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Influence of relict milldams on riparian sediment biogeochemistry

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Abstract

Purpose Riparian zones are important modifiers of nutrient flux between terrestrial and aquatic ecosystems. However, dams alter riparian zones—trapping fine-grained, organic matter-rich sediment and creating poorly mixed, low oxygen conditions—thereby affecting sediment biogeochemistry in poorly understood ways.

Methods We characterized the impact of two relict US mid-Atlantic milldams (one from a primarily agricultural watershed and one from a mixed land use/urban watershed) on spatial patterns of bioavailable element concentrations (Mehlich-3 extractable P, K, Ca, Mg, Mn, Zn, Cu, Fe, B, S, and Na) in sediments upstream and downstream of milldams, with depth, and along transects running parallel and perpendicular to the stream.

Results Element concentrations were not clearly correlated with grain size or organic matter content and, although generally higher, were not significantly more concentrated in upstream riparian sediments when similar (shallow, variably saturated) depths were compared. Pronounced differences were observed: upstream of milldams, sediment concentrations of Ca and Mg were highest in variably saturated shallow sediments, while Fe and Mn were highest in deeper, continuously saturated, low-oxygen sediments. Additionally, data was significantly different by milldam site, a result of differences in land-use histories (e.g., road salt and fertilizer application/runoff) and dominant bedrock geology.

Conclusion Overall, results highlight the combined importance of milldams (and associated influences on groundwater hydrology and sediment redox conditions) and external drivers (other land-use legacies and bedrock geology) in influencing spatial patterns of bioavailable elements in riparian sediments.

Keywords Milldam · Riparian · Sediment · Biogeochemistry

1 Introduction

Sediment and sediment-bound nutrients and contaminants pose particularly serious risks to water quality and aquatic organisms (US EPA 2019), including reduction of light penetration and food resources (Henley et al. 2000); eutrophication and subsequent hypoxia (Yang et al. 2008); contamination of potentially toxic and harmful metals (Rothenberger et al. 2017); and degradation of drinking water quality (Dodds and Whiles 2004). As interfaces between terrestrial and aquatic ecosystems, riparian zones can however, mitigate these deleterious effects through sediment and pollution trapping and nutrient processing by a variety of physical, chemical, and biological processes (Lowrance et al. 1997). Thus, characterizing sediment and sediment-bound elements stored in riparian zones—and the natural and anthropogenic actives that alter riparian biogeochemical conditions—is critical for watershed pollution assessment and mitigation.

Anthropogenic alterations of fluvial landscapes, such as dams, can have profound impacts on riparian ecosystem structure and function, and increasing interest has been placed on biogeochemical characterization of legacy sediments, defined as sediment deposits resulting from past anthropogenic activities (James 2013), in riparian zones (Knox 1972;

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Jacobson and Coleman 1986; Niemitz et al. 2013; Fajer and Rzetala 2018; Lutgen et al. 2020; Sullivan et al. 2022). In particular, milldams constructed in prior centuries, such as those found across the eastern USA and Europe, dramatically altered the geomorphology, hydrology, and biogeochemistry of valley bottoms (Groffman et al. 2003; Walter and Merritts 2008; Wegmann et al. 2012; Brown et al. 2018; Brykała and Podgórski 2020; Pizzuto et al. 2022). Concurrently, erosion of upland forests due to land clearance and poor agricultural practices resulted in elevated downstream sediment transport (Meade and Trimble 1974; Costa 1975). Thus, following milldam construction, legacy sediments rapidly accumulated upstream within millponds creating deep, wide riparian terraces (Merritts et al. 2011). Given the prevalence of these relict impoundments across the eastern USA and Europe (Walter and Merritts 2008; Brown et al. 2018) and the need for mitigating downstream transport of legacy sediments upon dam breaching/removal (Wohl 2019; Cashman et al. 2021), improved understanding of the biogeochemistry of riparian sediments upstream of intact relict milldams is required (sensu Yorke et al. 1985; Ashley et al. 2006).

Hydraulic conditions created by the milldams, including reduced stream flow and increased water residence time upstream of the obstructions, result in greater deposition of fine-grained sediments within millponds (Walter and Merritts 2008). In the Piedmont across the Eastern USA especially, legacy sediments are composed predominantly of clay and silt interspersed with buried organic material above existing and breached milldams (Merritts et al. 2011; Wegmann et al. 2012). Sediment texture, especially surface area, and organic matter content strongly influence sediment bound element concentrations, with higher surface area clays and silts serving as important sorption surfaces (e.g., Malcolm and Kennedy 1970; Ye et al. 2019; Lutgen et al. 2020). Thus, dam modification of sediments could be one key control on sediment biogeochemistry (Fig. 1A).

In addition, milldams alter riparian hydrologic and biogeochemical regimes by raising stream and groundwater levels upstream of the dam (Hripto et al. 2022; Sherman et al.2022). Shallow sediments ($\leq$ ~1 m) in riparian areas upstream of milldams undergo moisture and redox fluctuations due to groundwater level variations, while deeper sediments (below ~0.5–1 m) are continuously saturated (Sherman et al. 2022). Upstream groundwaters are therefore mostly hydrologically stagnant or poorly mixed causing hypoxic or anoxic conditions in these sediments, while downstream sediments are more variably saturated and oxic (Inamdar et al. 2022; Sherman et al. 2022). Contrasting hydrologic and redox regimes could have differential implications for sediment-bound elements upstream and downstream of the dams as well as vertically in the upstream soil profile (Fig. 1A). Redox-sensitive elements (e.g., Fe and Mn) could undergo reductive dissolution under anoxic conditions, thereby increasing their mobility (Sun et al. 2018; Yuan et al. 2021). Similar hydrologic and redox conditions are created by beaver dams (Westbrook et al. 2006; Hill and Duval 2009; Janzen and Westbrook 2011; Wang et al. 2018; Smith et al. 2020), which alter the concentrations and processing of bioavailable elements (especially N; Hill and Duval 2009; Wang et al. 2018). Indeed, the chemical conditions created by beaver systems have been observed to increase leaching of heavy metals and major cations (Fe, Mn, Ca, and Mg; Brazier et al. 2021 and citations within).

Chemistry of riparian sediments could also be affected by historic and contemporary, local and watershed-wide, agricultural, industrial, and other land-use activities (Fig. 1A). These could include direct inputs of metals and nutrients from historic milling activities and/or contemporary agricultural and urban sources (e.g., Niemitz et al. 2013). Additionally, increasing attention is being paid to road salt inputs to riparian zones, as salinization could alter chemical mobilization (e.g., desorption) of sediment-bound elements and nutrients (e.g., Kaushal et al. 2005; Wilhelm et al. 2019; Hintz et al. 2022).

Beyond external influences, riparian sediment biogeochemistry is also shaped by the local and regional geologic and lithologic conditions that influence the weathering and release of elements (Fig. 1A; Bain et al. 2012; Niemitz et al. 2013). Dense forest vegetation, often present in riparian zones surrounding milldams, may additionally impact sediment biogeochemistry directly through plant uptake and decomposition and also indirectly through microbial stimulation (Rule 1999; Hefting et al. 2005; Ye et al. 2019).

Given the various factors and conditions that regulate the chemistry and fate of sediment-bound elements in riparian zones, the distribution of element concentrations in the riparian sediment profile could be highly variable and complex. The overarching goal of this study was to assess this variability and investigate the spatial distribution of bioavailable elements in riparian sediments impacted by milldams. We focused on the bioavailability of major cationic species that serve as both nutrients (macro = P, K; micro = Ca, Mg, Mn, Zn, Cu, Fe, B, S, Na) and also contaminants at concentrations that impair soil function and lead to plant and animal mortality (He et al. 2005). In addition to affecting in situ ecological functioning, these elements may pose water quality threats to streams and coastal waters if chemically mobilized and/or physically eroded following dam removal/breaching (Fleming et al. 2019; Jiang et al. 2020). We addressed the following key questions: (1) How do bioavailable element concentrations in riparian sediments differ upstream and downstream of the milldams? (2) How do bioavailable elements vary transversely, longitudinally, and with depth in sediments upstream of milldams? (3) What role do sediment texture, organic matter content, hydrology driven redox conditions, and watershed land use and geology play

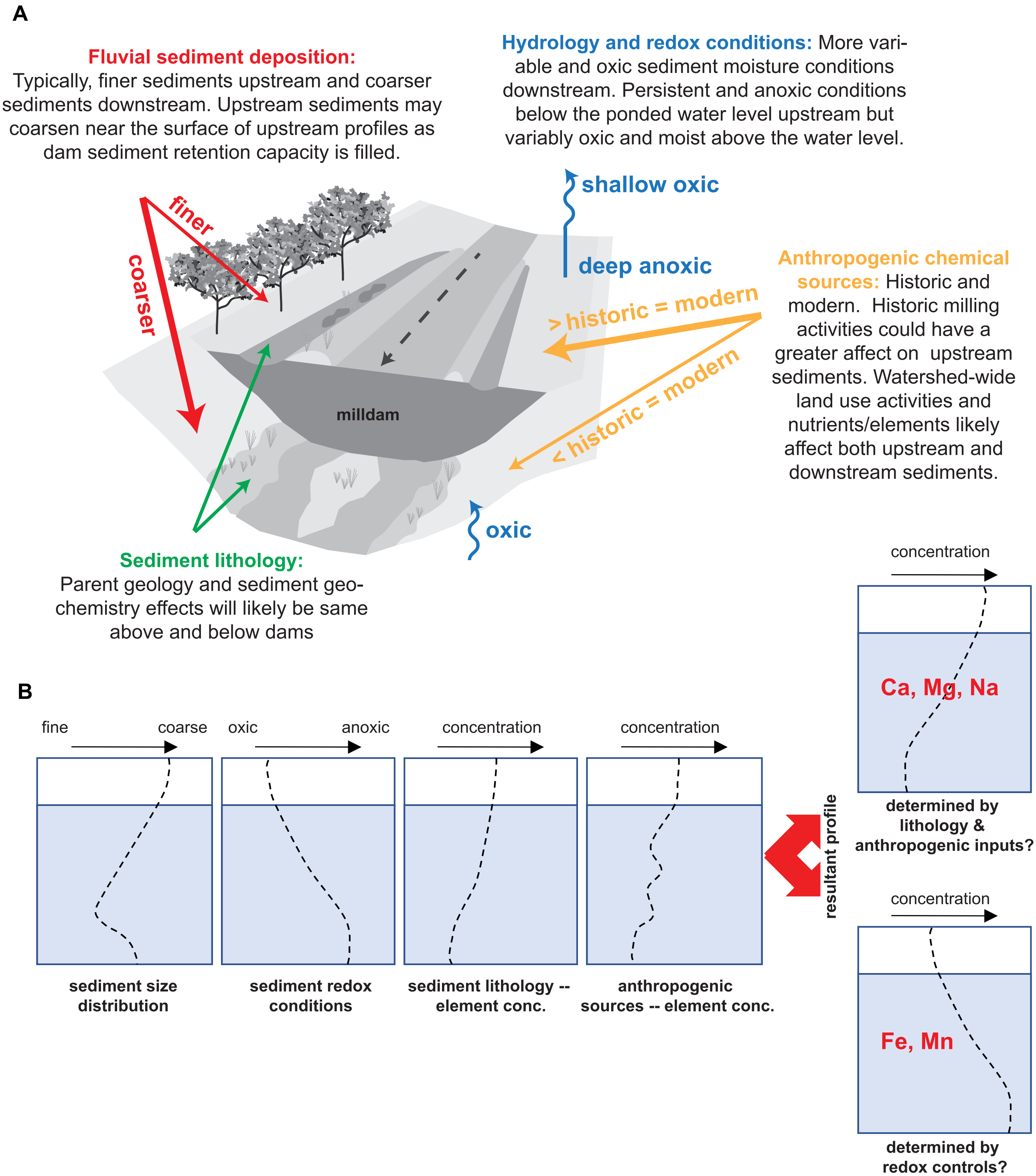


Fig. 1 **A** Conceptual model highlighting the various factors that could affect riparian sediment chemistry upstream and downstream of milldams. **B** Hypothesized profiles of various controls with sediment depth upstream of the dam and the final potential elemental concentration profile shaped by dominant influence of either lithology and anthropogenic inputs or redox conditions

in shaping element concentrations in riparian sediments? Overall, we hypothesized that while multiple processes influence sediment concentrations in riparian zones affected by milldams, individual processes may dominate and thus dictate the distribution of specific elements (Fig. 1B for conceptualization). To address these questions, we measured bioavailable element concentrations (Mehlich-3 extractable P, K, Ca, Mg, Mn, Zn, Cu, Fe, B, S, and Na) at various sediment depths in riparian areas upstream and downstream of two relict milldams in the US mid-Atlantic.

2 Methods

2.1 Sites and sampling

Roller milldam, which is 2.4 m tall, was built along Chiques Creek, Manheim, PA, in the 1700s but was repaired/rebuilt several times until the 1930s (original dam heights and repair dates are unknown; Fig. 2A, B). Above Roller milldam, sediments, which are predominately silty clay, extend > 3 m in depth adjacent to the stream. Sediment at 3 m was ^{14}C dated at ~600 years (Peck et al. 2022). The Chiques Creek watershed, which drains into the Susquehanna River and is part of the larger Chesapeake Bay basin, is 128 km^2 above the dam and the bedrock is mostly dolomite/limestone (rich in Ca and Mg) and shale. The basin is dominated by the Bedington, Hagerstown, and Ungers soil series which has a mixed clay minerology of illite, kaolinite, vermiculite, and montmorillonite (USDA Web Soil Survey 2021). Land use is predominately agriculture (54%), and 22% of land is forested and 20% is developed (USGS National Landcover Database 2011). The Chiques Creek Watershed is considered impaired, being highly impacted by excess suspended sediment and nutrients, and altered hydrology (e.g., dams, culverts, and channelization; Susquehanna River Basin Commission).

Cooch milldam is 4.0 m tall and was built in 1792 along the Christina River, New Castle County, DE (Fig. 2A, C). Above the Cooch milldam, sediments are predominately clay loam, > 3 m in depth adjacent to the stream, and ~230–250 years old at 3 m depth (Peck et al. 2022). The Christina River watershed, which drains into the Delaware River and is part of the Delaware Bay basin, is 51 km^2 upstream of the dam. The basin is dominated by gabbro (rich in Fe, Ca, and Mg) and gneiss (rich in K and Na). Soil types are mostly Hatboro-Codorus, Keyport, and Mattapex series, with a dominant kaolinite minerology (USDA Web Soil Survey). The Christina River Basin, which is part of the USGS Critical Zone Observatory program, is 47% urban/developed, 30% forested, and 23% agricultural land (USGS Land Cover Database 2011). The Cooch site is located downstream of

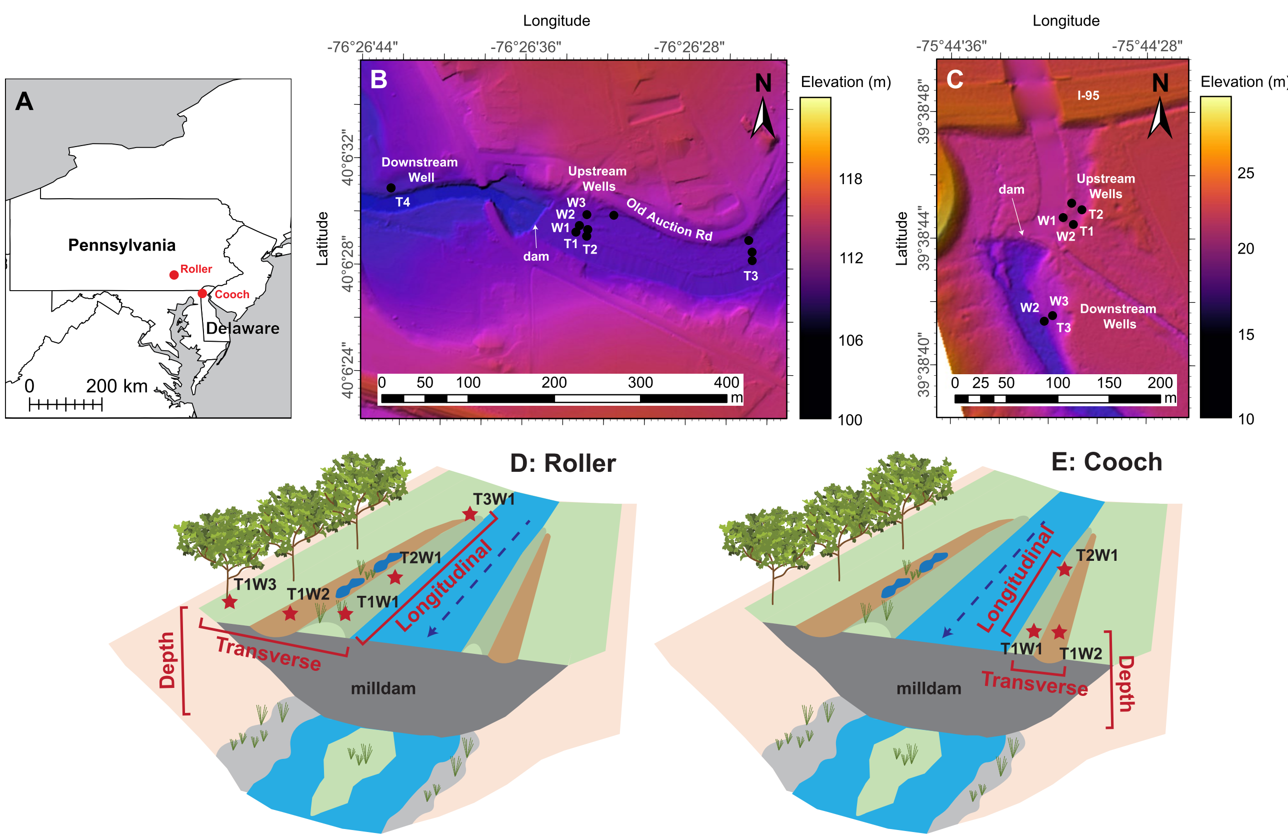


Fig. 2 **A** Portion of Eastern USA with Roller milldam in Pennsylvania and Cooch milldam in Delaware labeled. **B**–**C** Digital elevation models for the Roller and Cooch milldam sites and associated groundwater well locations. **D**–**E** Site layout for Roller and Cooch

a major interstate highway (I95), from which runoff rich in deicing road salt enters the riparian area and river following winter storms (Inamdar et al. 2022; Sherman et al. 2022).

Chiques Creek and Christina River are comparably temperate in climate, with similar mean annual air temperatures (15.5 and 12.2 °C, respectively) and precipitation amounts (104 and 114 cm, respectively, with ~50 cm of snowfall; NOAA 2021). Both riparian areas are forested with dominant tree species including sugar maple (*Acer saccharum*), black walnut (*Juglans nigra*), and American sycamore (*Platanus occidentalis*). Both Roller and Cooch milldams are unbreached. Roller and Cooch milldams are in the Chesapeake (Roller) and Delaware Bay (Cooch) drainages and thus provide valuable datums and insights for monitoring and managing two important US east coast estuaries.

At Roller and Cooch, groundwater wells (5-cm diameter screened PVC pipes) were installed starting in summer 2019 using a hand-operated auger to a depth of refusal, which varied from 2 to 4 m and 1 m in upstream and downstream sediments, respectively. Groundwater flow regimes and chemistry at these wells are not the focus of this study (see Inamdar et al. 2022; Sherman et al. 2022) but groundwater levels (assessed using U20L HOBO sensors that have measured groundwater level every 30 min). During augering, distinct soil horizons/layers were not observed, likely a result of poorly drained, hypoxic/anoxic sediment conditions, which would have prevented full formation of these horizons in the time since sediment accumulation behind the dams. While it is possible that some distortion of the soil layers could have occurred during auguring, we did not visually observe indication of smearing. Sediment samples were collected at ~0.3-m depth intervals in ziplock bags. Seven and five sediment cores were retrieved from Roller and Cooch, respectively (uneven sampling scheme was due to differences in the number of groundwater wells across the riparian widths; Fig. 2B, C; Table S1). Upstream of the Roller dam, three transects (T1–T3) were installed perpendicular to the creek. At T1, which was closest to the dam, sediment cores were recovered from three wells (W1–W3), with T1W1 collected on the berm closest to the creek, T1W2 in the swale/depression, and T1W3 at the riparian-upland edge. At T2, one core was collected on the berm (T2W1) and one in the swale (T2W3). At T3, which was furthest from the dam, one core on the berm was retrieved (T3W1). At Cooch, sediment cores were collected for two transects, which had two wells each (Fig. 2C). W1s were located on the berm and W2s were in the swale (Fig. 2B and C). As a comparison with the upstream wells, one and two wells were installed downstream of Roller and Cooch milldams, respectively. At Cooch, sediment was only collected from one downstream well for analysis (T3W3). Downstream sediments were coarse-grained and frequently dry, so no additional wells were installed.

2.2 Sample analysis

Bioavailable element concentrations were measured by the University of Delaware (UD) Soil Testing Program by ICP-OES following extraction by the Mehlich-3 (M3) method, which was performed using ammonium fluoride, EDTA, ammonium nitrate, acetic acid, and nitric acid (Mehlich 1984; Sims et al. 2002). This method was developed for determining bioavailability of several plant macro- and micro-nutrients and is specifically optimized for acidic Utisols and calcareous soils of the US mid-Atlantic (Sims et al. 2002; Wang et al. 2004). Elements analyzed included P, K, Ca, Mg, Mn, Zn, Cu, Fe, B, S, and Na and will be denoted as M3 (all elements are included in analyses though we focus discussion on those that displayed significant spatial trends). While no extraction method is optimized for all elements, the M3 method is considered appropriate for estimating a wide range of soils and has been found to successfully extract a wide array of available soil nutrients when compared to other chemical and nonchemical methods (Ziadi and Tran 2008; see Table S2 for list of studies that have reported significant correlations between M3 and other extraction methods).

Twelve sediment samples from W1–W3 along Roller T1 were additionally assessed for total sorbed element concentrations at the UD Soil Testing Program by ICP-OES following microwave digestion (using nitric and hydrochloric acids; EPA Method 3051; EPA 1986).

2.3 Groundwater hydrology, sediment particle size, and organic matter contents

Groundwater level variations and associated dynamics (measured every 30 min using U20L HOBO sensors) were previously described by Sherman et al. (2022). Sherman et al. (2022) found that berm wells (W1 wells), which were closest to the rivers, groundwater levels were deepest from the sediment surface due to the berm topography and displayed limited mixing with stream water (based on comparison of stream and groundwater specific conductance and tracer elements) even during high discharge events. Groundwater levels were closer to or above the soil surface in the swale wells (W2) and displayed greater chemical variations during high discharge events. During storms, water from overland flow and rising stream levels flood the swales; these areas are covered in standing water during wet periods of the year (see the conceptual model in Sherman et al. 2022). At Roller, groundwater levels for the upland-edge well T1W3 were deeper than the swale and berm wells, and subject to greater variation and mixing. Groundwater was rarely observed in the downstream wells at both dams. Further, dissolved oxygen concentrations measured in groundwater wells were significantly lower upstream (typically ≤ 1 mg

L^{-1}) than downstream (Inamdar et al. 2022). At Roller and Cooch, groundwater levels in upstream wells were binned into depths every 0.1 m and cumulative percent time was determined for each binned depth; depths above the level saturated 100% of the time (≤ 1 m) were considered variably saturated and depths below the 100% saturation level were considered consistently saturated (Peck et al. 2022).

Particle size—sand, silt, and clay contents—were measured using the standard hydrometer method (Ashworth et al. 2001) for riparian sediments upstream and downstream of Roller and Cooch milldams were previously described by Peck et al. (2022). Sand, silt, and clay contents were consistent with depth, with silt and clay ranging from 48 to 100% upstream of the milldams. While fine sediment fractions have higher surface areas than coarse, which result in greater capacity for nutrient and metal sorption (e.g., Malcolm and Kennedy 1970; Ye et al. 2019; Lutgen et al. 2020), this relationship may not be linear depending on the dominant clay minerology (Horowitz and Elrick 1987). We did not specifically measure surface area, and instead relied on particle size, though future studies should assess the relationship between particle size and surface area in these sediments.

Organic matter contents measured by loss on ignition (Schulte and Hoskins 1995) for riparian sediments upstream and downstream of Roller and Cooch milldams were also previously described by Peck et al. (2022). Organic matter contents, which were similar for the two milldam sites, ranged from 0.7 to 9.8% in upstream sediments.

2.4 Data and statistical analysis

All statistical analyses were performed in MATLAB (R2022a).

To assess reproducibility, percent standard deviations of M3 element concentrations were calculated on replicates from three Roller sediment profiles and two Cooch sediment profiles ($n = 2$–3). Coefficients of variance were calculated for each sediment element concentration across all wells and depths to assess spread in the data around the mean concentration.

Clay and silt percentages, sediment organic matter contents, and sediment element concentrations were compared between upstream and downstream sites at Roller and Cooch using box plots and Kruskal–Wallis H tests ($\alpha = 0.05$). Statistical comparisons with downstream sediments were made using upstream depths shallower than the 100% groundwater depth (i.e., depths that were variably saturated; Table S1 for depths) as hydrology and redox conditions are most comparable. To further compare upstream and downstream elements at Roller and Cooch, depth-integrated element masses (g m^{-2}) were determined by calculating mean concentrations for each 1-m depth increment and summing across all sediment depths.

Correlation analyses between clay and silt percentages, organic matter contents, and element concentrations were performed using Spearman's rank ($\alpha = 0.05$). Linear regressions were fit between M3 bioavailable element concentrations and total sorbed element concentrations for sediment cores from the three wells (W1–W3) along Roller (RM) transect 1 (T1) to evaluate the influence of milldams on different forms (especially Fe).

To assess the influence of unbreached, relict milldams on bioavailable element concentrations in legacy sediments, Kruskal–Wallis H tests ($\alpha = 0.05$) and percent differences in mean concentrations for M3 elements were compared in upstream sediments at Roller and Cooch with those reported by Lutgen et al. (2020) for mid-Atlantic stream banks (~1–4 m height) where most milldams were breached.

Principal component analyses (PCAs) were performed on upstream and downstream sediment samples for all depths from Roller, Cooch, and the two milldams combined to further explore biogeochemical patterns spatially. Methods were similar to PCAs performed by others on legacy sediments (Sullivan et al. 2022) and sediments along dammed reaches (Sun et al. 2018). PCAs were performed for M3 elements and trends were identified through comparison of eigenvectors for each element and the principal component scores for each sediment sample. Upstream sediments were categorized by those that were shallower than the 100% groundwater saturation depth (i.e., variably saturated) and those that were deeper than the 100% groundwater saturation depth (i.e., always saturated).

To visualize transverse (perpendicular to creek) and longitudinal (parallel to the creek) elemental trends with depth, surface plots of sand and silt content, organic matter content, and element concentration were generated using a linear interpolation, similar to those presented by Lu et al. (2022). Box plots and Kruskal–Wallis H tests ($\alpha = 0.05$) between upstream depths above and below the 100% groundwater saturation depth additionally assessed differences between saturation and redox conditions created by the dams.

3 Results

Percent standard deviations of replicate M3 measurements ranged from 0.5 to 107% (median = 18%) and were expectedly highest for elements that had low concentrations (< ~100 mg kg^{-1}; Table S3). Percent standard deviations were lower for elements of interest (medians: Ca = 14%, Mg = 11%, Fe = 14%, Na = 15%), as identified by the PCA (discussed more below), and therefore these measurements support the analyses presented herein. The coefficients of variance ranged from 36 to 151% (Table S4). M3-Mg, -Fe, and -K having the lowest variances (36, 38, and 48%, respectively) and M3-Cu, -P, and -Na having the highest variances (151, 126, and 118%, respectively).

Results of Kruskal–Wallis tests between downstream and upstream sediments were made using upstream sediments from depths shallower than the 100% groundwater saturation depth as hydrology and redox conditions are most comparable (Fig. 3). Downstream sediments were significantly coarser at both Roller ($p=0.01$, $n=53$) and Cooch ($p<0.01$, $n=36$), with sand fractions up to 62 and 84%, respectively. Downstream sediment organic matter contents were lower than for upstream sediments, significantly so at the Cooch site ($p<0.01$, $n=36$). At Roller, M3 element concentrations were similar upstream and downstream except for M3-Mg, which was significantly more concentrated in downstream sediments ($n=19$, $p<0.01$; Fig. 3). At Cooch, M3-K, -Mn, -Fe, and -Na were significantly greater in upstream sediments ($n=21$, $p\leq0.01$; Fig. 3). Most strikingly, median M3-Na concentrations were ~10× greater in upstream sediments at Cooch compared to downstream. On a depth-integrated, per-area basis (units = g m^{-2}), masses of all elements were greater upstream than down at both Roller and Cooch (Table S4).

Based on Spearman's rank correlation (Table S5), no elements correlated significantly with clay and silt content in riparian sediments above the milldam ($n=79$, $p\geq0.05$). A few elements were significantly correlated with organic matter content (M3-P, Mn, Zn, Cu; $n=79$; $p\leq0.01$). Correlations among bioavailable elements revealed a number of significant relationships between element pairs, with M3-Ca and -Mg most highly correlated ($n=79$; rho = 0.89; $p<0.001$).

Compared to M3 element concentrations reported for mid-Atlantic legacy sediments where most milldams were breached (Lutgen et al. 2020), M3 elements were significantly more concentrated in sediments upstream of Roller and Cooch milldams ($n=146$; $p\leq0.01$) with the exceptions of M3-Cu and -S ($n=146$; $p\geq0.1$). Mean upstream element concentrations at Roller and Cooch were 9–350% greater than those reported by Lutgen et al. (2020), with M3-Ca (350%) and M3-Fe (120%) having the greatest percent differences (Table S4).

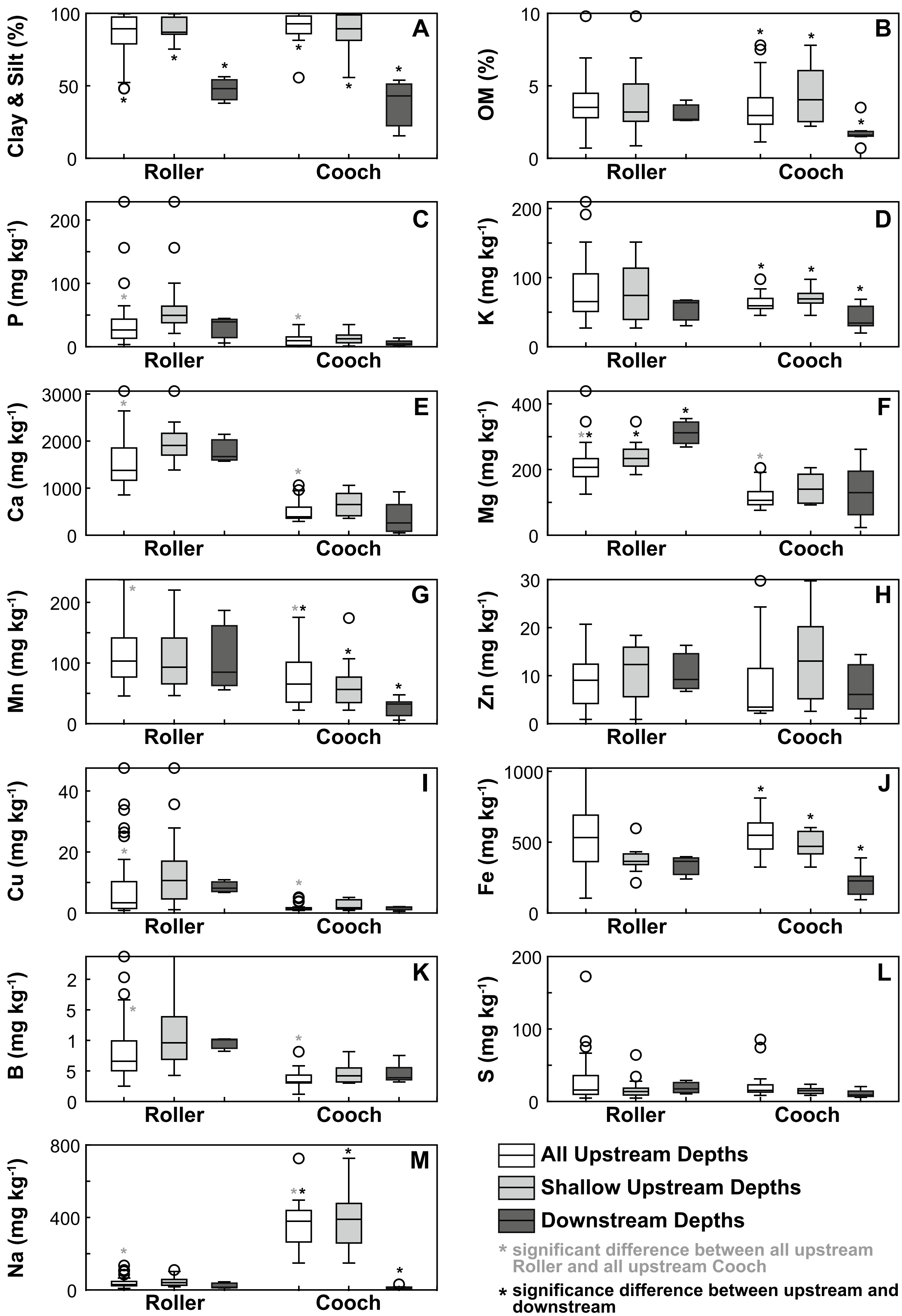
Results of the PCA on M3 elements revealed that the first two principal components explained 97 and 90% of variability in all M3 elements at Roller and Cooch, respectively (Fig. 4A, B). At both milldams, principal component 1 displayed most variability in M3-Ca, while M3-Mg and -Fe additionally had coefficients ≥ |0.1|. M3-Na had the second largest coefficient in the first principal component for the Cooch site. For individual milldam PCAs, sediment M3 element concentrations displayed a distinct separation between saturated (depths below 100% saturation) and variably saturated sediments (above the 100% saturation depth) with some overlap. Downstream sediments (primarily unsaturated) clustered most closely to shallow, variably saturated upstream sediments, especially at Roller. Upstream sediments were not clustered based on riparian well location for either Roller or Cooch sites. When Roller and Cooch sediments were assessed together (95% of variability explained), sediment M3 concentrations separated out primarily by the milldam site and along the first principal component axis, with Roller sediments occupying the positive quadrants (dominated by high M3-Ca and -Mg) and Cooch sediments clustering along the negative quadrants (dominated by M3-Na and M3-Fe; Fig. 4C).

Of the elements with high (≥ |0.1|) PCA coefficients, M3-Ca and -Mg were significantly greater at Roller; M3-Na was significantly higher at Cooch (df = 79, $p<0.01$); and M3-Fe was not significantly different (df = 79, $p=0.6$). Above both milldams, M3-Ca concentrations were significantly higher in the surficial sediments that were variably saturated (Figs. 3 and 5). Transversely, M3-Ca concentrations were moderately higher in the swales (T1W2 locations) and at the Roller upland well (T1W3). Longitudinally, M3-Ca concentrations were highest at T2W1 at both Roller and Cooch (Fig. 5). M3-Mg displayed similar spatial trends to M3-Ca at Cooch, though at Roller the highest M3-Mg concentration was at the deepest T1W3 depth (Fig. 5). M3-Fe concentrations were significantly highest in fully saturated, deeper sediments (Figs. 3 and 5). At Roller, M3-Fe concentrations were highest in sediments closest to the creek (W1s), with the highest concentrations at the furthest transect (T3W1; Fig. 5). While M3-Fe did not display a distinct transverse trend at Cooch, concentrations increased with distance from the dam (T2W1; Fig. 5), though the depth of T2W1 relative to T1W1 may have contributed to this increasing trend. M3-Na did not display consistent depth trends, and transverse and longitudinal patterns were different between Roller and Cooch (Fig. 5). At Roller, M3-Na concentrations were highest in shallow swale sediments (T1W2) and deep upland sediments (T1W3). Conversely, at Cooch, M3-Na was highest at the site closest to the creek and dam (T1W1), though concentrations were elevated overall. Of elements with lower PCA coefficients (<|0.1|), concentrations for M3-P, -Zn, -Cu, and -B were higher in shallow sediments, while M3-Mn and -S were typically most concentrated at depths below the 100% groundwater saturation depth (Fig. S1; also see Fig. S1 for transverse and longitudinal trends of M3-P, -K, -Mn, -Zn, -Cu, -B, and -S).

M3 element concentrations were generally linearly well correlated with total sorbed element concentrations, important exceptions being Fe and Mn ($n=12$; $p>0.01$; Fig. S2).

4 Discussion

Results indicated that although particle sizes were significantly finer and organic matter medians were higher upstream of both milldams, few bioavailable elements were significantly more concentrated upstream (exceptions being


A
Clay & Silt (%)
B
OM (%)
C
P (mg kg-1)
D
K (mg kg-1)
E
Ca (mg kg-1)
F
Mg (mg kg-1)
G
Mn (mg kg-1)
H
Zn (mg kg-1)
I
Cu (mg kg-1)
J
Fe (mg kg-1)
K
B (mg kg-1)
L
S (mg kg-1)
M
Na (mg kg-1)
Roller
Cooch
All Upstream Depths
Shallow Upstream Depths
Downstream Depths
* significant difference between all upstream Roller and all upstream Cooch
* significance difference between upstream and downstream

◂**Fig. 3** Box plots (box represents first and third quartile, center line indicates medians, whiskers are minimums and maximums, and circles are outliers) of **A** clay and silt contents, **B** organic matter (OM) contents, and **C**–**M** element concentrations for sediments upstream (depths below the 100% groundwater saturation depth are constantly saturated and depths above are variable saturated) and downstream of Roller and Cooch milldams. Asterisks indicate significance ($\alpha = 0.05$) determined by Kruskal–Wallis test

M3-K, -Mn, -Fe, and -Na at Cooch). Thus, neither particle size nor organic matter were dominant controls on concentrations (though this result requires further investigation, as discussed below). However, some elements (e.g., M3-Ca, -Mg, -Fe, and -Na) did display pronounced spatial differences in sediments upstream of both milldams. Depth (fully versus variably saturated sediment) was a strong predictor of element concentrations with M3-Ca and -Mg peaking in shallow sediments that were variably saturated, and M3-Fe expectedly peaked in deeper, continuously saturated, low-oxygen sediments. M3-Na, which has likely been introduced into the riparian zones through road salt runoff at both milldams, was especially concentrated at Cooch, which is located immediately downstream of the high-traffic Interstate 95 (Inamdar et al. 2022; Sherman et al. 2022). Most other M3 elements (M3-P, -K, -Ca, -Mg, -Mn, -Cu, and -B) were higher at Roller likely reflecting the combined influence of limestone-dominated bedrock and fertilizer/manure/sewage runoff from the primarily agricultural watershed. Overall, these results supported our conceptual model (Fig. 1), highlighting the importance of relict milldam-driven groundwater hydrology and redox environment combined with watershed land-use legacies and bedrock geology in affecting the spatial patterns of bioavailable elements in riparian sediments. We elaborate further on these controls in the discussion below.

4.1 Upstream vs downstream sediment biogeochemistry

We expected M3 element concentrations in upstream sediments to significantly exceed those measured downstream given the trends in particle size and organic matter content at Roller and Cooch. Numerous studies indicate that particle size is a strong control on element concentrations in riparian sediments as smaller particle sizes have higher surface area for sorption (e.g.,Malcolm and Kennedy 1970; Ye et al. 2019; Lutgen et al. 2020). Particle sizes were significantly finer upstream of milldams (Fig. 3) due to the deposition/accumulation of legacy sediments under slow velocity flows behind the dams (Merritts et al. 2011), though particles coarsen at shallower depths after millponds have filled to capacity (Lutgen et al. 2020). Relatedly, median organic matter contents were higher in sediments above both milldams (though only significantly at Cooch; Fig. 3) due likely to depositional trapping of organic matter above the dam, increased surface area on the fine-grained sediments, higher algal productivity in the pond-like environment compared to free-flowing water, and reduced decomposition in the anoxic sediment conditions above the dam (Pinay et al. 1992; Berhe et al. 2012). Combined with its relationship with particle size, organic matter also tends to correlate with bioavailability of micro- and macro-nutrients as decay of organic matter is a direct input (Rule 1999; Ye et al. 2019).

Although bioavailable element concentrations were elevated in upstream sediments, none was significantly higher upstream at Roller compared to downstream; while at Cooch, the M3 elements that were significantly more concentrated upstream were M3-K, -Mn, -Fe, and -Na (Fig. 3). Further, when all elements are considered together in the PCA (discussed more in "Sect. 4.2"), downstream and shallow, variably saturated upstream sediments clustered together, away from deeper, fully saturated upstream sediments (Fig. 4), highlighting similarities in overall elemental makeup despite significant differences in sediment texture.

The absence of a pronounced difference in M3 element concentrations in comparable sediment depths above and below the dams indicates controls on bioavailable elements beyond sediment particle size and organic matter content—likely hydrology, redox conditions, and anthropogenic/geologic sources (discussed further in "Sect. 4.2"). Thus, our initial assumption that we would observe strong correlations between element concentrations and particle size and element concentrations and organic matter was not supported by the data. We observed no strong correlation between M3 elements and clay and silt content, and most M3 elements either displayed no correlation or only a weak positive correlation (e.g., M3-P) with organic matter content (Table S5). Lack of significant correlations could be a result of limited ranges of particle sizes observed in these millpond riparian sediments (48–100% clay and silt with the majority > 80%; Fig. 5), though organic matter contents varied more widely (0.7–9.8%). Increased density of measurements (additional sediment cores) or measurements of surface area may have produced more significant correlations and should be investigated in the future.

As an additional explanation for the lack of significant correlation, mechanisms causing bioavailable element loss may be greater in upstream versus downstream sediments. Vegetation, for instance, controls bioavailable element concentrations (especially macro-nutrients like P and K) directly through plant uptake and decomposition (Hill 1990; Tabacchi et al. 2000), and also indirectly through microbial stimulation (Hefting et al. 2005; Ye et al. 2019). Unfortunately, vegetation assemblages were not quantified at our sites and should be in the future to assess whether plant uptake of bioavailable macro- and micro-nutrients could have suppressed upstream concentrations. Physiochemical conditions (especially pH

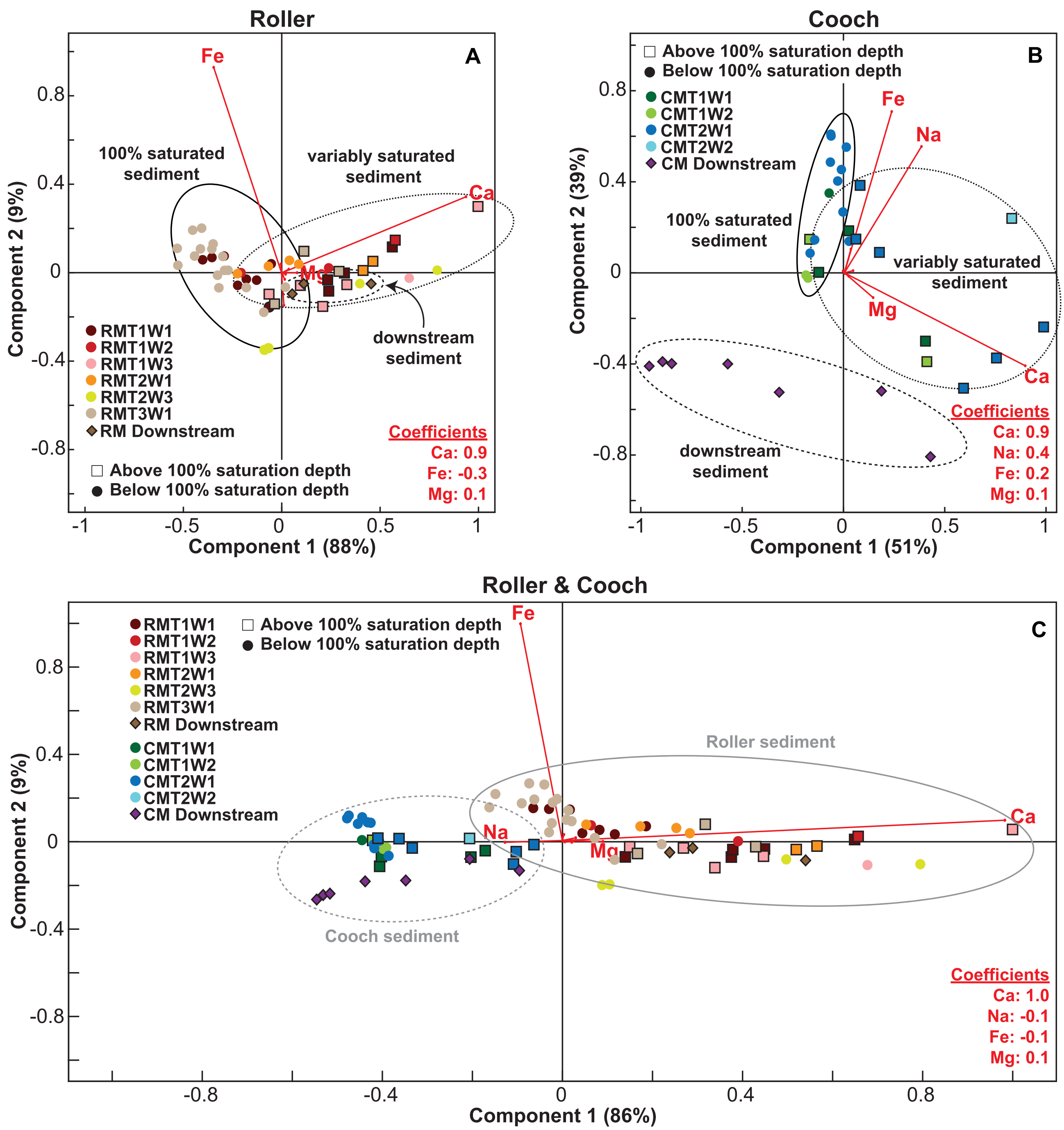


Fig. 4 Results of the principal component analyses represented by biplots of first two principal components (scores associated with each component are noted in axis labels) with eigenvectors (plotted as red lines) of M3 elements for **A** Roller, **B** Cooch, and **C** Roller and Cooch combined. Elements with short eigenvectors (coefficients < |0.1|) are not labeled. Observations are plotted as symbols with color indicating well location, and shape indicating downstream sediments as diamonds and upstream as either squares (variable saturated) or circles (constantly saturated). Circles highlight clusters in the data

and redox) created by groundwater saturation additionally affect the mobility of micro- and macro-nutrients (Yuan et al. 2021; Zhang and Furman 2021; Lu et al. 2022). For instance, low pH conditions created by sediment saturation behind dams can cause cation (especially Fe and Mn) release through H^+ replacement (Yuan et al. 2021). Further, low oxygen/reducing conditions in saturated sediments additionally cause reductive dissolution and increased mobility of many cations, with redox-sensitive Fe and Mn being especially susceptible (Yuan et al. 2021; Lu et al. 2022). Downstream sediments at Roller and Cooch were well-drained and mostly dry except during and immediately after the largest storms. In

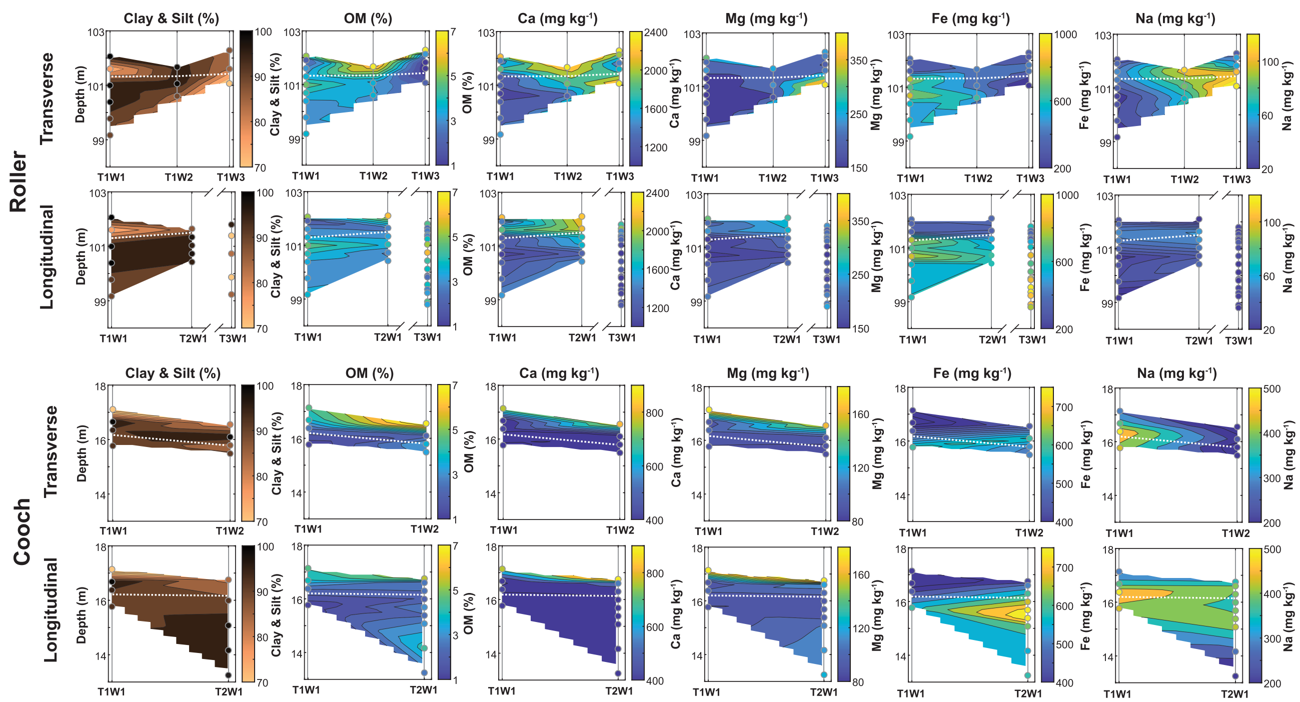


Fig. 5 Transverse (along transect 1 axis perpendicular to the stream—see conceptual models in Fig. 2 for site layouts) and longitudinal (along well 1 axis parallel to the stream) trends with depth in clay and silt content; organic matter (OM) content; and Ca, Mg, Fe, and Na concentrations measured in riparian sediment upstream of Roller and Cooch. Circles with gray outlines indicate depths at which measurements were taken, with internal colors indicating measured contents/concentrations. Colored surface plots indicate interpolated contents/concentrations between measured points. At Roller, a longitudinal surface is not interpolated between T2W1 and T3W1 given the distance between well locations (180 m). White dashed lines are the 100% groundwater saturation depth (values below are always saturated)

comparison, a more nuanced pattern of hydrologic drainage and mixing was observed for riparian sediments upstream of the dam (Sherman et al. 2022). Deeper upstream groundwaters (> 100% saturation depth) were generally poorly mixed and flushed, whereas shallow groundwaters (< 100% saturation depth) in the swales (location of W2 wells) were subject to greater hydrologic variation and flushing from overbank flooding from stream water and surface runoff from adjoining roads during large storms (see conceptual model—Fig. 8 in Sherman et al. 2022). Moreover, dissolved oxygen concentrations measured in groundwater wells are significantly lower for upstream versus downstream riparian locations with mean upstream values close to or lower than 1 mg L^{-1}, indicating hypoxic (< 2 mg/L) groundwater conditions (Inamdar et al. 2022). Thus, upstream sediments experience a wider range of variability in saturation and redox conditions, which may influence element mobility thereby further altering upstream sediment-bound concentrations. Additionally, road salt, which may be an especially important factor at Cooch (discussed more in "Sect. 4.2"), may increase cation leaching from soil cation exchange sites (Shanley 1994; Baldwin et al. 2006; Ostendorf et al. 2009; Kaushal et al. 2018).

When the full riparian sediment depth and width are considered, per area element masses (summed over depths; units = g m^{-2}) are much higher upstream than downstream (Table S4). For this reason, riparian sediment terraces upstream of milldams may be important reservoirs of bioavailable nutrients in regions heavily impacted by milldams, as others have noted, especially in relation to N and P (Miller et al. 2019). Calving of the upstream banks, which would occur if the dam was removed, would therefore result in high bioavailable element input to creeks, much more so than erosion of downstream areas. Furthermore, compared to previously measured bioavailable, M3 elements in legacy sediments along mid-Atlantic stream banks (~1–4 m height) where milldams have breached or been removed (Lutgen et al. 2020), M3 elements were more concentrated in sediments upstream of Roller and Cooch relict milldams (Table S4). It is possible that oxidative transformation and leaching of many of these bioavailable nutrients occurred with hydrologic drainage (Du Laing et al. 2009) associated with dam breaching/removal. Indeed, differences in mean concentrations between dammed and undammed legacy sediments were as great as 350% and 120% for Ca and Fe, respectively (Table S4 for other elements). Given the likelihood of differences in starting concentrations across sites due to differences in watershed geology and land use, more studies are needed to measure element losses before and after dam removal (e.g., Lewis et al. 2021). Clearly assessing these macro- and micro-nutrient additions (via erosion of tall, wide, exposed sediment banks or via oxidative transformation and leaching) to stream waters is critical for determining the legacy of milldams on landscape biogeochemistry.

4.2 Sediment biogeochemistry spatial trends upstream of the dams

The PCAs for individual milldam sites revealed separation in upstream riparian sediment by depth as a result of groundwater hydrology (Fig. 4). When Roller and Cooch were compared together, sediments clustered most by milldam, suggesting the importance of site-specific differences related to geology and land use in controlling bioavailable element concentrations. Others have similarly observed the importance of upstream anthropogenic activities on cation concentrations in sediments upstream of dams (e.g., Sun et al. 2018).

M3-Ca and -Mg displayed pronounced vertical depth trends with concentrations highest in shallow, variably saturated sediments along both transverse and longitudinal axes (Fig. 5). Both Ca and Mg may be related to bedrock weathering, with significantly higher values at Roller given that limestone/dolomite dominates in this region. Indeed, at Roller the ratio of M3-Ca:Mg in sediment (mean $=7.2\pm1.4$) was high compared to Cooch (mean sediment $=3.7\pm1.0$), and typical of regions with limestone and dolomite bedrocks (Jacobson and Langmuir 1970; Toran and Roman 2006). Furthermore, as road salt may increase Ca and Mg leaching from soil cation exchange sites (Shanley 1994; Ostendorf et al. 2009; Kaushal et al. 2018), the increased influence of road salt at Cooch, as evident in higher M3-Na concentrations (discussed more below), may also partially account for higher M3-Ca and -Mg concentrations at Roller. Fertilizer (which may include dolomitic limestone and manure) and sewage runoff could have additionally contributed to the high M3-Ca and -Mg concentrations, especially at Roller as agriculture is a dominant land use in the Chiques Creek watershed and common reliance on septic tanks. Cement use and production in urban and industrial areas can be an additional anthropogenic source of Ca in riparian sediments as has been documented in other mid-Atlantic riparian sediments downstream of urban and industrial areas (Bain et al. 2012). Overbank flow during flood events or even precipitation may deposit Ca and Mg over the riparian area, resulting in high surface concentrations (Dezzeo et al. 2000; Bain et al. 2012). While disentangling the relative importance of bedrock weathering and agricultural and industrial runoff is particularly challenging in the Piedmont where these activities simultaneously contribute to enrichment (Bain et al. 2012), consistently high element concentrations in Roller sediment compared to Cooch indicate the importance of fertilizer rich in macro- and micro-nutrient runoff. As additional evidence of the role of fertilizer/manure/sewage input in the Chiques watershed, median nitrate–N concentrations were 2 × higher in sediments upstream of Roller compared to Cooch (Peck et al. 2022). Carbonate-dominated lithology, as is found in the Chiques watershed, can act as a buffer, inhibiting changes in acidic-alkaline conditions, limiting metal(loid) solubilization (Yuan et al. 2021), and thereby further contributing to higher element concentrations observed at Roller versus Cooch. At Roller, deep sediments at the T1 upland edge well (T1W3) were concentrated in both M3-Ca and -Mg, suggesting groundwater input either naturally or anthropogenically enriched in these elements. Despite the strong correlation between M3-Ca and -Mg (Table S5), there exists somewhat of a discrepancy in the relative M3-Mg concentration in these deep T1W3 sediments compared to M3-Ca, which is similarly concentrated in surface sediments across the riparian zone. This M3-Mg may be sourced from the deicing (Cunningham et al. 2008) and dust control (Goodrich et al. 2009) agent magnesium chloride applied to the road that runs parallel to the creek or some other source preferentially enriched in M3-Mg over M3-Ca. Lower concentrations of M3-Ca and -Mg with depth, especially in W1 locations closest to the stream, may simply be related to the highly soluble nature of these elements.

Na is primarily delivered to mid-Atlantic riparian zones and streams through road salt runoff (Kaushal et al. 2005; Robinson et al. 2017; Moore et al. 2019; Hintz et al. 2022), especially at the Cooch milldam site, which is located just downstream of Interstate 95. As such, Na is consistently elevated across sediments at Cooch, and Na concentrations peak in upland-edge sediments at Roller where the other deicing agent, Mg, is also highly concentrated (Fig. 5). Salinization of riparian areas can cause additional feedbacks between elements (Kaushal et al. 2019; Lazur et al. 2020). For instance, Na may displace sorbed metals and base cations, such as Ca and Mg, especially in clay-rich soils, thereby reducing sediment concentrations as these species are leached from the area (Walker et al. 2021). Given that Na is significantly elevated at Cooch compared to Roller, element mobilization due to Na may partially contribute to the lower overall concentrations of bioavailable elements observed in Cooch sediments. As evidence, many elements were similar to or significantly more concentrated in Cooch groundwater samples despite overall higher concentrations of bioavailable elements in Roller sediments (Inamdar et al. 2022). Further, salinization also impacts vegetation species density and richness (Walker et al. 2021) and could therefore impact macro- and micro-nutrient uptake and turnover/mineralization.

Bioavailable Fe was most concentrated at depths below the 100% groundwater saturation depth (i.e., depths that were always wet; Fig. 5). Although Fe displayed little difference along the first transect at Cooch, Fe was highly concentrated in moderate to deep depths at the T2W1 location at Cooch. Vertical redox gradients strongly control Fe speciation and thus mobility and sediment concentration with depth (e.g., Zhang and Furman 2021; Lu et al. 2022). Previous work within the Christina River Basin, specifically White Clay Creek, observed distinct differences in iron speciation across vertical sediment profiles in riparian areas along undammed reaches (Chen et al. 2017). Sediment that undergoes oscillations in redox conditions, as occurs in shallow, variably saturated sediments above Roller and Cooch, may create Fe species that are more resistant to reductive dissolution, thereby resulting in Fe accumulation within sediments, especially the less mobile Fe(III) (Hansel et al. 2003; Thompson et al. 2006; Chen et al. 2017). Simultaneously, within poorly mixed, anoxic sediments reductive dissolution of Fe oxides often occurs preferentially forming Fe(II) (Chen et al. 2017). Lu et al. (2022) observed increases in total sorbed Fe and Fe(II) below the groundwater table, upstream of dams where conditions were anoxic. While we did not characterize Fe speciation, future studies should strive to do so as it may help characterize the integrative effects of low dissolved oxygen concentrations on Fe. Transversely, sediment M3-Fe concentrations peaked at the near-stream location W1 in Roller and were lowest at the upland-edge riparian wells, while longitudinally, M3-Fe was most concentrated at T3W1 (Fig. 5). This near stream enrichment of M3-Fe, also observed at Cooch T2W1, may be related to particularly poorly mixed and persistently anoxic groundwater conditions in the deeper near-stream groundwaters (Inamdar et al. 2022; Sherman et al. 2022). Additionally, although not a large coefficient in the first principal component, M3-Mn appears to be similarly influenced by groundwater stagnation and redox conditions created upstream of the dams (as observed by others: Yuan et al. 2021; Lu et al. 2022). M3-Mn peaks at depths at or below the 100% groundwater saturation depth (Fig. S1). Interestingly, comparison of M3 and total sorbed Fe and Mn in a subset of Roller samples revealed little correlation (unlike most other elements including Ca, Mg, and Na; Fig. S2), perhaps indicating greater controls of redox conditions on bioavailable forms of Fe and Mn. Both Fe and Mn oxides are important sinks or reservoirs for toxic trace elements like Cd, Cr, Cu, Zn, and Pb (Farnsworth and Hering 2011). Reductive dissolution of these oxides under anoxic conditions in riparian sediments, upstream of milldams, could result in a downward spiral in water quality with the release of such sorbed metals. Thus, dam-associated low-oxygen choke points could serve as hotspots for release of additional sediment-bound contaminants.

5 Conclusions

This study investigated the concentrations of bioavailable elements in riparian sediments above and below milldams and with depth in sediments upstream of the milldams. Key conclusions that can be derived are:

(a) Bioavailable element concentrations were not correlated with grain size or organic matter content and, although generally higher, were not significantly concentrated in upstream riparian sediments when similar (shallow, variably saturated) depths were compared.
(b) Ca and Mg concentrations were highest in the variably saturated, shallow sediments upstream of the dam and were attributed to the effect of land-use histories (e.g., road salt and fertilizer application/runoff) and dominant bedrock geology. In contrast, Fe and Mn concentrations were highest for the deepest, continuously saturated, anoxic sediments upstream of the dam and were dictated by redox conditions.
(c) These results underscore that milldams represent a complex depositional environment for riparian sediments with a myriad of factors regulating the concentrations of sediment-bound elements. Understanding these controls is essential for making water quality and watershed management decisions that account for the buffering role of riparian zones.
(d) While this study focused on sites in the US Piedmont where sediments have greater proportion of clays and silts, future studies should target regions with differing sediment texture (e.g., the Coastal Plain where sediments have a higher fraction of sand) and geology to develop more broadly applicable models characterizing milldam influence on riparian sediment geochemistry.
(e) Finally, given that > 14,000 dams still exist across the Northeast USA (Martin and Apse 2011), with many in disrepair and actively being removed for public safety and aquatic habitat considerations, a better understanding of status and fate of riparian legacy sediments above milldams is urgently needed.

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Data availability All data are available on Hydroshare (http://www.hydroshare.org/resource/89bc711455b644ac9871f20dc763aed1).

Declarations

Competing interests The authors declare no competing interests.

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