ambrose AR, Carroll AL, Antoine ME, Mifsud BM. 2010. Increasing wood production through old age in tall trees. Forest Ecology and Management 259(5):976–994.

Slessarev EW, Nuccio EE, McFarlane KJ, Ramon CE, Saha M, Firestone MK, Pett-Ridge J. 2020. Quantifying the effects of switchgrass (panicum virgatum) on deep organic c stocks using natural abundance ^{14}C in three marginal soils. GCB Bioenergy 12:834–847.

Steinaker DF, Wilson SD. 2005. Belowground litter contributes to nitrogen cycling at a northern grassland-forest boundary. Ecology 86(10):2825–2833.

Stuiver M, Polach HA. 1977. Reporting of C-14 data. Radiocarbon 19:355–363.

Thomas GW. 1996. Soil ph and soil acidity. In: Agronomy SSSA, ASA, editor. Methods of soil analysis part 3 chemical methods. Madison: SSSA. p. 475–490.

Torn MS, Trumbore SE, Chadwick OA, Vitousek PM, Hendricks DM. 1997. Mineral control of soil organic carbon storage and turnover. Nature 389:170–173.

Veirs S. 1987. Vegetation studies of Elk Prairie, Prairie Creek Redwoods State Park, Humbolt County, California. Humbolt County, California: Cooperative Park Studies Unit.

Vogel JS, Southon JR, Nelson DE, Brown TA. 1984. Performance of catalytically condensed carbon for use in accelerator mass-spectrometry. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 5(2):289–293.

Vorony RP, Paul EA, Anderson DW. 1989. Decomposition of wheat straw and stabilization of microbial products. Canadian Journal of Soil Science 69(1):63–77.

Wang W, Zhang X, Tao N, Ao D, Zeng W, Qian Y, Zeng H. 2014. Effects of litter types, microsite and root diameters on litter decomposition in pinus sylvestris plantations of northern china. Plant and Soil 374(1–2):677–688.

Webster E, Chudek J, Hopkins D. 2000. Carbon transformations during decomposition of different components of plant leaves in soil. Soil Biology and Biochemistry 32(3):301–314.

Wiedemeier DB, Hilf MD, Smittenberg RH, Haberle SG, Schmidt MWI. 2013. Improved assessment of pyrogenic carbon quantity and quality in environmental samples by high-performance liquid chromatography. Journal of Chromatography A 1304(0):246–250.

Yeasmin S, Singh B, Smernik RJ, Johnston CT. 2020. Effect of land use on organic matter composition in density fractions of contrasting soils: a comparative study using ^{13}C NMR and drift spectroscopy. Science of The Total Environment 726:138395.

Young IM, Blanchart E, Chenu C, Dangerfield M, Fragoso C, Grimaldi M, Ingram J, Monrozier LJ. 1998. The interaction of soil biota and soil structure under global change. Global Change Biology 4(7):703–712.

Zhang D, Hui D, Luo Y, Zhou G. 2008. Rates of litter decomposition in terrestrial ecosystems: Global patterns and controlling factors. Journal of Plant Ecology 1(2):85–93.

Zhang K, Cheng X, Dang H, Ye C, Zhang Y, Zhang Q. 2013. Linking litter production, quality and decomposition to vegetation succession following agricultural abandonment. Soil Biology and Biochemistry 57(0):803–813.

Ziter C, MacDougall AS. 2012. Nutrients and defoliation increase soil carbon inputs in grassland. Ecology 94(1):106–116.