

Molecular Nature of Mineral–Organic Associations within Redox-Active Mountainous Floodplain Sediments

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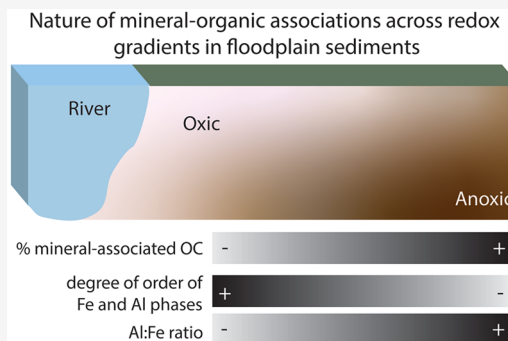
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ABSTRACT: Floodplains are critical terrestrial–aquatic interfaces that act as hotspots of organic carbon (OC) cycling, regulating ecosystem carbon storage as well as export to riverine systems. Within floodplain sediments, regular flooding and textural gradients interact to create dynamic redox conditions. While anaerobic protection of OC upon burial is a well-recognized carbon storage mechanism in redox-active floodplain sediments, the impact of protective mineral–organic associations is relatively unknown. Here we determined the quantitative importance and chemical composition of mineral–organic associations along well-defined redox gradients emerging from textural variations and depth within meander sediments of the subalpine East River watershed (Gothic, CO). We characterized mineral–organic associations using a combination of sequential extractions, physical fractionation, and high-resolution mass spectrometry. Across the meander, we found that mineral-associated OC constitutes a significant fraction of total OC, and that extractable iron (Fe) and aluminum (Al) phases are quantitatively important for floodplain sediment OC protection. Our mass spectrometry results showed OC associated with increasingly ordered Fe and Al phases are relatively enriched in low-molecular weight, oxidized, aromatic compounds. Surprisingly, however, total OC content showed weak or no correlation with indicators of anaerobic protection, such as relatively bioavailable OC pools (water-extractable and particulate OC) or the molecular weight and oxidation state of OC. Overall, this work highlights that protection of OC bound to reactive mineral phases—in addition to anaerobic protection—can play a quantitatively important role in controlling soil carbon storage in redox-active floodplain sediments.

KEYWORDS: Soil organic carbon, Floodplains, Redox gradients, Mineral–organic associations, Climate change



INTRODUCTION

Floodplains are important terrestrial–aquatic interfaces that can act as carbon sinks or sources, regulating ecosystem carbon storage within and export to riverine systems.^{1,2} Floodplain ecosystems are estimated to account for up to 8% of soil organic carbon (OC) stocks globally, despite covering only 1% of the land area surface.³ Each year, 0.25 Pg OC are transferred from floodplain to riverine systems, and eventually exported to oceans.⁴ OC stored within floodplains is increasingly precarious in the Anthropocene, as climate change and human alteration affect the timing and magnitude of flooding cycles.⁵ These changes are particularly pronounced in headwater systems of the mountainous western United States, with a current megadrought⁶ foreshadowing further predicted declines in snow water equivalent.⁷ To predict the impact of these drastic hydrological changes on OC retention and loss within floodplain sediments, specifically those in mountainous systems, a mechanistic understanding of the rate-controlling mechanisms is critical.

Seasonal flooding and the resulting depositional environment create a mosaic of floodplain sediments with varying characteristics and propensities to sequester OC. The storage of sediment OC is temporally and spatially heterogeneous, depending on factors including grain size distribution, soil moisture dynamics, and biogeochemical processes.^{8,9} For example, seasonal flooding events result in particle sorting and accumulation of fine sediment, resulting in distinct textural patterns across floodplain meanders and with sediment depth.³ While sediment burial is a major factor governing OC storage in floodplains,^{1,10–12} the mechanisms governing floodplain OC

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storage, and how burial interacts with texture, moisture, and biogeochemical gradients, are poorly understood.

In depositional floodplain sediments, textural gradients give rise to spatially dynamic redox conditions. Reducing conditions dominate both when sediments are saturated during flooding and in fine-textured sediments. It is commonly assumed that oxygen limitations experienced under reducing conditions are primarily responsible for OC preservation in the floodplain.^{13–15} The absence of oxygen imposes both kinetic and thermodynamic constraints on microbial activity and can limit depolymerization and respiration of organic compounds,^{16,17} resulting in anaerobic protection of OC in the floodplain. Under anaerobic conditions, the activity of oxidative enzymes capable of catalyzing depolymerization reactions is restricted,¹⁸ causing the preservation of complex particulate organic carbon (POC).¹⁷ Additionally, the degree of microbial respiration in anaerobic environments is not just dependent on the energetics of available terminal electron acceptors (e.g., Fe(III) or sulfate), but also on the oxidation state of the electron donor, i.e., the organic substrate utilized by microbes.¹⁹ Boye et al.¹⁹ found that in floodplain sediments, reduced organic compounds, with nominal oxidation state of carbon (NOSC) values below a thermodynamic threshold that makes microbial respiration unfavorable, are selectively preserved. The influence of such kinetic and thermodynamic constraints, here termed anaerobic protection, will likely vary along spatial redox gradients within floodplain environments, which can form within microsites, along textural transitions, or along the capillary fringe.^{16,18,20}

While anaerobic protection of OC within sediments has received widespread attention,^{16,19,21,22} it is less clear how reactive metals influence OC preservation within floodplain environments. Associations with reactive minerals effectively protect organic compounds from microbial access²³ and represent an important C storage mechanism in upland soil systems.^{21,24,25} Iron (Fe) and aluminum (Al) (oxy)(hydr)-oxides (in the following abbreviated as “oxides”) are particularly important for the formation of mineral-organic associations,^{26,27} especially in humid and/or redox-active systems.^{28–30} This contrasts with relatively arid and alkaline systems, where organic complexes with calcium (Ca) can be an important OC stabilization mechanism.³⁰ Although the abundance of reactive metal phases can constitute a significant component of the mineral matrix in floodplain sediments,^{8,31,32} their quantitative importance for OC retention has not been considered.

The importance of reactive metals in driving OC cycling likely shifts depending on the redox regime, because Fe, unlike Al and Ca, is redox-active.^{33–35} The stability of Fe-OC associations is impacted by redox oscillations: reducing conditions can lead to their disruption through reductive dissolution of Fe oxides and subsequent leaching;²¹ conversely, oxic conditions promote the formation of protective Fe-OC associations through precipitation reactions.^{36–39} In floodplains, it is expected that spatiotemporal variations in oxygen availability (and thus redox) as imposed by water table depth or textural gradients cause local variation in Fe reduction and oxidation, likely regulating the relative importance of Fe-OC associations^{12,31} as compared to protective associations between OC and Al or Ca.^{30,35,40} This is in contrast to organic soils, where anaerobic protection can combine with low pH in regulating OC storage, where O₂ limitation, low pH,

and high phenol concentrations combine to limit organic matter decomposition.^{41,42}

In mineral-rich sediments, redox fluctuations alter both the degree of microbial OC transformation and mineral reactivity. Consequently, such fluctuations dictate the chemical nature of mineral-associated OC (MAOC) that might form. For example, plant-derived aromatic OC preferentially binds to increasing short-range order mineral content^{43–45} in tropical and volcanic soils, which may be stabilized on Fe oxide surfaces during redox fluctuations.³⁸ However, because redox fluctuations affect the crystallinity of Fe oxides,^{38,46,47} we expect that MAOC composition varies in redox-active soils. For example, in humid tropical soils which undergo frequent redox oscillations, Coward et al.⁴³ found that varying Fe mineral phases, as determined by sequential extraction, associated with unique OC compounds. Together, these observations suggest that the chemical composition of mineral-organic associations in floodplains will vary with redox regime.

In this study, we determined the quantitative importance and chemical composition of mineral-organic associations within redox-active subalpine floodplain sediments. To assess the impact of redox conditions on the characteristics of mineral-organic associations, we sampled along well-defined redox gradients emerging from textural variations and depth within an active floodplain meander of the East River (Gothic, CO). This study area is representative of headwater catchments in the Upper Colorado Basin, an area that supplies water resources to a large portion of the Western United States.⁴⁸ We quantified the amount of mineral-associated OC (MAOC) using physical density fractionation and chemical extractions. To characterize the chemical composition of MAOC, we used a combination of selective dissolution with subsequent analysis by Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). Finally, we compared abundance and chemical composition of bioavailable OC and MAOC to infer the relative importance of mineral protection versus anaerobic protection on floodplain C cycling. We hypothesized that the chemical composition of mineral-organic associations is dictated by changes in mineral reactivity across redox gradients, and that the quantitative importance of MAOC will be lowest within more reducing environments.

■ MATERIALS AND METHODS

Field Site Description. We established a sampling transect across an active meander of the East River floodplain (Gothic, CO; Figure 1). This location was chosen as it is a representative meander of the subalpine region of the East River watershed, and has been studied extensively in terms of geochemical dynamics^{49,50} and carbon chemistry.⁵¹ Sediment profiles across the transect consisted of fine-grained material (<2 mm) overlaying more coarse-grained alluvium, all underlain by Mancos shale.⁵¹ Floodplain vegetation included dwarf shrubs (e.g., American dwarf birch and mountain willow), potentilla, and grasses.⁵² Water table depth was calculated using pressure transducers (Hobo U20L-04) installed along the sampling transect:⁵³ over the course of seasonal flooding, the water table declined by 0.4 m at the near river position and 0.9 m at the midmeander position (Table S1 of the Supporting Information, SI). Measurements of soil moisture (Acclima TDR-315L) and redox potential (in-house platinum-tipped electrodes) were taken at the same sampling locations and depths in 2019, a year that experienced similar

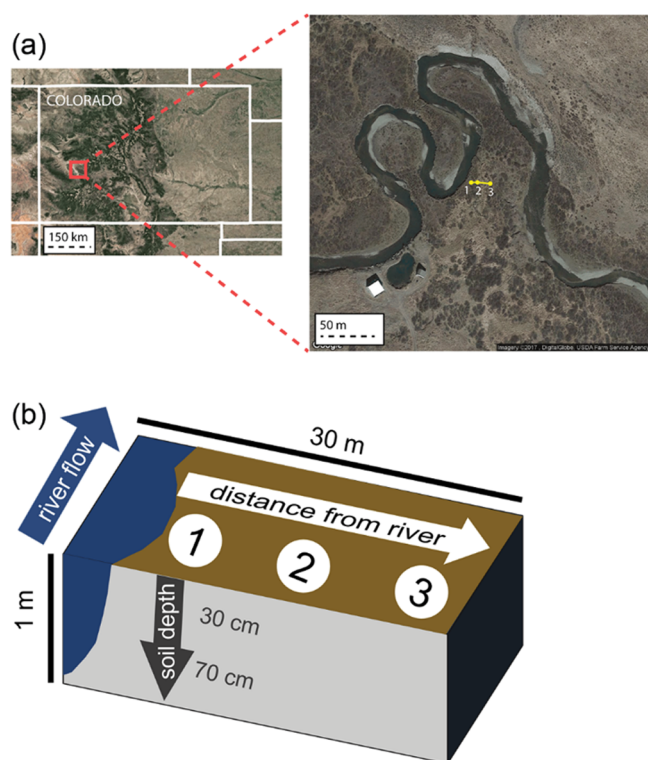


Figure 1. (a) Location of East River sampling transect in Colorado, and (b) schematic of the transect across the meander with distance from the river (positions 1, 2, and 3 representing near river, intermediate, and midmeander positions, respectively) and sampled depths (30 and 70 cm). East River discharge values and corresponding sediment moisture and redox values are provided in SI (Figure S1, Table S1).

levels of river discharge and subsequent flooding as 2017 (Figure S1).

Sediment Sampling. We collected sediment samples in triplicate in June 2017 at three positions along the sampling transect, at shallow (30 cm) and deep depths (70 cm) (Figure 1, Table S2); these depths were chosen based on visual assessment of sediment redoximorphic features during field sampling. Sediments were air-dried and sieved to 2 mm. Sediments across the transect dry out to 27–59% volumetric water content upon drainage in September (Table S1); thus, precipitation of redox-active metal phases may have occurred during sample processes and the data reported here likely represent the state of mineral-organic associations present within the sediments during fully drained, oxic periods spanning from midsummer to the following spring. No unexpected or unusually high safety hazards were encountered in the sampling and subsequent analysis of sediment samples.

Bulk Sediment Characterization. We determined total sediment carbon and nitrogen in triplicate using an ECS 4010 CHNS-O elemental analyzer (Costech Analytical Technologies, Inc., Valencia, CA, U.S.A.). We measured total metals (Fe, Al, Ca, Si, etc.) on finely ground samples using X-ray fluorescence (Spectro Xepos HE XRF Spectrometer). We determined sediment texture after loss on ignition to remove organic matter (4 h at 550 °C) by a laser diffraction particle size analyzer (Beckman Coulter LS 13 320, Indianapolis, IN). We estimated root biomass by picking out coarse roots from air-dried sediments. Analytical error was orders of magnitude lower than the variance among biological replicates, and thus

only standard error of the means of biological replicates are reported.

Density Fractionation. To isolate organic matter of decreasing bioavailability (e.g., particulate to mineral-associated organic carbon), we used a density fractionation procedure modified from the literature.^{54,55} Briefly, two sodium polytungstate (SPT) solutions were prepared in DI water at the following densities: 1.6 g cm³ and 2.2 g cm³ (solutions #1 and #2, respectively). Particulate organic carbon (POC) was determined by adding and gently vortexing 30 mL of solution #1 and 7.5 g of sediment, shaking for 2 h at low speed, and centrifuging for 1 h at 1000g. The supernatant was filtered (0.8 μm, Millipore), rinsed thoroughly with DI water to remove excess SPT, and the filter was oven-dried at 60 °C and weighed to determine the amount of POC. To determine the intermediate density fraction (>1.6 and <2.2 cm³), 30 mL of solution #2 was added to the remaining sediment pellet, and the above steps were repeated. The final density fraction (>2.2 g cm³) was determined by thoroughly cleaning the remaining sediment pellet with DI water. Thirty mL of DI water was added and vortexed until the pellet was suspended, then centrifuged for 1 h at 2000g. The supernatant was removed, and this process was repeated three times. The dry mass of the remaining sediment pellet was recorded. The intermediate and heavy fractions together comprised the MAOC pool. We determined carbon and nitrogen content of density fractions in triplicate as described above for bulk sediment.

Sequential Extractions. To selectively dissolve mineral phases of varying degrees of order and their associated OC, sediments were extracted sequentially with four reagents.^{56–58} After each extraction, the supernatant was filtered using 0.22 μm filters (Sigma-Aldrich). Briefly, 0.33 g sediment was extracted with 10 mL deionized (DI) water to extract bioavailable phases of minerals and OC (shaken 2 h at 200 rpm, centrifuged 20 min at 510g); this extraction represented water-extractable organic carbon (WEOC). The same pellet was then extracted with 10 mL of 0.1 M sodium pyrophosphate to target amorphous metal–organic complexes^{57,59} (shaken 16 h at 200 rpm, centrifuged 1 h at 4000g) and combined with the filtered extract of a 6.7 mL DI water rinse (shaken 2 h at 200 rpm, centrifuged 1 h at 4000g). Then, 10 mL of 0.5 M hydrochloric acid (HCl) was added to the remaining pellet to target short-range order phases⁵⁶ (shaken 4 h at 200 rpm, centrifuged 20 min at 4000g) and combined with the filtered extract of a 6.7 mL DI water rinse (shaken 2 h at 200 rpm, centrifuged 20 min at 510g). Lastly, 10 mL of 0.049 M sodium dithionite was added to the pellet to target total reducible oxide phases⁵⁸ (shaken 16 h at 200 rpm, centrifuged 20 min at 510g) and combined with the filtered extract of a 6.7 mL of 0.05 M HCl rinse (shaken 1 h at 200 rpm, centrifuged 20 min at 510g).

Metal and TOC Analysis of Sequential Extractions.

Extracts were analyzed for metals using Microwave Plasma-Atomic Emission Spectrometry (Agilent, Santa Clara, CA), diluting to a final concentration of 2% nitric acid. Extracts were analyzed for total organic carbon using a TOC-L Analyzer (Shimadzu, Kyoto, Japan), diluting in DI water.

Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) Analysis of Sequential Extractions. Extracts were analyzed for organic matter composition using a 12 T Bruker Solarix FTICR spectrometer located at the Environmental Molecular Science Laboratory in Richland, WA. Samples were first desalted and concentrated

using solid phase extraction⁶⁰ with bond elute PPL cartridges. The analyte was eluted from the PPL cartridge in HPLC grade methanol and introduced directly to a standard Bruker electrospray ionization source operating in negative mode. The instrument was externally calibrated weekly to a mass accuracy of <0.1 ppm using a tuning solution from Agilent. The ion accumulation time varied to account for differences in C concentration between samples. A Suwannee River Fulvic Acid standard, obtained from the International Humic Substance Society, was used as a control to monitor potential carryover from one sample to another and ensure instrument stability in day-to-day operation. The instrument was flushed between samples using a mixture of Milli-Q water and HPLC grade methanol. One hundred forty-four individual scans were averaged for each sample and internally calibrated using OM homologous series separated by 14 Da ($-\text{CH}_2$ groups). The mass measurement accuracy was <1 ppm for singly charged ions across a broad mass-overcharge (m/z) range (i.e., $100 < m/z < 1100$). The mass resolution was 350 000 at 339.112 Da. BrukerDaltonik data analysis software (version 4.2) was used to convert raw spectra to a list of m/z values applying FT-MS peak picker module with a signal-to-noise ratio threshold of 7 and absolute intensity threshold of 100. Formularity software⁶¹ was used to assign chemical formulas based on the criteria previously described.⁶² Peaks were filtered to only include masses between $200 < m/z < 900$. Compounds were grouped into molecular classes (e.g., lipid-, protein-, carbohydrate-, lignin-, tannin-, condensed aromatic-like) based on C, H, and O for H/C and O/C ranges according to previous literature.⁶³ Each assigned molecular formula was used to calculate the nominal oxidation state of C (NOSC), double bond equivalence (DBE), and aromaticity index (AI) as in previous work.²¹

Statistical Analysis. All statistical analyses were performed using R version 4.2.2.⁶⁴ We used Shapiro-Wilk and Levene's tests to assess normality and equality of variances for all data. Parametric tests were used in cases in which data met assumptions for normality. To test our hypotheses, we grouped by sediment depth and assessed differences among meander positions or extractions using analysis of variance (ANOVA), combined with Tukey's honestly significant difference post hoc test ($\alpha = 0.05$ indicates significant differences), using the R package *agricolae*.⁶⁵ Specifically, we compared values within surface (30 cm) and deep (70 cm) sediments across the lateral meander transect from near river to midmeander locations (Figure 1) and among extractions. We performed linear regressions to determine relationships between sediment C and sediment properties ($\alpha = 0.05$ indicates significant differences).

RESULTS AND DISCUSSION

Physical and Chemical Characteristics of Floodplain Sediments Dictate Redox Regime. Along the meander transect and with depth, spatial variations in sediment texture, moisture, and root C inputs resulted in pronounced redox gradients. Clay and silt content was 53% greater in shallow (30 cm, 89.6%) than deep sediments (70 cm, 58.7%), and in deep sediments the clay and silt content was 105% greater at the meander center (79.6%) compared to the near river position (39.9%) (Table 1). Due to the finer texture in the meander center, the moisture content remained higher across both depths (65–67% volumetric water content, VWC) compared to the near river position (43%–47% VWC) during early

Table 1. Physical and Chemical Characteristics of Floodplain Sediments (mean $\pm$ standard error) Across Meander Position and Depth^a

position	depth (cm)	sand (%)	silt + clay (%)	pH	root biomass (mg)	bulk Fe (%)	bulk Al (%)	bulk Ca (%)	bulk Si (%)	POC (mmol C/g)	MAOC (mmol C/g)
near river	30	13.9 $\pm$ 0.8	86.1 $\pm$ 0.8	7.3 $\pm$ 0.02	2011 $\pm$ 932	3.07 $\pm$ 0.08	4.97 $\pm$ 0.11	2.22 $\pm$ 0.08	23.91 $\pm$ 0.49	4.28 $\pm$ 1.22	3.88 $\pm$ 0.59
	70	61.1 $\pm$ 6.0	38.9 $\pm$ 6.0	8.3 $\pm$ 0.08	309 $\pm$ 183	3.34 $\pm$ 0.18	5.60 $\pm$ 0.04	2.42 $\pm$ 0.07	26.55 $\pm$ 0.09	2.44 $\pm$ 0.29	1.24 $\pm$ 0.21
intermediate	30	8.7 $\pm$ 1.1	91.3 $\pm$ 1.1	6.5 $\pm$ 0.03	460 $\pm$ 84	3.25 $\pm$ 0.09	5.29 $\pm$ 0.08	1.25 $\pm$ 0.10	24.43 $\pm$ 0.57	3.41 $\pm$ 1.23	4.81 $\pm$ 0.53
	70	42.3 $\pm$ 9.1	57.7 $\pm$ 9.1	7.7 $\pm$ 0.10	128 $\pm$ 71	3.32 $\pm$ 0.12	5.72 $\pm$ 0.09	1.58 $\pm$ 0.12	26.89 $\pm$ 0.40	1.45 $\pm$ 0.02	1.18 $\pm$ 0.10
midmeander	30	8.6 $\pm$ 0.3	91.4 $\pm$ 0.3	6.7 $\pm$ 0.11	2062 $\pm$ 1705	3.75 $\pm$ 0.07	5.56 $\pm$ 0.11	1.01 $\pm$ 0.08	25.77 $\pm$ 0.55	3.40 $\pm$ 0.51	3.66 $\pm$ 0.73
	70	20.4 $\pm$ 2.0	79.6 $\pm$ 2.0	7.5 $\pm$ 0.02	223 $\pm$ 76	4.15 $\pm$ 0.27	5.30 $\pm$ 0.43	0.71 $\pm$ 0.01	25.55 $\pm$ 1.47	0.95 $\pm$ 0.12	0.93 $\pm$ 0.06

^aBulk metals included iron (Fe), aluminum (Al), and silicon (Si). Density isolates included particulate organic carbon (POC) and mineral-associated organic carbon (MAOC).

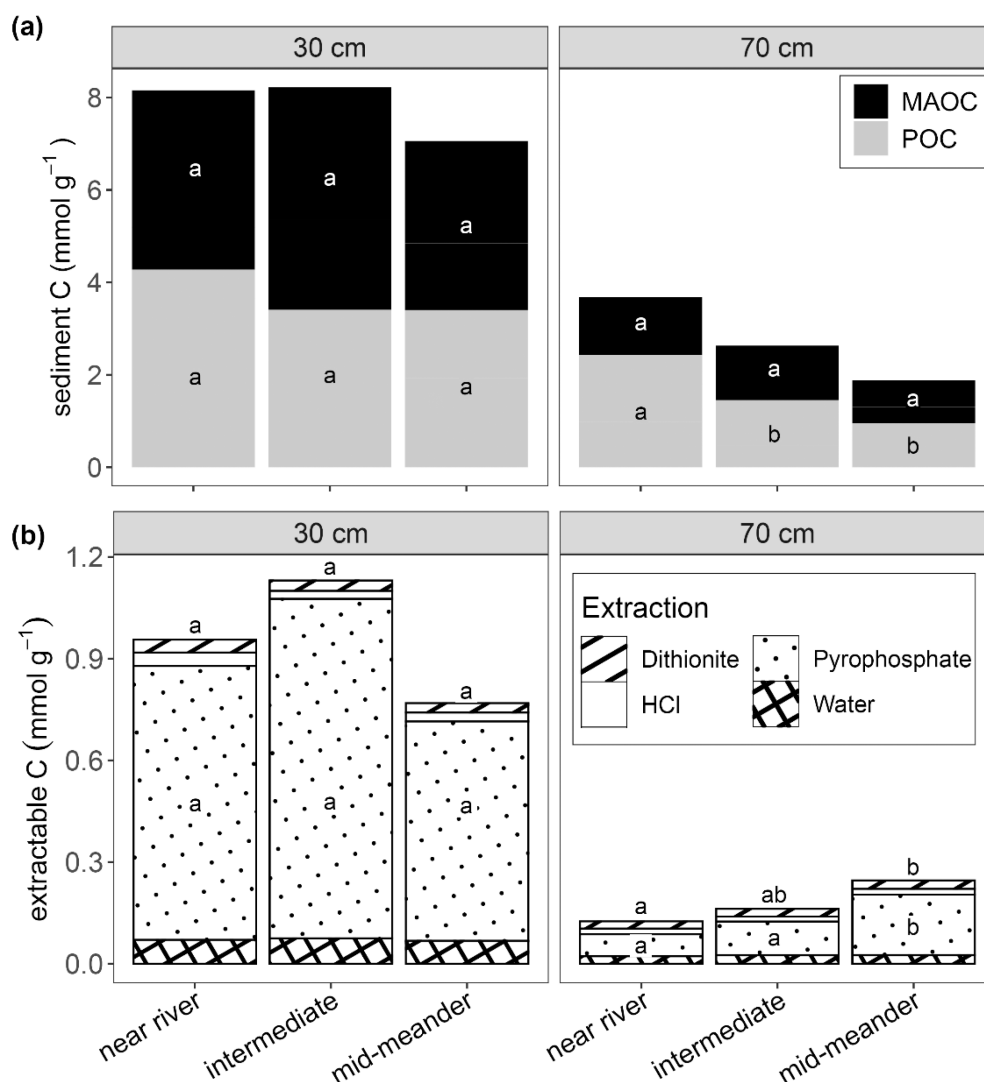


Figure 2. OC in shallow (30 cm) and deep (70 cm) sediment across the floodplain meander in (a) bulk pools separated by mineral-associated organic carbon (MAOC) and particulate organic carbon (POC) (denoted by black and gray shading, respectively) and (b) extractable pools separated by extraction (denoted by pattern fills). Units for both panels are mmol C per g sediment. Letter designations are Tukey's honestly significant difference test results ($p < 0.05$) based on differences along the meander in each depth: differences in MAOC and POC in panel (a) and differences in total extractable OC and pyrophosphate-extractable OC in panel (b). Mean and standard errors are reported in Table 1 for bulk pools, and in Table S3 for extractable OC.

season flooding (Table S1). As a result of these texture and moisture patterns during flooding, the midmeander position experienced lower redox potentials at both depths (−180 to 240 mV), while the coarse textured and well-drained near-river position remained relatively oxic (9 to 355 mV, Table S1). Root biomass, used here as a proxy for root C inputs, decreased by 85% from shallow (1510.7 mg) to deep sediments (220.3 mg), with no significant differences among the meander positions (Table 1). Total metals varied significantly across the meander, but not with depth: total Fe in the midmeander position (3.9%) was 22% greater than the near river position (3.2%), while total Ca in the near river position (2.3%) was 156% higher versus the midmeander position (0.9%). There were no significant trends in total Al. Sediment pH was greater in the near river position (7.9) than midmeander position (7.1), and greater in the deep (7.8) compared to shallow horizons (6.9) (Table 1).

Mineral-Associated Organic Carbon Pools Vary Spatially Across the Floodplain. Total OC, as well as

POC, MAOC, and root biomass, were significantly greater in the surface compared to deep sediments (Figure 2a, Table 1, $p < 0.05$). No significant changes in root biomass were observed across the floodplain meander (Table 1). However, contrary to our original hypothesis, total sediment C and POC significantly declined toward the finer textured, more reducing meander center, a trend particularly pronounced with depth (Figure 2a, $p < 0.05$). Burial of POC and subsequent kinetic and thermodynamic protection due to limited oxidative depolymerization are common mechanisms of floodplain sediment C storage.^{1,10–12,18} If such protection mechanisms were dominant, we would expect the highest sediment OC and POC contributions in the more reducing meander center; however, we find both pools lowest at the meander center compared to the relatively oxic near-river position. This finding suggests that kinetic and thermodynamic constraints do not solely explain the patterns of C storage across the meander.

Our proxies for MAOC better predict the spatial distribution of total OC across the meander than POC. Notably, in deep

sediments, the relative contribution of MAOC (isolated by density fractionation) compared to POC increased by 38% toward the center of the meander (Figure 2a, $p < 0.05$). Similarly, the total amount of extractable OC (sum of water, pyrophosphate, HCl, and dithionite extractable OC) increased in the deep sediment at the midmeander position (Figure 2b, $p < 0.05$). Both independent lines of evidence indicate that mineral protection becomes relatively more important toward the finer-textured, more reducing meander center, especially in deep sediments. This finding is counter to our expectation that mineral protection, particularly via bonds to Fe oxides, would decrease toward the more reduced deeper sediments of the meander center due to microbial Fe reduction.³¹ Rather, this suggests that mineral-organic associations play an important role in C storage, even in temporarily reduced locations of the floodplain meander.

Sequential extractions further highlight the importance of Fe and Al oxides in driving patterns of OC accumulation across the meander. Along the floodplain meander, total extractable Fe and Al concentrations as well as MAOC isolated by density fractionation strongly and significantly correlated with sediment C content (Figure 3, $p < 0.05$). Extractable Ca, which can effectively protect OC in alkaline soils (Rasmussen et al. 2018), only significantly correlated with OC content in the more alkaline deep soils (Figure S2a, $p < 0.05$). In contrast, clay content did not significantly correlate with total sediment C content (Figure S2b). Our results therefore suggest that mineral protection of OC in our floodplain sediments is due to pedogenic (extractable) Fe and Al oxides, and possibly Ca-organic complexes at depth, rather than phyllosilicates.

Total extractable OC was higher in surface compared to deep sediments and increased toward the meander center in the deep sediments (Figure 2b, $p < 0.05$). Pyrophosphate extracted significantly more OC than other extractants across both depths and all meander positions (Figure 2b, $p < 0.05$). Comparison of the OC pools extracted during selective dissolutions shows that in deep sediments, pyrophosphate-extractable OC is principally responsible for the significant increase in total extractable OC toward the meander center (Figure 2b, $p < 0.05$). This increase in the contribution of pyrophosphate-extractable OC toward the more reducing meander center suggests protection of C within metal–organic complexes,^{57,66} although this pool might include nanoparticulate metal oxide phases⁶⁷ and base-extractable organic matter.⁵⁷ Together, these results show that OC associated with extractable metals explains total sediment C distribution across the floodplain better than POC, signifying the quantitative importance of mineral-organic associations for C storage within floodplain sediments.

Changing Composition of Mineral–Organic Associations Across Redox Gradients. Detailed examination of the extractable metal pools yielded further insights into the impact of mineralogical composition on MAOC pools across the floodplain meander. Shallow sediments contained greater amounts of extractable Fe and Al compared to deep sediments (Figure 4, $p < 0.05$), which predominantly reside in less extractable (HCl and dithionite) pools. Similarly, the relative abundance of HCl- and dithionite-extractable Fe and Al pools was significantly greater near the river than in the meander center (Figure 4, $p < 0.05$; except dithionite-extractable Al: $p = 0.052$). The dominance of these pools in sediments at the surface and close to the river are suggestive of the formation and preservation of more crystalline Fe oxides phases in the

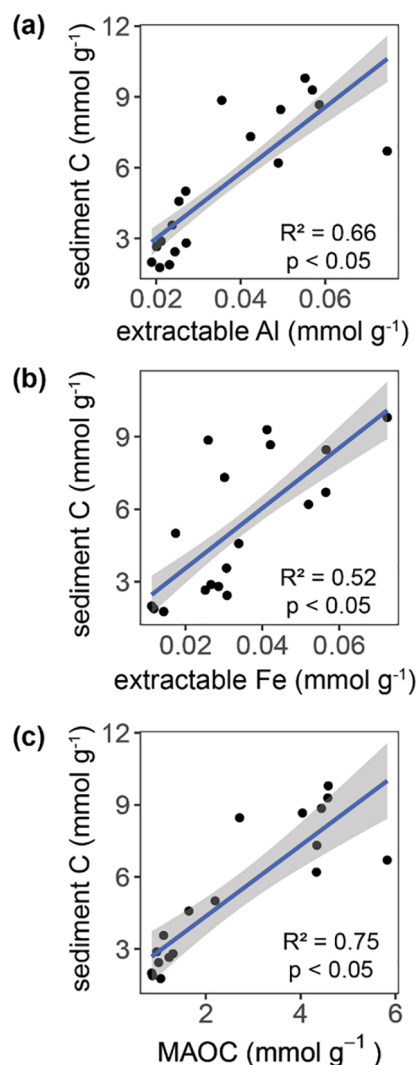


Figure 3. Correlations between sediment OC and (a) extractable aluminum (Al), (b) extractable iron (Fe), and (b) mineral-associated organic carbon (MAOC). Units for all panels are mmol C per g sediment. The blue line is the linear regression and statistics are provided, including the R^2 and p -value for model significance.

oxic meander domains. In contrast, although the total extractable Fe concentrations declined toward the meander center, and total extractable Al remained constant, pyrophosphate-extractable Fe and Al concentrations increased toward the meander center, especially at depth (Figure 4, $p < 0.05$). These results suggest that the more intense redox cycling in the meander center (Table S1) may have caused the loss of more crystalline Fe and Al phases but maintained a larger pool of short-range order Fe and Al phases that may be subject to repeated dissolution and precipitation reactions. We suggest further research examine the impact of redox oscillations on the mobilization of reactive metal phases in floodplain sediments.

In both surface and deep sediments, total extractable Fe decreased toward the meander center, whereas total extractable Al remained relatively constant across the meander (Figure 4, $p < 0.05$). Consequently, the ratio of extractable Al/Fe increased by 93% from the near river position (0.82 ± 0.03) toward the meander center (1.58 ± 0.09 , Figure S3). These results suggest a relative enrichment of Al phases in the more reducing

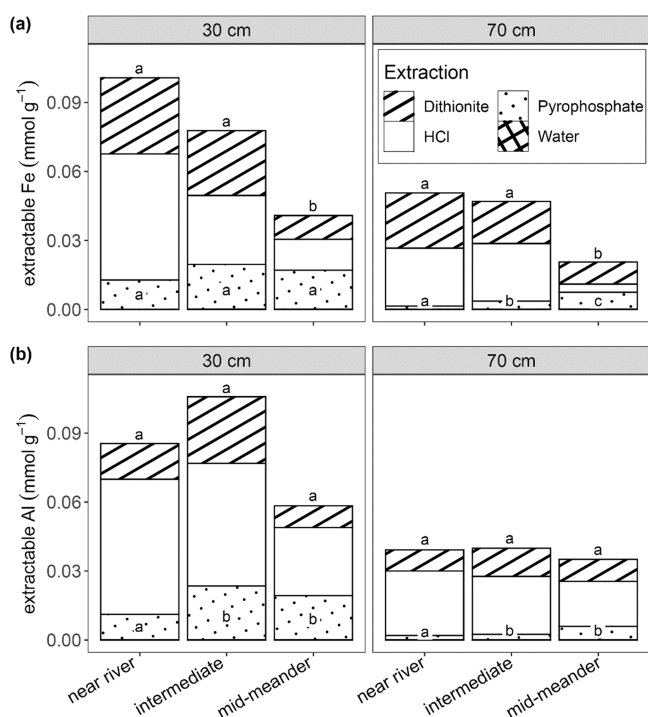


Figure 4. Composition of (a) extractable iron (Fe) and (b) extractable aluminum (Al) in shallow (30 cm) and deep (70 cm) sediment, across the floodplain meander. Extractable pools are denoted by pattern fills. Units for both panels are mmol metal per g sediment. Letter designations are Tukey's honestly significant difference test results ($p < 0.05$) based on differences along the meander in each depth: differences in total extractable Fe and pyrophosphate-extractable Fe in panel (a), and differences in total extractable Al and pyrophosphate-extractable Al in panel (b). Mean and standard errors are reported in Table S4 for extractable Fe and Table S5 for extractable Al.

meander center, potentially due to loss of Fe oxides minerals via reductive dissolution ("gleying"). In deep sediments, while the pyrophosphate-extractable Al/Fe ratio decreased toward the meander center, the HCl-extractable Al/Fe ratio increased (Figure S3). This result suggests that, at least in deep sediments, short-range order phases are relatively enriched in Fe, while relatively ordered phases are enriched in Al. Amorphous Al oxides have been shown to strongly sorb and thus protect OC,⁶⁸ particularly in redox-active systems.³² Notably, similar shifts from Fe- in oxic domains to Al-protected OC in anoxic domains have been observed in soils experiencing seasonal flooding^{21,34,35} or contrasting precipitation.⁶⁹

Together, while the overall abundance of reactive Fe and Al phases declined toward the more redox-active meander center, we observed a relative increase in the abundance of water-extractable and pyrophosphate-extractable Fe and Al phases in comparison to the near river position. The greater abundance of such dissolved and short-range order Fe phases is likely a product of the more intense redox cycling that occurs here, which prevents formation of more crystalline phases due to repeated cycles of Fe reduction and subsequent export.^{70,71} The concurrent decline in extractable Fe relative to Al suggests a redox-induced preferential loss of Fe phases and effective protection of remaining C within associations with Al phases. These results provide strong evidence for the role of redox dynamics in shaping the composition of mineral-organic

associations in the sediments. However, it is important to acknowledge that there may have been differences in their original composition of mineral-organic associations upon deposition. While it was beyond the scope of this study, the question to what extent the composition of mineral-organic associations in floodplain sediment is a function their original composition upon deposition versus subsequent biogeochemical transformations warrants further research.

Imprints of Mineral versus Anaerobic Protection on Organic Matter Composition. To assess variations in OC composition along the floodplain meander, we used high-resolution mass spectrometry (FT-ICR-MS) on our sequential extractions. Our results confirm our hypothesis that variable mineral characteristics and contrasting redox environments impact the composition of relatively accessible WEOC and less accessible MAOC pools. Across both depths, WEOC had significantly lower NOSC values and significantly higher molecular weights compared to other extracts (Figure 5a and b, $p < 0.05$), suggesting that this relatively accessible OC has undergone less depolymerization and oxidation than OC protected within associations to minerals, potentially due to kinetic and thermodynamic constraints on its decomposition.^{18,19} With each extraction step, the NOSC of extracted OC consistently increased while molecular weight decreased (Figure 5a and b, $p < 0.05$). This result indicates that MAOC becomes more oxidized and depolymerized the less extractable (and presumably more ordered) the Fe and Al phases become. WEOC contains relatively more lipid-, amino sugar-, and protein-like compounds compared to MAOC (Figure 5c), suggesting that WEOC is more microbial in nature (i.e., more microbial metabolites and extracellular enzymes).^{72,73} With each subsequent extraction step, the coextracted OC becomes relatively more enriched in condensed hydrocarbon-, lignin-, and tannin-like compounds (Figure 5c), suggesting that plant-derived aromatic compounds accumulate in association with increasingly stable Fe and Al oxides. These observations are consistent with evidence that low-molecular weight, oxidized, aromatic compounds preferentially bind to positively charged surfaces of Fe and Al oxides.^{43,45,74} While our results are supported in other studies, it is important to note that extraction conditions may alter SOM and thus impact downstream FT-ICR-MS analyses.⁷⁵

We also found that the chemical composition of OC changed with sediment depth, specifically in the pyrophosphate-extractable pool that accounted for the largest portion of MAOC (Figure 2b). As discussed above, OC co-extracted by pyrophosphate represents metal-organic complexes, although it possibly also includes a significant fraction of base-extractable OM⁵⁷ or nanocrystalline phases.⁶⁷ Compared to shallow sediments, pyrophosphate-extractable OC in deep sediments consistently had lower NOSC (Figure 5b) and aromaticity (double-bond equivalence, DBE; aromaticity index, AI, Figure S4), relatively more lipid-, amino sugar-, and protein-like compounds (Figure 5c), and a higher proportion of N-, P-, and S-containing compounds (Figure S5). Furthermore, sediment C/N ratios also decreased with depth, especially toward the meander center (Figure S6), which can be indicative of greater microbial processing.^{45,76} Together, these observations suggest that OC associated with amorphous metal complexes in deep sediments may have a stronger microbial signature compared to shallow sediments.

While lower NOSC values at depth possibly indicate that anaerobic protection (i.e., kinetic and thermodynamic

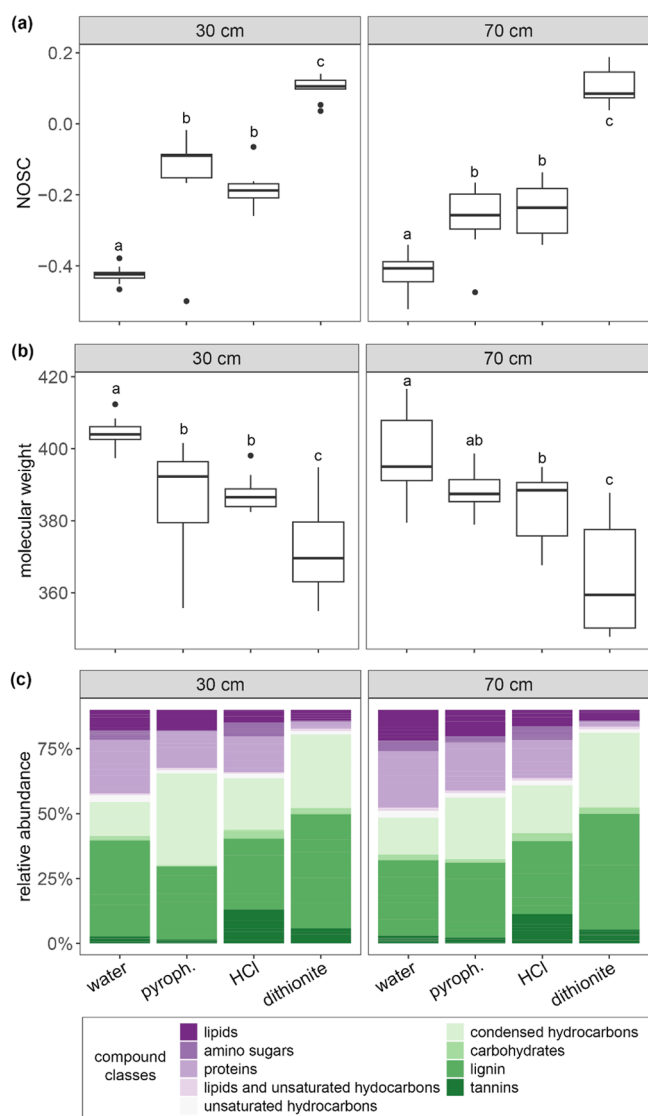


Figure 5. Composition of extracted organic matter in shallow (30 cm) and deep (70 cm) sediment: (a) nominal oxidation state of carbon (NOSC), (b) molecular weight, and (c) compound classes by extractant (i.e., water, pyrophosphate, HCl, and dithionite). Letter designations are Tukey's honestly significant difference test results ($p < 0.05$) based on differences across extractions in each depth.

constraints) is a stronger control on OC storage in deeper sediments than in shallow sediments, we did not find evidence that anaerobic protection becomes stronger in the more reducing meander center. Rather than decline toward the more reduced meander center, NOSC of pyrophosphate-extractable OC increased toward the center of the meander (Figure S7), albeit not significantly, suggesting a limited role for anaerobic protection in explaining the observed OC accumulation in this pool (Figure 2b). Because, as discussed above, MAOC (Figure 2) and pyrophosphate-extractable metals (Figure 4) increased toward the meander center, these results indicate that mineral protection via metal–organic complexes, rather than solely anaerobic protection, drives OC accumulation patterns along this floodplain meander transect. In sum, these results suggest that mineral protection of OC in metal–organic complexes imprints on its composition in redox-dynamic floodplain sediments.

Dynamic Nature of Mineral–Organic Associations across Floodplain. Storage of OC within floodplain sediments is often attributed to constraints on microbial metabolism under reducing conditions, with oxygen limitations restricting both oxidative depolymerization and aerobic respiration, thus protecting OC anaerobically. However, redox transitions experienced by hydrodynamic floodplain environments also impact mineral transformations, with relatively unknown consequences on the importance of mineral–organic associations in OC storage. Our detailed investigation of defined redox gradients emerging from textural variations and depth offers important insights on the quantitative importance and chemical nature of mineral–organic associations within floodplain sediments.

Overall, we found a strong correlation between total sediment C and different proxies for MAOC (isolated by density fractionation and sequential extraction), suggesting that mineral–organic associations contribute to OC storage within the sediments of this mountainous floodplain. The fact that extractable Fe and Al, rather than clay content, predicted OC content across the meander points to a critical role of Fe and Al oxides in the formation of mineral–organic associations within these floodplain sediments. While the importance of Fe and Al oxides for OC storage in upland soils⁵⁸ and even marine sediments⁷⁷ has long been established, our results support the notion that mineral protection, in addition to anaerobic protection, is also critical for OC storage in floodplain sediments with high mineral content. This observations contrasts with floodplains and wetland systems dominated by organic soils, such as peat-dominated wetlands, where OC storage may be a consequence of anaerobic conditions,⁷⁸ low pH,⁴² or the inhibiting effects of phenolics.⁷⁹

Interestingly, the chemical nature of MAOC showed no significant spatial variations across the meander but rather varied with crystallinity of the Fe and Al phases: with increasing crystallinity, we saw greater contributions of oxidized, low-molecular weight, aromatic compounds (Figure 5). These results contrast with longer-term studies that examine the turnover of OC,^{44,45} perhaps because of loss of more reactive short-range order phases in redox oscillating soils over longer time scales. In contrast, the absolute amount of MAOC showed significant spatial variations (Figure 2). MAOC concentrations were greatest in the relatively oxic surface horizons, coinciding with greater contents of less extractable, and presumably more ordered, Fe and Al oxides (Figure 4). In deeper sediments, despite the lower amounts of MAOC, the relative contribution of MAOC to total sediment OC increased toward the more reducing meander center (Figure 2a). This increase in the apparent importance of mineral protection (relative to anaerobic protection, as discussed above) in the meander center coincided with increases in the OC pool bound in amorphous metal–organic complexes. This result suggests that while the overall pool of extractable oxides declines (Figure 4), a greater portion of the OC is sequestered in short-range order or amorphous metal–organic complexes (Figure 2b). Given the concurrent increases in deep sediment clay content (Table 1) and pyrophosphate-extractable metals (Figure 4), it is possible that nanoparticulate Fe/Al oxide phases or phyllosilicates may also play a role in OC protection, although we did not directly measure phyllosilicate content.

Examination of the relative importance of mineral and anaerobic protection along redox gradients within the

floodplain sediments yielded unexpected results. We initially hypothesized anaerobic protection to be most dominant in the more reduced meander sediments,¹⁹ resulting in greater OC concentrations. Instead, sediment OC concentrations were significantly lower in the fine-grained, reduced center of the meander and increased in the more oxic sediments near the river (Figure 2a). If burial and subsequent anaerobic protection on floodplain C solely explained the C patterns along the floodplain meander, we would expect more relatively undegraded particulate or reduced OC to accumulate in the reduced meander center. However, in the deep sediments, we found that POC declined toward the more reduced portion of the meander, while water-extractable OC and NOSC remained relatively constant. Conversely, we found that the relative contribution of MAOC increased toward the more reduced center of the meander (Figure 2). Together, these results suggest that the relative importance of mineral protection increased toward the reduced meander center, while that of anaerobic protection remained steady or diminished. While our study was qualitative in nature, future studies should consider quantifying the contribution of mineral versus anaerobic protection to floodplain sediment OC storage.

The prevalence of metal–organic complexes in the meander center could be attributed to more dramatic and persistent reducing conditions with seasonal flooding compared to sediments near the river (Table S1). Reducing conditions prompt reductive Fe oxide dissolution and leaching of dissolved Fe from the system (i.e., gleying),^{31,38} consistent with the loss of extractable Fe (and Al) phases observed here. While the sediments become reoxygenated every season, the oxidation–reduction cycles may be dramatic enough to prevent formation of crystalline Fe oxides as has been observed in humid tropical soils that experience redox heterogeneity due to frequent rainfall.^{38,80} Instead, repeated oxidation–reduction cycles in response to flooding may only allow for short-range order Fe (and Al) phases to form and persist.^{70,71} Because those short-range order Fe phases are likely dissolved and reprecipitated during each oxidation–reduction cycles, their presence may indicate that MAOC within such metal–organic complexes may not be as protected as the MAOC bound to crystalline Fe and Al oxides within the more oxic meander sediments. It is also possible that redox cycling increases the formation of reactive oxygen species, which can also stimulate organic matter decomposition,⁸¹ and we suggest that further studies of carbon cycling in dynamic floodplains should incorporate this mechanism.

Environmental Implications. Together, our results support the notion that mineral–organic associations are more important for OC storage in redox active floodplain environments than previously recognized and may act in combination with anaerobic protection to limit OC export through microbial decomposition (as CO₂) and leaching (as DOC). Our results demonstrate that, depending on the redox regime, the quantitative importance of mineral protection as well as the chemical nature of mineral–organic associations controlling their stability vary across floodplain sediments. High elevation floodplains like that of the East River, CO, experience dynamic redox transitions with seasonal flooding events. The magnitude and timing of these seasonal flooding cycles is expected to change due to greater variability in snowpack,⁸² declines in snowpack depth,^{7,83} or slower snowmelt rates,⁸⁴ which will directly impact the redox regime in the floodplains. Combined, our results suggest that such

changes will not only directly affect anaerobic protection but may also have immediate consequences for protection in redox-sensitive mineral–organic associations, warranting further exploration of potential impacts on OC storage within and export from floodplain sediments.

■ ASSOCIATED CONTENT

Data Availability Statement

The data used in this work will be available online at the ESS-DIVE database (<https://ess-dive.lbl.gov/>). Analysis code will be available on <https://github.com/camganderson>.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsearthspacechem.3c00037>.

East River discharge data; correlations between total sediment C and clay and extractable Ca; extractable Al/Fe ratios; organic matter compositional differences; C/N ratios of mineral-associated organic matter; water table depth, soil moisture, and soil redox potential across the transect and over time; detailed sampling location information; and means and standard errors for extractable OC, Fe, and Al (PDF)

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Notes

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