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Nitrogen Sinks or Sources? Denitrification and Nitrogen Removal Potential in Riparian Legacy Sediment Terraces Affected by Milldams

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Key Points:

- Riparian denitrification rates are similar above and below milldams but deeper, wider upstream zones result in more nitrogen removal
- Denitrification rates peak in shallow sediments of riparian areas above milldams with higher hydrologic variability
- Stagnant hydrologic conditions upstream of milldams promote nitrogen processes that result in ammonium accumulation at deep sediment depths

Supporting Information:

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

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Abstract

Riparian zones are key ecotones that buffer aquatic ecosystems through removal of nitrogen (N) via processes such as denitrification. However, how dams alter riparian N cycling and buffering capacity is poorly understood. Here, we hypothesized that elevated groundwater and anoxia due to the backup of stream water above milldams may enhance denitrification. We assessed denitrification rates (using denitrification enzyme assays) and potential controlling factors in riparian sediments at various depths upstream and downstream of two relict U.S. mid-Atlantic milldams. Denitrification was not significantly different between upstream and downstream, although was greater per river km upstream considering deeper and wider geometries. Further, denitrification typically occurred in hydrologically variable shallow sediments where nitrate-N and organic matter were most concentrated. At depths below 1 m, both denitrification and nitrate-N decreased while ammonium-N concentrations substantially increased, indicating suppression of ammonium consumption or dissimilatory nitrate reduction to ammonium. These results suggest that denitrification occurs where dynamic groundwater levels result in higher rates of nitrification and mineralization, while another N process that produces ammonium-N competes with denitrification for limited nitrate-N at deeper, more stagnant/poorly mixed depths. Ultimately, while it is unclear whether relict milldams are sources of N, limited denitrification rates indicate that they are not always effective sinks; thus, milldam removal—especially accompanied by removal of ammonium-N rich legacy sediments—may improve riparian N buffering.

Plain Language Summary

Floodplains adjacent to rivers are important ecosystems that provide valuable services including nutrient removal, especially nitrogen, from stream water. Because nitrogen is a major polluter of coastal waters, river floodplains are increasingly being restored as part of watershed best management practices. For example, millions of dollars are being spent annually in the Chesapeake Bay to install 900 miles of riparian buffers and on other watershed practices to mitigate nutrient pollution. However, the impact of small, colonial-era milldams on floodplain nitrogen mitigation is poorly understood, despite >14,000 such structures still present across streams of the eastern United States. We studied the impact of two small milldams (Roller mill on Chiques Creek, Lancaster, Pennsylvania, and Cooch mill on Christiana River, Newark, Delaware) on the ability of floodplains to remove or store nitrogen. We found that the stagnant water that accumulates behind milldams restricts floodplains from effectively removing nitrogen and may actually cause the accumulation of nitrogen. Whether accumulated nitrogen is released back into streams is unknown but concerning. Removal of dams would likely improve many ecosystem services of both streams and floodplains, with minimal consequences for the nitrogen mitigation abilities of these ecosystems.

1. Introduction

Watershed export of excessive reactive nitrogen (N) is a major environmental concern globally, as eutrophication of coastal waters causes hypoxia, habitat degradation, and loss of biodiversity (Howarth, 2008; Schaefer et al., 2009). Functioning riparian zones that are hydrologically connected to streams and rivers help mitigate downstream N transport through N removal by numerous biogeochemical pathways (Vidon et al., 2010; Zhao et al., 2021). Complete denitrification is a particularly important removal pathway by which facultative anaerobic bacteria reduce nitrate and nitrite to N_2 gas, permanently removing N from reactive pools (Groffman et al., 1992; Hill, 2019; Lutz et al., 2020). Denitrification occurs in areas with available organic carbon (C), high concentrations of nitrate, and wet, low oxygen sediments (Zhao et al., 2021). These conditions are often present in riparian zones, and hot spots of denitrification may account for the majority of total landscape denitrification (Duncan et al., 2013; Vidon et al., 2010). In part because of their N buffering capacity, riparian zones are increasingly being promoted as part of watershed best management practices (Cole et al., 2020; Sweeney et al., 2004). For example, millions of dollars are being spent in the Chesapeake Bay to install 1,500 km of riparian buffers annually to mitigate nutrient pollution (Chesapeake Bay Program, 2016).

While riparian zones along undammed rivers and streams are well studied and are known to be effective filters for upland N inputs in surface and subsurface runoff (Lowrance et al., 1997; Peterjohn & Correll, 1984), their behavior in the presence of dams (Inamdar et al., 2021) is poorly understood. This is particularly so in landscapes that have been widely altered by low-head milldams (e.g., <5 m in height), such as those in the mid-Atlantic United States (which includes Delaware, Maryland, New Jersey, New York, Pennsylvania, Virginia, and West Virginia). An estimated >65,000 water-powered mills were constructed by 1840 across the eastern United States, with densities up to 0.61 mills per km^2 (Walter & Merritts, 2008). Coupled with accelerated sediment erosion from widespread land clearance and agriculture (Costa, 1975; Meade, 1982), milldams inundated valley bottoms with fine-grained (silt and clay) legacy sediments (defined as sediments deposited because of past anthropogenic activities; James, 2013) resulting in tall riparian terraces upstream of the dams and lower floodplains downstream. While many of the dams are gone (Merritts et al., 2011, 2013; Pizzuto & O'Neal, 2009; Walter & Merritts, 2008; Wegmann et al., 2012), many remain intact (>14,000 in the mid-Atlantic and northeast United States; Martin & Apse, 2011) and are continuing to influence stream and riparian corridor processes and functions. Where dams have been removed or breached, streams have incised through legacy sediments leaving upstream riparian terraces hydrologically disconnected and perched above the stream (Inamdar et al., 2021; Merritts at al., 2011; Wegmann et al., 2012).

Low-head milldams, like beaver dams, typically raise the base level of streams resulting in increased stream and riparian groundwater levels upstream of the dam (Ecke et al., 2017). Elevated groundwater levels could potentially foster wet and anoxic riparian sediment conditions that favor denitrification. Furthermore, clay- and silt-rich legacy sediments are often concentrated in both nitrate (denitrification electron acceptor) and organic matter (OM; denitrification electron donor) (Weitzman & Kaye, 2017; Weitzman et al., 2014). Indeed, enhanced denitrification has been observed in riparian zones impacted by beaver dams (Hill & Duval, 2009; Lazar et al., 2015) that create similar, though more transient, hydrologic and redox conditions (Hill & Duval, 2009; Westbrook et al., 2006). Similar nitrate declines in the presence of milldams are unknown but could be providing a valuable ecosystem service.

Conversely, milldams may create conditions unfavorable for denitrification. For instance, denitrification rates may be limited by the stagnant/poorly mixed groundwater conditions (Peralta et al., 2013; Reverey et al., 2018) found on the riparian terraces. Dynamic conditions tend to produce oxic periods that increase the supply of nitrate-N via nitrification and organic C via mineralization (Peralta et al., 2013, 2014; Tomasek et al., 2019). Under these anoxic, nitrate-limited conditions, other pathways may compete with denitrification, such as suppression of nitrification of ammonium (Hefting et al., 2004) or dissimilatory nitrate reduction to ammonium (DNRA; Pandey et al., 2020; Rütting et al., 2011). If DNRA is significant, riparian sediment terraces may be net sources of reactive ammonium, which would either accumulate in the sediment and/or become released into streams via desorption (Doussan et al., 1998; Giblin et al., 2013; Rütting et al., 2011).

A key aspect for understanding the behavior of riparian zones in the presence of dams is to determine whether they act as net nitrogen sinks or sources. This is particularly critical given the increasing trend toward dam removal across the United States. An estimated 1,490 dams have been removed since 1912 in the United States (American Rivers, 2020), primarily for safety and improvement of aquatic habitat (Foley et al., 2017), and little attention is given to water quality consequences. If milldams enhance riparian N consumption, milldam removal could increase N pollution in streams and coastal waters. On the other hand, if milldams result in riparian N sources, their removal could be a valuable tool and supplement watershed efforts for N mitigation.

Thus, we address the questions: How do riparian denitrification rates vary upstream and downstream of the milldams and along the riparian transect? How do the denitrification rates vary with depth in the upstream riparian terraces? What are the key factors affecting riparian denitrification?

We hypothesize that (a) denitrification will be elevated in riparian terraces above milldams because of fine-grained, saturated, and anoxic sediment conditions, whereas denitrification rates will be lower at riparian areas downstream of the milldams where sediment texture is coarser, less saturated, and more oxic. (b) Denitrification rates will be highest adjacent to the creek where sediments are typically more saturated and will decrease with distance from the creek as sediments become generally drier. (c) Along riparian terraces above milldams, denitrification rates will peak near the sediment surface and decrease with depth, mirroring sediment nitrate-N depth profiles. (d) Given previously identified conditions conducive to denitrification, these rates will be most strongly impacted by sediment saturation, nitrate-N concentration, and OM content.

To address the questions and test these hypotheses, we collected sediment cores from riparian sediment terraces above and floodplains below two relict milldams in the U.S. mid-Atlantic. Roller milldam was located on Chiques Creek in Pennsylvania (PA) and Cooch milldam on Christina River in Delaware (DE). Roller and Cooch milldams are also being evaluated to investigate the impacts of milldams on instream nitrogen processing (Hripto, 2022) and riparian groundwater hydrology (Sherman, 2022). In this study, estimated denitrification rates, sediment texture; OM, C, and N contents; and nitrate-N and ammonium-N concentrations were determined for sediments collected at various depths from 0 to 3 m.

2. Methods

2.1. Site Descriptions

The two milldam sites, Roller and Cooch, were selected for study as they are both long-standing, low-head dams that are relatively tall (≥3 m) and still largely intact. Both sites are accessible with permissions for long-term monitoring. In addition to these similarities, upstream watershed characteristics, especially dominant land use, differs between sites allowing for comparisons. The two rivers, Chiques and Christina, drain into the Chesapeake and Delaware Bays, respectively, and thus these findings are relevant for management of two greatly important U.S. East Coast estuaries.

Roller milldam is located on Chiques Creek in Lancaster County, PA (40.1083, −76.4431), ∼13 km upstream of the confluence with the Susquehanna River, which drains into the Chesapeake Bay (Figure 1a). The dam was first built in the early 1700s at 3 m tall but was rebuilt in the 1930s and is 2.4 m tall and 30 m wide (Figures 1c and 1e). Above the dam, fine-grained riparian sediment extends >3 m in depth adjacent to the stream, while below the dam coarser sediment extends ∼1 m in depth. A radiocarbon date collected at 3 m depth, upstream of the dam, was dated to 526 cal BP (95% CI = 501–550 cal BP; IntCal20; Reimer et al., 2020; Beta Analytic 536900, bulk sediment), indicating overlying sediment has accumulated in the last ∼600 years, though likely much of this has accumulated since dam construction (∼300 years). The upstream catchment drains 128 km^2, which is comprised of 54% agricultural, 22% forested, and 20% developed land (USGS National Landcover Database, 2011).

The Cooch milldam is located on the Christina River in New Castle County, DE (39.6456, −75.7425), 23 km upstream of the confluence with the Delaware River, which drains into the Delaware Bay (Figure 1b). The dam was built in 1792 and is 4.0 m tall and 45 m wide (Figures 1d and 1f). Above the dam, fine-grained riparian sediment extends >3 m in depth adjacent to the stream, while below the dam coarser sediment extends ∼1 m in depth. A radiocarbon date collected at 3 m depth, upstream of the dam, was dated to 184 cal BP (95% CI = 142–221 cal BP; IntCal20; Reimer et al., 2020; Beta Analytic 538549, wood), indicating overlying legacy sediment has likely accumulated since dam construction (∼230–250 years). The upstream catchment drains 51 km^2, which is comprised of 47% urban/developed, 30% forested, and 23% agricultural land (USGS National Land Cover USGS National Landcover Database, 2011).

Both Roller and Cooch have stream water residence times much slower (∼8x) above than below the dams (Hripto, 2022; Hripto et al., 2022). Though mean in-stream water concentrations of ammonium-N (0.10 and 0.04 mg L^{-1}) and dissolved organic C (3.3 and 4.7 mg L^{-1}) are similar between creeks, nitrate-N (4.3 and 1.1 mg L^{-1}) and total dissolved N (9.3 and 6.7 mg L^{-1}) concentrations are greater in Chiques than Christina (∼5 and 4x), respectively (Hripto, 2022).

2.2. Sampling

Groundwater wells (5-cm diameter screened PVC pipes) were installed beginning in August 2019 above and below both dams using a hand-operated auger to a depth of refusal (∼2–4 m upstream and ∼1 m downstream; Table S1 in Supporting Information S1; Sherman, 2022). Water level data, measured every 30 min using U20L

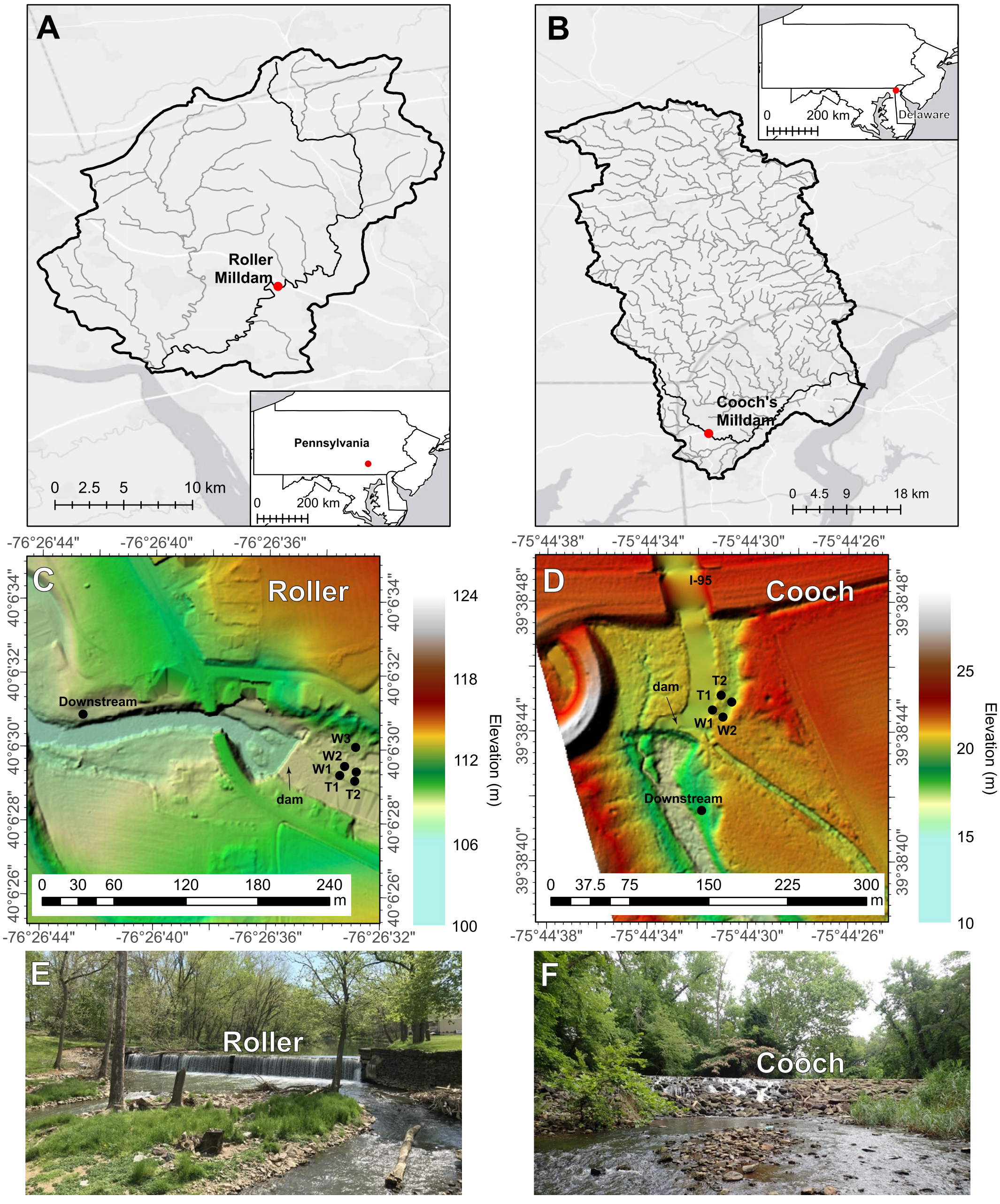

Figure 1. (a–b): Watershed maps of Chiques Creek and Christina River with Roller and Cooch milldams marked by red dots. Insets indicate the location of each watershed in the U.S. mid-Atlantic. (c–d): Digital elevation models of the Roller and Cooch milldams and well locations. (e–f): Photographs of Roller and Cooch milldams.

HOBO sensors, were utilized to assess riparian sediment saturation at various depths. Dissolved oxygen was measured monthly using a YSI EcoSense ODO200 in each groundwater well (the probe was lowered into the well and measurements were recorded after readings stabilized) and associated depths were calculated as the mean on the day of measurement. During well installation, augered sediment samples at roughly 0.3 m depth intervals from the surface to the depth of refusal were obtained and preserved in ziplock bags. To provide greater depth resolution following the initial augering (some depths had been discarded during initial well installation), additional samples were collected at each well location in 2020 and 2021 within ~5 m of the groundwater wells (Table S1 in Supporting Information S1). We did not divide sediment depth samples based on soil horizons as we did not visually observe distinct horizons or layering during collection. The absence of distinct soil horizons is likely due to the recent sediment deposition (200–300 years) and continuously wet or poorly drained soil conditions. Although groundwater monitoring incorporated 10 wells from Roller and 6 wells from Cooch (uneven sampling scheme was due to differences in riparian width), we focused sediment analyses on well locations that were comparable topographically between milldams. At both Roller and Cooch, three well locations with associated sediment cores were located above the milldams. Transect 1 (T1) was closest to the milldam with two wells (W1 and W2); W1 located on the berm closest to the creek and W2 located in a swale further from the creek (Figure 1). Transect 2 (T2) was further from the milldam and had one well (W1) located on the berm. At Roller, which had a wider riparian zone, a third well (W3) located along T1 at a higher elevation behind the swale was additionally included to assess the impact of distance from the creek on rates of denitrification. Additionally, as downstream riparian sediments were shallow, coarse, and mostly dry, only one comparison well was installed downstream at Roller and two at Cooch to the depth of refusal (∼1 m; though sediment was collected from only one downstream site at Cooch).

2.3. Sediment Measurements

Denitrification enzyme activity (DEA) assays, which provide an estimate of the maximum potential denitrification rates (Groffman et al., 1993, 2006), were performed on sediments (undried and refrigerated but not frozen) as soon as possible after collection. Unamended and amended (addition of glucose and nitrate-N) DEA assays were performed at the University of Rhode Island Watershed Hydrology Laboratory. Sediment was homogenized with DI water and sodium nitrate ($NaNO_3$) and incubated in sample containers purged with helium and acetylene gas to induce anoxia and to prevent the conversion of N_2O to N_2 gas. Headspace gas was sampled from the sample container and analyzed using gas chromatography to quantify the denitrification product (N_2O) gas.

Remaining sediment samples were oven dried at 60°C for ∼24 hr, disaggregated, and sieved through a 2-mm sieve. Using a portion of this dried sediment, percent sand (2,000–63 μm), silt (63–2 μm), and clay (<2 μm) fractions were measured at the University of Delaware's (UD) Soil Testing facility by the standard hydrometer method (Ashworth et al., 2001).

Dried and disaggregated samples were also analyzed for %C, %N, and C:N mass ratios at the University of Maryland Center for Environmental Science using elemental combustion (4010 CHNSO analyzer, Costech). OM content was determined by loss on ignition (Schulte & Hoskins, 1995) at UD's Soil Testing facility. Nitrate- and ammonium-N were measured colorimetrically using a Bran & Luebbe Autoanalyzer 3 after KCl extraction at the UD's Soil Testing facility.

2.4. Data Analysis

All statistical analyses were performed in MATLAB (2022).

To assess the effects of riparian GW levels and sediment saturation on DEA, we determined the cumulative distribution of the water levels below the soil surface in 0.1 m depth increments. Negative water level depths indicative of water levels above the sediment surface (i.e., standing/flooding water) were classified as 0 m or at the sediment surface. Sediment clay and silt fractions were combined when analyzing the effects of particle size data.

As additional augering was performed to supplement depth profiles, we assessed the effect of collecting sediments on different dates by comparing nitrate-N and ammonium-N concentrations and unamended and amended DEA rates measured in sediment samples collected from the same wells (Roller T1W1 and Cooch T2W1) during different times of the year using Kruskal-Wallace H tests ($\alpha = 0.05$). As they revealed no statistical difference (Figure S1 in Supporting Information S1), biogeochemical measurements collected on different dates were combined for each well location to create integrated depth profiles. When depths had multiple sediment measurements, means were calculated.

Surface (depths ≤ 1 m) unamended and amended DEA rates; C:N mass ratios; OM contents; and nitrate-N and ammonium-N concentrations were compared between upstream and downstream sites for Roller and Cooch using box plots and Kruskal-Wallis H tests ($\alpha = 0.05$). Additionally, variations with sediment depth were investigated using box plot depth profiles for upstream riparian locations. To compare this sediment depth data between well locations with slightly variable sampling depths, downcore biogeochemical data were binned into 1-m increments (Figure S2 in Supporting Information S1 for unbinned depth data). Depths were then normalized to the deepest depth to groundwater for each well to allow for depth comparisons between sites with differing groundwater levels. To determine N loss by denitrification per unit riparian area, mean volumetric DEA amounts (calculated

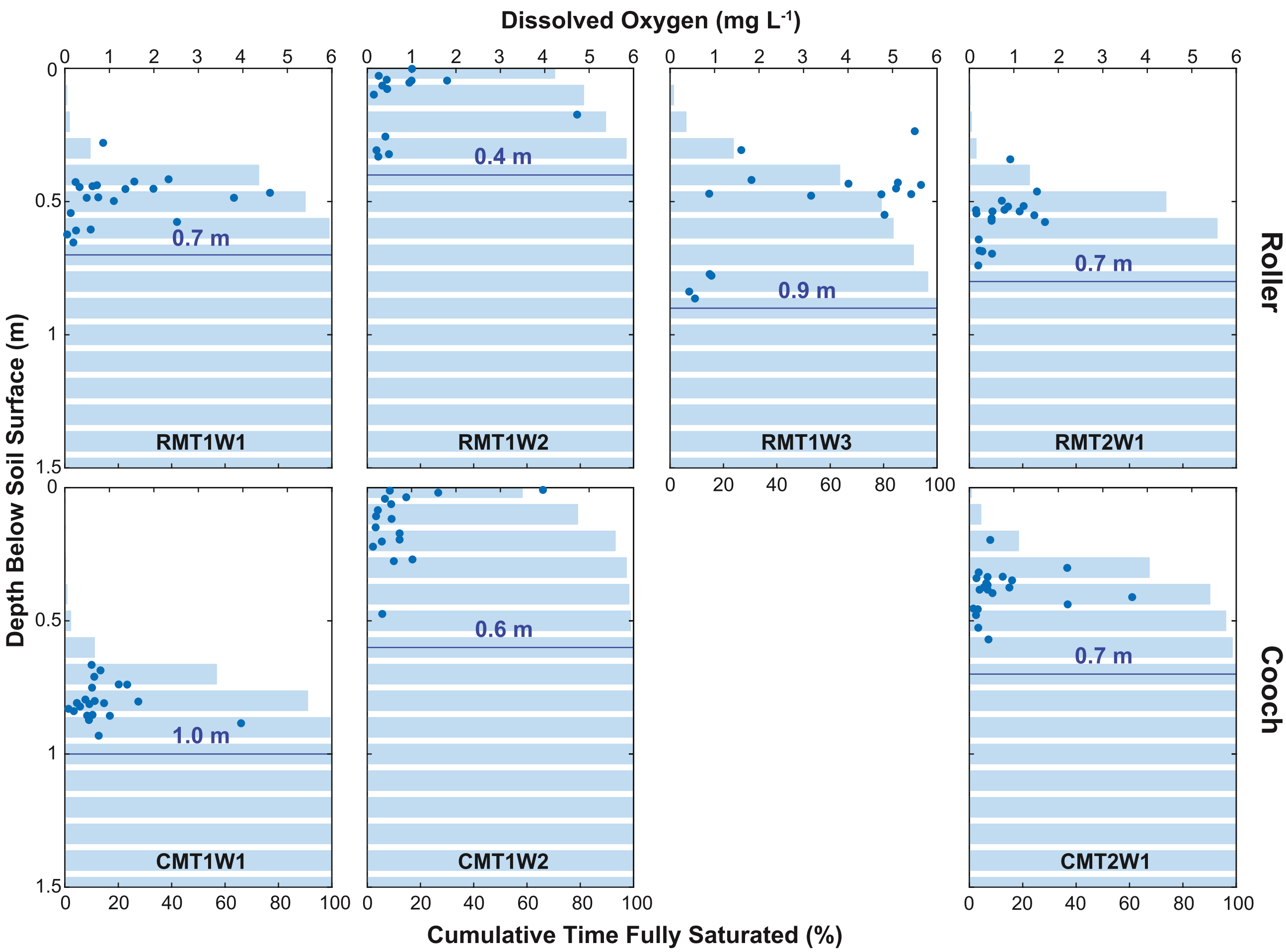

Figure 2. Bar charts of cumulative percent time that groundwater levels were at binned depths (every 0.1 m) below the sediment surface for wells on the riparian sediment terraces upstream of Roller and Cooch milldams. Dark blue lines and labeled depths indicate the deepest depth to groundwater. Depths below the blue line were always saturated and those above were sometimes saturated. Dissolved oxygen concentrations are plotted as blue dots at mean groundwater depths on the day of measurement.

assuming a sediment dry density of 1.13 g cm^{-3} based on a standard dry-weigh-dry method on a known volume) were multiplied by the total depth (depths in Table S1 in Supporting Information S1; final units mg N m^{-2} d^{-1}).

Pearson correlation ($\alpha = 0.05$) was performed to determine variables that correlated with unamended and amended DEA rates in W1 and W2 sediments, which are locations most comparable between Roller and Cooch. Correlations were made between DEA rates and C:N mass ratios, OM, nitrate-N, ammonium-N, depth specific cumulative percent saturation time, and clay and silt fraction, which were chosen based on previously identified mechanistic relationships (Covatti & Grischek, 2021; Matheson et al., 2002; Pinay et al., 2000). C:N was included as an indicator of OM lability (Hill & Cardaci, 2004). Because C and OM ($R^2 = 0.67$, $p < 0.01$, $n = 35$) and N and OM ($R^2 = 0.58$, $p < 0.01$) are highly correlated, only OM was assessed. Additionally, cumulative percent saturation time was used as a surrogate for oxygen availability with small values of percent saturation indicating oxic conditions and large values associated with hypoxic or anoxic conditions.

3. Results

3.1. Riparian Sediment Saturation, Textural Characteristics, and Groundwater Oxygen

Groundwater levels below the sediment surface were deepest at wells closest to the creek/river on berms (W1 wells) and also further from the creek (W3 well), whereas levels were closer to the surface in W2 wells, which were located in the depressions/swales (Figure 2). Well water levels at W1 never reached the sediment surface, while

W2 levels were at or above the surface 71% and 59% of the observation period at Roller and Cooch, respectively. Well water dissolved oxygen concentrations for all sites ranged from 0.05 to 5.64 mg L^{-1}.

Textural analysis revealed that upstream riparian sediments at both Roller and Cooch were predominantly silty clay and silty clay loam, respectively. Sand, silt, and clay contents were consistent with depth, with silt and clay ranging from 56% to 100% (Figure S3 in Supporting Information S1). In contrast to the upstream terrace, downstream riparian sediments were significantly coarser at both Roller ($p < 0.01$, $n = 17$) and Cooch ($p < 0.01$, $n = 16$), with sand fractions up to 62% and 84%, respectively.

3.2. Denitrification Rates and Sediment Biogeochemistry

Amended DEA rates were significantly higher than unamended DEA rates ($p = 0.001$, $n = 70$). The highest rates of unamended and amended DEA were observed in downstream sediments at Roller, though these ranges were driven by a single depth with high rates that could not be disregarded due to the small sample size ($n = 4$). However, downstream DEA rates were not significantly different from upstream rates at either Roller (unamended: $p = 1$, $n = 17$; amended: $p = 0.4$, $n = 17$) or Cooch (unamended: $p = 0.09$, $n = 14$; amended: $p = 0.1$, $n = 14$; Figures 3a and 3b). Along-transect comparison at Roller revealed that maximum and mean DEA rates were highest at upslope W3 position (Figure 4). Both unamended and amended DEA rates displayed similar depth patterns, generally peaking in shallow sediments (Figures 5a and 5b); however, neither unamended (Roller: $p = 0.1$, $n = 18$; Cooch: $p = 0.8$, $n = 17$) nor amended (Roller: $p = 0.1$, $n = 18$; Cooch: $p = 0.2$, $n = 17$) DEA rates changed significantly with depth. When compared across all depths, unamended DEA rates were higher on average in upstream sediments at Roller than those at Cooch, though not significantly ($p = 1$, $n = 35$), while amended DEA rates were higher on average at Cooch, though also not significantly ($p = 0.5$, $n = 35$). Rates of unamended DEA are likely more representative of in situ conditions than the amended DEA rates enriched with glucose and nitrate; however, both unamended and amended DEA rates displayed similar upstream versus downstream and depth patterns.

When incorporated over the depth profile, mean per-area N loss through denitrification was greater upstream (Roller mean: 202 ± 137 mg N m^{-2} d^{-1}; Cooch mean: 46 ± 32 mg N m^{-2} d^{-1}) than downstream (Roller: 39 mg N m^{-2} d^{-1}; 5 mg N m^{-2} d^{-1}; Table S1 in Supporting Information S1). Along Roller T1, per-area DEA amounts increased with distance from the stream, peaking at W3. At Cooch, W1 locations had the highest per-area DEA amounts.

C:N ratios were significantly larger at Cooch than Roller ($p < 0.01$, $n = 35$). Additionally, C:N ratios were significantly larger at downstream locations than upstream (Roller: $p < 0.01$, $n = 17$; Cooch: $p < 0.01$, $n = 14$; Figure 3c). OM contents and nitrate-N and ammonium-N concentrations ranged higher at Roller than Cooch, though they were not significantly different ($p \geq 0.1$, $n = 35$). The highest mean nitrate-N concentrations were observed in downstream sediments at Roller (5.0 ± 3.2 mg kg^{-1}) but were not significantly larger than those upstream at Roller when similar depths were compared ($p = 0.4$, $n = 17$; Figure 3e). Nitrate-N concentrations peaked at the sediment surface especially at Roller where values ranged up to 21 mg kg^{-1} and varied significantly with depth (Roller: $p < 0.01$, $n = 18$; Cooch: $p = 0.2$, $n = 17$; Figure 5e). At both milldams, ammonium-N was higher at upstream locations when similar, surface depths were compared, especially at Cooch (Roller: $p = 0.3$, $n = 17$; Cooch: $p < 0.01$, $n = 14$; Figure 3d). Ammonium-N concentrations peaked at deeper sediment depths at both Roller and Cooch; these depth trends were significant (Roller: $p < 0.01$, $n = 18$; Cooch: $p = 0.01$, $n = 17$; Figure 5f).

Nitrate-N and OM were significantly correlated with unamended DEA rates, with nitrate-N being most strongly correlated (Table 1; Figure S4 in Supporting Information S1). OM and clay and silt content were significantly correlated with amended DEA rates, with OM the most well correlated.

4. Discussion

We did not find strong evidence supporting our hypothesis of elevated denitrification rates in riparian sediment terraces upstream of Roller and Cooch milldams. Indeed, although estimated rates of denitrification (amended and unamended) varied widely, they were generally low and not significantly different upstream and downstream of the milldams when compared between similar, surface depths (≤1 m). However, when summed across all

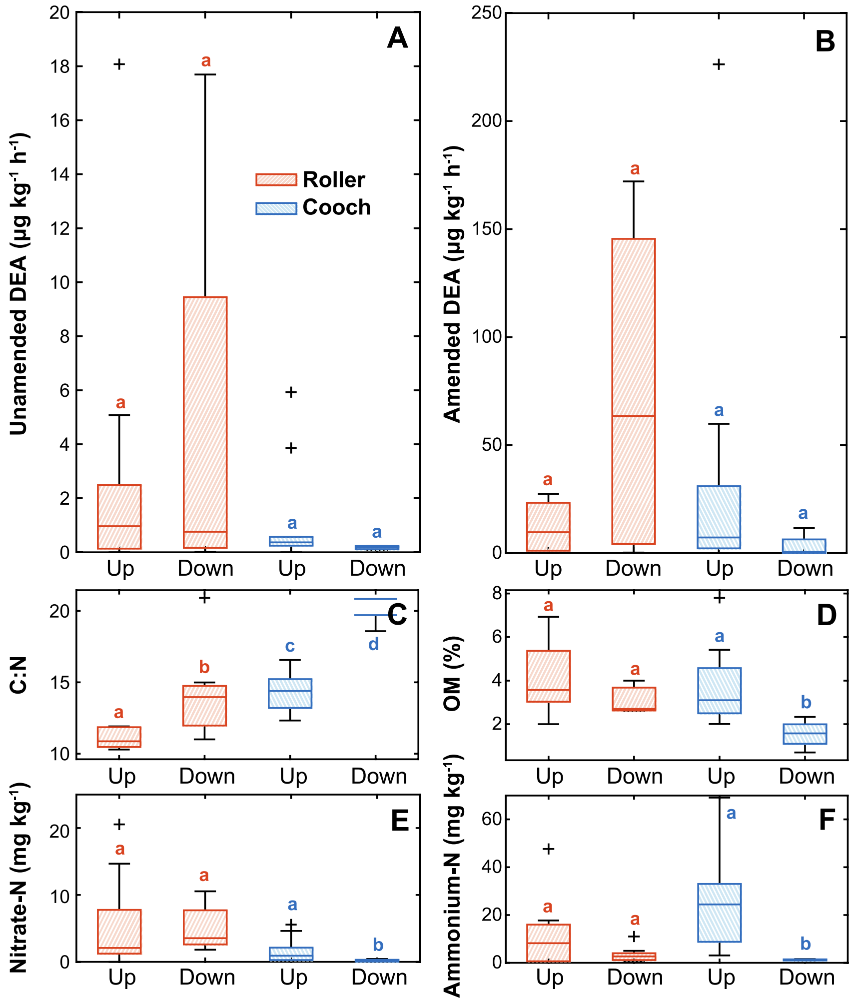

Figure 3. Comparison of upstream and downstream sediment denitrification and biogeochemistry to test hypothesis 1. (a–b): Sediment unamended denitrification enzyme assay (DEA) and amended DEA rates; (c): C:N ratios; (d): organic matter contents; and (e–f): nitrate-N and ammonium-N concentrations plotted as box plots (boxes represent first and third quartile, center lines indicate medians, whiskers are minimums and maximums, and +'s are outliers) for Roller and Cooch binned into upstream (labeled Up) and downstream (labeled Down) sites. Depths ≤1 m were used for comparison of upstream sediments to shallower downstream sediments. Letters indicate significant differences based on a Kruskal-Wallace test.

depths, denitrification amounts where much larger upstream than downstream on a per area basis. Denitrification rates and amounts were especially elevated at wells further from the creek when viewed along the Roller upstream terrace, indicating the importance of hydrodynamic variability in controlling denitrification, perhaps through stimulation of nitrification and mineralization during dry periods and of nitrate-rich upland groundwater runoff. Moreover, while we did observe elevated rates of denitrification in shallow sediments in riparian sediment terraces that mirrored nitrate-N and OM concentrations, DEA rates were not significantly different across depths.

4.1. Denitrification Upstream Versus Downstream of the Milldam and Along the Riparian Transect—Role of Hydrologic Variability

Denitrification rates were overall much lower than expected. The DEA method tends to underestimate denitrification rates as acetylene inhibits nitrification and subsequent nitrate supply (Groffman et al., 2006), perhaps explaining low rates. However, other studies from comparable environments that utilized similar methods observed higher rates. Indeed, estimated denitrification rates in active beaver ponds (150–370 μg kg^{-1} h^{-1}; Lazar et al., 2015) and in riparian zones along undammed streams (5–1,750 μg kg^{-1} h^{-1}; Bettez & Groffman, 2012) ranged much higher. Moreover, unamended and amended DEA rates for the riparian terrace above the recently removed Krady dam

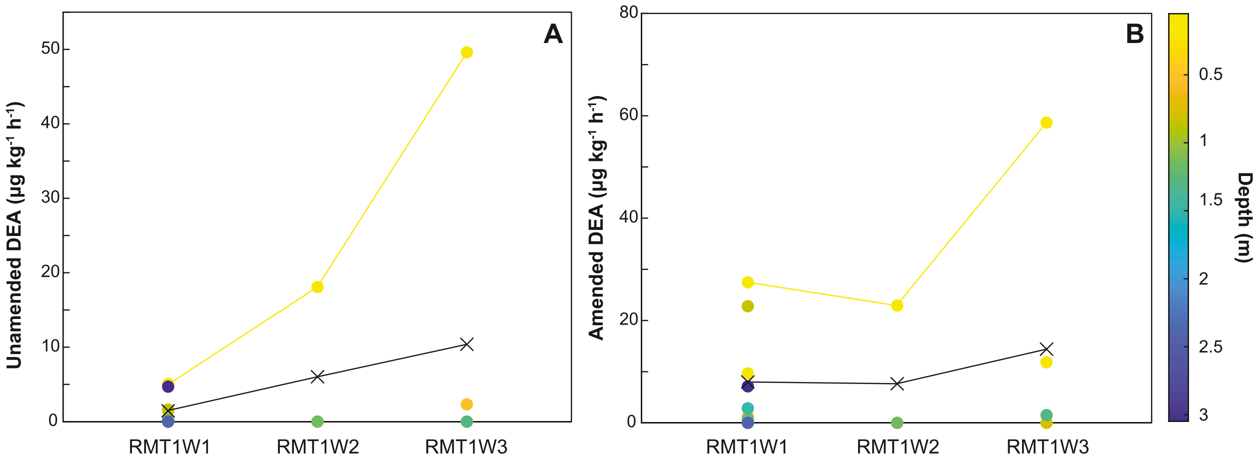

Figure 4. Comparison of sediment denitrification rates with distance from the stream to test hypothesis 2. (a) Unamended and (b) amended denitrification enzyme assay (DEA) rates for sediment collected from wells 1, 2, and 3 (W1–W3) along transect 1 (T1) at Roller. Dot colors indicate depth; black x's indicate mean values; and lines through surface and mean points help illustrate trends.

(1.5 m, Lewis et al., 2021) ranged up to 320 and 664 μg kg^{-1} h^{-1}, respectively (Lewis et al., 2021), even though this dam was also on Chiques creek, just ~8 km downstream of the Roller milldam site. Thus, despite similar C and N contents, Krady DEA rates were 20x times greater than the Roller values (though conditions prior to dam removal were not assessed by Lewis et al., 2021).

Comparison between riparian sediment terraces located upstream of milldams with riparian areas located downstream in the free-flowing reaches provides further insight into how these relict structures have (or have not) influenced N cycling. Although we hypothesized that sediments located upstream of the milldams would display greater evidence of denitrification than downstream, DEA rates were not significantly different when compared across similar surface depths (≤1 m). In part, these results highlight consistently low rates of denitrification in riparian zones of both rivers. However, when unamended DEA amounts were computed for the entire depth profile, the deeper, wider terraces above the milldams removed more nitrate via denitrification than the shallower, narrower riparian zones below by up to an order of magnitude (Table S1 in Supporting Information S1).

Additionally, when viewed across the riparian terrace upstream of Roller milldam, denitrification rates increased with distance from the creek, peaking at W3 (Figure 4; Table S1 in Supporting Information S1). This was somewhat surprising as we expected the swales (well W2), which were saturated for most of the observation period, would be important N sinks given these anoxic conditions. However, upland runoff of nitrate-N-rich water combined with transverse differences in hydrodynamic variability (Figure 2) could explain these patterns in denitrification rates (Figure 6). Hydrodynamic variability, such as was observed at wells located further from the creek above milldams and downstream, may stimulate microbial communities, promoting both nitrification and mineralization during dry periods when OM is more exposed to oxygen (Peralta et al., 2013, 2014; Racchetti et al., 2011; Tomasek et al., 2019; Ye et al., 2017). Nitrification produces nitrate-N and mineralization produces organic C, both of which stimulate denitrification during wet, more anoxic periods. Conversely, stagnant/poorly mixed groundwater, with more limited fluctuations in level such as those located closer to the creek upstream of the milldam (Figure 2), may limit nitrification and mineralization rates, thereby starving denitrification of new nitrate inputs. Similar couplings between nitrification and denitrification in hydrologically dynamic systems have been observed by others (Peralta et al., 2013; Reverey et al., 2018; Tomasek et al., 2019). Moreover, this relationship likely explains the enhanced DEA rates observed in legacy sediment upstream of Krady dam, as dam removal would have increased moisture variability along the depth profile (Lewis et al., 2021).

4.2. Denitrification With Sediment Depth

Our hypothesis that denitrification rates would be highest near the sediment surface in riparian sediment terraces upstream of milldams was substantiated by patterns of DEA rates at both Roller and Cooch, though these rates were not significantly different with depth. At both milldams, the highest rates of unamended and amended DEA

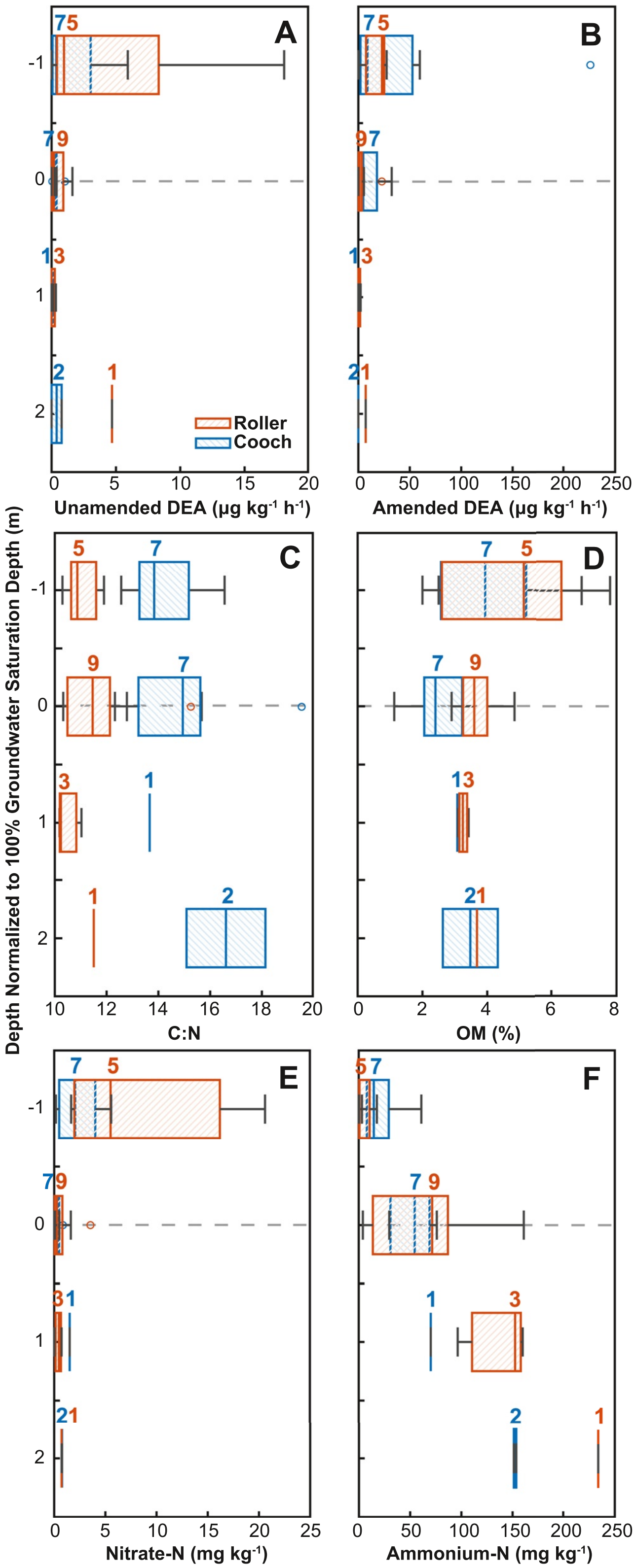
A
B
C
D
E
F
Roller
Cooch
Unamended DEA (µg kg⁻¹ h⁻¹)
Amended DEA (µg kg⁻¹ h⁻¹)
C:N
OM (%)
Nitrate-N (mg kg⁻¹)
Ammonium-N (mg kg⁻¹)
Depth Normalized to 100% Groundwater Saturation Depth (m)

Figure 5.

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Table 1
Pearson Coefficients (r) and P-Values (α = 0.5) for Biogeochemical Characteristics Compared With Unamended and Amended Denitrification Enzyme Assay (DEA) Rates Measured in Roller and Cooch Sediments From W1 and W2 Locations to Test Hypothesis 4

	Unamended DEA		Amended DEA	
	r	*p*-value	*r*	*p*-value
C:N	−0.080	0.7	0.16	0.4
OM	0.51	<0.01	0.62	<0.01
Nitrate-N	0.67	<0.01	0.16	0.3
Ammonium-N	−0.13	0.4	−0.28	0.1
Cumulative time fully saturated	−0.22	0.2	−0.18	0.3
Clay and silt	0.096	0.6	−0.37	0.03

were measured in shallow sediments at or above the minimum groundwater level. Nitrification and mineralization likely predominately occur in shallow oxic sediments during dry periods, thereby supplying nitrate-N and OM. As evidence, depths near the sediment surface also had the highest concentrations of nitrate-N and OM, both required for denitrification. When surface sediments were saturated, these depths maintained reducing conditions favorable to denitrification, with groundwater dissolved oxygen concentrations frequently <2 mg L^{-1} (Figure 2). Denitrification thus appears to occur at depths that experience more dynamic changes in groundwater level and therefore more dynamic saturation and redox conditions (e.g., Tomasek et al., 2019).

Others have identified riparian denitrification occurring in dynamic zones of intersecting flow paths, where surface and ground waters or ground and hyporheic waters converge and mix (Hedin et al., 1998; Vidon et al., 2010). In certain riparian settings where groundwater intersects, root zone microsites serve as denitrification hotspots where small volumes of sediment disproportionally account for the majority of nitrate-N removal (e.g., Jacinthe et al., 1998; Parkin, 1987). Elevated denitrification rates for surficial sediments (vs. the subsurface) have also been reported for legacy sediment terraces upstream of breached/removed milldams, reflecting nutrient profiles that sharply decline with depth (Lewis et al., 2021; Weitzman et al., 2014). This was despite the fact that groundwater levels were observed at considerable depth from the sediment surface because of the removal/breach of the dam. While it is possible that only the potential for denitrification was high, as Weitzman et al. (2014) suggested, wet periods of elevated denitrification can occur following dry periods of elevated nitrification (Kolbjørn Jensen et al., 2017; Peter et al., 2011). Indeed, following the initial decline in DEA rates just after the Krady dam removal, potential denitrification rates showed evidence of seasonality (Lewis et al., 2021). These results are in line with our conceptual framework between hydrodynamic variability and coupled nitrification and denitrification rates (Figure 6) but in situ measurements of denitrification and nitrification rates across seasons are needed.

4.3. Drivers of (and Competitors to) Denitrification

Based on the correlation analysis, unamended DEA rates at both Roller and Cooch milldams appear correlated with nitrate-N concentration and OM content (Table 1). Given that denitrification requires both nitrate as the terminal electron acceptor and OM as an electron donor, it is unsurprising that these were related. Nitrate-N became less important in controlling amended DEA rates, which were most correlated with OM and clay and silt contents (Table 1).

It appears that nitrate-N concentrations are limiting rates of denitrification in milldam riparian terraces. As evidence, nitrate-N concentration was more correlated than OM content with unamended DEA rates, and this was apparent in the spatially consistent patterns of nitrate-N concentrations and estimated rates of denitrification. Indeed, above the milldams, estimated denitrification rates were highest in shallow sediments where nitrate-N was most abundant (Figure 5). In contrast, OM content was relatively consistent with depth, indicating a more limited correlation. Unlike the total OM content, the OM type (especially lability) may vary with depth. Often, OM lability is greatest in shallow sediments and could therefore drive higher DEA rates in shallow sediments (e.g., Hill & Cardaci, 2004; Matheson et al., 2002). However, C:N ratios, a proxy for organic matter quality/lability (Hill & Cardaci, 2004), were not significantly correlated with unamended or amended DEA rates (Table 1) and did not vary much with depth (Figure 5c), similar to OM content. Assays that incorporate nitrate-only and carbon-only amendments should be performed to tease these limitations out further.

Overall, despite the presence of a small number of high DEA rates in shallow sediments, these denitrification estimates were not as high as expected. We are therefore still left with the question: What other N reductive processes are occurring in saturated milldam riparian sediment terraces, especially at depths below the minimum

Figure 5. Comparison of sediment denitrification and biogeochemistry with depth to test hypothesis 3. (a–b): Sediment unamended denitrification enzyme assay (DEA) and amended DEA rates; (c): C:N ratios; (d): organic matter contents; and (e–f): nitrate-N and ammonium-N concentrations for upstream sites at Roller and Cooch binned every 1 m with depth and plotted as box plots (boxes represent first and third quartile, center lines indicate medians, whiskers are minimums and maximums, and dots are outliers). Depths were normalized to the 100% groundwater saturation depth, where depths below 0 m were observed to always be saturated, and depths above 0 m (gray dashed line) were observed to be saturated or dry depending on precipitation. Sample sizes are labeled above the corresponding box plots.

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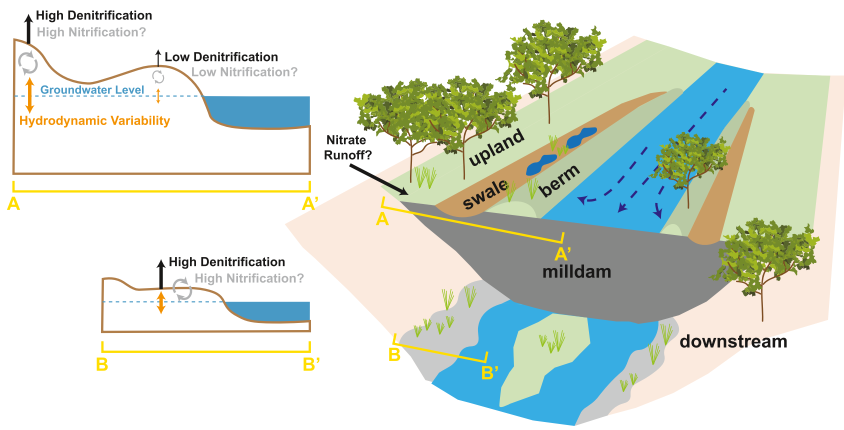

Figure 6. Conceptual model of the relationship between hydrologic variability and denitrification rates. Riparian areas upstream of milldams and close to the creek are hydrologically stagnant and as such denitrification is limited. Conversely, riparian areas further from the creek or downstream of milldams are hydrologically more variable, and wet/dry phases stimulate nitrification, producing nitrate to fuel denitrification rates.

groundwater level? Ammonium-N concentrations may provide insights into other major N processes as they are inversely related to nitrate-N concentrations (Figure 7). While nitrate-N was maximum at the surface and decreased sharply with depth, ammonium-N was lowest in surface sediments and increased significantly with depth (Figures 5e and 5f). Suppression of ammonium consumption by nitrification and/or DNRA could result in accumulation of ammonium-N. However, the strong opposing relationship between nitrate-N and ammonium-N suggests DNRA may be occurring as denitrification and DNRA are metabolically competitive processes for nitrate-N usage under reducing conditions (Minick et al., 2016; Pandey et al., 2020; Silver et al., 2001). Furthermore, DNRA is favored over denitrification under low nitrate-N conditions (Pandey et al., 2020; Rütting et al., 2011; Sgouridis et al., 2011; Wang et al., 2020). Thus, denitrification may be occurring in more hydrologically variable shallow sediments where dry periods stimulate production of nitrate-N via nitrification and upland groundwater runoff may provide an additional source of nitrate-N. Conversely, DNRA may become a more significant N process at deeper, more consistently saturated sediments with lower nitrate-N concentrations

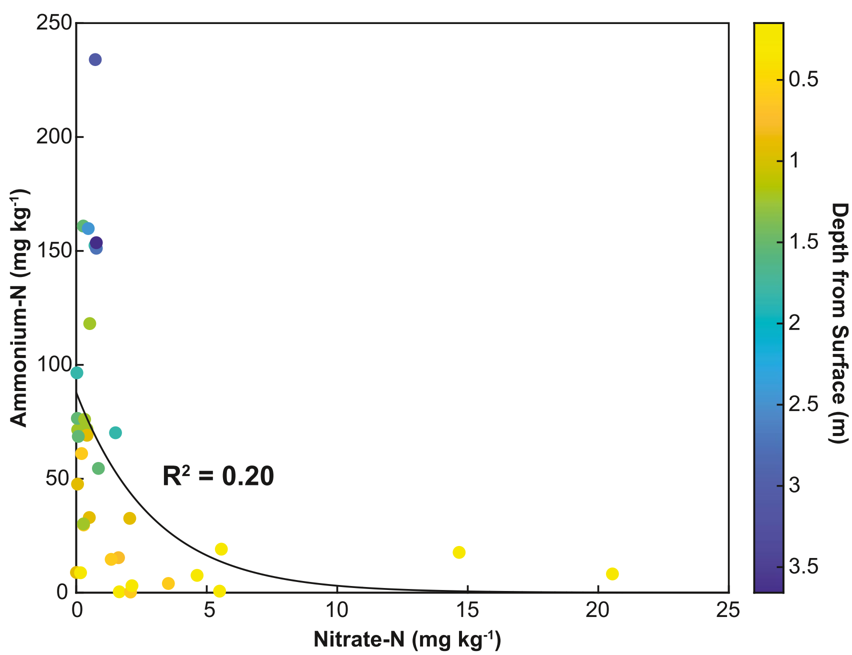

Figure 7. Negative exponential relationship (black line; $R^2 = 0.20$; $p < 0.01$; $n = 35$) between ammonium-N and nitrate-N concentrations for upstream riparian sediment terrace sediments colored with depth from the surface.

(Inamdar et al., 2021). Unfortunately, our analysis did not include direct measurements of DNRA, which should be performed in the future as it is an understudied, potentially important component of riparian N cycling. Indeed, zones of concentrated ammonium-N have been observed in other riparian systems with similar groundwater hydrodynamics, such as beaver ponds (Duval & Hill, 2006; Lazar et al., 2015; Naiman et al., 1994) and urban "accidental" wetlands (Handler et al., 2022). While many early studies have typically attributed high ammonium-N concentrations to ammonification and suppression of nitrification, there is increasing appreciation of the importance of DNRA as a mechanism for N production in anoxic soils/sediments. If DNRA occurs widely above mid-Atlantic milldams and is significant in riparian sediments, removal of milldams (and accompanied mitigation of legacy sediment concentrated in ammonium) may contribute to improved water quality goals.

5. Conclusions

Overall, this study indicates that wet conditions and elevated groundwater levels in riparian terraces upstream of milldams may not necessarily translate into high N buffering capacity through denitrification. In fact, consistently wet, stagnant/poorly mixed conditions above dams may actually be suppressing denitrification. In contrast, more hydrodynamically variable conditions in shallow sediments, especially those further from the creek (possibly receiving nitrate-rich upland runoff) or downstream of the milldam, lead to a coupling of nitrification/mineralization and denitrification. These two N pathways dominate during wet/anoxic and dry/oxic periods, respectively. Despite the more variable conditions downstream of the milldam, the deeper, wider terraces upstream of the milldams result in greater N buffering capacity per unit length of the stream. At depths below the seasonal high water table, which make up the majority of the sediment depth profile in riparian areas upstream of milldams, nitrate-N concentrations decrease while ammonium-N concentrations increase. It is likely that processes such as ammonification and/or DNRA are responsible for producing ammonium-N.

Whether these findings extend to milldams in other regions and landscapes needs to be investigated since this would affect watershed N management, dam removal decisions, and riparian buffering potentials. Moreover, whether a similar N cycling behavior extends to coarse grained riparian sediments (greater sand content) also needs to be investigated. In situ, push-pull type of denitrification assays could also provide valuable insights into N removal rates as opposed to laboratory-based DEA assays. The fate of the ammonium-N accumulating in riparian sediment terraces upstream of intact milldams should be assessed as well, given its propensity to contribute to degraded water qualities across riverscapes.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All data are available on Hydroshare (https://www.hydroshare.org/resource/dae70b4130b04b95aca4081522ccfe78/).

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