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Association with pedogenic iron and aluminum: effects on soil organic carbon storage and stability in four temperate forest soils

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Abstract Soil organic carbon (SOC) can be stabilized via association with iron (Fe) and aluminum (Al) minerals. Fe and Al can be strong predictors of SOC storage and turnover in soils with relatively high extractable metals content and moderately acidic to circumneutral pH. Here we test whether pedogenic Fe and Al influence SOC content and turnover in soils with low Fe and Al content and acidic pH. In soils from four sites spanning three soil orders, we quantified the amount of Fe and Al in operationally-defined poorly crystalline and organically-complexed phases using selective chemical dissolution applied to the soil

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fraction containing mineral-associated carbon. We evaluated the correlations of Fe and Al concentrations, mean annual precipitation (MAP), mean annual temperature (MAT), and pH with SOC content and ¹⁴C-based turnover times. We found that poorly crystalline Fe and Al content predicted SOC turnover times ($p \leq 0.0001$) consistent with findings of previous studies, while organically-complexed Fe and Al content was a better predictor of SOC concentration ($p \leq 0.0001$). Greater site-level MAP ($p \leq 0.0001$) and colder site-level MAT ($p \leq 0.0001$) were correlated with longer SOC turnover times but were not correlated with SOC content. Our results suggest that poorly crystalline Fe and Al effectively slow the turnover of SOC in these acidic soils, even when their combined content in the soil is less than 2% by mass. However, in the strongly acidic Spodosol, organo-metal complexes tended to be less stable resulting in a

more actively cycling mineral-associated SOC pool.

Keywords ^{14}C · Soil carbon stabilization · Selective chemical dissolution · Soil fractionation · Soil organic carbon · Mineral-organic associations

Abbreviations

Al Aluminum

Al_o Oxalate extractable Al

Al_p Organically complexed Al extractable in sodium pyrophosphate

Al_{o-p} Poorly crystalline Al

C	Carbon		
Fe	Iron		
Fe _o	Oxalate extractable Fe		
Fe _p	Organically complexed Fe extractable in sodium pyrophosphate		
Fe _{o-p}	Poorly crystalline Fe MAP	Mean annual precipitation MAT	Mean annual temperature
SOC	Soil organic carbon		

Introduction

Adsorption and complexation reactions with Fe and Al soil constituents are important mechanisms of storage and stabilization of soil organic carbon (SOC; Oades [1988](#), Conant et al. [2011](#)). Recent studies using spatial gradients indicate that soil mineralogy may be a better predictor of SOC storage and turnover than climatic factors (Doetterl et al. [2015](#); Mathieu et al. [2015](#)).

Iron (Fe) and aluminum (Al) cations initially enter the soil environment via dissolution of primary minerals. The free metal cations can react with organic anions in the soil solution to form organo-metal complexes that exhibit a range of stabilities depending on a number of factors including the number of chemical bonds formed by the organic ligand to the metal, ligand size, charge properties of the metal and ligand, and solution characteristics such as temperature, pH, and ionic strength (McLean and Bledsoe [1992](#)). Once formed, organo-metal complexes may either sorb to solid mineral surfaces, facilitating their retention within the horizon, or they may be transported with the soil solution to down-profile (Stevenson [1994](#); McLean and Bledsoe [1992](#)).

Solution phase Fe and Al can precipitate to form solid metal oxide and hydroxide phases (Cornell and Schwertmann [2003](#)), which can react with and stabilize organic soil constituents via sorption to reactive surface sites or coprecipitation with the solid phase (McLean and Bledsoe [1992](#)). The reactivities of metal oxide and hydroxide mineral phases vary primarily as a result of crystallinity and surface area but also in response to solution pH, and ionic strength. The most reactive are freshly precipitated poorly crystalline oxyhydroxides. Reactivity generally decreases as weathering progresses, causing short-range order Fe and Al minerals to transform to more crystalline phases with decreased surface area and correspondingly lower surface site densities (Goldberg [2014](#)).

The capacity of pedogenic Fe and Al to stabilize organic soil constituents has been shown by previous empirical studies that reported a positive correlation between Fe and Al content and organic C stocks and ¹⁴C-based turnover time (Masiello et al. [2004](#); Torn et al. [1997](#); Rasmussen et al. [2005](#); Heckman et al. [2009](#)). These studies used controlled gradients in which soil type and mineralogy varied but climate, vegetation, and other soil-forming factors were relatively constant. All of these studies involved soils with relatively high extractable metals content and moderately acidic to circumneutral pH. Less is known about whether pedogenic Fe and Al influence soil organic carbon (SOC) in soils with low reactive-metals content and acidic pH where factors like climate vary. The soils in the Enriched Background Isotope (EBIS)—AmeriFlux study (McFarlane et al. [2013](#)) span three soil orders that differ with respect to their physical and chemical properties. Climate differences among the sites did not explain variation in SOC content and turnover time as originally hypothesized by McFarlane et al. ([2013](#)). SOC turnover times were shortest at the warmest and coldest sites, while the longest turnover times were at sites with intermediate temperatures (Tables [1](#), [2](#)). McFarlane et al. ([2013](#)) suggested that mineralogy and pedogenic processes might explain the observed differences in SOC storage and stability among these sites. The soils are strongly acidic and characterized by lower Fe and Al content than soils in previous studies of organo-mineral interactions (see above). Thus, they provide us with an opportunity to examine the influence of poorly crystalline Fe and Al phases and organo-Fe- and Al- complexes on the storage and stability of SOC in strongly acidic soils where they are present in low concentrations.

Methods

We characterized mineralogy and carbon content in soils from four forested sites in the eastern deciduous forest zone that span three soil orders. Using selective chemical dissolution applied to the soil fraction containing mineral-associated carbon (hereafter referred to as the dense fraction, DF), we quantified the amount of Fe and Al in operationally-defined poorly crystalline and organically-complexed phases, and correlated these with previously published SOC

Table 1 Summary of soil series names and orders, soil properties, mean annual temperature (MAT), and mean annual precipitation (MAP) for the four EBIS Ameriflux forest sites used in this study (McFarlane et al. 2013)

Site	Series name and soil order	Texture (%sand, %silt, %clay)	Bulk mineralogy	pH _w (1:1)	MAT (OC)	MAP (mm)
BEF	Berkshire series spodosol	Coarse loam (65,26,9)	F, A, Mi, Qz	3.9 ± 0.2	7.3	1300
HAF	Gloucester series inceptisol	Coarse loam (63,25,12)	En, F, A, Mi, Qz	4.1 ± 0.7	8.2	1141
MOZ	Weller series alfisol	Silt loam (4,75,21)	F, A, Mi, Qz	4.9 ± 0.6	13	1037
UMBS	Rubicon/bluelake series spodosol	Sand (89,10,1)	F, A, Mi, Qz	4.4 ± 0.6	6.8	608

Abbreviations for bulk mineralogy are as follows: *F* Na and K Feldspar, *A* Albite, *En* Enstatite, *Mi* Mica, *Qz* Quartz

Table 2 Mean ¹⁴C-based turnover times, C concentration, and extractable metals content in the dense fraction across all sites and depths

Site	Depth (cm)	Turnover time (year)	C (wt%)	Fe _{o-p} (g/kg)	Fe _p (g/kg)	Al _{o-p} (g/kg)	Al _p (g/kg)
BEF	0–5	349 ± 34	1.90 ± 0.40	1.53 ± 0.89	2.65 ± 1.21	0.13 ± 0.03	0.61 ± 0.25
	5–15	482 ± 28	2.80 ± 0.53	0.07 ± 0.05	6.03 ± 1.27	1.52 ± 0.43	6.03 ± 1.27
HAF	0–5	284 ± 49	4.15 ± 0.54	1.72 ± 0.56	3.88 ± 0.86	0.99 ± 0.61	2.10 ± 0.61
	5–15	553 ± 82	3.62 ± 0.47	5.10 ± 1.75	4.82 ± 0.65	3.77 ± 1.90	4.68 ± 0.31
MOZ	0–5	90 ± 5	1.46 ± 0.69	1.08 ± 0.35	1.59 ± 0.11	0.00 ± 0.00	1.36 ± 0.11
	5–15	209 ± 29	0.68 ± 0.08	0.51 ± 0.33	2.32 ± 0.29	0.27 ± 0.27	1.63 ± 0.43
UMBS	0–5	147 ± 8	0.88 ± 0.18	0.54 ± 0.21	0.14 ± 0.04	0.06 ± 0.02	0.10 ± 0.04
	5–15	252 ± 39	0.21 ± 0.06	1.03 ± 0.46	0.14 ± 0.04	1.03 ± 0.46	0.08 ± 0.01

Error bars represent standard error (n = 5; turnover and C data from McFarlane et al. 2013)

content and ¹⁴C-based turnover times (McFarlane et al. 2013).

Site description

Our study focused on four temperate forest sites: Missouri-Ozarks Baskett Wilderness, MO (MOZ), Bartlett Experimental Forest, NH (BEF), Harvard Forest, MA (HAF), and University of Michigan Biological Station, MI (UMBS). All four sites are located within the temperate broadleaf deciduous forest zone. The vegetation is classified as eastern deciduous hardwood but dominant species differ by site. The UMBS soils are sandy, mixed, frigid, Entic and Lamellic Haplorthods, BEF soils are coarse, loamy, isotic, frigid, Typic Haplorthods, and the MOZ soils are fine, smectitic, mesic, Aquertic, Chromic Hapludalfs all of which are all considered “mature” soils, while the HAF soils are sandy, skeletal, mixed, mesic, Typic Dystrudepts that are classified as intermediate weath- ering-stage soils (Schaetzel and Anderson 2005). All soils are of Holocene age with similar mineralogic composition (Table 1) forming on glacial sediments deposited during the Wisconsin glaciation (11.0–11.7 kya) (Thompson et al. 1999; USDA Soil Survey 2001; Bergquist 2009). The soils from UMBS, HAF, and BEF were formed on glacial till and the MOZ soils were formed on loess (McFarlane et al. 2013).

Soil cores (10 cm in diameter 9 90 cm deep or depth to bed rock) (Table [1](#)) were collected in November–December 2007 from five 2 m 9 2 m square plots located at each of the four study sites. The soils from all four sites have similar mineralogical composition except for enstatite, which was identified at HAF. Enstatite is a pyroxene group mineral, which tends to weather rapidly. Its presence at HAF is consistent with the assignment of an earlier weather- ing stage for the soils at this site based on the Jackson- Sherman weathering stage criteria (Sposito [2008](#)). More detailed descriptions of site characteristics, as well as laboratory methods for physical fractionation of bulk soils, pH measurements, texture analysis, and

results for the initial ^{14}C characterization study are found in McFarlane et al. (2013).

Laboratory methods

Surface bulk (≈ 2 mm) soils from 0–5 and 5–15 cm depths were fractionated by density using a 1.65 g cm^{-3} density SPT solution as described in McFarlane et al. (2013). We performed all chemical extractions non-sequentially on the dense fraction (DF) isolated from the bulk soils. DF contained on average 70% of the soil mass and 60% of SOC across all sites and depths (McFarlane et al. 2013). In the current study, poorly crystalline Fe and Al oxides were selectively dissolved via a 4 h extraction in 0.2 M acid ammonium oxalate in the dark (Schwertmann 1964; Fey and LeRoux 1977; Hodges and Zelazny 1980). Operationally-defined organically-complexed Fe and Al (Fe_p and Al_p) were extracted via reaction with

0.1 M Na-pyrophosphate (McKeague 1967; Ross and Wang 1993). Post reaction, samples were centrifuged at 3000 rpm followed by syringe filtration of the extract at 0.45 μm . Under the conditions of this study, it is not possible to assume the Na-pyrophosphate extractable Fe and Al were completely free of suspended colloidal material which has been noted in previous studies and attributed to the alkaline conditions of the extractant solution (e.g., pH 10; Schuppli et al. 1983); however, the effect was most pronounced in tropical soils characterized by clay content $\geq 40\%$, and Schuppli et al. (1983) concluded the method is appropriate for use in temperate soils. Al and Fe in the filtered extractant solutions were quantified by inductively coupled plasma mass spectrometry (ICP-MS). Process and reagent blanks were used to correct for Fe and Al impurities introduced during sample preparation. Operationally-defined poorly crystalline Fe (Fe_{o-p}) and Al (Al_{o-p}) contents were estimated as the difference between Fe_o – Fe_p and Al_o – Al_p , where the o subscript denotes acid ammonium oxalate-extractable Fe and Al and the p subscript denotes sodium pyrophosphate extractable Fe and Al (McKeague et al. 1971).

SOC concentration of the dense fraction was determined via solid phase combustion using a Costech ECS 4010 Elemental Analyzer. Radiocarbon content of the dense fraction prior to selective dissolution was measured at the Center for Accelerator Mass Spectrometry, Lawrence Livermore Laboratory

on a Van de Graff FN AMS and ^{14}C -based turnover times were calculated from measured D^{14}C values using a single-pool steady state model. Soil OC concentration and radiocarbon results as well as modeled turnover times are described in McFarlane et al. (2013).

Statistical analyses

Differences in the abundance of extractable Fe and Al amongst sites and with depth were tested using analysis of variance (ANOVA) with soil core as a random effect using the nlme package (Pinheiro et al. 2011) in R 2.14.1 (R Development Core Team 2011). For ad hoc interpretation of two-way interactions, multiple comparisons were made with a Holm adjustment using the Multicomp Package (Hothorn et al. 2008) with $\alpha = 0.05$.

The relative contributions of climate, pH, extractable Fe & Al soil constituents, and soil depth on SOC concentration and stability (estimated from turnover time) across all study sites were examined using mixed effect multiple regression. Model parameters included mean annual temperature, mean annual precipitation, pyrophosphate extractable aluminum and iron (Fe_p & Al_p), poorly crystalline iron and aluminum (Fe_{o-p} & Al_{o-p}), pH, and soil depth (as a factor) as explanatory variables. With exception of Fe_p & Al_p and MAP ($r = 0.7$), none of these explanatory values were highly correlated ($r \leq 0.6$) with each other, which could have interfered with model interpretation. Graphical exploration of the data and preliminary model comparisons did not reveal any significant interactions, so none were included in the models. Percent clay was not included because it did not have a statistically significant relationship with either carbon content or turnover time. The relationship between turnover time and Fe_{o-p} & Al_{o-p} visually appeared to be non-linear; however, the linear relationship was better than piecewise, accumulating exponential, and polynomial relationships based on model AIC. We used the full linear model to optimize random effects and variance structures using AIC following Zuur et al. (2009). Both the turnover time and percent-carbon models included soil core as a random effect. The turnover time model included a variance structure based on soil depth. Once random effects were optimized, we performed a series of

pair- wise model comparisons using the F test, dropping the

least significant explanatory variable each time (highest p value) until only significant explanatory variables remained (Zuur et al. 2009). The models were fitted with the lme command in the nlme package in R (Pinheiro et al. 2011) using restricted maximum likelihood. The effect of extractable Fe and Al constituents on soil carbon storage and stability within individual sites was assessed via least squares linear regression analysis.

Results

Trends for SOC concentration, turnover, and Fe and Al oxides

For context, we include results from McFarlane et al. (2013): Soil OC concentrations and turnover times in dense fractions were highest and longest at HAF and BEF, and lowest and shortest at MOZ and UMBS (Table 2). With the exception of BEF, soil C concentrations decreased with depth. At all sites, SOC turnover times increased from the 0–5 to the 5–15 cm depths (Table 2).

Soils from HAF and BEF had greater total extractable Fe and Al than soils from MOZ and UMBS, and they had significantly more organically-complexed Fe and Al than those from MOZ and UMBS (Table 2; depth \times site interaction, $p < 0.05$, $n = 40$ for Fe_p and $p < 0.01$, $n = 40$ for Al_p). Organically-complexed Fe increased significantly with depth at all sites (Table 2; depth effect,

$p = 0.04$, $n = 40$), but organically-complexed Al did not. Poorly crystalline Fe and Al was not significantly different among soils from the four sites at the 0–5 cm depth (site effect, $p = 0.2796$, $n = 20$), but at the 5–15 cm depth, soils from Harvard Forest had significantly more poorly crystalline Fe and Al than did the other three sites (depth \times site interaction, $p = 0.0038$, $n = 20$). Poorly crystalline Al (Table 2, depth effect, $p = 0.04$, $n = 40$) and Fe (Table 2, depth effect, $p = 0.018$, $n = 40$) increased significantly with depth at all sites.

Fe and Al: effect on soil carbon and turnover Across sites

We used multiple regression across sites to determine whether variation in SOC concentration and turnover times was explained by variation in depth, MAT, MAP, pH, organically-complexed Fe \times Al, and poorly crystalline Fe \times Al content. Soil OC concentration increased with the concentration of organically-complexed Fe \times Al, decreased with pH, and was not significantly explained by MAT, MAP, or poorly crystalline Fe and Al (Table 3; Fig. 1). Carbon concentration was significantly lower, by 0.75 percentage points, between soil depth on average across all sites (Table 3). The pseudo r-squared value, assessing the multiple regression model fit by regressing the actual data versus the model-predicted values, was 0.98.

In contrast, ^{14}C -based turnover times increased significantly as a function of poorly crystalline

Table 3 Multiple regression results [Results are from models run using only significant predictors after model selection (see “Methods” section)] for turnover time and percent carbon of EBIS soils

Variable	Coefficients	Estimate	E	t value	p value
Carbon concentration	Intercept (0–5 cm)	3.78	0.95	3.97	<0.0010
	Depth (5–15 cm)	–0.76	0.15	–4.96	0.0001
	$Fe_p \times Al_p$	0.254	0.02	10.6	<0.00001
	pH	–0.60	0.22	–2.75	0.0137

Turnover time	Intercept (0–5 cm)	158		45.2	3.50	0.0026
	Depth (5–15 cm)	115		16.0	7.24	\0.00001
	Fe _{o-p} ? Al _{o-p}	23.5	3.06		7.70	\0.00001
	MAT	–29.3	3.68		–7.98	\0.00001
	MAP	0.277	3.68		7.70	\0.00001

The estimates are the intercept for 0–5 cm depth, the change in the intercept for the 5–15 cm depth, and the slopes for the continuous variables

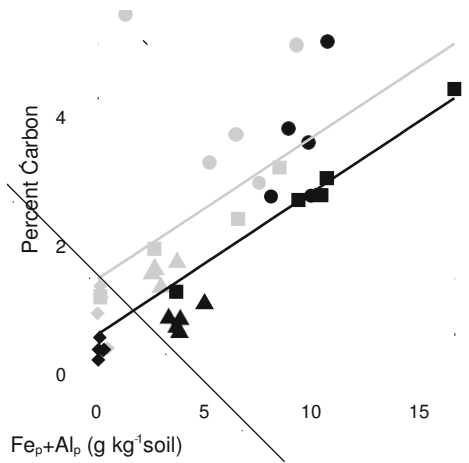


Fig. 1 Percent soil carbon increased with increasing organically-complexed iron and aluminum. The points are the actual data, and the lines show the predicted relationship with the other significant predictor, pH, held at its mean. The squares represent samples from BEF, the circles samples from HAF, the triangles samples from MOZ, and the diamonds samples from UMBS. The grey symbols and lines are the data and predicted values from the 0–5 cm depths, and the black symbols and lines are the data and predicted values from the 5–15 cm depths

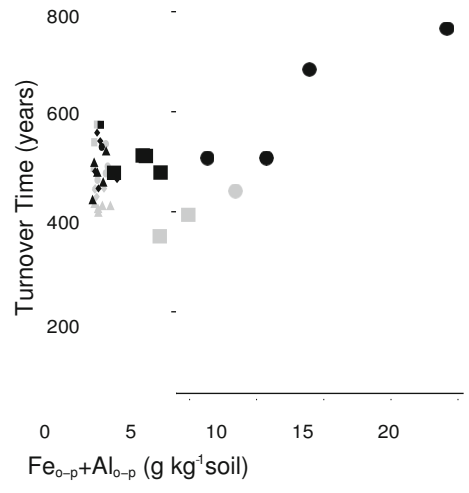


Fig. 2 ¹⁴C-based turnover time increased with poorly crystalline Fe and Al content at all sites. The squares represent samples from BEF, the circles samples from HAF, the triangles samples from MOZ, and the diamonds samples from UMBS. Grey symbols are 0–5 cm and black symbols are 5–15 cm depths

Fe ? Al content but were not significantly correlated with organically-complexed Fe ? Al or pH (Table 3; Fig. 2). Variation in turnover time was also affected by climate with greater site-level MAP associated with significantly longer turnover times, and warmer site-

level MAT associated with significantly faster turnover times (Table 3; Fig. 3). Turnover time increased significantly with soil depth, by an average of 115 years (Table 3). The pseudo r-squared value for the multiple regression model was 0.94.

Effect of Fe and Al on C storage and turnover within individual sites

Pedogenic processes differ across sites, so we also examined the relationship between Fe, Al, and Fe ? Al

forms on SOC concentration and turnover times within individual sites. Bartlett Experimental Forest was the only site in which variation in SOC concentration among the five replicate blocks depended significantly on organically-complexed Fe and Al content (Table 4). In both depths, SOC concentration increased significantly with the amount of organically-complexed Fe and Al. None of the sites had any significant relationships between SOC concentration and poorly crystalline Fe and Al in either 0–5 or 5–10 cm depths (Table 4), meaning that within-site variation in poorly crystalline Fe and Al did not explain within-site variation in SOC concentration at any site.

At BEF, turnover time was significantly and negatively correlated with organically-complexed Fe and Al in the 0–5 cm depth but not 5–15 cm (Table 5). A different trend was found at HAF, where turnover time was significantly and positively correlated with organically-complexed Al (only) at 0–5 and 5–15 cm depths (Table 5). At HAF, turnover times were also significantly and positively correlated with poorly crystalline Fe and Al at 0–5 and 5–15 cm (Table 5). There were no statistically significant relationships between SOC turnover time and organically-complexed or poorly crystalline Fe or Al within the MOZ or UMBS soils.

Discussion

Across these forest soils, Fe- and Al-(hydr)oxide mineral phases and Fe and Al organo-mineral complexes, despite being present in low concentrations, influenced the amount and stability of dense fraction SOC. Dense fraction SOC concentrations increased with increasing amounts of organically-complexed Fe and Al, but were unaffected by climate. These results

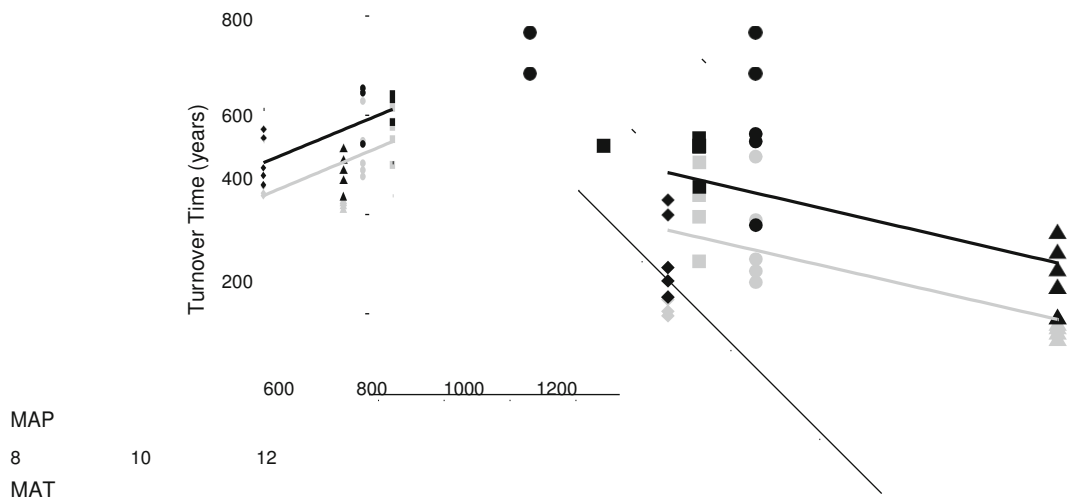


Fig. 3 Turnover time of soil organic carbon increased with increasing mean annual precipitation (MAP) and decreased with increasing mean annual temperatures (MAT) at the site level. The points are the actual data, and the lines show the average predicted relationship with the other significant predictors ($FeAl_{op}$ and MAT or MAP; see Table 3) are held at their respective means. The squares represent samples from BEF, the circles samples from HAF, the triangles samples from MOZ, and the diamonds samples from UMBS. The grey symbols and lines are the data and predicted values from the 0–5 cm depths, and the black symbols and lines are the data and predicted values from the 5–15 cm depths

are similar to those from studies in a grassland soil (Masiello et al. 2004) and volcanic soil (Lawrence et al. 2015) that also found SOC storage was highly correlated with organically-complexed Fe and Al, but these soils had higher Fe and Al concentrations than ours. Our findings show that complexation with free Fe and Al cations can be an important mechanism for storing SOC even in soils with relatively low Fe and Al concentrations. Heckman et al. (2009) suggest a regulatory role of pH with respect to the mode of OM stabilization, with complexation being the dominant stabilization mechanism in the more acidic soils at their study sites owing to the increased solubility of Fe and Al with decreasing pH in the acidic range (Lindsay 1979; Wagai and Mayer 2007). The soils in the current study were more acidic (3.9–4.9) than those described by Heckman et al. (2009). Adding support to the hypothesis that pH might be driving this trend, SOC concentrations and organically-complexed Fe and Al were greatest at the sites with the lowest pH, BEF and HAF.

Contrary to previous findings (Torn et al. 1997; Rasmussen et al. 2006), poorly crystalline metals content was not consistently correlated with SOC concentrations across our study’s forest soils, which may reflect their comparatively lower abundances of poorly crystalline metals, as postulated for grassland soils by Masiello et al. (2004). The range in poorly crystalline metals content observed in our study’s soils was 0–0.18%, while the poorly crystalline metals content ranged from 0.1 to 1.9% in temperate coniferous forest soils (Rasmussen et al. 2006) and from 2 to 75% in Hawaiian volcanic soils (Torn et al. 1997). The lower abundances of poorly crystalline metals in our forest soils may be due the following factors. First, we focused on the top 15 cm of soil, and the importance of poorly crystalline metals for C storage is greater in deeper soil horizons (Masiello et al. 2004; Torn et al. 1997). Second, the formation of organo-metal complexes, which were significantly related to carbon storage in our soils, can prevent the formation of more weathered secondary minerals (Lawrence et al. 2015).

Despite the lower amounts of poorly crystalline metals in the soils from this study, our results are consistent with previous findings that the turnover time of organic C is slowed with increased poorly crystalline Fe and Al content (Torn et al. 1997) and are also consistent with the finding of Rasmussen et al. (2006) that soil C mineralization appears to be inhibited in soils as poorly crystalline Fe and Al content increases. Heckman et al. (2009) examined the effect of mineralogy on carbon cycle dynamics in forest soils derived from rhyolitic, granitic, basaltic and limestone parent material and found, in agreement with our results, that association with reactive Fe and

Table 4 Linear regression results for C concentration versus extracted Fe and Al and pH for each site and depth (n = 5 for each)

Site	Depth	Fe _p	Al _p	Fe _p ? Al _p	Fe _{o-p}	Al _{o-p}	Fe _{o-p} ? Al _{o-p}	pH _w (1:1)
BEF (spodosol)	0–5 cm	R ² = 0.95, p = 0.0045 (1)	R ² = 1.0, p < 0.0001 (1)	R ² = 0.96, p = 0.0028 (1)	R ² = 0.36, p = 0.29	R ² = 0.39, p = 0.26	R ² = 0.35, p = 0.29	R ² = 0.6, p = 0.0040 (1)
	5–15 cm	R ² = 0.88, p = 0.020 (1)	R ² = 0.88, p = 0.019 (1)	R ² = 0.99, p = 0.0002 (1)	R ² = 0.0006, p = 0.97	R ² = 0.52, p = 0.17	R ² = 0.47, p = 0.20	R ² = 0.081, p = 0.6
HAF (inceptisol)	0–5 cm	R ² = 0.027, p = 0.79	R ² = 0.27, p = 0.37	R ² = 0.12, p = 0.57	R ² = 0.56, p = 0.16	R ² = 0.40, p = 0.25	R ² = 0.47, p = 0.20	R ² = 0.30, p = 0.3
	5–15 cm	R ² = 0.68, p = 0.085	R ² = 0.61, p = 0.12	R ² = 0.41, p = 0.24	R ² = 0.48, p = 0.19	R ² = 0.63, p = 0.11	R ² = 0.57, p = 0.14	R ² = 0.91, p = 0.01 (2)
MOZ (alfisol)	0–5 cm	R ² = 0.096, p = 0.61	R ² = 0.15, p = 0.52	R ² = 0.14, p = 0.54	R ² = 0.12, p = 0.57	NA ^a	NA ^a	R ² = 0.041, p = 0.7
	5–15 cm	R ² = 0.24, p = 0.40	R ² = 0.024, p = 0.80	R ² = 0.5294, p = 0.1635	R ² = 0.033, p = 0.77	R ² = 0.0080, p = 0.89	R ² = 0.011, p = 0.87	R ² = 0.24, p = 0.40
UMBS (spodosol, 90% sand)	0–5 cm	R ² = 0.30, p = 0.35	R ² = 0.75, p = 0.058	R ² = 0.5593, p = 0.1461	R ² = 0.12, p = 0.57	R ² = 0.44, p = 0.22	R ² = 0.14, p = 0.53	R ² = 0.82, p = 0.033 (2)
	5–15 cm	R ² = 0.015, p = 0.84	R ² = 0.047, p = 0.73	R ² = 0.0201, p = 0.8201	R ² = 0.70, p = 0.078	R ² = 0.66, p = 0.093	R ² = 0.67, p = 0.078	R ² = 0.11, p = 0.58

Regression parameters in bold indicate a statistically significant correlation with C concentration

The subscript “p” denotes organically-complexed phases and the subscript “o-p” denotes poorly crystalline phases

^a Only 1 of 5 samples had measurable extractable Al_{o-p}

Table 5 Linear regression results for ¹⁴C-based turnover time versus extracted Fe and Al and pH for each site and depth (n = 5 for each)

Site	Depth	Fe _p	Al _p	Fe _p ? Al _p	Fe _{o-p}	Al _{o-p}	Fe _{o-p} ? Al _{o-p}	pH _{H2O}
BEF (spodosol)	0–5 cm	R² = 0.89, p = 0.021 (2)	R² = 0.92, p = 0.0096 (2)	R² = 0.88, p = 0.018 (2)	R² = 0.55, p = 0.15	R² = 0.52, p = 0.17	R² = 0.55, p = 0.15	R² = 0.85, p = 0.025 (2)
	5–15 cm	R² = 0.007, p = 0.90	R² = 0.16, p = 0.58	R² = 0.053, p = 0.71	R² = 0.19, p = 0.69	R² = 0.045, p = 0.73	R² = 0.06, p = 0.69	R² = 0.72, p = 0.071
HAF (inceptisol)	0–5 cm	R² = 0.11, p = 0.59	R² = 0.81, p = 0.037 (1)	R² = 0.40, p = 0.26	R² = 0.88, p = 0.021 (1)	R² = 0.82, p = 0.034 (1)	R² = 0.86, p = 0.024 (1)	R² = 0.75, p = 0.059
	5–15 cm	R² = 0.47, p = 0.20	R² = 0.93, p = 0.0072 (1)	R² = 0.094, p = 0.62	R² = 0.85, p = 0.025 (1)	R² = 0.88, p = 0.018 (1)	R² = 0.91, p = 0.013 (1)	R² = 0.66, p = 0.095
MOZ (alfisol)	0–5 cm	R² = 0.30, p = 0.34	R² = 0.35, p = 0.11	R² = 0.15, p = 0.52	R² = 0.024, p = 0.81	NA ^a	NA ^a	R² = 0.56, p = 0.14
	5–15 cm	R² = 0.27, p = 0.38	R² = 0.0009, p = 0.97	R² = 0.31, p = 0.33	R² = 0.60, p = 0.12	R² = 0.067, p = 0.67	R² = 0.30, p = 0.34	R² = 0.31, p = 0.33
UMBS (spodosol, 90% sand)	0–5 cm	R² = 0.45, p = 0.21	R² = 0.45, p = 0.21	R² = 0.55, p = 0.17	R² = 0.12, p = 0.57	R² = 0.49, p = 0.19	R² = 0.15, p = 0.52	R² = 0.18, p = 0.48
	5–15 cm	R² = 0.0029, p = 0.93	R² = 0.0001, p = 0.99	R² = 0.0020, p = 0.94	R² = 0.10, p = 0.61	R² = 0.16, p = 0.50	R² = 0.11, p = 0.59	R² = 0.070, p = 0.69

Regression parameters in bold indicate a statistically significant correlation with ¹⁴C-based turnover

The subscript “p” denotes organically-complexed phases and the subscript “o-p” denotes poorly crystalline phases

^a Only 1 of 5 samples had measurable extractable Al_{o-p}

Al phases effectively slowed decomposition of soil organic matter. The positive relationship between turnover and poorly crystalline mineral content in our study was driven by HAF soils, which had both the widest range and greatest amounts of poorly crystalline Fe and Al. Their high amounts of poorly crystalline Fe and Al may be due to differences in parent material. However, the granite-till parent material that the HAF soils formed on (Latimer and Smith [1932](#)) and the granite/schist deposits from which the BEF and UMBS soils formed (Latimer and Lanphear [1929](#); Dorr and Eschman [1977](#)) yield similar weathering products, including K-feldspar (Al, Si), Quartz (SiO₂), plagioclase feldspar (Na, Ca), and biotite (Fe), consistent with our soils' mineral assemblages (Table [1](#)) although their abundances likely vary spatially. The high poorly crystalline Fe and Al content at HAF may also be related to weathering stage—HAF soils appear to be the least weathered of the soils examined based on the presence of enstatite, a rapidly weathering pyroxene group mineral typically absent in intermediate to late weathering stage soils. As soil weathering progresses, the abundance of poorly crystalline reactive minerals increases initially but then decreases as they are further weathered into secondary clay minerals (Torn et al. [1997](#)). In a Hawaiian chronosequence, poorly crystalline minerals peaked at 150 kya (Torn et al. [1997](#)). However, our soils are much younger (development began following deglaciation near the start of the Holocene ~11.7 kya), and their parent material had less potential for poorly crystalline mineral formation than the andesitic parent material in Hawaii. For the more weathered UMBS, BEF, and MOZ soils this developmental peak likely occurred much earlier and poorly crystalline mineral phases now appear to be on the decline. However, the less weathered HAF soils may still be approaching the poorly crystalline mineral peak.

MAT and MAP were also important factors determining turnover time across sites, with increasing precipitation and decreasing temperatures resulting in longer turnover times. The four sites in the present study are well-drained (McFarlane et al. [2013](#)), therefore it is unlikely that the slower turnover times for the wettest sites, HAF and BEF, could be attributed to saturation. However, greater precipitation and higher soil moisture at these two sites may have indirectly contributed to SOC stability by promoting dissolution of Fe and Al constituents from parent minerals, thereby increasing their concentration in the soil solution where they are available to react with and stabilize soil OC constituents via complexation or adsorption. In fact, across all sites, annual average volumetric soil moisture was positively related to both organically-complexed Fe and Al ($p = 0.035$, $n = 20$) and to total extractable Fe and Al (sum of organically-complexed and poorly crystalline; $p = 0.005$, $n = 20$) and MAP was positively correlated to organically-complexed Fe + Al ($p < 0.0001$, $n = 40$). Thus, the positive relationship between precipitation and turnover time could be explained in part by the enhanced effect of increased moisture on soil weathering processes.

Decreasing turnover times with warmer temperatures was expected, as warming temperatures tend to increase SOC decomposition rates (Davidson and Janssens [2006](#)). However, temperature could not explain variation in turnover times across all our sites, since HAF and BEF, which had MATs intermediate between the warmest site (MOZ) and the coldest site (UMBS) had the longest turnover times.

Slow turnover times at HAF were explained by the soils' comparatively higher poorly crystalline Fe and Al content, suggesting stabilization via adsorption to solid metal oxide surfaces. Fe and Al metal oxide minerals exhibit variation in surface charge as a function of pH, affecting how they react with soil organic matter (Sposito [1984](#); Zhang and Zhao [1997](#)). At pH values below the point of zero charge (PZC) for a given mineral, hydroxylated surfaces will be protonated and characterized by a net positive charge. pH also plays an important regulatory role with respect to the activity of organic anions in organic matter or within the soil solution, which increases with increasing pH as the pKa of the anion is approached. When pH is equal to the pKa, acidic groups are 50% ionized and when pH is about two units above the pKa, acidic groups are 100% ionized (McKenzie [1983](#); Bowden et al. [1974a](#), [b](#), [1980a](#), [b](#)). Adsorption of organic anions via anion exchange (or electrostatic interaction) is greatest within the range of pH values below the PZC and above the pKa wherein the charge on mineral surfaces and acidic organic groups are opposite (Murphy et al. [1990](#), [1992](#); Tipping [1981](#); Davis [1982](#)). A theoretical optimal range for reaction of carboxylic acid moieties with surface hydroxyl groups on Fe and Al oxide mineral phases of opposite charge

as a function of pH can be calculated from the Nernst equation (Tomba'cz [2009](#)) to estimate surface charge potential for metal oxides and the percent of dissociated carboxylic acid groups can be obtained from the Hendersson–Hasselbach equation (Supplemental Material). Assuming a PZC value for hydrous ferric oxide of 8.1 and 6–7 for goethite (Smith [1999](#)) and a pKa of 4.4 for IHSS humic acid representing a model of soil organic matter (Ritchie and Perdue [2003](#)), we found an optimal range for electrostatically mediated adsorption of humic acid at 4–8.1 and 4–7.5 for ferrihydrite and goethite respectively. A similar optimal range was found for Al hydrous oxide, hydroxide, and oxyhydroxide (PZC \approx 9.1, Komulski [2006](#)). The lower bound of this estimated range coincides with the mean pH (4.1) of the HAF soils however at this pH value COOH groups would be only 10% ionized. Thus, based on these estimates, electrostatic interaction with variable charge metal oxides represents a potential, but likely not a dominant, C stabilization mechanism in the HAF soils.

A more probable stabilization mechanism on oxide surfaces in HAF soils is via specific (i.e., short range, inner sphere) non-electrostatically mediated interactions (Schlautman and Morgan [1994](#); Perrot [1977](#)). Maximum surface loadings of organic C on Fe hydroxides is estimated to be 0.22 g C g⁻¹ Fe within the pH range of 4–7 (Kaiser and Guggenberger [2007](#)). An adsorption maximum of organic C on Al mineral phases was determined to be 0.82 g C g⁻¹ Al by Kaiser and Zech ([1997](#)). For HAF, surface loadings for both poorly crystalline Fe and Al were found to be well in excess of these amounts implying that most of the organic C is likely not in direct contact with mineral surfaces, which is consistent with a more complex inter- and intra- molecular bonding mechanism (OM–OM) (Feng et al. [2015](#); Ellerbrock et al. [2005](#); Kaiser and Guggenberger [2007](#)) that is likely to be operating at this site. Hydrogen bonding has also been shown to occur under acidic conditions at high surface coverages (Schlautman and Morgan [1994](#)) and therefore cannot be ruled out.

In contrast to HAF, at BEF where turnover times were significantly and inversely related to organically-complexed Fe and Al in the 0–5 cm depth, other pedogenic processes may be important in determining C stability. The inverse relationship suggests that organo-metal complexes do not persist in the surface soils and is likely indicative of a more actively cycling

mineral-associated SOC pool at BEF. We found that SOC content and abundance of organically-complexed Al and Fe increase significantly as a function of pH in the 0–5 cm depth at BEF. This is consistent with a regulatory effect of pH on the reactivity of dissolved Fe and Al, solution phase organic acid constituents, as well as acidic functional groups on soil organic matter. As soil pH approaches the pKa (negative log of the acid dissociation constant) of acidic functional groups on SOC, an increasing proportion become deprotonated and thus increasingly reactive with positively charged Fe and Al in the soil solution. An adsorption maximum for carboxylic acids has been observed when the solution pH approached the pKa of the acid (Parfitt [1978](#); Bowden et al. [1974a, b](#); Lacourmet et al. [2001](#)). A strongly acidic pH for BEF soils in the 0–5 cm depth would limit the number of polycarboxylic acids capable of forming chelates, and would thus tend to favor the formation of less stable soluble OM-metal complexes. Furthermore, in Spodosols, these complexes tend to be mobile and can be translocated within the soil profile (McLean and Bledsoe [1992](#)). This mechanism is consistent with the decreasing turnover times with organically complexed Fe and Al in BEF 0–5 cm soils. Formation of mobile organo-metal complexes in the A horizon and their subsequent transport to the B horizon has been identified as a dominant soil formation process for Berkshire series soils where the BEF study site is located.

In the two most acidic forest soils from our study sites (BEF and HAF), a single mechanism of stabilization could not be uniformly applied across soil orders to accurately predict carbon storage and turnover. Site-specific factors, such as pedogenic processes and possible differences in parent material, must be also taken into consideration. Our results suggest at least three hypotheses for further study. First, poorly crystalline Fe and Al can effectively slow the turnover of soil organic matter, even when their combined content in the soil is less than 2%. Second, our results suggest weathering stage contributes to the capacity of soil to stabilize SOC via association with poorly-crystalline metal oxide surfaces; the least-weathered soil in our study (Harvard Forest, Inceptisol) had the longest turnover times and these were strongly correlated with poorly crystalline Fe and Al content. Finally, the effect of pH on organic matter chemistry is such that as pH decreases, dissolution of

Fe and Al is enhanced, thus increasing the concentration of Fe and Al cations in the soil solution. However, at low pH the stability of organo-metal complexes also decreases. This would explain why organo-metal complexes were correlated with SOC concentrations but not with turnover times and also why, in the most acidic site, organo-metal complexes were negatively correlated with turnover time.

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