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RESEARCH ARTICLE

Effects of relic low-head dams on stream denitrification potential: seasonality and biogeochemical controls

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Abstract

The majority of dams in the contiguous United States are small, low-head dams that are no longer operational but can influence the water quality of contemporary stream ecosystems. Potential effects of low-head dams on stream nitrogen removal (denitrification) have been rarely quantified, and yet they can be an important part of the decision-making process of removing low-head dams. Here, we provide novel empirical data on potential denitrification rates and their biogeochemical controls above and below two mid-Atlantic low-head dams over a 2-year period. Our results show that low-head dams did not increase streambed potential denitrification in comparison to dam-free sections in the same rivers. In our study sites, potential denitrification above low-head dams was generally low (15.7 ± 3.5 μg N [kg sediment]$^{-1}$ h^{-1}) despite recurring events of water hypoxia (< 50% dissolved oxygen saturation) and high NO_3^- and DOC concentrations. Overall, we observed higher potential denitrification during winter samplings (9.2 and 50.1 μg N [kg sediment]$^{-1}$ h^{-1} on average) and significant effects of sediment surface area and organic matter content on potential denitrification rates above the dams. Results from this study suggest limited effects of relic low-head dams on nitrogen removal and transport in stream ecosystems, and can contribute to the decision-making process of removing low-head dams.

Keywords Low-head dams · Streams · Nitrogen · Denitrification · And anoxia

Introduction

Although much of the previous research has focused on the environmental impacts of large dams (Poff and Hart 2002; Barbarossa et al. 2020), the vast majority of dams in the US are small (less than 4.5 m in height), *aka* low-head dams (Brewitt and Colwyn 2020; USACE 2020). In the mid-Atlantic region, most of the existing low-head dams are 17th- to 19th-century milldams that are no longer operational and currently filled to capacity with sediment (Walter and Merritts 2008). These relic low-head dams are one of the most pressing environmental challenges in the mid-Atlantic and northeast regions (Martin and Apse 2011), and a prime example of the legacy effects of human land use on contemporary ecosystems (Inamdar et al. 2021). Ecological effects of low-head dams on fish (Tiemann et al. 2004; Gillette et al. 2005; Yan et al. 2013), invertebrates (Tiemann et al. 2005; Smith et al. 2015), and sediment (Pearson and Pizzuto 2015; Casserly et al. 2020) have been documented, but the influence of relic low-head dams on stream nutrient processing and removal (e.g., denitrification) has seldom been investigated.

Denitrification is a microbially mediated process that results in a net loss of nitrogen (N) from aquatic ecosystems and has a major role in regulating N removal in streams (Groffman et al. 2006; Seitzinger et al. 2006; La Notte et al. 2017). Stream denitrification rates are typically higher in the top 2–5 cm of stream sediments where low oxygen conditions and organic carbon sources are frequently encountered (Burgin and Hamilton 2007). Relic low-head dams generally result in deeper and wider stream channels above them (Stanley et al. 2002; Csiki and Rhoads 2014; Fencl et al. 2015), increasing water residence time and deposition of organic matter (OM) (Proia et al. 2016; Casserly et al. 2020). Accordingly, from a hydrological perspective, relic low-head

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dams can create favorable conditions for denitrification and could act as hotspots of nutrient removal in stream networks. Previous studies have estimated an important contribution of small dams and reservoirs to riverine denitrification using empirical relationships between N removal and water residence time (Seitzinger et al. 2002; Powers et al. 2015; Gold et al. 2016). However, these models were based on limited available data and do not separate biological and hydrologic processes controlling N removal. To further assess how relic low-head dams can affect stream N removal and transport, it is also necessary to determine the magnitude of biological activity (*i.e.,* areal uptake) relative to hydrological conditions (Wollheim et al. 2006). At present, site-specific measurements of denitrification activity above low-head dams have—to the best of our knowledge—never been documented, limiting our ability to predict N delivery estimates (Gold et al. 2016) and to quantify the role of relic low-head dams as denitrification hot spots, here in defined as a localized area of comparatively high denitrification rates.

Here, we address this key data and knowledge gap by measuring potential denitrification rates and their biogeochemical controls at two mid-Atlantic low-head dams. Over 2 years, we measured nutrient concentrations, sediment particle size distribution, sediment incubations, and denitrification enzyme assays at each stream site. Then, we investigated the seasonality and controls of potential denitrification rates in sediments upstream and downstream of these two relic low-head dams, Roller (2.4 m height) and Cooch-Dayett (4 m height) milldams, located in two streams of the mid-Atlantic region with contrasting land uses (i.e., agricultural and urban dominated). Specifically, we examined how potential denitrification rates upstream of dams compare to downstream, how these rates vary among seasons, and what are their main controlling factors. We hypothesized that stream sediments upstream of relic low-head dams would have greater potential denitrification rates compared to free-flowing downstream locations due to enhanced fine sediment and OM deposition, enhanced hypoxia, and increased water–sediment interaction (longer water residence time) in impounded waters.

Methods

Study sites

The Cooch-Dayett milldam (*circa* 1792) sits on the Christina River (39.6455, − 75.7425), a third-order tributary of the Delaware River in New Castle Country, DE (Fig. 1a). The dam is roughly 40 m wide and 3.7 m high. At the Cooch-Dayett milldam, hereafter referred to as Cooch dam, the Christina River has an average annual flow of 0.75 $m^3\ s^{-1}$ (USGS station 01478000) and drains a 50.7 km^2 watershed dominated by approximately 24% forest, 23% cropland, and

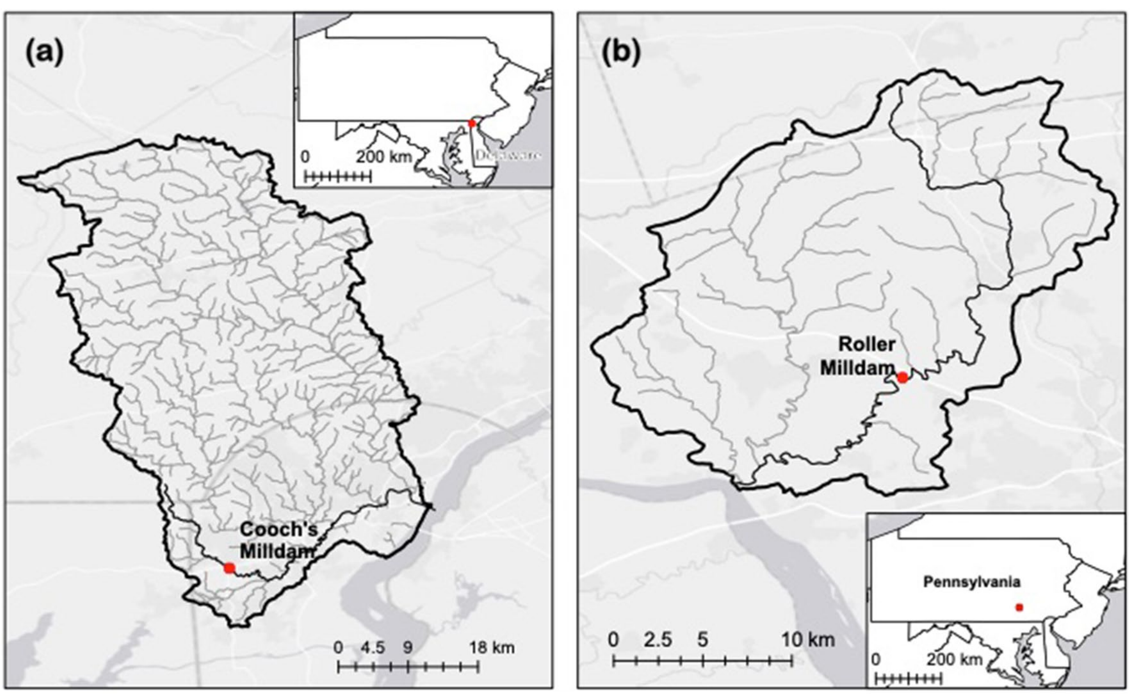

Fig. 1 Watershed maps for the Christina River (**a**) and Chiques Creek (**b**). Inserts indicate the location of each watershed in the US mid-Atlantic. Cooch and Roller dam sites are highlighted with red dots (color figure online)

47% developed land (NLCD 2011). Catchment soils are dominated by sand, loamy sand, or sandy loam with low runoff potential and high infiltration rates (Ries et al. 2008). The Roller milldam (*circa* 1730) is located on Chiques Creek (40.1083, − 76.4431), a third-order tributary of the Susquehanna River in Lancaster County, PA (Fig. 1b). Roller dam is smaller than Cooch dam, measuring approximately 30 m wide and 2.4 m in height. The average annual flow of Chiques Creek near the Roller dam is 1.45 $m^3 s^{-1}$, corresponding to a drainage area of 127 km^2 composed of 24% forest cover, 19% developed, and 56% agricultural lands (NLCD 2011). The catchment and surrounding riparian zone consist mostly of silty-loam soils dominated by Glenelg loam (Ries et al. 2008).

Hydrologic and physicochemical monitoring

Starting in November of 2019, we collected stream water samples every other week above each dam (within ~ 10 m) in 250 mL Nalgene bottles. In March of 2020, we switched to a monthly sampling frequency due to transport, access, and capacity limitations derived from the COVID pandemic. All samples were immediately stored in ice after collection and filtered within 24 h using glass microfiber filters (Whatman 1825-047 GF/F Glass Microfiber Filters, 0.7um pore size). First, filtered water samples were sub-sampled for the analysis of optical absorbance at 254 nm using an Aqualog spectrophotometer (HORIBA Europe GmbH, Oberursel, Germany). The remaining filtered volume was acidified with high-purity HCl 34–37% until pH decreased below 2.0 to preserve each sample. Later, samples were analyzed for total dissolved N (TdN) and dissolved organic carbon (DOC) concentrations using a Vario-Cube total organic carbon (TOC) analyzer (ELEMENTAR Americas Inc, New York, US), and for nitrate–N (N-NO_3^-) and ammonium-N (NH_4^+-N) by colorimetric analysis using an AutoAnalyzer 3 continuous-flow analyzer (Bran & Luebbe, Norderstedt, Germany) at the University of Delaware Soils Laboratory following standard procedures (APHA 2006). Specific ultraviolet absorbance values were divided by DOC concentrations to estimate $SUVA_{254}$ values following Weishaar et al. (2003). High values of $SUVA_{254}$ indicate more aromatic/recalcitrant DOC. On a seasonal basis, we also collected water samples at ~ 100 m increments for a distance of ~ 500 m upstream and downstream of Cooch dam, and only upstream of Roller dam due to access limitations. These water samples were paired to sediment collection for benthic N processes quantification, and were analyzed for N-NO_3^- (EPA-126-D) and NH_4^+-N (EPA-148-D) concentrations using an AQ300 discrete analyzer (SEAL Analytical, Wisconsin, US) and for total N (TN) from an unfiltered sample using a persulfate alkaline digestion followed by N-NO_3^- analysis (EPA-126-D). All chemical analyses were done following standard procedures (APHA 2006).

In January of 2020, we installed an AquaTroll 600 multiparameter sonde 150 m downstream of the Cooch dam to measure dissolved oxygen (DO) concentrations and water temperature every 30 min. At the Roller dam, dissolved oxygen and water temperature data were obtained 300 m downstream of dam using an EXO II multiparameter sonde (Yellow Spring Instrument, Ohio, US) recording every 15 min owned and maintained by the Susquehanna River Basin Commission (SRBC) for the duration of the study period. The sondes were routinely cleaned and calibrated on a monthly basis. Later, in July of 2020, we installed DO and water temperature loggers (HOBO Onset, Massachusetts, US) upstream of both dams to record data every 30 min. Stream flow at Chiques Creek was measured by SRBC 300 m downstream of the Roller dam and by USGS (station 01,478,000) in the Christina River 600 m downstream from the Cooch-Dayett milldam.

Streambed sediment sampling and analysis

Streambed sediment cores were collected seasonally from fall 2019 to summer 2021($n = 8$) with their corresponding stream water samples. At each sampling event, ten sediment cores were taken at Cooch dam, five upstream and five downstream, at 100-m increments. At Roller, due to site access restrictions, five sediment cores were collected above the dam. Sediment was collected from a modified canoe to provide greater stability when using an extensible AMS Multi-Stage Sediment Sampler to collect sediment cores from the stream bottom. Cores included sediment from the surface to a varying depth of 15–30 cm depending on the site and sampling date. In the laboratory, cores were homogenized and sub-sampled for further analyses. At Roller dam, cores were collected in October 2019; January, May, July, and September 2020; January, May, and August 2021. At Cooch dam, cores were collected in October and December 2019; May, July, and September 2020; January, May, and August 2021. Samples were collected in 16 oz amber HDPE Nalgene bottles, immediately placed on ice, and kept in the dark until processed within the next 24 h in the laboratory.

To quantify potential denitrification rates in stream sediments (as μg N [kg sediment]$^{-1}$ h^{-1}), we performed denitrification enzyme assays (DEA) following the procedures described in Dodds et al. (2017). This method uses acetylene gas to prevent the reduction of N_2O to N_2, allowing estimation of denitrification activity based on the net accumulation of N_2O. This technique typically relies on promoting anoxia in each bioassay by flushing with an oxygen-free gas (Seitzinger et al. 1993, Groffman et al. 2006). For this reason, all denitrification rates measured in our study are considered to represent potential denitrification rates. The assay consists of two treatments, unamended and amended (DEA), and thus the approach tests each sample in duplicate. Unamended denitrification samples quantify potential denitrification rates under field conditions of carbon and nutrient concentrations, whereas DEA samples measure potential denitrification rates under optimal conditions of C and N supply for denitrification. We hereafter refer to these two treatments as unamended denitrification samples and DEAs. For each treatment, we added 25 mL of wet sediment to 250 mL media septa bottles and mixed it with 20 mL of stream water collected from the same location. DEA samples received 5 mL of DEA media (1.01 g KNO_3 L^{-1}, 0.30 g $C_6H_{12}O_6$ L^{-1}, and 1 g chloramphenicol L^{-1}). Unamended denitrification samples only received 5 mL of chloramphenicol (1 g L^{-1}) to inhibit protein synthesis to stop the production of de novo nitrate reductase enzymes to create measurements close to in situ measurements (Murray and Knowles 1999). Samples were then flushed three times with N_2 to create an anaerobic environment and vented to atmospheric pressure prior to adding approximately 20 mL of acetylene gas (10% of headspace). DEA samples were shaken (175 rpm) at room temperature (18 °C) for 3 h during which we collected 3 mL N_2O gas samples at 0.5, 1, 1.5 and 3-h increments. Unamended denitrification samples were shaken (175 rpm) for 6 h at 18 °C during which we collected 3 mL N_2O gas samples at 1, 2, 4, and 6-h increments. Vials (LabCo 46 W Exetainer® 4.5 ml) were stored upside down, underwater, until N_2O analysis using an Agilent 6890 N gas chromatograph (Agilent Scientific Instruments, California, US) equipped with a 30 m 19091P-Q04 column (Agilent Scientific Instruments, California, US). The injection volume was 10uL, the oven was set at 50 °C, the inlet at 200 °C, and the temperature of the electron captured detector (ECD) was 350 °C. We measured OM content at the end of each DEA analysis by weighing samples oven-dried at 60 °C for 72 h, combusting these samples at 500 °C for 5–6 h, and reweighing them for calculation of dry mass and ash-free dry mass (*i.e.,* organic matter).

We also separately performed sediment incubations to characterize net nitrification and net mineralization rates in each sediment core following procedures described in Groffman et al. (2005) and Dodds et al. (2017). Specifically, 25 mL of wet sediment from each core were sieved using a 2 mm sieve and then mixed in a 125 mL Erlenmeyer flask with 85 mL of stream water collected at the same time of each sediment collection (i.e., all sediments received the same stream water), covered with tin foil, and incubated in the dark while shaken at 135 rpm for four days. Three 20 mL water samples are collected from each flask at 0, 1, and 4 days for NH_4^+-N and N-NO_3^- analysis to characterize net mineralization and nitrification, respectively. Net nitrification rates are the result of both accumulation (from nitrification) and removal (from uptake) of N-NO_3^-. When negative, net nitrification values indicate greater uptake rates than nitrification, although the contribution of assimilatory and dissimilatory (denitrification) uptake processes is not determined. Similarly, positive values of net mineralization indicate greater NH_4^+-N accumulation (from ammonification) than removal (uptake).

Finally, sediment samples from October 2019 to September 2020 ($n = 74$) were analyzed for particle size using a Beckmann Coulter LS 13 320 Particle Size Analyzer (Beckman Coulter, Indiana, US). Samples were disaggregated and sieved to 2000 µm as the particle size detection ranged from 17 to 2000 µm. Vials and the column were cleaned prior to each analysis and background checks run every 10 samples. Additionally, all streambed sediment subsamples ($n = 121$) were dried for 24 h at 60 °C, disaggregated, and sent to the University of Maryland's Central Appalachians Stable Isotope Facility (Frostburg, MD) for δ^{15}N, δ ^{13}C, %C and %N analysis using a Carol Erba NC2500 elemental analyzer (Carol Erba Reagents, Val de Reuil, France) interfaced with a Thermo Delta V + isotope ratio mass spectrometers (IRMS) (ThermoFisher, Massachusetts, US).

Data analysis

We evaluated the effects of relic dams on water temperature and DO concentrations by comparing mean daily differences above and below each dam. We used repeated-measures ANOVA (RM-ANOVA) with 'location relative to dam' as an independent factor and 'sampling date' as our blocking (within-subject) factor to compare nitrogen forms (NH_4^+-N and N-NO_3^-), DOC concentrations, unamended denitrification samples, DEAs, and net N processing rates above and below each dam. Similarly, we also employed RM-ANOVA to compare unamended denitrification samples versus DEAs within each stream and location. When necessary, we $\ln(x + 1)$–transformed our data to ensure model residuals were normally distributed with constant variance among levels. Following statistical analyses, measurements were back-transformed and corrected before being presented as mean values along with standard errors (SE). To assess biogeochemical controls on potential denitrification, we included only data collected above the dams and conducted the same analysis separately for unamended denitrification samples and DEAs. To do so, we used linear mixed-effects (LME) models accounting for the repeated-measures design employed in our sampling by including 'sampling date' as a random effect and 13 variables (Stream, OM, NH_4^+-N, N-NO_3^-, TN, δ^{15}N, δ ^{13}C, %C, %N, %Clay, %Sand, %Silt, and net nitrification) as fixed effects. All explanatory and response variables were log-transformed previously to the analysis. To select the optimal structure of fixed effects we individually dropped explanatory variables from the full LMEs and compared models with the likelihood ratio test following procedures described in Zuur et al. (2009). Error structures were applied in both models (for unamended and DEAs) to normalize variance in model residuals across sampling dates. LME models were finally fitted using restricted log-likelihood with the *lme* function in the 'nlme' package (Pinheiro et al. 2016) in the R environment (R Core Team 2022). We estimated the marginal R^2 of final LME models, which represents the proportion of variance explained by the fixed factors, and the conditional R^2, which corresponds to both fixed and random factors, using the *r.squaredGLMM* function in the 'MuMIn' package (Nakagawa and Schielzeth, 2013).

Results

Physicochemical differences above and below relic low-head dams

During the study period, the stream water temperature was on average 0.4 and 0.8 °C warmer above the Roller and Cooch dams than below them. Daily mean water

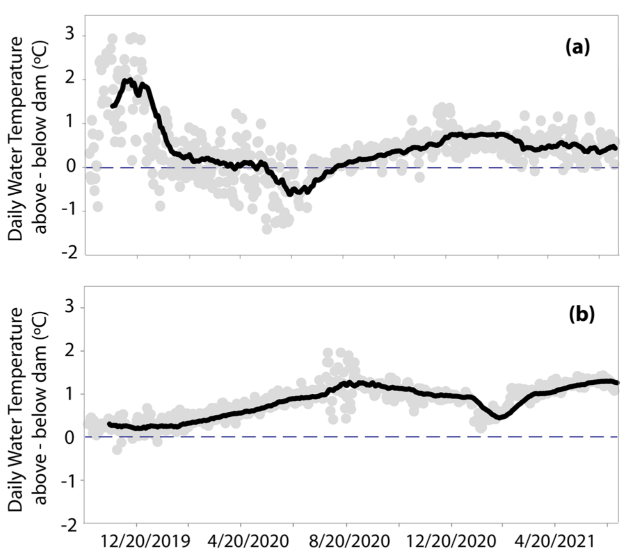

Fig. 2 Average daily difference in water temperature, (calculated as above minus below daily average values, at the Roller (**a**) and Cooch (**b**) dams. Black line represents the 7-day moving average of the mean daily difference in water temperature. Dotted line indicates equal water temperature above and below the dam (color figure online)

temperatures were consistently warmer above the Roller dam during winter months, and similar or even colder than below the dam during summer months (i.e., negative values in Fig. 2a). In contrast, differences in daily water temperature above and below the Cooch dam were always positive, indicating a more permanent warming effect of the dam on stream temperatures throughout the year (Fig. 2b). Dissolved oxygen saturation (DO_{sat}) was typically lower, and more variable, in impounded waters (above dams) than in free-flowing sections (below dams) over the period of record (Fig. 3). Abrupt drops in DO_{sat} to hypoxic conditions (< 50%, Carter et al. 2021) were usually preceded by storm events (Fig. 3), suggesting mobilization of hypoxic water due to storm flows. Hypoxic and anoxic events were particularly pronounced in the summer after longer periods of base flow conditions (Fig. 3d–e).

Average concentrations of nitrate (6.4 ± 0.3 µg N L^{-1}) and TdN (6.9 ± 0.3 µg N L^{-1}) were five times higher at Roller than at Cooch dam (1.1 ± 0.1 and 1.9 ± 0.1 µg N L^{-1}, Fig. 4a, b), contrasting with similar average NH_4^+-N concentration between the two sites (0.05 ± 0.01 µg L^{-1}; Fig. 4c). Mean DOC concentration was higher at the Cooch dam than at Roller, averaging 4.7 and 3.3 mg L^{-2}, respectively (Fig. 4d). Mean $SUVA_{254}$ values at Cooch dam (3.1 ± 0.4 L mg-M^{-1}) were also higher compared to Roller dam (2.2 ± 0.4 L mg-M^{-1}). Across seasons, N-NO_3^- and TdN concentrations at both sites were generally highest in the winter, lowest in the summer, and slightly rising again in the fall (Fig. 4a). Overall, we found no significant differences in inorganic (N-NO_3^- and NH_4^+-N) or total (TdN) concentrations when comparing conditions above and below each impoundment (Table 1). We also found no differences in $SUVA_{254}$ above and below the dam at neither sites (RM-$ANOVA_{0.24–0.78,\ 1}$, *p* value > 0.6 and > 0.9).

Composition and particle size of low-head dam sediments

We found similar volumetric contributions of silt, clay, and sand fractions to sediment collected above both dams. Sand dominated at both sites and smaller size fractions (silt and clay) were more abundant at Roller than at Cooch dam (Fig. 5a). However, small differences in clay fractions by volume between sites translated into large differences in clay's contribution to sediment surface area (Fig. 5b). At Roller dam, an average of 75% of sediment surface area was attributed to clay, while at Cooch dam, most of sediment surface area (64% on average) was associated with sand (Fig. 5b). While we observed substantial variation in sediment particle size over space and time, we found no consistent patterns based on seasonality and/or proximity to the dam. Similarly, OM content in stream sediments above Roller (4.7%) and Cooch (3.2%) dams was similar

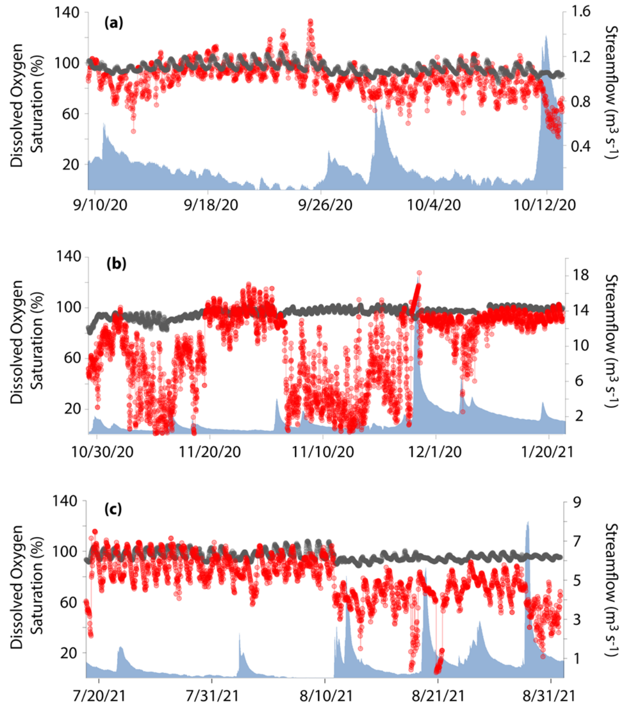

Fig. 3 Dissolved oxygen saturation every 30 min during three time periods above (red dots) and below (grey dots) Roller (**a**–**c**), and two time periods above and below Cooch (**d**–**e**) dam. Concurrent stream flow is plotted (in blue) in the background for each time period and location (color figure online)

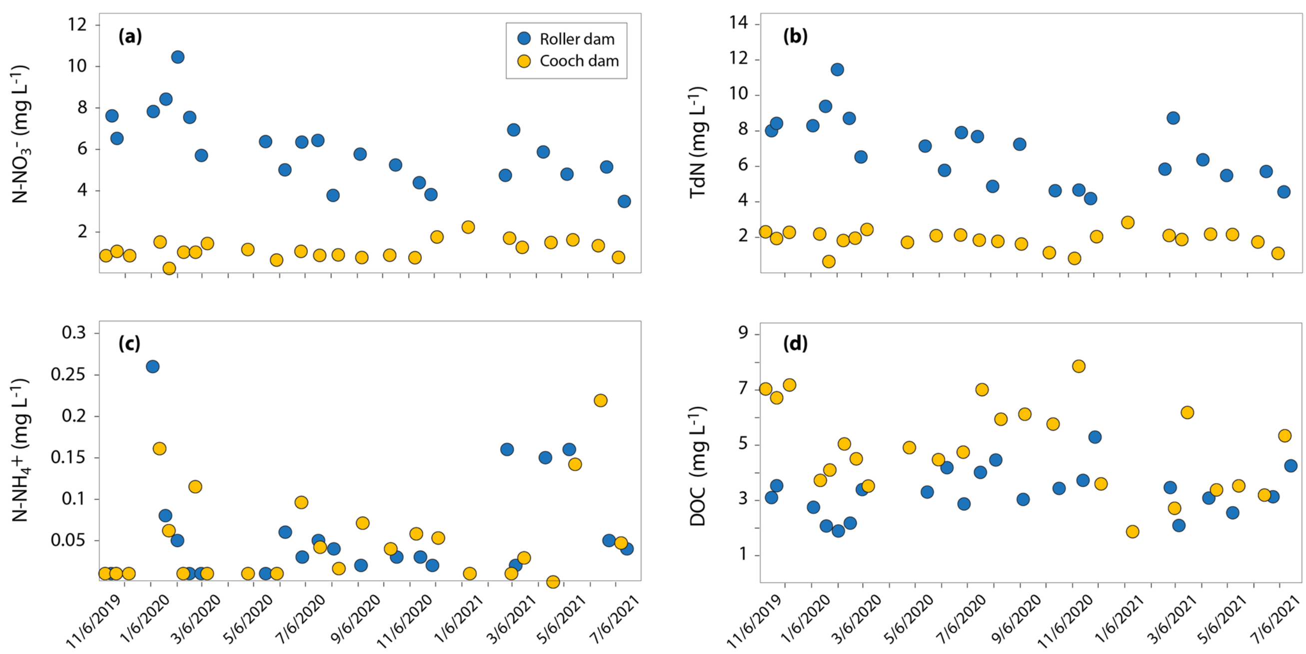

Fig. 4 Monthly concentrations of nitrate (N-NO_3^-) (**a**), total nitrogen (TdN) (**b**), ammonium (N-NH_4^+) (**c**), and dissolved organic carbon (DOC) (**d**) over 2 year period above Roller (blue dots) and Cooch (yellow dots) dams (color figure online)

Table 1 Summary of stream nitrogen concentrations above and below low-head dams

Site	N	$N\text{-}NO_3^-$	$N\text{-}NH_4^+$	TN
Roller dam				
Above	20	4.3 ± 0.4	0.10 ± 0.06	9.3 ± 0.5
Below	20	4.4 ± 0.3	0.06 ± 0.03	10.1 ± 0.4
Cooch dam				
Above	7	1.1 ± 0.3	0.04 ± 0.02	6.7 ± 0.2
Below	7	1.1 ± 0.3	0.04 ± 0.01	6.5 ± 0.3

Data are arithmetic mean ± standard error where N = total number of observations. All values are in mg N L^{-1}

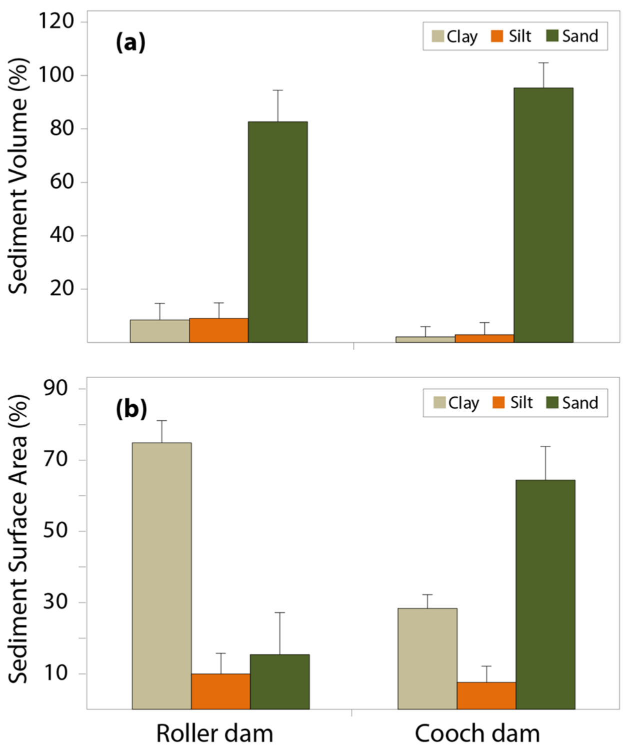

Fig. 5 Percent sediment particle size by volume (**a**) and by surface area (**b**) at each study site. Bars represent mean values above each dam and error bars correspond to standard errors

(RM-ANOVA$_{1.09,\ 1}$; p value = 0.314) and highly variable within each site—3.9 and 5.5% standard deviation values at Roller and Cooch, respectively.

Low-head dam effects on stream nitrogen processes

Comparisons between the two stream sites showed that both unamended denitrification samples and DEAs were more than two times higher above the Roller dam than above the Cooch dam (Table 2). Using the proportional area-to-volume ratio in our sediment cores, we estimated a similar difference in areal denitrification rates above Roller and Cooch dams—92.8 ± 16.5 and 44.7 ± 7.8 µg N m^{-2} h^{-1}, respectively. Net nitrification and mineralization rates were also highest at the Roller dam, regardless of the location relative to the dam (Table 2).

At each stream site, potential denitrification rates in unamended samples were lower than DEA samples (Table 2), indicating higher potential denitrification when additional C and N substrates were provided. However, differences between unamended denitrification and DEA rates were only statistically significant below the Cooch dam (RM-ANOVA$_{9.22,\ 1}$; p value = 0.003). Overall, potential denitrification rates (µg N [kg sediment]$^{-1}$ h^{-1}) were generally higher above dams than below them, but no statistically significant differences were found (Table 2). Net mineralization rates were also higher above the Roller dam than below it, but not at the Cooch dam (Table 2). In contrast, net nitrification rates below the two dams were higher than above them, although only significantly at the Roller site (Table 2).

Seasonal patterns of unamended denitrification and DEA rates were generally similar at both sites (Fig. 6). Potential denitrification rates at Roller dam showed a robust seasonality over the 2-year period with high rates in the winter and low in the summer (Fig. 6a, b). In the winter, unamended potential denitrification was negatively related to net nitrification with similar values of opposite sign that suggest a high contribution of denitrification to

Table 2 Summary of potential denitrification and nitrogen transformation rates above and below each low-head dam

Site	N	DEA (ug N kg $^{-1}$ h^{-1})	Unamended denitrification (ug N kg^{-1} h^{-1})	Net mineralization (ug N kg^{-1} h^{-1})	Net nitrification (ug N kg^{-1} h^{-1})
Roller dam					
Above	38	40.5 ± 9.8	22.3 ± 4.9	0.66 ± 0.16	0.25^{A} ± 0.14
Below	4	7.7 ± 7.7	7.1 ± 3.7	0.43 ± 0.14	0.41^{B} ± 0.39
Cooch dam					
Above	35	19.4 ± 4.2	9.2 ± 2.2	− 0.18 ± 0.09	− 0.01 ± 0.09
Below	35	23.5 ± 8.3	5.3 ± 1.3	0.03 ± 0.11	0.11 ± 0.08

Data are arithmetic mean ± standard error where N = total number of observations. All rates are expressed per kg of sediment. For a given stream, mean values within a column with unique superscripts are significantly different (p < 0.05) following RM-ANOVA

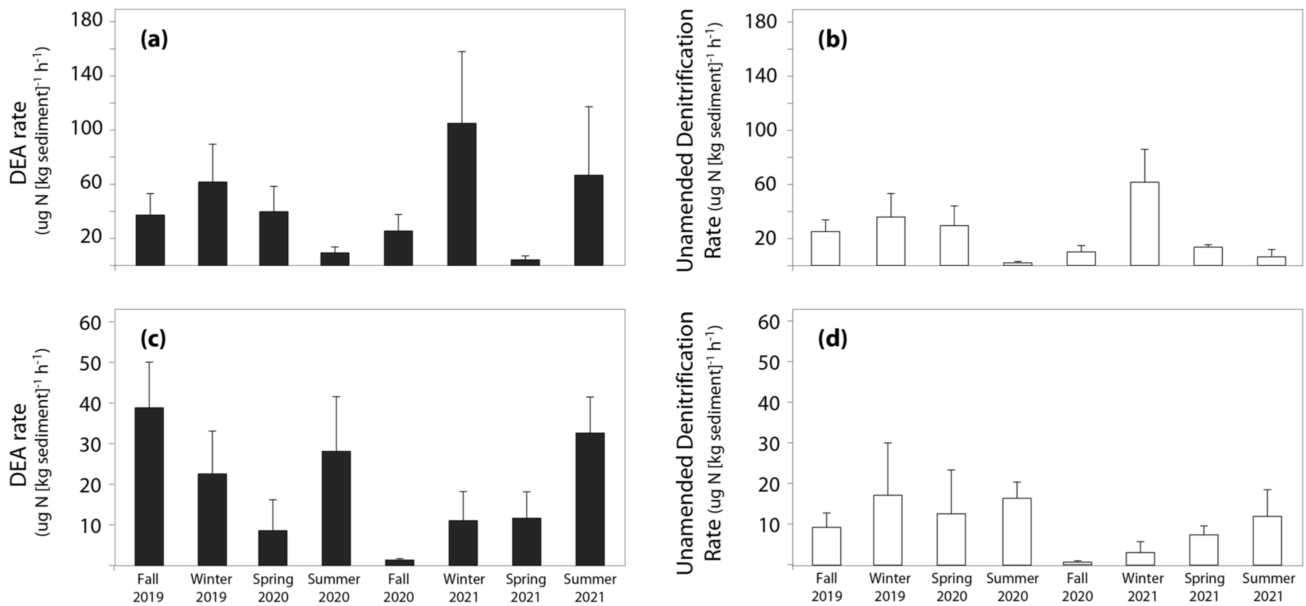

Fig. 6 Seasonal trends of potential denitrification rates (μg N [kg sediment]$^{-1}$ h^{-1}) above Roller (**a**, **b**) and Cooch (**c**, **d**) dams. Black columns correspond to mean values of DEAs (**a**, **c**) and white columns (**b**, **d**) to mean values of unamended denitrification samples. Error bars correspond to standard errors (color figure online)

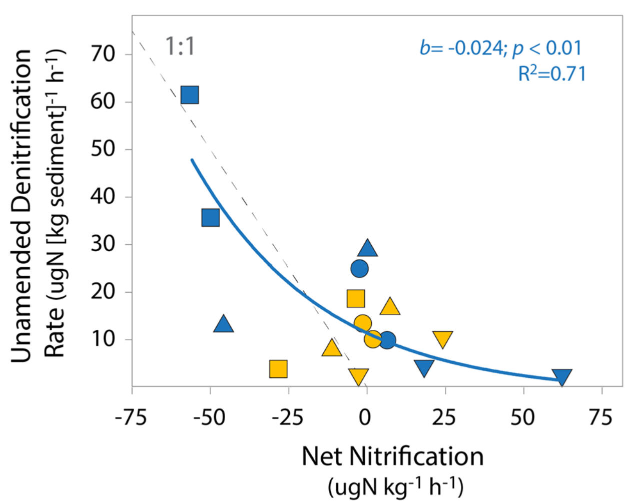

Fig. 7 Relationship between unamended denitrification samples (μg N [kg sediment]$^{-1}$ h^{-1}) and net nitrification (μg N [kg sediment]$^{-1}$ h^{-1}) at Roller (blue dots) and Cooch (yellow dots) dams. Dotted line indicates equal values on both axes. Seasonal averages are displayed as follows: winter (squares), fall (triangle up), spring (circles), and summer (triangle down). Solid line represents the significant relationship between unamended denitrification samples and net nitrification at Roller dam (color figure online)

net N uptake. In contrast, near-zero unamended potential denitrification during the summer matched with the highest net nitrification values (Fig. 7). Seasonal denitrification patterns were much less consistent at the Cooch dam, where summer potential denitrification rates were among the highest values observed at this site, and even higher than summer denitrification at Roller dam (Fig. 6c, d). We found no relationship between unamended denitrification samples and net nitrification rates at Cooch dam (Fig. 7). In the fall of 2020, we measured some of the lowest unamended denitrification and DEA rates observed in our study, suggesting large-scale conditions at the time limiting biological activity and stream N removal capacity in both streams (Fig. 6).

Biogeochemical controls of denitrification in low-head dams

Assessment of potential denitrification drivers within each stream site showed that unamended denitrification samples were correlated to silt surface area in both dams (Fig. 8a) and to sediment OM at Cooch dam (Fig. 8b). No clear correlations were found between DEAs and biogeochemical predictors within each study site. On the other hand, LME models including above-dam data from both stream sites showed similar effects of sediment surface area and N content on both unamended denitrification and DEAs. For unamended denitrification samples, silt surface area was the only significant predictor, which along with sediment N content accounted for only 7% of the observed variation in unamended denitrification (Table 3). In total, our LME model could only explain less than 20% of the observed variation in unamended denitrification samples, of which a large portion was associated with the effects of sample date as a random effect (Table 3). For DEAs, both clay volume and surface area were significant predictors of denitrification potential, and along with sediment

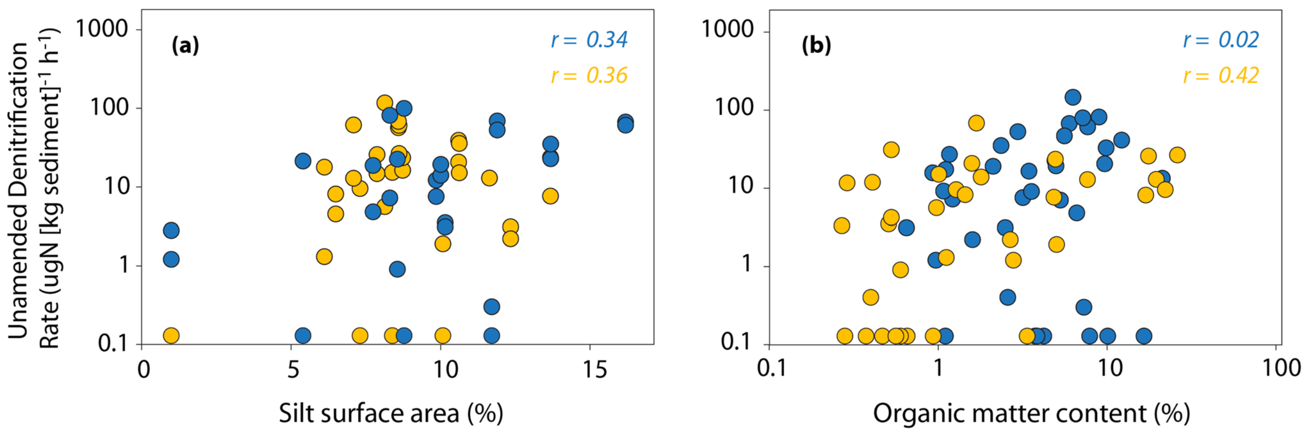

Fig. 8 Relationships of unamended denitrification samples (μg N [kg sediment]$^{-1}$ h^{-1}) with silt surface area (**a**) and with organic matter content (**b**) above Roller (blue dots) and Cooch (yellow dots) dams. Note log-scale in both vertical axes and one horizontal axis (color figure online)

Table 3 Summary of linear mixed-effects models for unamended denitrification samples and DEAs

Model variables	Fixed effects				Variance explained	
	Estimate	Std. Error	*t* value	*p* value	Marginal R^2	Conditional R^2
Unamended denitrification						
Intercept	0.01	0.85	0.01	0.989	0.07	0.17
Nitrogen content (%)	− 0.09	0.27	− 0.35	0.731		
Silt content (% by surface area)	1.10	0.51	2.14	0.044*		
DEA						
Intercept	3.86	1.04	3.72	0.001**	0.41	0.41
Nitrogen content (%)	0.84	0.59	1.42	0.171		
Clay content (% by volume)	− 2.87	0.83	− 3.44	0.003**		
Clay content (% by surface area)	0.59	0.24	2.44	0.024*		

Both models included sample date as the random intercept factor and allowed for the variance of model residuals to vary among sampling dates

p-values of model parameters are indicated by superscripted symbols as: *$p < 0.05$; **$p < 0.01$; ***$p <$ 0.001

N content accounted for more than 40% of the observed variation in DEAs (Table 3). Random effects (sample date) in our final LME model for DEAs were negligible as indicated by the equal marginal and conditional R^2 values (Table 3). In both unamended denitrification and DEAs models, the surface area of fine sediment fractions (silt and clay) showed positive effects on potential denitrification (Table 3). In the case of DEAs, we also found a significant and negative effect of clay volume on potential denitrification rates (Table 3).

Discussion

We found limited support for our initial hypothesis that relic low-head dams increase stream denitrification. However, our results showed multiple episodes of hypoxia and significant control of fine sediments on potential denitrification rates in impounded waters above low-head dams. In light of this new evidence, we speculate that the present capacity of relic low-head dams to accumulate fine sediment and OM deposition is severely limited; which, in turn, reduces denitrification activity above low-head dams and limits their current contribution to watershed N removal in the mid-Atlantic region.

Hydrologic and physicochemical conditions above low-head dams

Our two study sites had clear and contrasting conditions of human influence and land-use legacies. Roller dam at Chiques Creek sits in a heavily agriculturally influenced watershed and exhibited high NO_3^- concentrations for the most part of our study. In contrast, N-NO_3^- concentrations were much lower in the more urbanized Cooch dam site in the Christina River watershed. Similarly, potential denitrification rates were also generally higher at

Chiques Creek, suggesting a positive effect of the high N availability on potential denitrification rates at this site. Nitrate concentrations in both streams were high enough to avoid threshold levels that can severely limit denitrification (0.88 mg N-NO_3^- L^{-1} in Inwood et al. 2005; and < 0.04 mg N-NO_3^- L^{-1} in Wall et al. 2005), with a few exceptions during summertime at the Cooch site. But marked differences in N-NO_3^- concentrations and unamended denitrification rates between our two study sites may indicate some degree of N-limitation on stream denitrification. In addition, and given our combined C and N amendment, higher DEA rates compared to unamended denitrification assays at both study sites can also indicate C-limitation, which would be concordant with the more recalcitrant DOC (i.e., high $SUVA_{254}$) observed at the Cooch dam.

Results from our study showed evident periods of hypoxia and anoxia above low-head dams that were synchronous with high DO saturation levels in adjacent free-flowing (below the dam) sections. Low DO levels upstream of several low-head dams have been observed elsewhere during base flow conditions (Santucci et al. 2005). However, we observed that hypoxia above low-head dams is most prevalent after stormflow events that can mobilize low-oxygen waters upstream of the dams. Similar DO responses to stormflow have been documented in rivers with DO-depleted pools (Dutton et al. 2018) and/or incised channels of urban watersheds (Blaszczak et al. 2019). Hypoxia and anoxia above dams are concordant with the high contribution of clay and silt particles to sediment surface area above dams that can promote microbe-water interaction and biological oxygen demand near the dam. However, clay and silt represented only 5 – 20% of the sediment volume within the stream channel above these two milldams, which likely prevented more severe anoxic conditions above each dam. Low fine-grained contribution to sediment volume in the channel upstream of each dam contrasts with the significant amounts of fine-grained particles in legacy sediment stored in fluvial floodplains behind historic milldams (Merritts et al. 2013). In addition, OM content in sediments above Roller and Cooch dams was generally low—5.2 and 3.4 g OM m^{-2} on average with some exceptions (20–40 g OM m^{-2})—and similar to average values found in free-flowing sections of 65 streams spanning eight US regions and three land-use types (Findlay et al. 2002). Together, the lack of exceptional deposits of fine sediment volume and OM above relic dams suggest that hypoxic conditions near them are more likely driven by increased exposure (water residence time) than by exceptionally high biological oxygen demand. Thus, low-head dam hypoxia seems to be strongly controlled by transport rates above the dams, which in turn suggests that low-head dam hypoxia can be a common phenomenon throughout the mid-Atlantic region and proportional to the size of low-head dams.

Previous studies have found a decrease in inorganic N and total phosphorus concentrations when comparing water entering and leaving small dams and attributed this change to net nutrient retention within the impoundment (Stanley and Doyle 2002; Doyle et al. 2005). In our study, we did not observe significant changes in stream nutrient concentrations when comparing conditions above and below low-head dams. Areal denitrification rates estimated from our study sites are in the low range of values found by previous work spanning multiple biomes and streams using both DEA measurements (Findlay et al. 2002) and ^{15}N labeling techniques (Mulholland et al. 2008). Low areal NO_3^- uptake combined with high N-NO_3^- fluxes due to high concentrations, particularly at Roller dam, will lead to a low proportion of the N-NO_3^- flux being removed by benthic denitrification uptake and per unit of stream length; therefore resulting in limited N removal capacity of low-head dams at the watershed scale. Our results suggest that relic low-head dams do not necessarily function as reservoirs and may have a smaller capacity to decrease river N transport than what others have quantified in human-made reservoirs (Powers et al. 2015).

Seasonality and controls of potential denitrification in low-head dams

Numerous studies have described how localized areas with favorable conditions for denitrification activity may exist within a stream network (Kreiling et al. 2019), leading to high spatial heterogeneity and hot spots of denitrification depending on watershed location and biogeochemical constraints (Korol et al. 2019; Comer-Warner et al. 2020; Wu et al. 2021). Accordingly, we hypothesized that stream reaches upstream of relic low-head dams could behave as hot spots of N removal due to the expected increase in accumulation of detritus, water residence time, sediment–water interaction, and hypoxia in these impounded waters. Instead, potential denitrification rates in our study were low or near average compared to what others have found in old and new beaver dams (27–79 µg N [kg sediment]$^{-1}$ h^{-1}; Lazar et al., 2015), high OM debris dams (185–4955 µg N [kg sediment]$^{-1}$ h^{-1}; Opdyke et al., 2006), or in geomorphic structures of urban streams (2.6–4955 µg N [kg sediment]$^{-1}$ h^{-1}; Groffman et al., 2005). Our findings also showed a lack of significant differences in streambed denitrification when comparing above and below dam conditions. Unamended denitrification analyses using the acetylene-block method can underestimate denitrification by inhibiting nitrification and subsequent nitrate supply (Groffman et al. 2006). However, the lack of clear differences in unamended denitrification samples above (lower DO_{sat}) and below (higher DO_{sat}) the dams suggest that nitrification inhibition was not a relevant factor for the lack of above-below differences in denitrification.

Denitrification rates are known to vary seasonally and can be highly site specific (Wall et al. 2005; David et al. 2006; Lazar et al. 2015), although common controlling factors are well known (Hall et al. 2009; Beaulieu et al. 2011). One of the most fundamental controlling factors of denitrification and microbial respiration in stream sediments is water temperature (Wall et al. 2005; Jankowski et al. 2014). Small impoundments can cause significant warming in low- to mid-order streams (Gómez-Gener et al. 2018; Zaidel et al. 2021). In our study, stream water above low-head dams was indeed predominantly warmer than below them throughout the year. However, seasonal patterns of denitrification above low-head dams were not coherent with thermal control of microbial activity. We observed robust denitrification seasonality with winter highs and summer lows at Roller dam, and to a certain extent at Cooch dam as well. This seasonal pattern contrasts with typical variation in stream water temperature. We contend that low DEAs in the summer are the result of strong competition between denitrifiers and river algae for NO_3^- uptake. Filamentous algae were abundant above the Roller dam during spring and summer samplings (J. Hripto personal observation). Previous studies have shown the capacity of benthic algae to reduce stream NO_3^- concentrations when solar irradiance is high (McKnight et al. 2004; Mulholland et al. 2006), as is the case in the wide stream channel above Roller dam in which canopy cover is sparse. High similarity in absolute values of unamended denitrification samples and net NO_3^- removal (net nitrification rates) during the winter (Fig. 7) supports our hypothesis that algal N demand in the winter was minimal, decreasing competition for NO_3^- uptake with denitrifying microbes.

While we found several individual relationships between biogeochemical attributes and DEAs above low-head dams, our LME models did not have a strong predictive capacity of the variation in potential denitrification above dams. The limited variance explained by our models (0.17 and 0.41%) may arise from the heterogeneity and complexity of the system, with multiple natural microhabitats with contrasting sediment particle size and OM content that create a heterogeneous biogeochemical template above relic milldams. Patchiness is commonly observed when assessing spatial variation of denitrification rates in undammed stream ecosystems (Royer et al. 2004), and it seems to also be the case in impounded waters above low-head dams. Our results highlight, with decreasing order of importance, physical (silt and clay surface area/volume) and biological (sediment N content and seasonality [as sample date]) controls of denitrification potential. Notably, the presence of fine sediments (silt and clay) was the most relevant factor to promote denitrification activity above low-head dams. Others have found similar effects of substratum particle size on potential denitrification rates when comparing coarse (cobbles, gravel) to finer (< 5 mm) sediments (e.g., Solomon et al. 2009), and attributed to greater availability of anoxic microsites (Groffman and Tiedje 1989; Kemp and Dodds 2002), greater OM content (Garcia-Ruiz et al. 1998), and larger surface area (Pattinson et al. 1998; Inwood et al. 2007). Our results generally support this proposed mechanism by showing measured hypoxia levels above relic dams, positive effects of sediment N content on denitrification, and a direct influence of silt and clay surface area on denitrification activity.

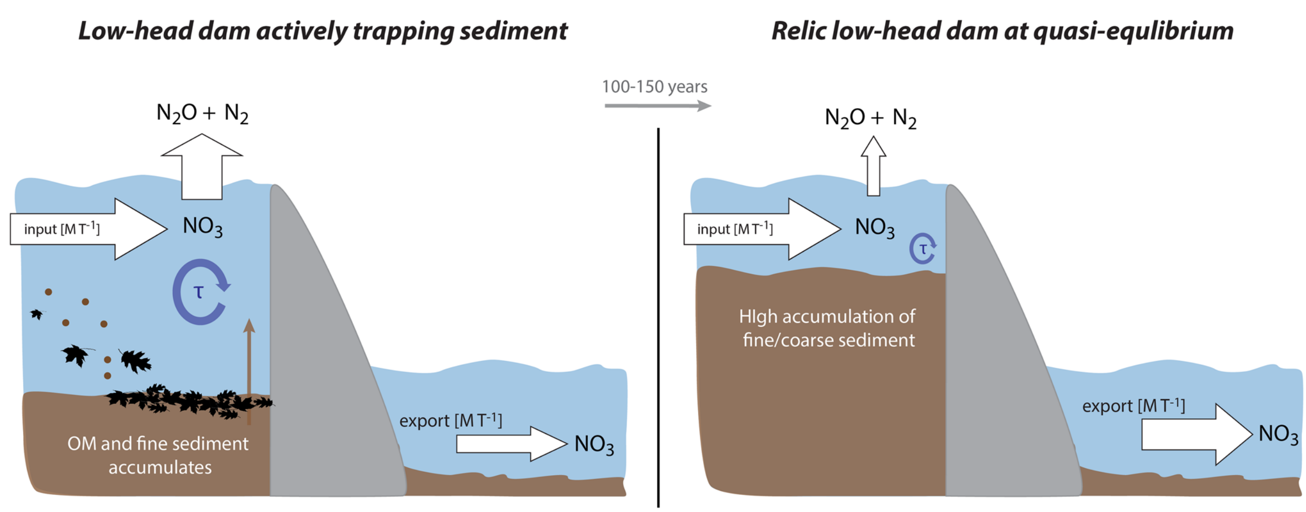

Fig. 9 Schematic diagrams of nitrogen transport and removal fluxes in low-head dams that are actively trapping sediment versus those at quasi-equilibrium filled with sediment to capacity. τ represents water residence time

Environmental implications of relic low-head dams in the Anthropocene

The large number of relic low-head milldams in the mid-Atlantic and northeast regions can influence many stream processes—sediment transport, DO availability, fish migration—but as these relic structures have filled with sediment due to age, the effect on biogeochemical cycling may wane over time, altering N removal and storage capabilities (Fig. 9). While we did find lower DO above the dam, no apparent "hotspots" of denitrification emerged, and significant differences in potential denitrification rates were not found when comparing above versus below dams. Numerous dams constructed during colonial times were effective at collecting and trapping sediment above the dam and preventing sediment and nutrients from continuing downstream (Walter and Merritts 2008), but as dams age their sediment storage capacity lessens as reservoirs become full and shallower upstream of the impoundments. Relic dams that are full and at quasi-equilibrium are no longer trapping fine sediments, and therefore may not be as efficient at removing N as initially hypothesized in this study. From this perspective, relic low-head dams at quasi-equilibrium may no longer contribute to decrease watershed N transport as do larger, and probably deeper, reservoirs (Powers et al. 2015). The large contribution of sand to sediment volume above the dams is in agreement with the current quasi-equilibrium state of relic low-head dams (Pearson and Pizzuto 2015). Site-specific investigations are necessary to better predict how N flux will change in individual watersheds post dam removal (Gold et al. 2016), and a better understanding of the effects of low-head milldams on N processes is integral as dams continue to age and reach full sediment capacity above the impoundments.

Conclusion

This study showed that two relic low-head dams in the US mid-Atlantic did not conspicuously increase streambed potential denitrification in comparison to free-flowing sections of the same river systems. Potential denitrification rates above low-head dams were in line with, or lower than, literature values from natural dams and human-impacted streams. Lack of an enhanced denitrification response above low-head dams occurred despite our observation of lower DO concentrations above dams, and high NO_3^- and DOC concentrations. Highest potential denitrification occurred primarily during winter and was significantly related to silt and clay surface area. Results from this study can contribute to the decision-making process of dam removal by providing empirical evidence for the current effects of low-head dams on stream N processes (or the lack of them) and the expected consequences after low-head dam removal.

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Availability of data and materials The datasets generated and analyzed in this study are available in the following Github repository https://github.com/mpstroud/Hripto2022_data.

Declarations

Conflict of interest The authors have no conflict of interest to declare.

References

APHA (2006) Standard methods for examination of water and wastewater, 21st edn. American Public Health Association, Washington

Barbarossa V, Schmitt RJP, Huijbregts MAJ, Zarfl C, King H, Schipper AM (2020) Impacts of current and future large dams on the geographic range connectivity of freshwater fish worldwide. Proc Natl Acad Sci USA 117:3648–3655

Beaulieu JJ, Tank JL, Hamilton SK, Wollheim WM, Hall RO, Mulholland PJ, Peterson BJ, Ashkenas LR, Cooper LW, Dahm CN, Dodds WK, Grimm NB, Johnson SL, McDowell WH, Poole GC, Valett HM, Arango CP, Bernot MJ, Burgin AJ, Crenshaw CL, Helton AM, Johnson LT, O'Brien JM, Potter JD, Sheibley RW, Sobota DJ, Thomas SM (2011) Nitrous oxide emission from denitrification in stream and river networks. Proc Natl Acad Sci USA 108:214–219

Blaszczak JR, Delesantro JM, Urban DL, Doyle MW, Bernhardt ES (2019) Scoured or suffocated: urban stream ecosystems oscillate between hydrologic and dissolved oxygen extremes. Limnol Oceanogr 64:877–894

Brewitt PK, Colwyn CLM (2020) Little dams, big problems: The legal and policy issues of nonjurisdictional dams. Wiley Interdiscip Rev Water. https://doi.org/10.1002/wat2.1393

Burgin AJ, Hamilton SK (2007) Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Front Ecol Environ 5:89–96

Casserly CM, Turner JN, O'Sullivan JJ, Bruen M, Bullock C, Atkinson S, Kelly-Quinn M (2020) Impact of low-head dams on bedload transport rates in coarse-bedded streams. Sci Tot Environ 716:136908

Carter AM, Blaszczak JR, Heffernan JB, Bernhardt ES (2021) Hypoxia dynamics and spatial distribution in a low gradient river. Limnol Oceanogr 66:2251–2265

Comer-Warner SA, Gooddy DC, Ullah S, Glover L, Kettridge N, Wexler SK, Kaiser J, Krause S (2020) Seasonal variability of sediment controls of nitrogen cycling in an agricultural stream. Biogeochemistry 148:31–48

Csiki SJC, Rhoads BL (2014) Influence of four run-of-river dams on channel morphology and sediment characteristics in Illinois, USA. Geomorphology 206:215–229

David MB, Wall LG, Royer TV, Tank JL (2006) Denitrification and the nitrogen budget of a reservoir in an agricultural landscape. Ecol Appl 16:2177–2190
Dodds WK, Burgin AJ, Marcarelli AM, Strauss EA (2017) Nitrogen transformations. In: Hauer R, Lamberti GA (eds) Methods in stream ecology. Elsevier, San Diego
Doyle MW, Stanley EH, Orr CH, Selle AR, Sethi SA, Harbor JM (2005) Stream ecosystem response to small dam removal: lessons from the Heartland. Geomorphology 71:227–244
Dutton CL, Subalusky AL, Hamilton SK, Rosi EJ, Post DM (2018) Organic matter loading by hippopotami causes subsidy overload resulting in downstream hypoxia and fish kills. Nat Commun. https://doi.org/10.1038/s41467-018-04391-6
Fencl JS, Mather ME, Costigan KH, Daniels MD (2015) How big of an effect do small dams have? Using geomorphological footprints to quantify spatial impact of low-head dams and identify patterns of across-dam variation. PLoS ONE. https://doi.org/10.1371/journal.pone.0141210
Findlay S, Tank J, Dye S, Valett HM, Mulholland PJ, McDowell WH, Johnson SL, Hamilton SK, Edmonds J, Dodds WK, Bowden WB (2002) A cross-system comparison of bacterial and fungal biomass in detritus pools of headwater streams. Microb Ecol 43:55–66
Garcia-Ruiz R, Pattinson SN, Whitton BA (1998) Denitrification in river sediments: relationship between process rate and properties of water and sediment. Freshw Biol 39:467–476
Gillette DP, Tiemann JS, Edds DR, Wildhaber ML (2005) Spatiotemporal patterns of fish assemblage structure in a river impounded by low-head dams. Copeia 2005:539–549
Gold AJ, Addy K, Morrison A, Simpson M (2016) Will dam removal increase nitrogen flux to estuaries? Water 8:522
Gómez-Gener Ll, Gubau M, von Schiller D, Marcé R, Obrador B (2018) Effect of small water retention structures on diffusive CO2 and CH4 emissions along a highly impounded river. Inland Waters 8: 449–460
Groffman PM, Tiedje JM (1989) Denitrification in north temperate forest soils-spatial and temporal patterns at the landscape and seasonal scales. Soil Biol Biochem 21:613–620
Groffman PM, Dorsey AM, Mayer PM (2005) N processing within geomorphic structures in urban streams. J N Am Benthol Soc 24:613–625
Groffman PM, Altabet MA, Bohlke JK, Butterbach-Bahl K, David MB, Firestone MK, Giblin AE, Kana TM, Nielsen LP, Voytek MA (2006) Methods for measuring denitrification: diverse approaches to a difficult problem. Ecol Appl 16:2091–2122
Hall RO, Tank JL, Sobota DJ, Mulholland PJ, O'Brien JM, Dodds WK, Webster JR, Valett HM, Poole GC, Peterson BJ, Meyer JL, McDowell WH, Johnson SL, Hamilton SK, Grimm NB, Gregory SV, Dahm CN, Cooper LW, Ashkenas LR, Thomas SM, Sheibley RW, Potter JD, Niederlehner BR, Johnson LT, Helton AM, Crenshaw CM, Burgin AJ, Bernot MJ, Beaulieu JJ, Arango CP (2009) Nitrate removal in stream ecosystems measured by N-15 addition experiments: Total uptake. Limnol Oceanogr 54:653–665
Inamdar S, Peipoch M, Gold AJ, Lewis E, Hripto J, Sherman M, Addy K, Merritts D, Kan JJ, Groffman PM, Walter R, Trammell TLE (2021) Ghosts of landuse past: legacy effects of milldams for riparian nitrogen (N) processing and water quality functions. Environ Res Lett 16:035016
Inwood SE, Tank JL, Bernot MJ (2005) Patterns of denitrification associated with land use in 9 midwestern headwater streams. J N Am Benthol Soc 24:227–245
Inwood SE, Tank JL, Bernot MJ (2007) Factors controlling sediment denitrification in midwestern streams of varying land use. Microb Ecol 53:247–258
Jankowski K, Schindler DE, Lisi PJ (2014) Temperature sensitivity of community respiration rates in streams is associated with watershed geomorphic features. Ecology 95:2707–2714
Kemp MJ, Dodds WK (2002) The influence of ammonium, nitrate, and dissolved oxygen concentrations on uptake, nitrification, and denitrification rates associated with prairie stream substrata. Limnol Oceanogr 47:1380–1393
Korol AR, Noe GB, Ahn C (2019) Controls of the spatial variability of denitrification potential in nontidal floodplains of the Chesapeake Bay watershed, USA. Geoderma 338:14–29
Kreiling RM, Richardson WB, Bartsch LA, Thoms MC, Christensen VG (2019) Denitrification in the river network of a mixed land use watershed: unpacking the complexities. Biogeochemistry 143:327–346
La Notte A, Maes J, Dalmazzone S, Crossman ND, Grizzetti B, Bidoglio G (2017) Physical and monetary ecosystem service accounts for Europe: a case study for in-stream nitrogen retention. Ecosyst Serv 23:18–29
Lazar JG, Addy K, Gold AJ, Groffman PM, McKinney RA, Kellogg DQ (2015) Beaver ponds: resurgent nitrogen sinks for rural watersheds in the Northeastern United States. J Environ Qual 44:1684–1693
Martin EH, Apse CD (2011) Northeast aquatic connectivity: an assessment of dams on Northeastern Rivers. The Nature Conservancy, Eastern Freshwater Program
McKnight DM, Runkel RL, Tate CM, Duff JH, Moorhead DL (2004) Inorganic N and P dynamics of Antarctic glacial meltwater streams as controlled by hyporheic exchange and benthic autotrophic communities. J N Am Benthol Soc 23:171–188
Merritts D, Walter R, Rahnis M, Cox S, Hartranft J, Scheid C, Potter N, Jenschke M, Reed A, Matuszewski D, Kratz L, Manion L, Shilling A, Datin K (2013) The rise and fall of Mid-Atlantic streams: millpond sedimentation, milldam breaching, channel incision, and stream bank erosion. In: DeGraff JV, Evans JE (eds) Challenges of dam removal and river restoration. Geological Society of America, Boulder, pp 183–203
Mulholland PJ, Thomas SA, Valett HM, Webster JR, Beaulieu J (2006) Effects of light on NO3- uptake in small forested streams: diurnal and day-to-day variations. J N Am Benthol Soc 25:583–595
Mulholland PJ, Helton AM, Poole GC, Hall RO, Hamilton SK, Peterson BJ, Tank JL, Ashkenas LR, Cooper LW, Dahm CN, Dodds WK, Findlay SEG, Gregory SV, Grimm NB, Johnson SL, McDowell WH, Meyer JL, Valett HM, Webster JR, Arango CP, Beaulieu JJ, Bernot MJ, Burgin AJ, Crenshaw CL, Johnson LT, Niederlehner BR, O'Brien JM, Potter JD, Sheibley RW, Sobota DJ, Thomas SM (2008) Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 452:202-U246
Murray RE, Knowles R (1999) Chloramphenicol inhibition of denitrifying enzyme activity in two agricultural soils. Appl Environ Microbiol 65:3487–3492
Nakagawa S, Schielzeth H (2013) A general and simple method for obtaining R^2 from generalized linear mixed-effects Models. Methods Ecol Evol 4:133–142
NLCD (2011) National land cover dataset. USGS, Reston
Opdyke MR, David MB, Rhoads BL (2006) Influence of geomorphological variability in channel characteristics on sediment denitrification in agricultural streams. J Environ Qual 35:2103–2112
Pattinson SN, Garcia-Ruiz R, Whitton BA (1998) Spatial and seasonal variation in denitrification in the Swale-Ouse system, a river continuum. Sci Total Environ 210:289–305
Pearson AJ, Pizzuto J (2015) Bed load transport over run-of-river dams, Delaware, USA. Geomorphology 248:382–395
Pinheiro JC, Bates DM, DebRoy S, Sarkar D, Team RC (2016) Nlme: linear and nonlinear mixed effects models

Poff NL, Hart DD (2002) How dams vary and why it matters for the emerging science of dam removal. Bioscience 52:659–668
Powers SM, Tank JL, Robertson DM (2015) Control of nitrogen and phosphorus transport by reservoirs in agricultural landscapes. Biogeochemistry 124:417–439
Proia L, von Schiller D, Gutiérrez C, Casas-Ruiz JP, Gómez-Gener L, Marcé R, Obrador B, Acuña V, Sabater S (2016) Microbial carbon processing along a river discontinuum. Freshw Sci 35:1133–1147
R Core Team (2022) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/
Ries KG, Guthrie JD, Rea AH, Steeves PA, Stewart DW (2008) StreamStats: a water resources web application. USGS, Reston
Royer TV, Tank JL, David MB (2004) Transport and fate of nitrate in headwater agricultural streams in Illinois. J Environ Qual 33:1296–1304
Santucci VJ, Gephard SR, Pescitelli SM (2005) Effects of multiple low-head dams on fish, macroinvertebrates, habitat, and water quality in the fox river, Illinois. N Am J Fish Manag 25:975–992
Seitzinger SP, Nielsen LP, Caffrey J, Christensen PB (1993) Denitrification measurements in aquatic sediments - a comparison of 3 methods. Biogeochemistry 23:147–167
Seitzinger SP, Styles RV, Boyer EW, Alexander RB, Billen G, Howarth RW, Mayer B, Van Breemen N (2002) Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. Biogeochemistry 57:199–237
Seitzinger S, Harrison JA, Bohlke JK, Bouwman AF, Lowrance R, Peterson B, Tobias C, Van Drecht G (2006) Denitrification across landscapes and waterscapes: a synthesis. Ecol Appl 16:2064–2090
Smith BR, Edds DR, Goeckler JM (2015) Lowhead dams and the downstream dispersal of zebra mussels. Hydrobiologia 755:1–12
Solomon CT, Hotchkiss ER, Moslemi JM, Ulseth AJ, Stanley EH, Hall RO, Flecker AS (2009) Sediment size and nutrients regulate denitrification in a tropical stream. J N Am Benthol Soc 28:480–490
Stanley EH, Doyle MW (2002) A geomorphic perspective on nutrient retention following dam removal. Bioscience 52:693–701
Stanley EH, Luebke MA, Doyle MW, Marshall DW (2002) Short-term changes in channel form and macro invertebrate communities following low-head dam removal. J N Am Benthol Soc 21:172–187
Tiemann JS, Gillette DP, Wildhaber ML, Edds DR (2004) Effects of lowhead dams on riffle-dwelling fishes and macroinvertebrates in a midwestern river. Trans Am Fish Soc 133:705–717
Tiemann JS, Gillette DP, Wildhaber ML, Edds DR (2005) Effects of lowhead dams on the ephemeropterans, plecopterans, and trichopterans group in a North American river (vol 20, pg 519, 2005). J Freshw Ecol 20:800–800
USACE (2020) National inventory of dams. U. A. C. O. Engineers and F. E. M. Agency, Washington
Wall LG, Tank JL, Royer TV, Bernot MJ (2005) Spatial and temporal variability in sediment denitrification within an agriculturally influenced reservoir. Biogeochemistry 76:85–111
Walter RC, Merritts DJ (2008) Natural streams and the legacy of water-powered mills. Science 319:299–304
Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37:4702–4708
Wollheim WM, Voosmarty CJ, Peterson BJ, Seitzinger SP, Hopkinson CS (2006) Relationship between river size and nutrient removal. Geophys Res Lett. https://doi.org/10.1029/2006GL025845
Wu X, Probst A, Barret M, Payre-Suc V, Camboulive T, Granouillac F (2021) Spatial variation of denitrification and key controlling factors in streams and ponds sediments from a critical zone (southwestern France). Appl Geochem 131:105009
Yan Y, Wang H, Zhu R, Chu L, Chen Y (2013) Influences of low-head dams on the fish assemblages in the headwater streams of the Qingyi watershed, China. Environ Biol Fishes 96:495–506
Zaidel PA, Roy AH, Houle KM, Lambert B, Letcher BH, Nislow KH, Smith C (2021) Impacts of small dams on stream temperature. Ecol Indic 120:106878
Zuur AF, Leno EN, Walker NJ, Saveliev AA, Smith GM (2009) Mixed effects models and extensions in ecology with R. Springer, New York, US