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Key Points:

- Soil pH, rather than reactive iron content, is a primary control on concentration of iron-associated carbon at the global scale
- Neither soil orders nor vegetation types have significant relationships with concentration of iron-associated carbon
- Iron-associated carbon represents a relatively small fraction of total soil organic carbon globally

Supporting Information:

Supporting Information may be found in the online version of this article.

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Association of Organic Carbon With Reactive Iron Oxides Driven by Soil pH at the Global Scale

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Abstract Association of organic carbon (C) with iron (Fe) minerals is one important mechanism for longterm terrestrial C storage. Yet, specific edaphic variables that directly contribute to Fe-associated C across diverse soil types are still unclear. Through analyzing soils from the National Ecological Observatory Network (NEON) and other published data, here we show that soil pH primarily controls Fe-associated C across the globe. Fe-associated C in most soils ranged from 0 to 20 g kg⁻¹ soil, with a strong increase from pH 4.2 to 3.5, but a small change in soils with pH > 4.2. A microcosm experiment further showed that raising soil pH by liming reduced the formation of Fe-associated C in an acidic Oxisol. Together, these findings demonstrate the dominant role of soil pH in controlling the abundance of Fe-associated C.

1. Introduction

Soils contain the largest near-surface reservoir of organic carbon (C) in terrestrial ecosystems (Jobbágy & Jackson, 2000; Scharlemann et al., 2014), which exceeds the sum of C stored in the vegetation and atmosphere. Even slight reduction in soil C stock could lead to significant increase in atmospheric carbon dioxide concentration, and accelerate climate warming (Crowther et al., 2016; Davidson & Janssens, 2006). Accumulating evidence has shown that physicochemical and biological influences of the soil environment play a primary role in organic C persistance (Doetterl et al., 2015; Lehmann & Kleber, 2015; Schmidt et al., 2011; von Fromm et al., 2021; Yu et al., 2021). Interaction with the mineral phases via mineral surface adsorption, occlusion and coprecipitation is a major mechanism that can potentially stabilize organic C in mineral soils for centuries or millennia (Kleber et al., 2015; Kögel-Knabner et al., 2008; Lehmann & Kleber, 2015). However, human activities such as fossil fuel combustion and fertilizer applications have considerably altered soil conditions such as increased soil nitrogen availability and soil acidification (Tian & Niu, 2015; Vitousek et al., 1997). These alterations likely affect mineral-associated C by influencing soil biochemical properties, given that mineral-associated C is surrounded with combinations of phyllosilicates, pedogenic oxyhydroxides, exchangeable cations and dissolved organic substances in soils.

A significant portion of mineral-associated C is adsorbed or co-precipitated with iron (Fe) minerals due to their high surface area and ubiquity in soils, and Fe-bound C is estimated to constitute 15%–38% of total soil organic C in sediments and upland soils (Lalonde et al., 2012; Wagai & Mayer, 2007; Wang et al., 2021; Zhao et al., 2016). Thus, quantification of the factors controlling Fe-associated C at continental to global scales is needed to predict the distribution of this C pool and its response to global change. However, it remains challenging to predict the quantity of C protected by Fe minerals despite the importance of Fe-C interactions for soil C persistence. For example, the abundance of Fe minerals is only weakly related with the abundance and/or percentage of Fe-associated C among diverse soils (Huang et al., 2021; Wang et al., 2021; Zhao et al., 2016). Recently, mean annual precipitation and potential evapotranspiration were demonstrated to be important drivers of the proportion (but not absolute amount) of subsoil organic C retained by Fe- and aluminum (Al)-bearing minerals over global scales, as defined by non-specific soil extractions (Kramer & Chadwick, 2018). However, Fe versus Al-bearing minerals may have distinct relationships with soil C persistence, because Fe has important catalytic roles that contribute to C decomposition as well as protection in humid ecosystems (Chen et al., 2020).

Increased solubility of Fe phases and increased net positive surface charge in response to decreases in soil pH play a key role in altering the sorption and co-precipitation reactions that affect Fe-associated C, although relatively few studies have studied these dynamics in soils as opposed to model laboratory systems (Gu et al., 1994; Kleber





Figure 1. Soil sampling locations for the NEON sites and other sites from published studies.

et al., 2015; Wang et al., 2017; Ye et al., 2018; Zhao et al., 2019). A synthesis study observed that effective soil moisture (precipitation minus potential evapotranspiration) determines a strong pH shift from 8 to 5 at a global scale (Slessarev et al., 2016), which implies that climate-induced changes in soil pH probably influence Fe-associated C.

Other than soil pH, climate also controls the global distribution of soil and vegetation types. Humid climates generally favor the formation of acid soils (generally represented by Oxisol, Spodosols and Ultisols) with accumulations of Fe- and Al-oxides by intensified weathering of the parent material and base cation leaching, while arid climates favor the formation of alkaline soils (generally represented by Alfisols, Aridisols and Mollisols) with an abundance of 2:1 phyllosilicates and exchangeable cations (Buol et al., 2011). Shifts in the composition of soil mineralogy and the surface activity of minerals during pedogenesis directly affect the potential of soils to store C (Doetterl et al., 2015; Rasmussen et al., 2018; Wiesmeier et al., 2019). Similarly, spatial patterns in vegetation type is strongly associated with soil C storage at multiple scales (Jobbágy & Jackson, 2000; Wiesmeier et al., 2019). Vegetation type effects on soil C often have been attributed to differences in plant inputs and plant litter chemistry (Wiesmeier et al., 2019). Despite considerable reports that soil and vegetation types significantly affect soil organic C, we have little understanding of how they influence soil C retention by reactive Fe minerals.

Here, we used soils provided by the National Ecological Observatory Network (NEON), along with additional samples and data collected from published studies, to characterize Fe-associated C and its relationships with climate and soil physicochemical factors across global mineral soils (Figure 1). To further assess the effect of soil pH on Fe-associated C, an incubation experiment was conducted to assess the formation of Fe-associated C in response to manipulated changes in soil pH values. Our objectives were to (a) ascertain how changes in soil pH affect Fe-associated C and (b) to understand distribution patterns of soil Fe-associated C as related to soil orders and vegetation. Given weak or inconsistent relationships between reactive Fe content and Fe-associated C observed previously (Huang et al., 2021; Wang et al., 2021; Zhao et al., 2016), along with evidence for pH control

of Fe-C interactions in laboratory studies (Gu et al., 1994), we hypothesized that soil pH, not Fe content, was the primary driver of global Fe-associated C among diverse soils. Because the soils in humid, forested regions are generally acidic and characterized by higher Fe content than the alkaline soils in water-limited ecosystems including grasslands and shrublands (Buol et al., 2011; Rasmussen et al., 2018), we also hypothesized that the soil and vegetation types characteristic of humid regions would have higher Fe-associated C concentration than those in arid regions.

2. Materials and Methods

2.1. Quantity and Distribution of Fe-Associated C Across the Globe

2.1.1. Soil Sampling and Analysis

We analyzed the content of extractable Fe phases and their associated C in soil samples spanning 32 sites in the NEON Megapit archive (Ayres, 2017), along with 10 additional soils that were sampled to expand diversity in biogeochemical characteristics. Both the soils from NEON Megapit archive and non-NEON samples were collected from the mineral horizon closest to the surface. More details on soil characteristics and sampling locations were described by Hall et al. (2020). All soils were air-dried and passed through a 2-mm mesh. Visible root fragments were removed with tweezers and soils were finely ground with a mortar and pestle prior to subsequent analyses.

Dithionite selectively removes secondary Fe (oxyhydro)oxide minerals (and any Fe³⁺) via reductive dissolution, including both crystalline and poorly crystalline Fe phases, with little effect on aluminosilicate clay minerals, crystalline primary mineral silicates, or Al oxides (Parfitt & Childs, 1988). Here, to quantify Fe-associated C, we used an inorganic dithionite extraction method adapted from Wagai and Mayer (2007), which was previously shown by these authors to dissolve a similar amount of Fe as the traditional citrate-dithionite extraction method (Parfitt & Childs, 1988). It should be noted that Al is commonly substituted within Fe mineral phases and is also released following dithionite extraction, and Al accounted for $20 \pm 15\%$ of total reducible Fe and Al on a molar basis in a previous study of diverse soils (Wagai & Mayer, 2007). A similar estimate of Al substitution in Fe phases was obtained from statistical comparison of dithionite- and oxalate-extractable metals from a broad range of NEON soils (Hall & Thompson, 2021). Therefore, the direct association of organic C with Fe atoms as opposed to Al atoms substituted in the Fe phase cannot be ascertained with the dithionite extraction. However, because dithionite is a strong reductant which has the principal effect of dissolving Fe (oxyhydr)oxide phases, the dissolved organic C released by inorganic dithionite extraction represents organic C that is bound either directly or indirectly to these Fe phases (Coward et al., 2017; Huang et al., 2020; Wagai & Mayer, 2007). Separate extraction with a control salt (typically sodium sulfate, which is the oxidation product of dithionite, or sodium chloride) is necessary to account for C that is released by ion exchange. This control extraction can be conducted prior to the dithionite extraction, or on a separate subsample of soil; both approaches have been used in the literature we summarize below.

In this study, Fe-associated organic C was measured using a sequential extraction method adapted from Huang et al. (2019). In order to remove organic C chemically bound with polyvalent cation bridges, soil subsamples were first extracted by sodium sulfate (0.5 M, 1:150 ratio of soil:solution) for 1 hr. Then, the residual soils were extracted with sodium dithionite (0.049 M, 1:150 ratio of soil:solution). The suspension was vortexed for 1 min and shaken for 16 hr, followed by centrifugation at 20,000 rcf for 10 min. The C concentration in the supernatant was quantified by measuring the CO_2 concentration produced from oxidizing dissolved organic C with persulfate in sealed gas-tight vials (Huang & Hall, 2017). The Fe (denoted Fe_d) in the same dithionite extraction was analyzed by inductively coupled plasma optical emission spectroscopy at Iowa State University (ICP-OES; Perkin Elmer Optima 5300 DV, Waltham Massachusetts). Subsamples were also extracted with ammonium oxalate (1:60 ratio of soil:solution) and analyzed by ICP-OES to quantify Fe in short-range-ordered phases and organo-metal complexes (termed Fe_o). Mean annual precipitation and temperature data of each NEON and additional site were extracted from published data (Hall et al., 2020; SanClements et al., 2020).

2.1.2. Literature Search for Published Data on Fe-Associated C

Peer-reviewed publications that reported Fe-associated C in soils were collected by searching Web of Science. To be included in our study, a study had to meet the following criteria: (a) surface mineral soils without amendment must be sampled from terrestrial ecosystems (soils from wetland and river delta were not included in this synthesis). (b) Bulk soil was used to determine Fe-associated C with dithionite extraction. (c) Bulk soil was also extracted with sodium chloride or sodium sulfate instead of sodium dithionite to remove or allow correction for water soluble, weakly exchangeable, and Ca- and/or Mg-associated organic C when calculating Fe-associated C. (d) Soil pH must be provided in the publication. In total, 14 publications were included in the synthesis. Information including site locations, site climate conditions (mean annual temperature and precipitation), sampling depth, soil orders, vegetation types, bulk soil organic C, soil pH, Fe-associated C, Fe_d, and Fe_o was extracted from each publication when possible (Table S1 in the Supporting Information S2). Together, the NEON and literature collected samples spanned a wide climatic range ($-9-28.6^{\circ}$ C mean annual temperature and 231-4500 mm mean annual precipitation). These samples also spanned a broad range of soil pH (3.9-9.2) and Fe_d content (0.08-245 mg g⁻¹) and included all of the 12 soil orders in the United States Department of Agriculture soil classification system. Given that most soil samples were located in North America and China (Figure 1), the unequal distribution of these samples geographically cannot completely represent global environments.

2.2. Impact of Lime Addition on Fe-Associated C Formation in an Acidic Oxisol

To explore the effect of soil pH on Fe-associated C formation, a microcosm incubation experiment was constructed using an acidic Oxisol (pH = 4.7) obtained from the Institute of Red Soil, Jinxian County (28°15' N, 116°20' E), Jiangxi Province, China. In order to raise the soil pH from acid to neutral in a short time, calcium hydroxide was selected in this incubation. In order to determine the appropriate addition rate, we set up eight levels of calcium hydroxide addition rate: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g kg⁻¹. Then, soil pH at each level was determined in a suspension using a 1:2.5 soil:water ratio. The soil had a pH value of \sim 7.0 with added 2.0 g kg⁻¹ calcium hydroxide, which was determined as the addition rate in the following incubation experiment. The litter we used was derived from maize leaf material. Specifically, 0 or 50 mg calcium hydroxide was added to sieved fresh soils (equal to 25 g dry soil mass, <2 mm), thoroughly mixed with soil and placed into a 500-mL glass jar (sealed with butyl rubber stoppers and aluminum caps) for each sample. The soils were then equilibrated for 1 week at 25°C and 60% water holding capacity. Following the initial equilibration, 0.3 g litter (finely ground and passed through a 0.2 mm mesh) was mixed into the soil (1.2% w/w). A sieved original soil with no litter was included as a control. This resulted in three treatment combinations (i.e., control, soil + litter, and soil + litter + lime) with 4 replicates per treatment combination. All jars were incubated in the dark up to 95 days at 25°C. To avoid excessive CO_2 accumulation in the headspace and maintain the water content, jars were flushed with air daily, and the soils were moistened as needed every 2 days.

To avoid interference from organic C released by litter, density fractionation of soil samples was performed to separate residual litter and mineral soils at the end of incubation, following a procedure from Ye et al. (2018). The mineral soil fractions were extracted with sodium sulfate followed by sodium dithionite as described above. The concentration of Fe-associated C in the extract was measured on a TOC analyzer (Elementar Vario Micro Cube, Germany).

2.3. Statistical Analyses

We combined the data from NEON sites and previous publications for subsequent statistical analyses. First, we used a linear mixed effects model to assess the impacts of soil orders or vegetation on Fe-associated C concentration, or the proportion of soil organic C associated with Fe (f_{OC-Fe}) and Fe_d, with soil orders or vegetation as fixed effects and sites as a random effect ("lmer" function in the "lme4" package). Then, one-way ANOVA was performed to compare the effects of soil orders or vegetation on Fe-associated C concentration, f_{OC-Fe} and Fe_d ("glht" function in the "multcomp" package). Second, both linear ("lm" function in R) and exponential ("nls" function in R) models were performed to analyze the relationships between Fe-associated C/ f_{OC-Fe} and predictive variables (soil pH, Fe_d, Fe_o, soil organic C, mean annual temperature and mean annual precipitation), and the optimal model fitted to the data was evaluated by comparing residual values. A broken stick analysis ("piecewise.linear" function in the "SiZer" package) was performed to quantify the pH value above which Fe-associated C concentration changed little. In addition, one-way ANOVA with Duncan's multiple-range tests was performed to estimate the responses of Fe-associated C formation to manipulated changes in soil pH in the incubation experiment.

Based on findings from the regression analyses, we developed a causal conceptual model that may explain Fe-associated C dynamics at the global scale. The variables included in this model were the best climatic (mean annual





Figure 2. Frequency distributions of iron (Fe) associated carbon (C), the fraction of Fe-associated C to soil organic C and dithionite extracted iron (Fe_d) at global scale (a, d, g) and among different soil orders and vegetations (b, c, e, f, h, i). Gray dots represent observations. Center lines are medians; box limits are upper and lower quartiles; whiskers are 1.5x the interquartile ranges. Several soil orders (Andisols, Anthrosols, Gellisols, and Vertisols) are not shown due to limited data.

precipitation) and soil (pH) predictor variables from the regression analyses (Figures 3 and S1 in the Supporting Information S1). Then, piecewise structural equation modeling (piecewise SEM) was performed to analyze the cascading pathways with the "piecewiseSEM" package using a *d-sep* approach, in which a set of linear structured equations are evaluated individually (Lefcheck, 2016). Good fit was assumed when Fisher's C values were non-significant (P > 0.05). All statistical analyses were performed using *R* software version 3.6.1.

3. Results

3.1. Iron-Associated C Distribution Across the Globe

Across all soils collected at NEON sites, non-NEON sites, and those in the published literature, concentrations of Fe-associated C and f_{OC-Fe} showed strong variation and ranged from 0.1 to 53 g kg⁻¹ and 2%–74%, respectively (Figures 2a and 2d). However, no significant differences in concentrations of Fe-associated C and f_{OC-Fe} were observed among soil orders or vegetation types (Figures 2b, 2c, 2e, and 2f) despite the fact that Fe_d varied 3062-fold and significantly differed among soil orders (P < 0.05; Figures 2g–2i).





Figure 3. Relationships between iron (Fe) associated carbon (C) and soil and climate variables at global scale. Soil variables include soil pH, soil organic C (SOC), dithionite extracted iron (Fe_d) and oxalate extracted iron (Fe_o); climate variables include mean annual temperature (MAT) and mean annual precipitation (MAP).

3.2. Relationships Between Fe-Associated C and Environmental Factors

To explore the potential mechanisms driving the observed variation in Fe-associated C concentrations and f_{OC-Fe} among soils, we analyzed their relationships with several climate and soil predictors (Figure 3). Among all the predictors, concentrations of Fe-associated C showed nonlinear correlations with soil pH only (Figure 3a). A threshold in Fe-associated C concentration (increasing from 1 g kg⁻¹ to 53 g kg⁻¹) occurred at soil pH from 4.2 to 3.5, according to the broken-stick regression. In the soils with pH > 4.2, concentrations of Fe-associated C were generally low (0.2–14 g kg⁻¹) but still measurable (Figure 3a). Mean annual precipitation and the ratio of Fe-associated C to dithionite extractable Fe showed negative correlations with soil pH (Figures S1b and S2



Figure 4. Effects of liming on soil pH, dithionite extracted iron (Fe_d), oxalate extracted iron (Fe_o) and formation of iron (Fe) associated carbon (C) in an acidic Oxisol with maize residue addition after incubation for 95 days.

in the Supporting Information S1). However, f_{OC-Fe} showed no significant correlations with any predictors (Figures 3g–3l). The piecewise SEM further revealed that the soils with more precipitation were associated with lower soil pH, which had a positive effect on Fe-associated C (Figure S3 in the Supporting Information S1).

3.3. Effects of Liming on the Formation of Fe-Associated C

Although lime + litter addition significantly increased soil pH from 4.6 to 5.5 at the end of the incubation (P < 0.05; Figure 4a), it did not affect Fe_o and Fe_d concentrations (Figures 4b and 4c). However, lime + litter addition significantly suppressed formation of new Fe-associated C relative to the treatment which received only litter, and no lime. Specifically, Fe-associated C was increased by 66%–87% in the two treatments with litter addition at the end of the experiment relative to the control, but it was significantly lower in the lime addition treatment compared with the treatment with litter addition only (P < 0.05; Figure 4d).

4. Discussion

The mean concentrations of Fe-associated C ($4.9 \pm 0.6 \text{ g kg}^{-1}$) and $f_{\text{OC-Fe}}$ (13.6 \pm 1.0%) in our global synthesis indicated that Fe-associated C typically represented a small fraction of surface mineral soil C in these samples, findings that are reasonably consistent with previous syntheses in alpine meadows (Fang et al., 2019) but slightly lower than those in forest

ecosystems (Zhao et al., 2016; Zong et al., 2021). A recent analysis of global soils found that large amounts of organic C (63% on average) could be retained by a combination of Al- and Fe-bearing minerals or metal complexes in subsurface soils (>30 cm) of wet biomes, as indicated by a combined pyrophosphate-dithionite extraction (Kramer & Chadwick, 2018). Comparing this finding with our results suggests that Al-bearing phases or Al complexes may play a particularly important role in C retention (Yu et al., 2021), and also supports previous assertions that Fe and Al oxides could be more important for organic C protection in deep soils as opposed to the relatively shallow soil samples that dominated our study (Coward et al., 2017; Kögel-Knabner et al., 2008; Zong et al., 2021).

A few studies have noted that pH dominantly determines Fe-associated C storage in soils at the site scale where Fe content and mineralogy are often similar (Wang et al., 2017; Ye et al., 2018; Zhao et al., 2019), whereas the role of pH versus other biogeochemical factors remains unclear over broader scales. Both our soil pH manipulation experiment (Figure 4d) and a previous acid addition experiment (Ye et al., 2018) indicated an acid-induced change in Fe-associated C, which support our first hypothesis that soil pH was the primary driver of Fe-associated C concentrations. The significant correlation between concentrations of Fe-associated C and soil pH, rather than Fe abundance (Figures 3a and 3c), implies that soil pH dominates Fe-associated C by regulating the propensity of organic C to bind to Fe oxides. Further, our observation that the ratio of Fe-associated C to dithionite extractable Fe increased with decreasing pH (Figure S2 in the Supporting Information S1) indicated that the same amount of Fe could adsorb (or perhaps, co-precipitate) more C at lower pH values. At some lower limit the abundance of Fe minerals must ultimately limit the amount of C that can be Fe-associated: the maximum sorption of C onto Fe (oxyhydr)oxides was estimated as 0.22 g C per g Fe, even though co-precipitation can lead to higher Fe:C mass ratios (Kaiser & Guggenberger, 2007; Wagai & Mayer, 2007). However, our data indicate that in many soils, secondary Fe phases may be sufficiently abundant that other factors such as pH (Figure 3a) or soil organic C input (Figure 4d) become more important than Fe abundance per se. This view is further supported by statistical analyses of relationships between bulk soil organic C concentrations and Fe_0 in large soil datasets, where soil organic C tends to increase with Fe₀ at very low Fe₀ concentrations, but the response plateaus as Fe₀ exceeds approximately 1 or 2 mg Fe_o g^{-1} (Hall & Thompson, 2021; Yu et al., 2021; von Fromm et al., 2021). Together, these results demonstrated that soil pH exerts strong control over the concentrations of C associated with reactive Fe minerals, consistent with previous work highlighting a central role for soil pH in modulating organo-metal complexation (Kleber et al., 2015; Wagai & Mayer, 2007).

Two potential mechanisms may explain the high association of organic C with reactive Fe in acidic soils. First, low pH increases the solubility of metal cations (e.g., Fe³⁺ and Al³⁺), promoting formation of organo-metal associations through sorption and/or co-precipitation reactions (Porras et al., 2017; Wagai & Mayer, 2007; Ye et al., 2018). Second, Fe oxide minerals exhibit variation in surface charge as a function of pH, with typical point of zero charge (PZC) values between pH 7 and 9 (Appel et al., 2003; Kleber et al., 2015; Tombácz et al., 2004). The surface of Fe minerals is protonated with an increasingly greater net positive charge as pH decreases below the PZC, and many studies have observed the sorption of organic C onto Fe oxides depending strongly on the pH (Gu et al., 1994; Kaiser & Guggenberger, 2000). Such positively charged surfaces are favorable for a strong sorption of the negatively charged organic molecules, and ligand exchange between carboxyl/hydroxyl functional groups of organic C and hydroxylated Fe oxide surfaces is likely a dominant mechanism of Fe-associated C formation (Gu et al., 1994; Guggenberger & Kaiser, 2003). Furthermore, Tombácz et al. (2004) found that the zero net proton surface excess of Fe oxides mixed with clays (simulated soil conditions) occurred at pH 5.5, which is roughly comparable to the pH threshold in the concentrations of organic C retained by Fe minerals in our study (Figure 3a). Thus, Fe oxide particles at low pH values have strong affinity for organic C (Gu et al., 1994; Silva et al., 2015). The SEM showed that the concentrations of Fe-associated C regulated by soil pH were ultimately related to mean annual precipitation (Figure S3 in the Supporting Information S1), highlighting the important role of water flux and related soil weathering as a mediator of soil pH (Figure S1b in the Supporting Information S1; Slessarev et al., 2016) and suggest that water-driven change in soil pH is the dominant pathway that controls soil C accumulation with Fe minerals.

We did not find significant correlations of f_{OC-Fe} with soil and climate parameters (Figures 3g–3l), likely because Fe-associated C and total soil organic C are regulated by different environmental factors and Fe-associated C was seldomly a dominant C pool (Doetterl et al., 2015; Rasmussen et al., 2018; Wagai & Mayer, 2007). Among soil taxa, Spodosols and Oxisol had the highest f_{OC-Fe} (Figure 2e). This may be due in part to Fe enrichment and soil acidification associated with humid and forested environments (von Uexküll & Mutert, 1995). Ultisols, which often have similar mineralogical characteristics as Oxisol, had the lowest f_{OC-Fe} , which was unexpected due to their typically high reactive Fe content (Figures 2e and 2h). However, our findings underscore that Fe abundance as determined in soil extractions (oxalate, citrate-dithionite) is not an effective predictor of Fe-associated C; rather, the surface characteristics of the Fe phases, and the particular compositions of the Fe phases, may play key roles in Fe-C interactions (Coward et al., 2017; Hall et al., 2018). In addition, Mollisols, with generally limited pedogenic development, had the second lowest f_{OC-Fe} (Figure 2e). This soil type is common in grasslands and shrublands with circum-neutral to alkaline pH values, which often accumulate calcium carbonate (Rasmussen et al., 2018). As a result, interaction with clay minerals by polyvalent cation bridges, especially Ca²⁺ and Mg²⁺ ions, should be a key stabilization mechanism for organic C in this kind of soil (von Lützow et al., 2006).

5. Conclusions

Our global-scale dataset accompanied by a complementary incubation experiment demonstrates that soil pH, not reactive Fe content, plays a dominant role in Fe-associated C concentration. This finding helps to reconcile weak associations between extractable Fe and SOC observed in previous data syntheses (Rasmussen et al., 2018; von Fromm et al., 2021; Yu et al., 2021), and is further important given significant soil acidification induced by excessive nitrogen fertilization and acid deposition over the past three decades globally (Guo et al., 2010; Tian & Niu, 2015), which suggests that Fe-associated C formation may be increasing in response to soil acidification. Finally, these findings highlight the importance of soil pH in regulating organic C retained by reactive Fe minerals, and suggest that soil pH should be included as an important factor in Earth system models that predict soil C accumulation and persistence under future acid deposition.

Data Availability Statement

The data supporting the results are available in the Environmental Data Initiative (https://doi.org/10.6073/pasta/7e9444b9b9ad8be100d4f39fc763782d).

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