



Divergent controls on carbon concentration and persistence between forests and grasslands of the conterminous US

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Abstract Variation in soil organic C (%OC) concentration has been associated with the concentration of reactive Fe- and Al-oxyhydroxide phases and exchangeable Ca, with the relative importance of these two stabilizing components shifting as soil pH moves from acid to alkaline. However, it is currently unknown if this pattern is similar or different with regard to measures of soil C persistence. We sampled soils from 3 horizons (uppermost A, uppermost B, C or lowest B horizons) across a pH gradient of 11 grass-

dominated and 13 deciduous/mixed forest-dominated NEON sites to examine similarities and differences in the drivers of C concentration and persistence. Variation in C concentrations in all soils could be linked to abundances of Fe, Al and Ca, but were not significantly linked to variation in soil C persistence. Though pH was related to variation in $\Delta^{14}\text{OC}$, higher persistence was associated with more alkaline pH values. In forested soils, depth explained 75% of the variation in $\Delta^{14}\text{OC}$ ($p < 0.0001$), with no significant additional correlations with extractable metal phases. In grasslands, soil organic C persistence was not associated with exchangeable Ca concentrations, but instead was explained by depth and inorganic C concentrations ($R^2 = 0.76$, $p < 0.0001$), implying stabilization of organic C through association with carbonate

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precipitation. In grasslands, measures of substrate quality suggested greater persistence is also associated with a more advanced degree of decomposition. Results suggest that explanatory variables associated with C concentrations differ from those associated with persistence, and that reactive Fe- and Al-oxyhydroxide phases may not be present in high enough concentrations in most soils to offer any significant protective capacity. These results have significant implications for our understanding of how to model the soil C cycle and may suggest previously unrecognized stabilization mechanisms associated with carbonates and forms of extractable Si.

Keywords Soil organic matter · Radiocarbon · Density fraction · Calcium carbonate · Oxyhydroxides

Introduction

Our understanding of the relative importance of drivers of soil organic C (SOC) persistence and turnover has been evolving over the past decades. Previous reliance on broad-scale climate variables (e.g., mean annual temperature and mean annual precipitation) for prediction of SOC turnover has fallen out of favor, and the examination of soil physicochemical properties as primary drivers of SOC persistence has garnered increasing attention (e.g. Schmidt et al. 2011; Davidson 2015). Fe- and Al-oxyhydroxide phases have been highlighted as possessing a unique role in the stabilization of SOC due to their ubiquitous nature, high specific surface area, and abundance of reactive hydroxyl groups. This is true of studies of both natural soils (Torn et al. 1997; Rasmussen et al. 2005; Kramer and Chadwick 2018, and others), and artificial soils used in laboratory incubation and batch flow-through experiments (see references in Kleber et al. 2015). More recently, exchangeable Ca has been associated with increasing SOC concentrations in more arid systems (Rasmussen et al. 2018; Rowley et al. 2018).

Similar to the diminished role of climate in soil organic matter (SOM) stabilization conceptual

models, humification has fallen out of favor as a primary stabilization mechanism for SOC (Sutton and Sposito 2005; Kleber 2010; Kleber et al. 2011). However, transformation of plant-derived organics to microbially-produced or microbially-associated forms is now thought to be a key process in the long-term preservation of soil organic matter (Cotrufo et al. 2013; Kallenbach et al. 2016).

In general, soil characteristics associated with increasing SOC concentrations are also thought to be associated with some degree of increased persistence. However, this hypothesis has not been directly tested through application of a large and diverse dataset which includes both measures of soil qualities thought to be associated with increased SOC persistence as well as measurements offering a proxy for SOC persistence (in this case, radiocarbon abundance of SOC, abbreviated as $\Delta^{14}\text{OC}$), in addition to C concentration data. Here, we seek to assess the relative importance of broad-scale climate properties, reactive mineral and metal phases, and SOC chemistry to the concentration (%OC) and persistence ($\Delta^{14}\text{OC}$) of SOC in well-drained, temperate soils from the National Ecological Observatory Network (NEON).

Drawing from the evolving paradigm of soil C stabilization, we hypothesized that both SOC concentration (%OC) and persistence ($\Delta^{14}\text{OC}$) would be linked to the abundance of reactive Fe and Al phases and exchangeable Ca, with a clear gradient in relative importance dependent primarily on soil pH. To further test robustness of connections between extractable Al, Fe, and Ca with SOC, we compared the predictive power of extractable Fe, Al and Ca to that of other extractable metals that have undergone lesser degrees of scrutiny (K, Mg, Mn, Na, Si) as well as a suite of climate, soil organic matter chemistry, and texture variables.

Methods

Site selection, soil sampling

We selected 24 NEON sites across the NEON network that met the precipitation and temperature requirements of a temperate seasonal forest (13) or a woodland/shrubland (11) according to the Whittaker biome classification system (Whittaker 1962, Supplementary Fig. 1). We refer to these two biome types as

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forest and grassland from this point forward for simplicity, and because grasses were generally more abundant than shrubs at the woodland/shrubland sites. We chose to contrast temperate forest and grassland soils specifically to capture variation in the abundance of reactive Fe/Al phases (Fe_{OX} and Al_{OX}) and exchangeable Ca (Ca_{EX}) across a pH gradient (Supplementary Fig. 2). These two biome classifications additionally represent temperate climate conditions, span a similar latitudinal gradient, and comprise over half of the total NEON terrestrial sites, indicating that these systems are widespread and therefore representative of a large portion of the soils in the conterminous US. NEON sites were not selected to incorporate any specific consideration of parent material, so variation in parent material could not be constrained in the current study (Fig. 1). Climate data for each site was generated with the ClimateNA v5.10 software

package, available at <https://tinyurl.com/ClimateNA>, based on methodology described by Wang et al. (2016). Soil parent material lithologies were extracted from the USGS map database for surficial materials in the conterminous United States (Soller et al. 2009). USGS data was used in lieu of geologic information supplied for NEON sites, as the geological formations associated with site descriptions often reflected bedrock geologic units rather than surficial materials.

At each site, five soil cores were extracted using a Giddings probe (Giddings Machine Company, Windsor, CO, USA) to either 2 m or the depth of refusal, collected between 2015 and 2018. The cores used in this study originate from the NEON soil arrays and associated soil sensor plots, specifically from the soil temperature and moisture sensor boreholes generated during sensor installation. At all terrestrial NEON sites, the soil array is comprised of five sensor plots

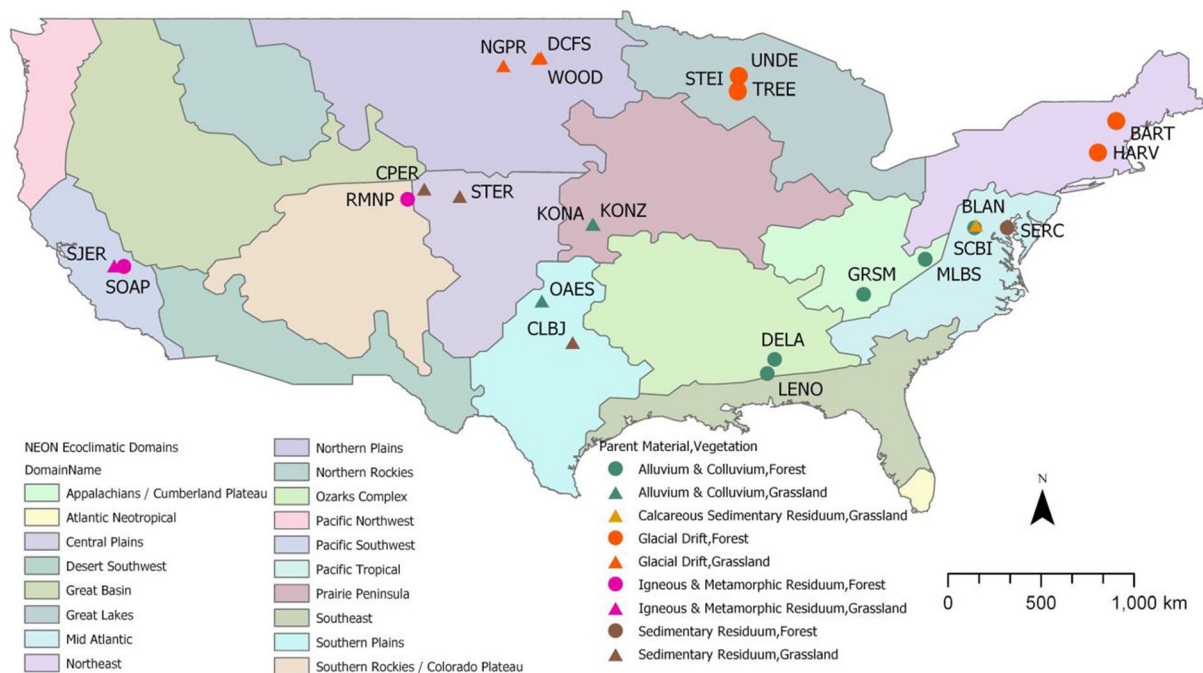


Fig. 1 Distribution of 24 NEON sites included in the current study. Grassland and forest sites span a similar latitudinal gradient and variety of parent materials. Parent materials were extracted from the USGS map database for surficial materials in the conterminous United States (Soller et al. 2009). Forest sites included: Bartlett Experimental Forest (BART), Dead Lake (DELA), Great Smoky Mountains National Park (GRSM), Harvard Forest (HARV), Lenoir Landing (LENO), Mountain Lake (MLBS), Rocky Mountain National Park (RMNP), Smithsonian Conservation Biology Institute (SCBI), Soaproot

Saddle (SOAP), Steigerwalt (STEI), Treehaven (TREE), and UNDERC (UNDE). Smithsonian Environmental Research Center (SERC). Grassland sites included Blandy Experimental Farm (BLAN), LBJ National Grassland (CLBJ), Central Plains Experimental Range (CPER), Dakota Coteau Field School (DCFS), Konza Prairie Biological Station (KONZ), Konza Prairie Biological Station—Relocatable (KONA), Northern Great Plains research Laboratory (NGPR), Klemme Range Research Station (OAES), San Juan Experimental Range (SJER), Sterling, CO (STER), and Woodworth (WOOD)

(typically arranged in a linear fashion) within the airshed of the NEON flux tower (Metzger et al. 2019). More information on NEON site layouts, the specific locations of soil sensors representing the origin of these cores, and proximity to other measurements (e.g. soil biogeochemistry data products) may be found by visiting neonscience.org. Cores were shipped on ice to the lab, air dried, and composited according to genetic horizon. Soils were sieved to < 2 mm. All further analyses were performed on the < 2 mm fraction. Supplemental Tables 1, 2, and the Discussion address what each of the following analyses are thought to approximate or represent.

Soil inorganic chemical and physical characterization

An extensive array of extractable metals and textural properties associated with soil organic matter (SOM) sorption and retention were measured. Soil texture and mass specific surface area (SSA) were determined by laser diffraction (Yang et al. 2019) following removal of organic matter with H_2O_2 at 50 °C overnight (Mikutta et al. 2005). Selective dissolution analyses (dithionite-citrate, ammonium oxalate, and sodium pyrophosphate) were conducted following standard USDA NRCS protocols (Soil Survey Staff 2014), and abundance of measured metals (Al, Fe, Mn, Si) is expressed on a mass percent of bulk soil basis. Dithionite-, oxalate-, and pyrophosphate-extractable metals are abbreviated, respectively, as: Al_{DC} , Fe_{DC} , Mn_{DC} , Si_{DC} ; Al_{OX} , Fe_{OX} , Mn_{OX} , Si_{OX} ; Al_{PY} , Fe_{PY} , Mn_{PY} , Si_{PY} . Exchangeable metals (abbreviated as Ca_{EX} , K_{EX} , Mg_{EX} , Na_{EX} , Al_{EX} , Fe_{EX}) were extracted using ammonium acetate at pH 7.1, and KCl-extractable metals (abbreviated as Al_{KCl} , Fe_{KCl}) were extracted using 1 M KCl at the Oregon State University Central Analytical Laboratory (Soil Survey Staff 2014).

Soil C characterization

Percent C and N and $\delta^{13}\text{C}$ were measured by EA-IRMS (Isoprime Ltd., Cheadle, UK). Samples containing carbonates, as determined by effervescence following application of 10% HCl solution, were measured both prior-to and following acid fumigation (Harris et al. 2001).

Samples were graphitized for radiocarbon measurement at the USDA Forest Service Carbon, Water & Soils lab in Houghton, MI. Graphite was measured for radiocarbon abundance at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory (LLNL) and the WM Keck Carbon Cycle Accelerator Mass Spectrometry facility at the University of California, Irvine (UCI). Sample aliquots containing carbonates were acid fumigated prior to graphitization if intended for radiocarbon analysis of organic C (Harris et al. 2001). Samples were dried and then weighed into quartz tubes with cupric oxide and silver while under vacuum. The tubes were sealed and then combusted at 900 °C for 6 h to convert the sample carbon into carbon dioxide (CO_2) gas. The CO_2 was then reduced to graphite through heating at 570 °C in the presence of hydrogen gas and a Fe catalyst (Vogel et al. 1987). Graphite targets were then analysed for radiocarbon abundance using an accelerator mass spectrometer (AMS; Davis et al. 1990). Values were corrected for mass-dependent fractionation using measured $\delta^{13}\text{C}$ values according to Stuiver and Polach (1977) at LLNL and corrected with inline AMS measurements at UCI. Dating of soil carbonates was carried out through reaction of bulk soil with concentrated H_3PO_4 under vacuum to produce CO_2 . The CO_2 was then reduced to graphite and measured by AMS as described above. Radiocarbon data for organic C is expressed in units of $\Delta^{14}\text{OC}$ (‰). Radiocarbon data for carbonates (inorganic C) is expressed in units of $\Delta^{14}\text{IC}$ (‰).

We specifically chose to examine bulk SOM $\Delta^{14}\text{OC}$ values as opposed to measurements on fractions or modeled turnover times, as we believe bulk $\Delta^{14}\text{OC}$ is the most effective integrative proxy of SOM persistence and its relationship to (de)stabilizing processes and properties (Bailey et al. 2018). Use of bulk $\Delta^{14}\text{OC}$ also allows for direct comparison of bulk $\Delta^{14}\text{OC}$ trends with trends in bulk %OC. Bulk SOM is composed of both fast- and slow-cycling pools which may have significantly different relationships to (de)stabilizing factors (Trumbore 2009). However, previous work has indicated significant relationships among bulk soil physicochemical properties and bulk $\Delta^{14}\text{OC}$ (Torn et al. 1997; Masiello et al. 2004; Lawrence et al. 2015).

We measured several metrics of SOM commonly used as indices of decomposition or metrics of plant versus microbial quality to explore how SOM

chemistry may or may not be related to C persistence. We additionally measured total pyrogenic C concentration to look for evidence of structural recalcitrance driving bulk C abundance or persistence. Measures of SOM chemistry included total pyrogenic carbon concentration ($g_C \text{ kg}_{\text{soil}}^{-1}$), ratio of diacids to lignin (diacid:lignin), double bond equivalents minus oxygen following chloroform extraction (DBE-O Chloroform), dissolved organic C biological index, and nominal oxidation state of C (NOSC) (Supplementary Table 2).

Total pyrogenic C concentration of bulk soils was quantified through the benzene polycarboxylic acid (BPCA) method (Matosziuk et al. 2019, 2020).

The diacid:lignin ratio of bulk SOC was determined through CuO oxidation (Goñi and Montgomery 2000; Hatten and Goñi 2016; Hatten et al. 2012), and is generally considered to be an indicator of SOM degradation, with SOM transitioning from “fresh” to “degraded” as the ratio increases. Lignin content is calculated as the sum of vanillyl phenols (vanillin, acetovanillone, vanillic acid), syringyl phenols (syringaldehyde, acetosyringone, syringic acid), and cinnamyl phenols (p-coumaric acid, ferulic acid). Diacids are calculated as the sum of pentane-1,5,-dioic acid, hexane-1,6-dioic acid, heptane-1,7-dioic acid, octane-1,8-dioic acid, nonane-1,9-dioic acid, decane-1,10-dioic acid, undecane-1,11-dioic acid, hexadecanoic acid, and octadecanedioic acid. CuO oxidation is considered semi-quantitative due to variance in extraction efficiency. However, previous work has supported this technique as highly repeatable and a valid approach for examination of natural soils (Hatten and Goñi 2016).

Double bond equivalents minus oxygen (DBE-O Chloroform), biological Index, fluorescence index, and nominal oxidation state of C (NOSC) were measured specifically on water-, methanol-, and chloroform-soluble extracts of bulk soils following standard procedures. Extractions and measurements were completed at the Environmental Molecular Sciences Lab, using a modified method from Tfaily et al. (2017). Extractions were carried out sequentially using a 1:5 soil to solution ratio, and mass spectra of extracts were collected using a 12 T Bruker Solarix Fourier transform ion cyclotron resonance mass spectrometer. Molecular formulas were assigned to mass spectra peaks using Formularity (Tolić et al. 2017). Abundance of DBE-O chloroform

extractable compounds specifically associated with the lipid-like fraction generally decrease with increasing degree of decomposition (Gonsior et al. 2009; Koch and Dittmar 2006). The DBE-O was calculated as the abundance of C=C bonds minus the number of oxygens and assumes all oxygen is bonded to carbon as a carboxyl group and thus the carbon is not included in the DBE-O (Koch and Dittmar 2006, 2016). The biological index broadly represents pools of dissolved organic matter associated with microbial activity and/or high bioavailability (Parlanti et al. 2000); values increase with increasing degree of decomposition. The fluorescence index is a proxy for plant- vs. microbially-sourced dissolved organic matter; values increase with increasing microbial nature (Cory and McKnight 2005; McKnight et al. 2001). NOSC values were averaged across all three extractions. More negative NOSC values are associated with a greater degree of reduction; more positive values are associated with a greater degree of oxidation. NOSC values are generally thought to decrease with increasing decomposition (Riedel et al. 2012).

Statistical analysis

Model testing was carried out through multiple linear regression and goodness of fit was determined through assessment of the skewness and kurtosis of the residuals of each model. Analyses were carried out in JMP Pro 14.0.0 (SAS Institute). When skewness of residuals fell between -0.5 and 0.5 and excess kurtosis fell between -1 and 1 , the model was determined to be a good fit. In cases where residuals were not normally distributed, predictor and response variables were transformed as necessary. Three modeling approaches were applied individually for %OC and $\Delta^{14}\text{OC}$: Hypothesis driven, stepwise, and best subset. Hypothesis driven models tested the explanatory power of depth, Al_{OX} , Ca_{EX} , pH, and PET/MAP for C concentrations (%OC) and long term persistence ($\Delta^{14}\text{OC}$) across our pH gradient of forest and grassland soils following recent work by Kramer and Chadwick (2018), Rasmussen et al. (2018), and Rowley et al. (2018). This hypothesis driven model replicates the model used previously in Rasmussen et al. (2018) that had strong explanatory power for %OC across a large dataset of soils from the U.S. Department of Agriculture’s National Cooperative Soil Survey (NCSS) Soil Characterization Database.

We additionally applied stepwise and best subset multiple regression approaches in order to explore the predictive power of less well-examined extractable metals in comparison to Al_{OX} , and Ca_{EX} . Stepwise and best subset both allow for the selection of predictive variables based on the individual or cumulative explanatory power of variables as they are selected from the pool of candidate variables. For stepwise and best subset models, we allowed for selection from the following extractable metal and textural properties: Al_{DC} , Fe_{DC} , Mn_{DC} , Si_{DC} ; Al_{OX} , Fe_{OX} , Mn_{OX} , Si_{OX} ; Al_{PY} , Fe_{PY} , Mn_{PY} , Si_{PY} ; Al_{EX} , Ca_{EX} , K_{EX} , Mg_{EX} , Na_{EX} ; Al_{KCl} , Fe_{KCl} ; % sand, % silt, % clay, SSA. We additionally tested for direct relationships among %OC, %IC, and $\Delta^{14}\text{OC}$, with %IC standing as a proxy for carbonate content (additional information in supplementary materials).

Spearman correlation matrices were constructed for the residuals of %OC and $\Delta^{14}\text{OC}$ versus depth against three suites of variables: extractable metals and textural variables, climate variables, and measures of SOC chemistry. Residuals were calculated for a linear relationship between depth and $\Delta^{14}\text{OC}$ and a ln-ln relationship between depth and %OC. *P*-values were adjusted for multiple comparisons following Benjamini and Hochberg (1995), which reduces false positives but also minimizes false negatives. This adjustment controls the false discovery rate (FDR) in comparison to the more traditional Bonferroni adjustment which controls only the false positive rate and may lead to significant type II errors (Jafari and Ansari-Pour 2019). These matrices allow for the comparison of the strength of monotonic relationships between large numbers of potential explanatory variables and %OC and $\Delta^{14}\text{OC}$ both across the complete forest and grassland pH gradient, and within each biome type. This approach offers an easy and quick way to illustrate the common and differing drivers of C concentration and persistence across and within biomes. This data visualization was carried out specifically to examine the relative importance of soil physicochemical properties in comparison to climate and SOM chemistry. Only correlations with $p < 0.05$ are shown.

Meta analysis

In order to place the results of the current study within the broader context of previous work, we also report a

brief meta analysis of data from the International Soil Radiocarbon Database v. 1.3.4 (ISRaD) (Lawrence et al. 2020). ISRaD is an open-source harmonized database which specifically compiles and archives data from soil studies which focus on soil radiocarbon measurements, fractionation methods, and soil respiration (incubation or field) measurements. ISRaD therefore offers a comprehensive and well-curated compilation of soil radiocarbon and C data from previously published works. We used ISRaD to extend our examination of the relationship between extractable metals and $\Delta^{14}\text{OC}$ by identifying all the studies in the database which reported both extractable metals (Fe or Al extracted by pyrophosphate, oxalate, or dithionite) and bulk soil $\Delta^{14}\text{OC}$. We additionally extracted all the bulk soil data which reported layer depth, $\Delta^{14}\text{OC}$, and %OC to examine the relationship between $\Delta^{14}\text{OC}$ and %OC. In order to probe connections between extractable metals in soils and parent material types, we compared the distribution of parent materials across the conterminous US (Soller et al. 2009) to the distribution of parent materials in the current study and across ISRaD studies (Lawrence et al. 2020).

Results

Pearson regression analyses

On average (Table 1), %OC values did not differ between grassland and forest soils ($p = 0.1228$, Fig. 2), although grasslands were significantly depleted in $\Delta^{14}\text{OC}$ in comparison to forests ($122.7 \pm 54.5 \text{ ‰}$, $p = 0.0275$, Fig. 3) and had lower C: N ratios (3.91 ± 1.38 , $p = 0.0060$). Grasslands were significantly drier and slightly warmer than forests, with higher pH (1.39 ± 0.21 , $p < 0.0001$) and Ca_{EX} ($0.26\% \pm 0.03$, $p < 0.0001$). Forests were enriched in Al_{OX} in comparison to grasslands ($0.13\% \pm 0.03\%$, $p < 0.0001$), but not significantly higher in Al_{PY} and Fe_{PY} ($p = 0.8299$ and $p = 0.0883$, respectively). Textural properties were similar between grasslands and forests (sand $p = 0.3211$, clay $p = 0.4260$, SSA $p = 0.6262$; Table 1).

After accounting for the influence of depth on %OC and $\Delta^{14}\text{OC}$, there was no significant relationship between %OC and $\Delta^{14}\text{OC}$ ($R^2 = 0.0032$, $p = 0.6497$, Supplementary Fig. 3a). The hypothesis-driven

Table 1 Mean and standard error values for commonly reported soil properties

	MAP/PET		MAT (°C)		Profile depth (cm)		% OC		C:N		$\Delta^{14}\text{OC}$		pH	
	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±
Grassland	0.60	0.03	10.5	0.8	98.0	11.2	0.91	0.17	11.1	0.7	-272.8	44.0	6.85	0.12
Forest	1.13	0.04	9.6	0.8	92.7	12.6	1.5	0.31	15.0	1.1	-150.1	33.4	5.46	0.18
<i>p</i> -value	< 0.0001		0.0467		0.7588		0.1228		0.0060		0.0275		< 0.0001	
	Al_{OX} (%)		Ca_{EX} (%)		Sand (%)		Clay (%)		SSA ($\text{m}^2 \text{g}^{-1}$)		Al_{PY} (%)		Fe_{PY} (%)	
	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±
Grassland	0.10	0.01	0.34	0.03	25.5	4.5	21.1	1.8	5.2	0.4	0.44	0.08	0.25	0.05
Forest	0.23	0.03	0.07	0.01	31.3	3.8	18.9	2.0	4.9	0.5	0.41	0.06	0.36	0.04
<i>p</i> -value	< 0.0001		< 0.0001		0.3211		0.4260		0.6262		0.8299		0.0883	

p-values were determined by one-way ANOVA by ecosystem type followed by Tukey's HSD post hoc test. *P*-values < 0.05 are bolded

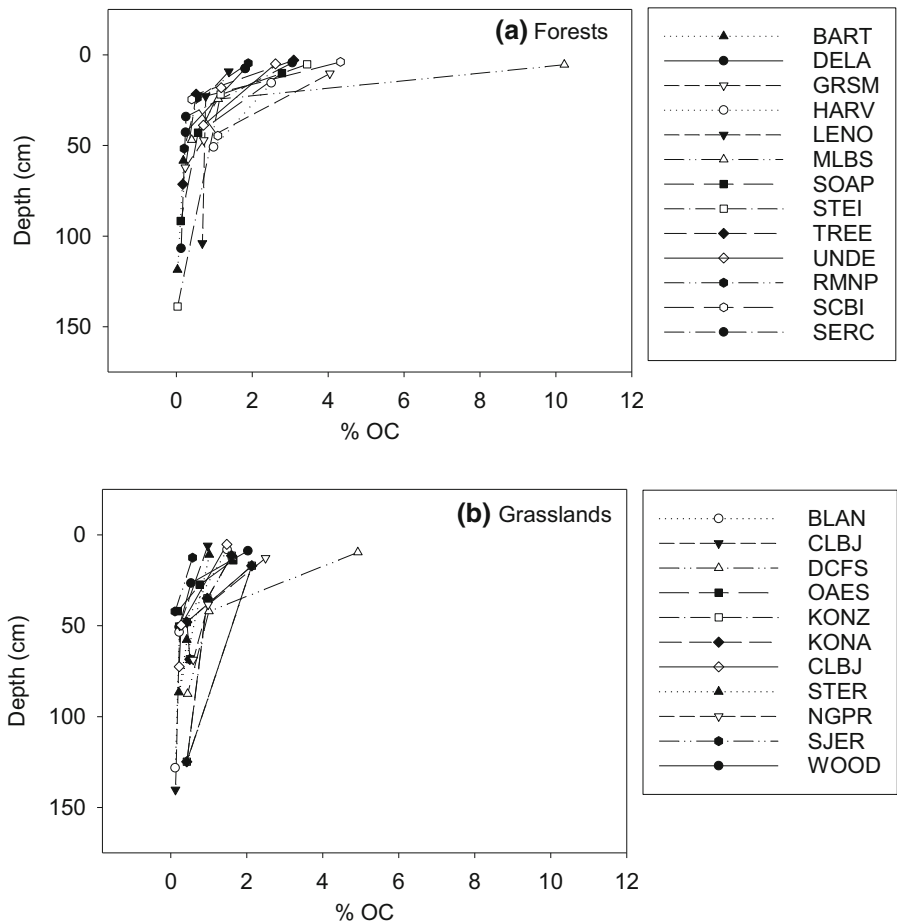


Fig. 2 Depth profiles of %OC for **a** forest ($n = 13$) and **b** grassland ($n = 11$) sites

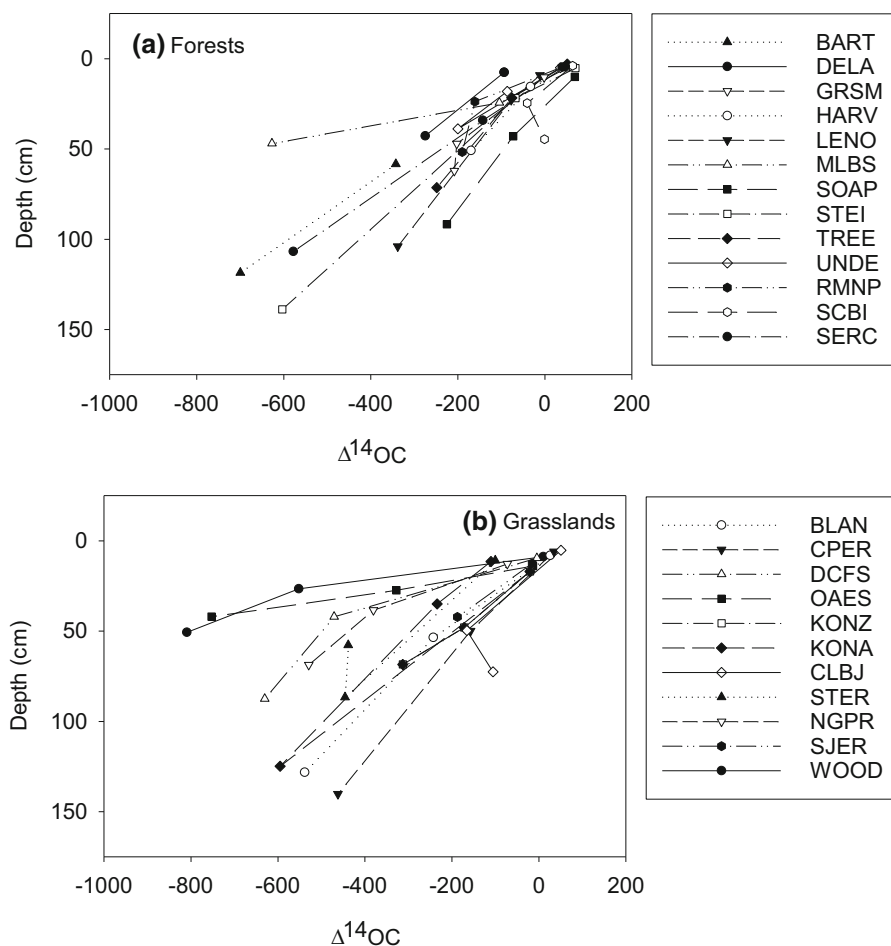


Fig. 3 Depth profiles of $\Delta^{14}\text{OC}$ for **a** forest ($n = 13$), and **b** grassland ($n = 11$) sites

regression test indicated that Al_{OX} and Ca_{EX} had significant explanatory power for %OC, but not for $\Delta^{14}\text{OC}$. The application of stepwise and best subset regression analyses indicated that extractable metals other than Al_{OX} had similar explanatory power and were selected either instead of, or in addition to, oxalate extractable phases for %OC models (Table 2). Only pH was selected as significant for $\Delta^{14}\text{OC}$ regardless of regression approach, with higher pH soils having lower $\Delta^{14}\text{OC}$ values (Table 3). Our original hypothesis partially centered around the importance of Ca_{EX} for the stabilization of OC in alkaline soils. Following a lack of significance of Ca_{EX} for explaining variation in $\Delta^{14}\text{OC}$, we explored inorganic C (%IC) as a potential explanatory factor, utilizing %IC as a proxy for carbonate abundance in alkaline grassland soils only, as forest soils had no

measurable inorganic C. %IC was significantly correlated with $\Delta^{14}\text{OC}$ values in grassland soils (Table 3).

Spearman regression analyses

We additionally examined nonparametric relationships among a large suite of explanatory values and %OC and $\Delta^{14}\text{OC}$ after accounting for variation associated with depth. Figure 4 shows the Spearman correlation coefficient values for %OC and $\Delta^{14}\text{OC}$ according to each individual biome type and across biomes. There was a general lack of significant relationships between almost all potential explanatory variables and $\Delta^{14}\text{OC}$ in forest soils. The majority of variation in %OC and $\Delta^{14}\text{OC}$ was explained by depth alone in forest soils (Table 4).

Table 2 Least squares regression models testing predictive power of extractable metals for OC concentration (%OC)

Approach	A priori selected				Approach				Stepwise				Approach				Best subset				
	R ² (adj)	RMSE	Parameter	Estimate	StdErr	SSE/SST	p-value	R ² (adj)	RMSE	Parameter	Estimate	StdErr	SSE/SST	p-value	R ² (adj)	RMSE	Parameter	Estimate	StdErr	SSE/SST	p-value
Intercept		0.806		1.8	0.3	< 0.0001				Intercept	2.6	0.2		< .0001			Intercept	2.0	0.2		< 0.0001
ln(depth)		0.526		− 0.9	0.1	0.63	< 0.0001			ln(depth)	− 1.0	0.1	0.66	< .0001			ln(depth)	− 1.010	0.056	0.702	< 0.0001
Al _{ox}				3.016	0.488	0.11	< 0.0001			% sand	− 0.01	< 0.01	0.03	0.0011			Si _{bc}	3.009	1.169	0.014	0.0124
Ca _{ex}				1.464	0.000	0.05	0.0002			Si _{ox}	13.451	2.613	0.07	< .0001			Al _{ox}	2.896	0.414	0.107	< .0001
										Fe _{KCl}	198.359	73.805	0.02	0.0092			Mg _{EX}	5.895	2.370	0.014	0.0155

For all models, n = 69, SST = 97.056. Extractable metals are in units of % by weight, depth is in units of ln(cm), and OC is in units of ln(% by weight)
 RMSE Root mean square error, SSE/SST ratio of the sum of squares explained by the individual effect and the total sum of squares

In general, we observed a large number of significant relationships between %OC, extractable metal phases and textural properties (Fig. 4a), but not for $\Delta^{14}\text{OC}$. Climate variables were weakly associated with %OC in grasslands, with hotter, drier sites having lower concentrations of C (Fig. 4b). Soil organic matter chemistry exerted a stronger influence on $\Delta^{14}\text{OC}$ than extractable metals and texture (Fig. 4c). Variables expressing degree of decomposition were strongly linked to $\Delta^{14}\text{OC}$ in grasslands but not in forests. In grasslands, increasing depletion in $\Delta^{14}\text{OC}$ was associated with increasing biological index, increasing diacid:lignin, and increasing fluorescence index values. Relative enrichment in grassland $\Delta^{14}\text{OC}$ was associated with increasing density of C=C bonds (DBE-O chloroform), and increasing NOSC values. Pyrogenic C concentration was a weak but significant predictor of %OC across all sites.

Meta-analysis of ISRaD data

Analysis of ISRaD data supported the findings of the current study. After accounting for depth, there was a significant relationship between %OC and $\Delta^{14}\text{OC}$. However, the explanatory power of the correlation is very low ($R^2 = 0.023$, $p < 0.0001$, $n = 1956$, Supplementary Fig. 3b). We identified a total of 15 studies included in ISRaD which reported both extractable Fe and Al concentrations (pyrophosphate, oxalate, dithionite) and $\Delta^{14}\text{OC}$ for bulk soils (Supplementary Table 4). Of these studies, eight were able to quantitatively or qualitatively link extractable metal concentrations/abundance to organic C concentrations or stocks, six were able to statistically link extractable metals with $\Delta^{14}\text{OC}$, and six were able to qualitatively draw connections between extractable metals and $\Delta^{14}\text{OC}$. Only three of the studies were conducted on grasslands, and two of these linked $\Delta^{14}\text{OC}$ to specific surface area, not extractable Fe and Al phases. The majority of these studies were conducted on what the USGS refers to as *volcanic* parent materials (Supplementary Table 5). This is in comparison to only a 1% abundance of volcanic parent materials across the conterminous US, and no sites located on volcanic parent materials in the NEON data used in the current study.

Table 3 Left panel: Least squares regression models testing predictive power of extractable metals for $\Delta^{14}\text{OC}$ for both forests and grasslands ($n = 69$, $\text{SST} = 3,367,529.6$)

Approach					Approach				
A priori selected, stepwise, best subset					Secondary hypothesis				
R ² (adj)					R ² (adj)				
RMSE					RMSE				
Parameter	Estimate	StdErr	SSE/SST	<i>p</i> -value	Parameter	Estimate	StdErr	SSE/SST	<i>p</i> -value
Intercept	304.3	99.2	0.00310	0.60	Intercept	396.5	80.2		0.79
Depth(cm)	− 4.4	0.5	0.43	146.812	ln(Depth(cm))	− 173.8	55.7	0.42	117.8894
pH	− 54.21	16.48	0.06	< 0.0001	IC (%)	− 136.9	23.5	0.25	< 0.0001
				0.0016					< 0.0001

Right panel: Least squares regression models testing predictive power of inorganic C for $\Delta^{14}\text{OC}$ of grassland soils only ($n = 32$, $\text{SST} = 1,919,988.7$)

Discussion

Recent work has illustrated variance in the soil physicochemical properties associated with increasing C concentrations across pH and moisture gradients (e.g. Rasmussen et al. 2018; Rowley et al. 2018; Kramer and Chadwick 2018). In general, Fe- and Al-oxyhydroxide phases have greater relative importance in wetter or more acidic soils, and Ca_{EX} and texture play a greater role in drier alkaline soils. These patterns have generally held true across C concentrations and/or stocks, and greater accrual of C would seem to imply a greater degree of stabilization. However, the current investigation suggests that soil properties associated with longer C persistence may not be the same properties associated with higher C concentrations.

Extractable metals linked to C concentrations but not persistence

A primary goal of this investigation was to leverage a pH gradient of temperate soils to test the explanatory power of reactive Fe and Al phases and exchangeable Ca for soil C abundance and persistence (Kramer and Chadwick 2018; Rasmussen et al. 2018; Rowley et al. 2018). Results suggested that although these extractable metals can successfully explain variation in SOC concentrations, they were not associated with variation in persistence (as inferred from $\Delta^{14}\text{OC}$ values). This result strongly suggests that a higher C concentration is not necessarily associated with a higher degree of persistence, a point of utmost

importance when considering how to model turnover of the terrestrial C pool.

We additionally found, through the application of self-selecting regression approaches, that other extractable metals can explain a similar amount of variation as Al_{OX} , Fe_{OX} and Ca_{EX} . Extractable pools of Si (e.g. pyrophosphate, oxalate, and dithionite soluble), for example, have not been thoroughly examined in the context of SOC stabilization mechanisms. The variation in %OC in grasslands was highly correlated to Si_{DC} , which may precipitate in amorphous forms in moisture limited systems (Chadwick et al. 1987; Kendrick and Graham 2004) and therefore may form similar associations with SOC as short-range-order Fe- and Al-oxyhydroxide phases do. Alternatively, Si_{DC} may be linked to pools of C preserved in phytoliths which can comprise a significant portion of total SOC and persist for millennia (Parr and Sullivan 2005).

These ideas are consistent with previous studies that found soil mineral phases other than oxyhydroxides associated with variation in C stocks, concentrations and $\Delta^{14}\text{OC}$ values. An examination of turnover of mineral-associated C across 36 forests and grasslands in Germany showed no connection of C persistence to oxalate-extractable Al and Fe (Herold et al. 2014). Similarly, Khomo et al. (2017) found smectite to be a better predictor of turnover than short-range-order phases in a series of well-developed soils across a wide variety of parent materials in South Africa. The concept of short-range-order phases dominating sorption and preservation of C was additionally challenged in Hall et al. (2018) which found short-range-order phases were associated with

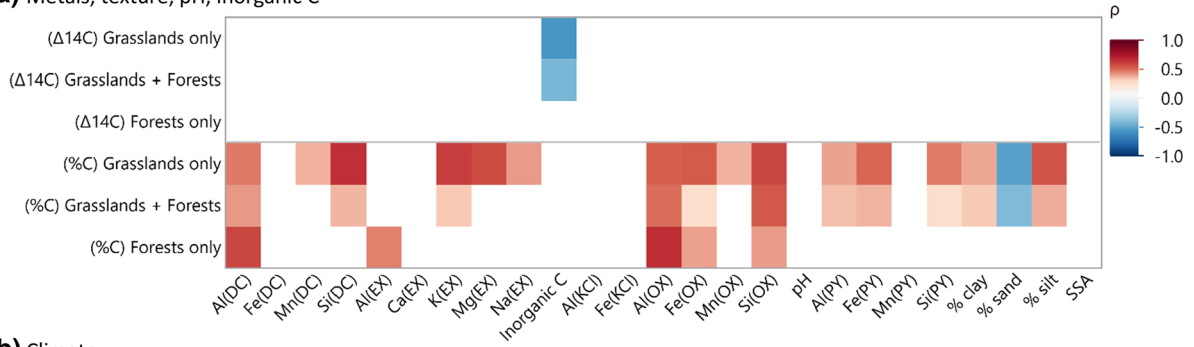
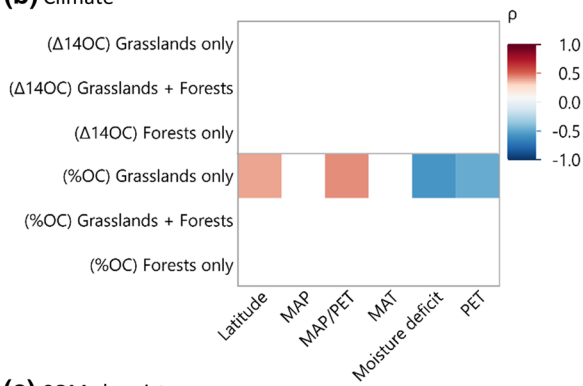
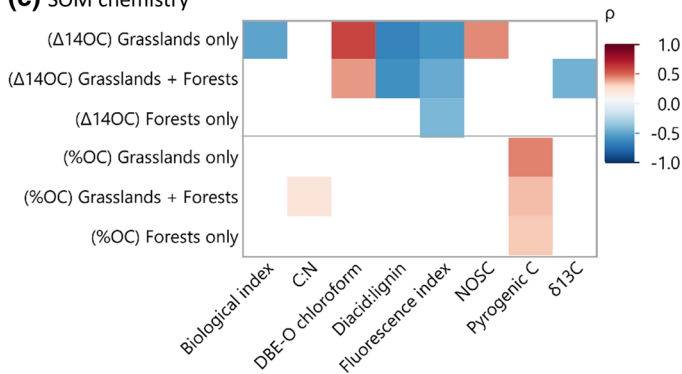
(a) Metals, texture, pH, inorganic C**(b) Climate****(c) SOM chemistry**

Fig. 4 Spearman correlation coefficients between potential explanatory variables and the residuals of linear regression models of $\ln(\%C)$ versus $\ln(\text{depth})$ and $\Delta^{14}\text{OC}$ versus depth. p values are only displayed for correlations with $p < 0.05$, after application of an FDR adjustment of p -values to account for multiple comparisons. Data is presented in this way to illustrate commonality and variation in the driving factors across and

between biome types. **a** Extractable metals, pH, texture variables, and inorganic C, **b** climate variables, **c** SOM chemistry. Suffixes are coded as follows: *DC* dithionite extractable, *EX* exchangeable, *KCl* KCl extractable, *OX* oxalate extractable, *PY* pyrophosphate extractable. Adjusted p -values for Spearman matrices are given in supplemental Table 3

faster-cycling pools of C, whereas more persistent pools were associated with crystalline oxides. Our results support the idea of variability in the particular mineral phases associated with C pools of higher persistence, and that this variance may be associated with differences in soil morphology and weathering status.

Additional meta-analysis of published literature indicated that only a handful of studies, the majority of which have been carried out on volcanic parent materials, have successfully linked abundances of selectively dissolved Fe and Al to $\Delta^{14}\text{OC}$. These volcanic parent materials make up less than 1% of surface area in the conterminous US and typically

Table 4 Least squares regression models testing predictive power of depth(cm) for %OC and $\Delta^{14}\text{OC}$

Response variable	Site type	R ²	p-value
% OC	Grasslands only	0.601	< 0.0001
	Grasslands + forests	0.696	< 0.0001
	Forests only	0.753	< 0.0001
$\Delta^{14}\text{OC}$	Grasslands only	0.414	< 0.0001
	Grasslands + forests	0.549	< 0.0001
	Forests only	0.735	< 0.0001

Depth was ln transformed prior to regression against ln(%OC)

have very high concentrations of extractable Fe and Al (Supplementary Table 4; Soller et al. 2009). The uniqueness of these soils may limit the applicability of a conceptual model which relies on reactive Fe- and Al-oxyhydroxide phases as primary regulators of SOC persistence and turnover. This is not to say that lower concentrations of extractable Fe and Al are not involved in stabilization mechanisms, only that they may be present in concentrations insufficient to substantially impact bulk soil C persistence in the majority of cases. This assertion is supported by our results, which showed that C persistence in forest soils was solely and strongly linked to depth ($R^2 = 0.735$, $p < 0.0001$) rather than extractable metals. The strong dependence of forest SOC persistence on depth may further support the importance of factors such as oxygen and moisture scarcity as well as reduced inputs at depth as a primary driver of SOC stabilization (Bernal et al. 2016; Keiluweit et al. 2016).

Soil pH and its relationship to climate and stabilization mechanisms

Soil pH has been invoked as a master variable in explaining variation in soil C abundance and persistence due to its ubiquitous influence on soil physicochemical and biological properties. Here we find higher pH values associated with greater depletion in $\Delta^{14}\text{OC}$, suggesting higher persistence in circum-neutral and alkaline soils compared to acidic soils across our constrained pH gradient of temperate sites. This seems to be contrary to our current conceptual understanding of pH effects on SOC stabilization, though few studies have directly contrasted SOC persistence in grasslands and forests. Acidity is

associated with Al toxicity, organo-metal coprecipitation, and sorption of nutrients such as P and N on mineral surfaces, all of which have been shown to discourage decomposition (c.f., Kleber et al. 2015). Alkaline pH values are associated with weaker stabilization mechanisms such as cation bridging and outer sphere sorption mechanisms, conditions thought to be more conducive to decomposition (Essington 2015). Because pH is associated with many soil physicochemical properties and varies consistently between forests and grasslands, relationships between pH and $\Delta^{14}\text{OC}$ may be spurious and may instead be indicative of differences in C cycling associated with leaching potential, soil morphology, or carbonate presence.

Soil pH is a reflection of both past and present climate conditions in these well-drained temperate soils, with increased leaching potential associated with lower pH values (Slessarev et al. 2016). The strong connections between leaching potential, pH and SOC stabilization mechanism have been illustrated through regional (Rasmussen et al. 2018; Mathieu et al. 2015) and global-scale investigations (Kramer and Chadwick 2018). We suggest that in moisture limited alkaline soils, moisture both limits productivity and associated increases in %OC but also promotes SOC persistence by limiting rates of turnover at depth. This is supported by greater depletion in $\Delta^{14}\text{OC}$ with depth in grasslands in comparison to forests (Fig. 3).

Inorganic C

Alkaline pH and limited leaching potential also promote pedogenic carbonate formation and precipitation, either disseminated throughout the soil matrix or deposited as localized concentrations and masses that may coalesce over time to form calcic horizons. The best explanatory variable in predicting SOC persistence in grasslands was depth, followed closely by inorganic C abundance. Two primary mechanisms may best explain these relationships: coinherance of lithogenic organics and carbonates, or stabilization of organics during dissolution/reprecipitation of pedogenic carbonates. The grassland sites containing carbonates were derived from glacial till (DCFS, WOOD), a combination of glacial till and loess (NGPR), sedimentary (STER), limestone (KONA), and unspecified unconsolidated (OAES) materials. These parent materials can contain lithogenic

carbonates and organics derived directly from the parent material. In the case of inheritance of lithogenic materials, carbonates may contain no detectable radiocarbon (“radiocarbon dead”), as the rocks that they are derived from are millions or more years old, and organic C age could also be radiocarbon dead or reflect the time of parent material deposition/reworking. If carbonates have experienced significant dissolution and reprecipitation, they will have incorporated more modern CO_2 from soil solution, rendering their radiocarbon ages much younger (Amundson et al. 1994; Pendall et al. 1994), and suggesting that SOC may become stabilized through coprecipitation and/or encapsulation within pedogenic carbonates as pedogenesis progresses. Radiocarbon values ($\Delta^{14}\text{C}$) of carbonates and SOC reflect some dissolution/reprecipitation over time, though neither concentrations nor $\Delta^{14}\text{C}$ values of inorganic and organic C were related to one another (Supplementary Fig. 4). Therefore, the exact mechanism which relates to stabilization of SOC by carbonates cannot be clearly discerned. It is notable that a relationship between Ca_{EX} and %OC was significant, but only when examined with an a priori selected pool of variables based on prior work, and no significant relationship to $\Delta^{14}\text{OC}$ was evident regardless of modeling approach. These relationships taken as a whole may argue for a greater importance of carbonate entrainment of organics during dissolution/reprecipitation reactions rather than cation bridging reactions with Ca.

Increasing degree of SOC decomposition associated with greater persistence

The historical view of the molecular complexity of “humics” acting as a primary factor limiting SOC decomposition has largely fallen out of favor over the past several decades (Sutton and Sposito 2005; Kleber 2010; Kleber et al. 2011). As discussed above, soil physicochemical factors have become more widely favored as the drivers of soil stabilization in more recent investigations. However, Weiglein et al., (*in review*) demonstrated a significant role of SOC chemistry in regulating SOC response to disturbance across NEON soils. In the current study, the broadest proxies for SOC quality and degree of decomposition, bulk soil C:N and $\delta^{13}\text{C}$, were unrelated to either % OC or $\Delta^{14}\text{OC}$ within biome type (we interpret the significance of $\delta^{13}\text{C}$ to $\Delta^{14}\text{OC}$ as being a product of

differences in C3 vs C4 vegetation dominance between biome types). However, more targeted measures of SOC molecular characteristics used as proxies for substrate quality were moderately-to-strongly linked to SOC persistence, though almost exclusively in grassland soils.

As biodegradation proceeds, the total substrate pool is transformed in two simultaneous but seemingly contradictory ways. As recognizable plant-derived compounds are broken down, structures become more heterogeneous and condensed, but a substantial fraction of the original substrate is also transformed into microbial necromass and metabolites which may appear structurally labile due to their comparatively low C:N and molecular weight (Miltner et al. 2012). We found that depletion in $\Delta^{14}\text{OC}$ of grassland soils was associated with increasing microbial nature (increasing biological index and fluorescence index, decreasing NOSC; Supplementary Table 2) and increases in metrics of the breakdown of primary substrates (DBE-O chloroform, diacid:lignin; Supplementary Table 2). The link between degree of decomposition and persistence may also be the product of increasing association of degraded organics with minerals and aggregates, as reactivity of organics increases as decomposition proceeds (Cotrufo et al. 2013). Though these relationships are significant and link an increase in biodegradation to a depletion in $\Delta^{14}\text{OC}$, the directionality and/or mechanistic nature of the relationship cannot be discerned with the current dataset.

Of the suite of SOM chemistry variables, only pyrogenic C was related (albeit weakly) to %OC. Increases in pyrogenic C ($\text{g kg}^{-1}_{\text{soil}}$) were associated with increasing %OC, possibly due to selective preservation of pyrogenic C (Brodowski et al. 2006; Heckman et al. 2014; Lavalley et al. 2019), increases in productivity following fire due to increases in cation exchange capacity, or changes in N dynamics (Johnson and Curtis 2001; Wan et al. 2001).

Summary

Across the suite of temperate forest and grassland soils from NEON we found substantial differences in the drivers of C concentration and persistence, both *across* and *between* biomes. In general, extractable metals were closely associated with %OC but not $\Delta^{14}\text{OC}$, in

both forests and grasslands. Depth alone was the strongest predictor of $\Delta^{14}\text{OC}$ in forest soils ($R^2 = 0.75$), with few other significant relationships among metals, climate and SOC chemistry variables. In contrast, grassland soil $\Delta^{14}\text{OC}$ had a variety of moderate-to-strong relationships with SOC chemistry variables, with increasing persistence associated with a higher degree of decomposition. Inorganic C was the strongest predictor of $\Delta^{14}\text{OC}$ in grassland soils, suggesting an underappreciated mechanism of organic C stabilization in these extensive, widespread systems. These results have significant implications for current approaches to modeling the soil C cycle, most of which have traditionally, if not implicitly, conflated measures of OC abundance with mechanisms of OC (de)stabilization. Given the large uncertainties associated with soil C modeling (Shi et al. 2020; Todd-Brown et al. 2018) and the strong influence of model conceptual structure on projections, disambiguating SOC amounts, (de)stabilization mechanisms and their relationships to soil properties is essential to model improvement. Furthermore, the contrasting relationships of SOC to climate and soil physicochemical properties in grasslands versus forests suggest that model parameterization may have to vary with biome, such that some processes, such as organic C association with carbonates, require organic–inorganic C linkages in models for some soil systems but not others.

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Data availability Additional information and data are available in the supplementary materials.

Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflict of interest.

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