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RESEARCH ARTICLE

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Saturated, Suffocated, and Salty: Human Legacies Produce Hot Spots of Nitrogen in Riparian Zones

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Key Points:

- The coupled effects of anthropogenic legacies for nitrogen dynamics are not well understood
- Ammonium-N may accumulate in riparian groundwater and sediments upstream of milldams due to stagnant, poorly mixed, and reducing conditions
- Road salt salinization may further enhance the concentrations of ammonium in riparian groundwaters

Supporting Information:

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

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Abstract

The compounding effects of anthropogenic legacies for environmental pollution are significant, but not well understood. Here, we show that centennial-scale legacies of milldams and decadal-scale legacies of road salt salinization interact in unexpected ways to produce hot spots of nitrogen (N) in riparian zones. Riparian groundwater and stream water concentrations upstream of two mid-Atlantic (Pennsylvania and Delaware) milldams, 2.4 and 4 m tall, were sampled over a 2 year period. Clay and silt-rich legacy sediments with low hydraulic conductivity, stagnant and poorly mixed hydrologic conditions, and persistent hypoxia in riparian sediments upstream of milldams produced a unique biogeochemical gradient with nitrate removal via denitrification at the upland riparian edge and ammonium-N accumulation in near-stream sediments and groundwaters. Riparian groundwater ammonium-N concentrations upstream of the milldams ranged from 0.006 to 30.6 mgN L^{-1} while soil-bound values were 0.11–456 mg kg^{-1}. We attribute the elevated ammonium concentrations to ammonification with suppression of nitrification and/or dissimilatory nitrate reduction to ammonium (DNRA). Sodium inputs to riparian groundwater (25–1,504 mg L^{-1}) from road salts may further enhance DNRA and ammonium production and displace sorbed soil ammonium-N into groundwaters. This study suggests that legacies of milldams and road salts may undercut the N buffering capacity of riparian zones and need to be considered in riparian buffer assessments, watershed management plans, and dam removal decisions. Given the widespread existence of dams and other barriers and the ubiquitous use of road salt, the potential for this synergistic N pollution is significant.

Plain Language Summary

Human activities can combine to exacerbate environmental pollution. We studied the effects of milldams and road salt runoff on nitrogen (N) pollution in streamside/riparian soil and groundwaters in Pennsylvania (Chiques Creek) and Delaware (Christina River). While nitrate-N concentrations in groundwaters and soils were low, ammonium-N concentrations for both sites were unexpectedly high. We attributed the high groundwater ammonium concentrations to processes of ammonification and/or dissimilatory nitrate reduction to ammonium that occurred under stagnant and persistently reducing riparian groundwater conditions. Road salt runoff inputs from an interstate highway above the Christina River site likely exacerbated the groundwater ammonium concentrations because of sodium displacement of ammonium-N from sediment surfaces into solution. We suggest that dam removals could enhance the natural variability in groundwater, induce nitrification-denitrification removal of N, and thus mitigate N pollution in riparian zones. Greater consideration needs to be given to environmental impacts of human legacies in watershed management.

1. Introduction

Human activities such as agriculture, urbanization, mining, logging, and damming have altered the inputs of nutrients like nitrogen (N) to the environment and legacies of these activities can persist for decades to centuries (Basu et al., 2022; Belletti et al., 2020; Kaushal et al., 2021; Van Meter et al., 2018; Walter & Merritts, 2008). While individual legacies are environmentally detrimental, the compounding effect of multiple legacies could be synergistic and is an important challenge for environmental sciences. Nowhere is this more critical than for N dynamics in mixed land use watersheds with extant and legacy loadings from agricultural, industrial, and urban activities that drain into coastal waters vulnerable to N-induced eutrophication (Basu et al., 2022; Van Meter

Tara L. E. Trammell, Dorothy J. Merritts, Robert C. Walter, Jinjun Kan

et al., 2018). Current mitigation practices and policies rarely account for these legacies (Basu et al., 2022; Van Meter et al., 2018), let alone the interactions or compounding effect of multiple legacies. Enhanced nutrient mobilization and inputs associated with land use legacies could undercut water quality targets and environmental goals for watershed programs in the United States (US; Carey, 2021; Van Meter et al., 2018) and elsewhere (Belletti et al., 2020).

In the US, one example of such land use legacy is milldams, which were built by early settlers to harness water power for mills and were established every few miles on streams and rivers (Merritts et al., 2011; Walter & Merritts, 2008). By 1840, there were more than 65,000 water-powered mills and associated dams in the eastern US (Walter & Merritts, 2008). While most milldams have breached or been removed, more than 14,000 still exist across the northeast US (Martin & Apse, 2011) and are actively being removed for aquatic habitat and public safety considerations (Foley et al., 2017; Magilligan et al., 2017; Tonitto & Riha, 2016). These dams, coupled with widespread agricultural erosion, resulted in large-scale accumulation of legacy sediments in valley-bottoms of the eastern US (James, 2019; Walter & Merritts, 2008).

Legacy sediment deposition has substantially altered the structure of riverine ecosystems. Upstream of the dams, legacy sediment deposition has resulted in tall riparian terraces, whereas lower floodplains prevail downstream (James, 2019; Johnson et al., 2019; Walter & Merritts, 2008; Wegmann et al., 2012). In US Piedmont watersheds, legacy sediment terraces are typically composed of fine-grained (silts and clay) sediments with buried organic horizons (Lutgen et al., 2020; Mattern et al., 2020; Merritts et al., 2011; Walter & Merritts, 2008; Wegmann et al., 2012). Where milldams exist, stream and groundwater levels upstream of the dams are high and close to the soil surface resulting in persistent wet and reducing conditions in riparian soils (Merritts et al., 2011; Peck et al., 2022; Sherman et al., 2022). In contrast, where milldams have been breached or removed, streams are incised through legacy sediments, resulting in drained and oxic riparian terraces/soils that may be "perched" and hydrologically disconnected from the stream waters (Inamdar et al., 2021; Merritts et al., 2011). While considerable attention has been paid to how milldams have affected stream geomorphology and fluvial erosion and transport (Cashman et al., 2018; Donovan et al., 2015; Miller et al., 2019), little research has focused on how milldams and associated hydrologic and biogeochemical conditions have altered riparian zone N processes and functions (Inamdar et al., 2021; Lewis et al., 2021; Peck et al., 2022).

At the interface of uplands and streams, riparian ecosystems have been shown to be important processors and "filters" of N (Cole et al., 2020; Dwivedi et al., 2018; Hill, 2019; Lowrance et al., 1997; Lutz et al., 2020; Vidon et al., 2010). Wet and variable reducing conditions in riparian soils encourage N cycle processes like denitrification that convert reactive nitrate-N to N_2O and N_2 gas and thus decrease the concentrations of nitrate-N in groundwaters (Gold et al., 1998; Hill, 2019; Lowrance, 1992). Denitrification losses of nitrate-N are particularly elevated when nitrate-rich groundwaters traverse organic rich soil layers that provide organic carbon electron donors for the heterotrophic process (Gurwick, Groffman, et al., 2008; Gurwick, McCorkle, et al., 2008; Hill, 2011). Fine grained sediments such as clay and silts have also been shown to enhance denitrification because of increased residence time and greater consumption of oxygen in soil pore spaces (Covatti & Grischek, 2021; Ranalli & Macalady, 2010; Zhang & Furman, 2021).

However, persistent hypoxic or anoxic (hypoxic <2 mg L^{-1}, anoxic ∼0 mg/L; Diaz & Rosenberg, 2008) and reducing soil conditions can increase N concentrations in riparian and wetland soils through accumulation of ammonium-N (Duval & Hill, 2007; Jantti et al., 2021; Liang et al., 2020; Reverey et al., 2018; Wang et al., 2020). Early studies attributed this ammonium-N accumulation to ammonification and suppression of nitrification (e.g., Doussan et al., 1998; Duval & Hill, 2007), whereas more recent studies increasingly attribute it to dissimilatory nitrate reduction to ammonium (DNRA; Chen et al., 2022; Covatti & Grischek, 2021; Liang et al., 2020; Murphy et al., 2020; Pandey et al., 2020; Su et al., 2022; Wang et al., 2020; G. Yin et al., 2017; Zhao et al., 2021). Stagnant and/or poorly mixed hydrologic conditions or flow paths with long residence time coupled with very low redox potentials and higher concentrations of electron donors such as organic carbon, dissolved iron (Fe), and sulfide have especially been shown to favor DNRA over denitrification (Burgin & Hamilton, 2007; Covatti & Grischek, 2021; Jantti et al., 2021; Reverey et al., 2018; Robertson & Thamdrup, 2017; Rutting et al., 2011; Sgourdis et al., 2011; Wang et al., 2020; G. Yin et al., 2017). Denitrification typically occurs for low organic C to nitrate-N ratios (OC limiting) while DNRA has been reported for high organic C to nitrate-N ratios (nitrate-N limiting; >10–15; Chen et al., 2022; Pandey et al., 2020; Wei et al., 2022; S. Yin et al., 1998). How this balance between N removal via denitrification versus accumulation through ammonification and/or DNRA occurs in reducing riparian sediments upstream of milldams is a key knowledge gap that needs to be addressed.

Over the last several decades, the sediment and hydrologic legacies of milldams have also been interacting with high salinity waters produced by road salting activities (Hintz et al., 2021; Kaushal et al., 2021). Road salt use tripled in the 1970s with substantial inputs of sodium (Na^+) and chloride (Cl^-) to soils and waterways (Hintz et al., 2021). Sodium displaces other cations off soil surfaces (Ardon et al., 2013; Herbert et al., 2015; Kaushal et al., 2021; Weston et al., 2010) and could directly enhance solubilization of reactive, soil-sorbed ammonium-N. Indirectly, salinization could increase ammonium-N production via its cascading effects on the iron and sulfur cycles and subsequent enhancement of mineralization and/or DNRA and depression of nitrification and denitrification (Giblin et al., 2013; Herbert et al., 2015; Noe et al., 2013). These mechanisms could be particularly pronounced in hypoxic, clay and silt-rich, reducing conditions upstream of milldams contributing to accumulation of legacy N.

How milldams and road salt legacies regulate N removal or transformation in riparian zones will be critical for water pollution and watershed management decisions. Based on the beneficial denitrification-N-removal ecosystem service, riparian zones are being promoted and adopted as a best management practice for N pollution mitigation in the US and worldwide (Cole et al., 2020; Lowrance et al., 1997; Stutter et al., 2019). For example, millions of dollars are being spent implementing riparian forest buffers with an annual goal of 900 miles of riparian buffers in the Chesapeake Bay (Chesapeake Bay Program, 2016). If relict milldams and road salt salinization foster N accumulation and mobilization in riparian soils, it would undercut the effectiveness of riparian buffers as a pollution mitigation practice. Furthermore, given the large number of remnant milldams in the northeast US, riparian N accumulation could also pose a threat to stream water quality, and could provide a new argument for removal of milldams, which is currently not recognized.

Here, we investigate how centennial-scale legacies of milldams and decadal-scale legacies road salt salinization affect N concentrations in riparian groundwaters and soils upstream of existing milldams. The study was conducted for two relict milldams, 2.4 and 4 m tall, that were originally built in the 1700s and are differentially impacted by road salt. The focus was to characterize the variation in groundwater and soil N concentrations along riparian transects from the upland to the stream and investigate the role of reducing conditions, hydrologic mixing, electron donors (dissolved organic carbon and Fe), and road salt salinization on the concentrations of nitrate- and ammonium-N.

Key questions we addressed were: (a) How do redox and biogeochemical conditions associated with milldams and road salt influence the concentrations of N in riparian groundwaters upstream of the dam? (b) What conditions and processes likely determine the N concentrations and how do they differ between the study sites? (c) What are the broader implications of the milldam and road salt legacies for riparian zone N buffering and watershed management? Our primary hypothesis, based on first principles, was that wet and reducing soil conditions upstream of milldams result in low nitrate-N concentrations in riparian groundwaters due to denitrification N removal. Alternately, stagnant hydrology and persistent hypoxic and reducing conditions of near-stream sediments could shift the reducing N regime toward N retention as ammonium-N through ammonification, suppression of nitrification, and/or DNRA. Further, sodium ions associated with road salt inputs could then enhance the leaching of ammonium-N off soil sorption surfaces via cation exchange. We present a new conceptual model for streams affected by milldams characterizing the N regime as a function of the reducing riparian gradient from the upland to the stream.

2. Materials and Methods

2.1. Site Description

The study was conducted at the Roller and Cooch milldam sites in Pennsylvania and Delaware, respectively. The Roller milldam is located on Chiques Creek near Manheim (coordinates 40.108306, −76.443111), and is about 2.4 m tall (previously ~ 3 m; Figure 1a and Figure S1 in Supporting Information S1). The Chiques Creek is ~21 m wide above the dam with a drainage area of 127 km^2 at the dam. The Cooch milldam is located on Christina River (coordinates 39.645556, −75.742500) in Newark and is about 4 m tall (Figure 1b and Figure S2 in Supporting Information S1). Christina River is ~45 m wide at the dam with a drainage area of 50.7 km^2. The drainage area in the Chiques Creek watershed is primarily agricultural while mixed land use dominates in the

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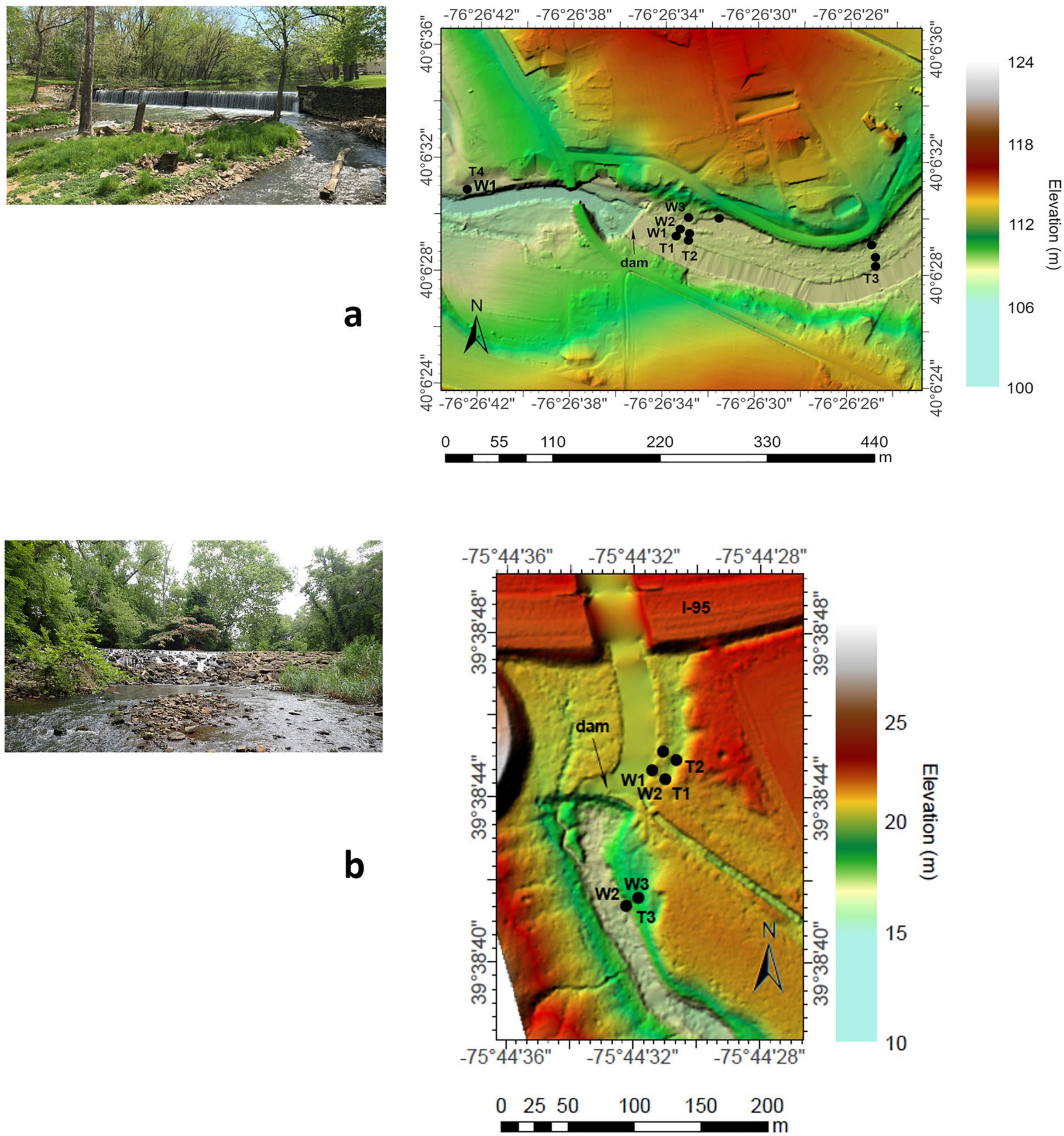

Figure 1. Photos and LIDAR DEMs indicating well transects for (a) Roller milldam on Chiques Creek and (b) Cooch milldam on Christina River sites. Chiques Creek riparian site has three upstream transects (T1–T3) with three wells each (W1–W3) and one downstream well (T4W1). The Christina River site had two upstream transects (T1–T2) with two wells each (W1, W2) and two wells in the downstream transect (T3W2 and T3W3). At the Christina River site, the interstate 95 was immediately above the dam location and a source of road salt.

Christina River watershed. The Christina River riparian site is also immediately downstream of a major multilane interstate highway (I-95) which receives substantial deicing road salt applications (storm drain indicated in Figure S2 in Supporting Information S1). Mean annual air temperature is 15.5°C and 12.2°C in Manheim and Newark, respectively, while mean annual precipitation is 104 and 114 cm (NOAA, 2021). The region receives ~50 cm of snowfall on an annual basis (NOAA, 2021).

Both watersheds are unglaciated. The soils in the Chiques Creek watershed and riparian zone are predominantly silt loams, but the riparian soils are classified as Hagerstown silt loam (HaB) and silty clay loam (HbD; Soil Survey, 2021). We should note here that the Soil Survey classifications are likely for undammed riparian conditions and do not account the drainage effects of the milldams. Riparian zones upstream of the dams at both sites were defined by a berm and swale topography (Figures S1–S3 in Supporting Information S1) which had a strong influence on local hydrology (Sherman et al., 2022). The thickness of the riparian terrace sediments, upstream of the milldams varies between 1 and 4 m depending on the height of the dam. Riparian terrace sediments also contain buried organic horizons at various depths. The geology of the Chiques Creek watershed is composed predominantly of dolomite/limestone (40%) and shale (30%) (DCNR, 2021). Soils in the Christina River watershed are predominantly silt loam with the poorly drained Hatboro-Codorus Complex (Hw) and the moderately well drained Keyport (KpB) and Mattapex (MtaB) silt loams (Soil Survey, 2021). The Cooch's Mill area is in the Piedmont physiographic province with the primary geologic unit being Iron Hill gabbro, a deeply weathered rock rich in iron oxides (Ramsey, 2005). Instrumented riparian areas at both milldam sites were forested and included sugar maple (*Acer saccharum*), black walnut (*Juglans nigra*), and American sycamore (*Platanus occidentalis*) among other species.

2.2. Instrumentation, Sampling, and Analytical Methods

Riparian zones on the north side of Chiques Creek (Roller milldam) and the east side of the Christina River (Cooch milldam) were instrumented (dictated by accessibility and permissions). At Chiques Creek, three groundwater well transects (T1–T3) with three wells each (W1–W3) were established upstream of the dam and one well (T4W1) was installed downstream of the dam (Figure 1a and Figure S1 in Supporting Information S1). At Christina River, two well transects (T1 and T2) with two wells (W1 and W2) each were installed upstream of the dam, and one transect with two wells was installed downstream of the dam (T3: W2 and W3, Figure 1b and Figure S2 in Supporting Information S1). The W1 wells at both sites are referred to as the “near-stream” or “berm” wells while the W2 wells located in the swale are indicated as “swale” wells. At Chiques Creek, W3 wells in transects T2 and T3 were both in the swale. The W3 well in transect T1 at Chiques Creek was above the swale on the hillslope and downslope of the Old Auction Road and represented the “upland edge” (Figure S1 in Supporting Information S1). A similar upland edge well was not installed at the Christina Creek site due to the sharper topographic transition in the riparian zone.

Near-stream or berm groundwater wells (W1) were augered through legacy sediments until we hit gravel or an impeding surface and were about 3 m deep at Chiques Creek and 4 m at Christina River (Figure S3 in Supporting Information S1). Upslope wells (W2 and W3) at both locations were shallower (1–1.5 m) and were augered to refusal. Soil/sediment samples collected during augering and analyzed using standard hydrometer analysis (Ashworth et al., 2001) indicated that at Chiques Creek, the average % sand, silt, and clay contents were 16%, 48%, and 35% (n = 24), respectively, while at Christina River the corresponding values were 11%, 58%, 33% (n = 12), respectively (Peck et al., 2022). The average soil bulk density across the sites was 1.12 ± 0.14 g cm^{-3}.

Manual grab water sampling was initiated in November 2019 and performed twice a week before COVID-19 (February 2020) and monthly thereafter until December 2021 for all wells and upstream locations (Sherman et al., 2022). Sampling was interrupted during the months of March–May 2020 due to COVID-19 travel bans. Groundwater samples were collected using a low-disturbance baler. During sampling of groundwater and stream water, dissolved oxygen (DO, mg L^{-1}) and oxidation reduction potential (ORP, mV) levels were measured in situ using a handheld YSI EcoSense ODO200 probe and a YSI Pro1030 probe, respectively.

All water samples were filtered within 24 hr of recovery using a glass microfiber filter (0.7 μm), acidified using HCl below a pH of 2, and analyzed at the University of Delaware Soils Laboratory. Dissolved organic carbon (DOC) was analyzed on an Elementar Vario-Cube TOC Analyzer; ammonium-N and nitrate-N were measured colorimetrically using a Bran&Luebbe AutoAnalyzer 3; and total dissolved Fe and Na^+ were quantified by inductively coupled plasma optical emission spectroscopy using an iCAP 7600 Duo View ICP-OES.

Sediment samples collected at various depths during augering for selected wells were analyzed for nutrients. Nitrate-N and ammonium-N were extracted from sediment samples with 2M KCl at the UD Soils Laboratory and the extract was analyzed colorimetrically using a Bran & Luebbe AutoAnalyzer 3. Fe and Na^+ were determined using a modified Mehlich-3 (M3) extraction procedure (Sims et al., 2002). Dried samples were analyzed for %C, and %N at the University of Maryland Center for Environmental Science using elemental combustion (4010 CHNSO analyzer, Costech).

2.3. Data Analysis

All statistical analysis was performed using JMP (SAS Institute) and Matlab (MathWorks). Significant difference among groups were determined using t tests ($\alpha = 0.05$). Multiple linear regressions were performed to assess the relative importance of potential predictors of ammonium-N concentration as the response variable. DO, ORP, DOC, DOC:NO_3^-, Fe, and Na+ were selected as potential predictors for ammonium-N. Given the high degree of correlation between DO and ORP (simple linear regression, $p < 0.001$, $n = 242$), and between DOC and DOC:NO_3^- (simple linear regression, $p < 0.001$, $n = 326$), only one of each pair, whichever contributed the highest predictive power, was included in final multiple linear regression models.

We built initial models by including all explanatory variables, and those that were not significant ($\alpha = 0.05$) were excluded (i.e., backward stepwise regression). We sought to optimize the adjusted coefficient of determination (R^2), which penalizes incorporation of many variables, by including only significant variables. To further ensure that our models maintained parsimony, we compared models using Akaike's Information Criterion (AIC). Models with the highest adjusted R^2 and the lowest AIC (a model i.e., lower in AIC by at least 2 is used to denote a model that explains variation without increasing model complexity; Burnham & Anderson, 2004) were accepted. We began by incorporating all well locations into a single model but found that the models performed better when milldams were separated and wells at each milldam were grouped. At Chiques Creek, the model performed the best when W1 locations were grouped together and compared to the other wells grouped together. At Christina River, the model performed best when it was run for T2W1 and for all other wells grouped. Residual variability was assessed for normality in all models (Figure S4 in Supporting Information S1). Simple linear regressions between ammonium-N and response variables are additionally shown ($\alpha = 0.05$; Figure S5 in Supporting Information S1).

2.4. Riparian Groundwater Hydrology and Mixing Regime Upstream of the Dams

The riparian groundwater hydrologic and mixing regime upstream of the dams for Chiques Creek and Christina River was characterized (Sherman, 2022; Sherman et al., 2022). Hydrologic response at the sites is influenced by the berm and swale topography, the thickness of the riparian sediments (Figure S3 in Supporting Information S1), and the hydraulic conductivities of the clay and silt-rich sediments. Hydraulic conductivity of the sediments across both sites was lowest for the near-stream berm sediments (wells W1; berm position; 59–108 cm day^{-1}) and greater upslope (wells W2 and W3; swale and hillslope positions; 85–468 cm day^{-1}). Because of stream water backing up above the dam, riparian groundwater levels upstream of the dam were close to soil surface year-round (Sherman et al., 2022). Groundwater flow gradients from the riparian zone to the stream were low for most of the year but reversed (stream to riparian) during the dry summer conditions (June through September) driven by high evapotranspiration (ET) loss (Sherman et al., 2022). High-frequency (30 min) specific conductivity data for the groundwater wells indicated that there was very little particle-to-particle groundwater mixing in the near-stream wells (W1) during storms. In comparison, swale and upslope wells were more frequently flushed and mixed. The low event-scale mixing for near-stream sediments was attributed to the larger sediment depths and low hydraulic conductivity, whereas greater mixing of upslope groundwaters occurred because of smaller depths and the routing of upland and overbank stream flows along the riparian swales during storms (Sherman et al., 2022; Figure S3 in Supporting Information S1). This differential hydrologic regime and mixing for the riparian transect was likely instrumental in shaping the redox and biogeochemical conditions described in the results.

3. Results

3.1. Groundwater and Stream Water DO and ORP Values

DO and ORP values differed between upstream and downstream groundwater locations, stream water, and across sites (Figures 2 and 3 and Table 1). Upstream groundwater DO values at Chiques Creek ranged between 0.05 and 8.7 mg L^{-1} (mean 1.25 ± 1.38 mg L^{-1}; Table 1) and were significantly lower ($p < 0.001$) than those for Chiques Creek stream water (mean 8.22 ± 2.42 mg L^{-1}) and downstream groundwater (10.9 mg L^{-1}; Table 1). Among the upstream groundwater wells at Chiques Creek, the highest DO concentrations were recorded for the well at the upland edge (T1W3; mean 2.73 ± 2.0 mg L^{-1}; Table 1) which was significantly greater than all other wells. The lowest DO value was observed for near-stream berm well T2W1 (0.70 ± 0.5 mg L^{-1}; Table 1).

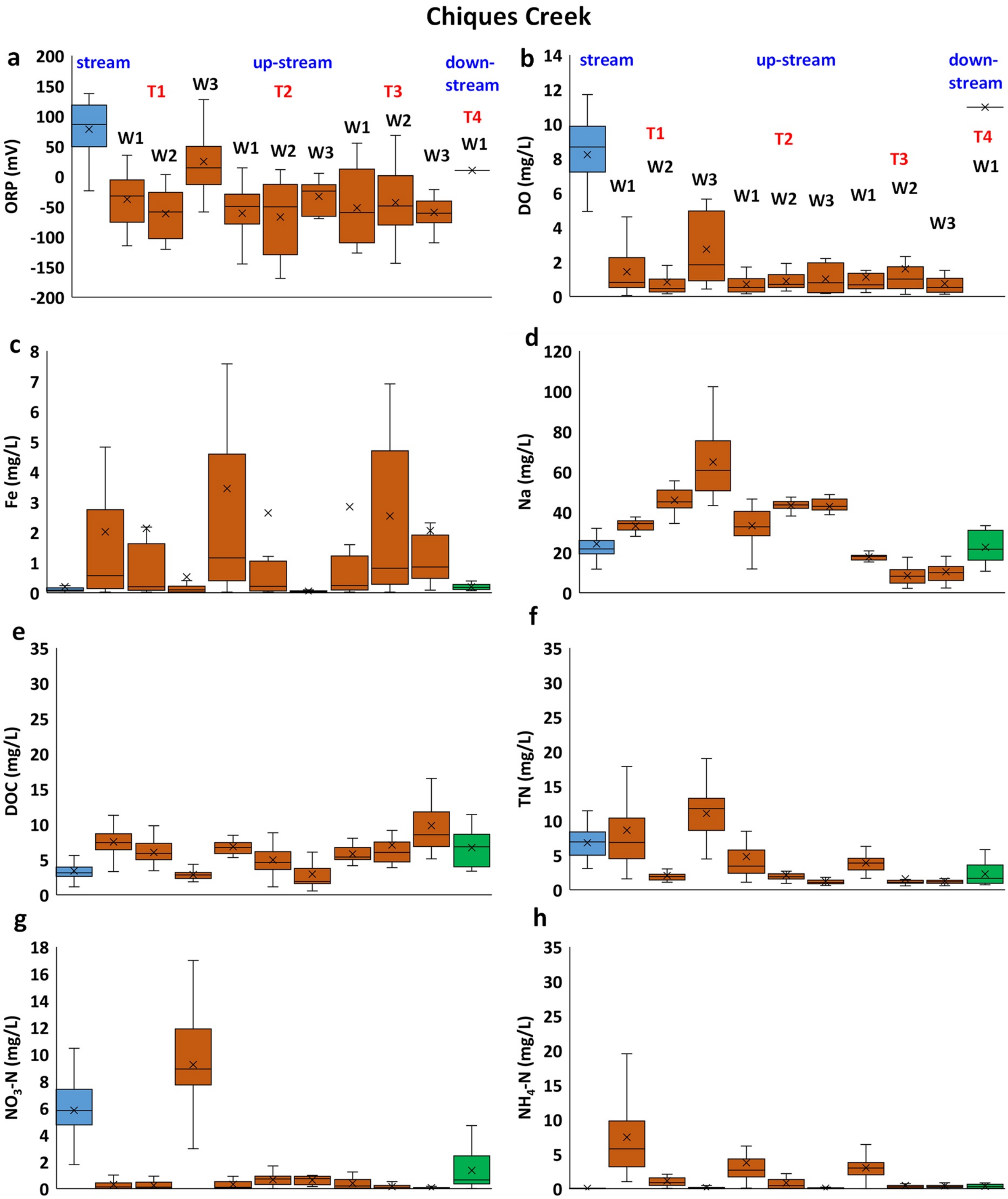

Figure 2. Box plots for Chiques Creek for (a) oxidation reduction potential (ORP, mV); (b) dissolved oxygen (DO, mgL^{-1}); (c) dissolved iron (Fe, mgL^{-1}); (d) dissolved sodium (Na, mgL^{-1}); (e) dissolved organic carbon (DOC, mgL^{-1}); (f) total dissolved N (TN) (mgL^{-1}); (g) nitrate-N (NO_3-N) (mgL^{-1}); and (h) ammonium-N (NH_4-N) (mgL^{-1}) in stream water (blue bar) and upstream (brown bars) and downstream (green bar) riparian groundwater wells. Sample numbers and numerical values with significant differences are reported in Table 1. The bounds of the boxes indicate the 25th and 75th percentiles (first and third quartile, respectively), the horizontal line is the median, the cross is the mean, and the whiskers identify the minimum and local maximum.

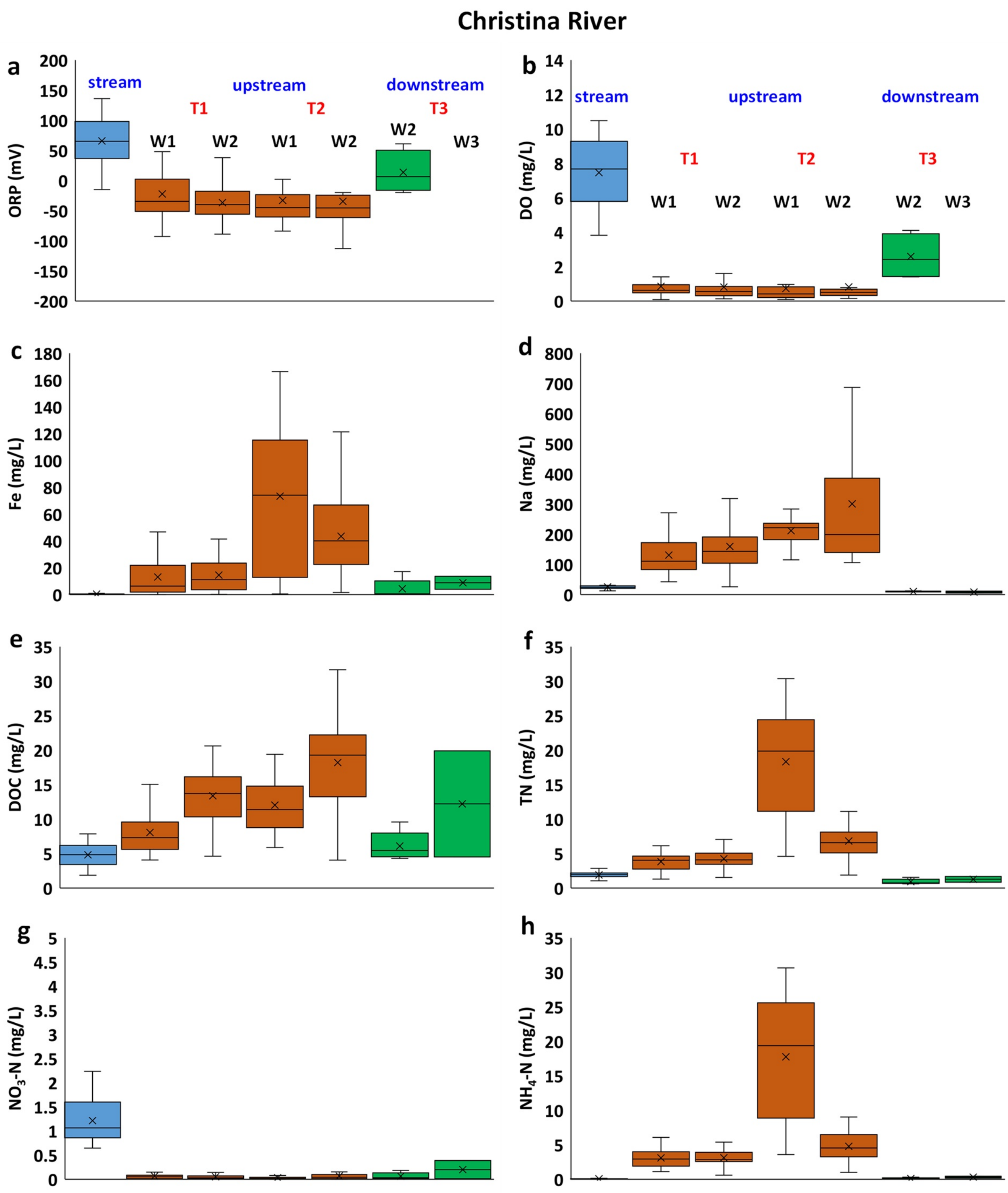

Figure 3. Box plots for Christina River for (a) oxidation reduction potential (ORP, mV); (b) dissolved oxygen (DO, mgL^{-1}); (c) dissolved iron (Fe, mgL^{-1}); (d) dissolved sodium (Na, mgL^{-1}); (e) dissolved organic carbon (DOC, mgL^{-1}); (f) total dissolved N (TN) (mgL^{-1}); (g) nitrate-N (NO_3-N) (mgL^{-1}); and (h) ammonium-N (NH_4-N) (mgL^{-1}) in stream water (blue bar) and upstream (brown bars) and downstream (green bar) riparian groundwater wells. Sample numbers and numerical values with significant differences are reported in Table 1. The bounds of the boxes indicate the 25th and 75th percentiles (first and third quartile, respectively), the horizontal line is the median, the cross is the mean, and the whiskers identify the minimum and local maximum.

Table 1
Mean and One Standard Deviation of Groundwater and Stream Water Concentrations for Christina River and Chiques Creek Sites

	ORP			DO			Fe			Na^+			DOC			NH_4-N			NO_3-N		
Location	#	Mean	Std.	#	Mean	Std.	#	Mean	Std.	#	Mean	Std.	#	Mean	Std.	#	Mean	Std.	#	Mean	Std.
Christina River																					
T1W1	20	−21.8BC	40.2	21	0.85C	0.8	29	13.50C	13.7	29	130.95CD	70.4	29	8.05C	2.9	29	3.08BC	1.3	29	0.07B	0.1
T1W2	20	−36.8C	29.5	21	0.81C	0.9	29	14.49C	11.6	29	159.51BC	100.0	29	13.38B	4.3	29	3.11BC	1.4	29	0.05B	0.1
T2W1	20	−32.5BC	46.7	21	0.73C	0.9	28	73.31A	52.7	28	211.67B	56.2	28	12.01B	3.8	28	17.74A	8.5	28	0.03B	0.0
T2W2	19	−33.7C	54.7	19	0.82C	1.0	28	43.43B	28.3	28	300.79A	286.1	28	18.18A	6.7	28	4.77B	2.0	28	0.06B	0.1
T3W2	4	13.5AB	35.3	4	2.58B	1.4	5	4.29C	7.3	5	9.79DE	1.5	5	6.08CD	2.1	5	0.09CD	0.1	5	0.06B	0.1
T3W3	-	-	-		-	-	2	8.76BC	6.9	2	8.20CDE	4.6	2	12.20ABC	10.9	2	0.29BCD	0.2	2	0.20B	0.3
stream	41	65.6A	38.2	20	7.46A	2.1	28	0.36C	0.2	28	25.29E	7.7	28	4.81D	1.7	28	0.05D	0.1	28	1.21A	0.4
Chiques Creek																					
T1W1	20	−43.4C	41.6	21	1.21CD	1.2	28	2.02ABC	2.9	28	33.19C	4.8	28	7.50B	1.9	28	7.44A	5.6	28	0.31CD	0.4
T1W2	20	−63.9C	40.5	21	0.83CD	1.0	28	2.13ABC	5.4	28	45.96B	5.2	28	6.02CD	1.5	28	1.14C	1.3	28	0.24CD	0.3
T1W3	20	25.8B	51.4	21	2.73B	2.0	27	0.53CD	1.9	27	64.84A	16.6	27	2.85E	0.8	27	0.14C	0.2	27	9.23A	3.5
T2W1	20	−62.9C	43.6	21	0.70D	0.5	28	3.45A	5.0	28	33.32C	8.4	28	6.84BC	2.1	28	3.75B	4.4	28	0.33CD	0.5
T2W2	19	−67.5C	56.5	20	1.02CD	0.8	26	2.64AB	5.5	26	43.31B	2.7	26	4.93D	1.8	26	0.87C	1.4	26	0.67CD	0.4
T2W3	5	−40.8C	24.6	6	1.01CD	0.8	10	0.06BCD	0.0	10	42.81B	5.1	10	2.93E	2.5	10	0.08C	0.1	10	0.64CD	0.3
T3W1	20	−53.1C	59.4	20	1.14CD	1.1	25	2.85AB	5.8	25	17.80E	1.6	25	5.79CD	1.1	25	3.02B	1.7	25	0.40CD	0.5
T3W2	19	−39.6C	56.3	21	1.60C	2.0	24	2.54ABC	3.1	24	8.50F	4.5	24	7.07BC	4.0	24	0.44C	0.8	24	0.15CD	0.2
T3W3	18	−59.3C	25.1	19	0.74CD	0.7	23	2.05ABC	3.4	23	10.42F	7.4	23	9.80A	4.6	23	0.42C	0.5	23	0.07D	0.1
T4W1	1	10ABC	-	1	10.97A	-	6	0.19ABCD	0.1	6	22.60DE	8.4	6	6.69BCD	2.9	6	0.35C	0.3	6	1.36C	1.7
Stream	38	78.5A	40.6	19	8.22A	2.4	28	0.21D	0.4	28	24.25D	8.7	28	3.39E	1.3	28	0.06C	0.1	28	5.83B	1.9

Note. Sampling locations with the same upper case letters are not significantly different.

Journal of Geophysical Research: Biogeosciences 10.1029/2022JG007138

DO concentrations for upstream wells at the Christina River site (mean 0.8 ± 0.87 mg L^{-1}) were significantly ($p < 0.001$) lower than those for Chiques Creek (1.25 ± 1.38 mg L^{-1}). At the Christina River site, while there were no significant differences among the upstream wells; taken together their DO concentrations were significantly lower than the stream water (mean 7.46 ± 2.1 mg L^{-1}, Table 1) and downstream well T3W2 (2.58 ± 1.4 mg L^{-1}).

Overall, ORP values displayed a similar trend as DO with low or negative values for upstream riparian wells and high or positive values for stream water and downstream wells (Figures 2 and 3 and Table 1). ORP values for Chiques Creek upstream wells ranged between −176 and 127 mV (mean −44 ± 53 mV) while those for Christina River ranged from −113 to 116 mV (mean −32 ± 42 mV) with no significant differences in upstream well values between the sites.

3.2. Dissolved Fe, DOC, and Na^+ Concentrations

The largest elemental differences between the two sites were in upstream groundwater Fe concentrations that ranged between 0.14 and 166 mg L^{-1} (mean 36 ± 3.9 mg L^{-1}) at Christina River, and from 0.02 to 25 mg L^{-1} (mean 2.18 ± 4.2 mg L^{-1}) at Chiques Creek. Stream water Fe values at both sites were much lower and significantly less ($p < 0.001$) than the upstream groundwater concentrations for Christina River. At both sites, the upstream wells closest to the stream (berm wells W1s) had the highest mean concentrations of Fe (T2W1 at Christina River [73 ± 52.7 mg L^{-1}]; and T2W1 [3.45 ± 5.0 mg L^{-1}] and T3W1 [2.85 ± 5.8 mg L^{-1}] at Chiques Creek, Table 1).

Overall, DOC followed a similar trend as Fe with some notable differences. DOC concentrations for upstream wells at Christina River (mean 12.8 ± 5.8 mg L^{-1}; range 4.0–31.6 mg L^{-1}) and Chiques Creek (mean 6.1 ± 3.1 mg L^{-1}; range 0.5–24.9 mg L^{-1}) were significantly greater ($p < 0.001$) than the corresponding stream water values (mean 4.8 ± 1.6 and 3.3 ± 1.3 mg L^{-1} for Christina River and Chiques Creek, respectively). While the near-stream berm wells (W1) had elevated DOC concentrations at both sites, the highest DOC concentrations were recorded in the swale wells - T3W3 (9.8 ± 4.6 mg L^{-1}) at Chiques Creek and T2W2 (18 ± 6.7 mg L^{-1}) at Christina River (Table 1). Riparian groundwater DOC concentrations at Chiques Creek progressively decreased from the stream edge W1 > W2 > W3 for the first two transects (T1 and T2) but the trend was reversed for T3 (Figure 2).

Sodium concentrations in upstream riparian groundwater wells at Christina River (mean 199 ± 167; range 25–1,504 mg L^{-1}) were significantly ($p < 0.001$) greater than those measured at Chiques Creek (mean 33 ± 19; range 2.2–102 mg L^{-1}). In contrast, stream water Na^+ values for the two sites were lower and not significantly different (25 ± 7.6 and 24 ± 8.7 mg L^{-1} for Christina River and Chiques Creek, respectively). At Christina River, the swale wells (W2) that received direct surface runoff input from the storm drain had higher Na^+ values than the adjacent, near-stream berm wells (W1) (Figure 3, Table 1). In contrast, at Chiques Creek, the upland edge well (T1W3; mean 64 ± 16 mg L^{-1}) adjacent to Old Auction Road (Figure 1) had the highest Na^+ concentration, but which was still an order of magnitude lower than the high concentrations for Christina River (Table 1). For both sites, downstream groundwater Na^+ concentrations (Figures 2 and 3) were lower than the upstream wells and stream water values.

3.3. Dissolved Ammonium-N and Nitrate-N Concentrations

Opposing trends in ammonium-N and nitrate-N concentrations were observed for the two sites. Other than one upland edge groundwater well at Chiques Creek (T1W3), nitrate-N concentrations in upstream groundwater wells for the two sites (mean 0.05 ± 0.07 and 1.4 ± 3.2 mg L^{-1} for Christina River and Chiques Creek, respectively) were significantly ($p < 0.001$) lower than the corresponding stream water concentrations (mean 1.2 ± 0.4 and 5.8 ± 1.9 mg L^{-1} for Christina River and Chiques Creek, respectively). At Chiques Creek, the highest nitrate-N concentration was recorded by the upland edge well T1W3 (mean 9.2 ± 3.5 mg L^{-1}) followed by stream water (5.8 ± 1.9 mg L^{-1}) and the downstream well (T4W1: 1.36 ± 1.7 mg L^{-1}, Table 1).

High ammonium-N concentrations were observed for upstream groundwater wells at both Chiques Creek (mean 2.2 ± 3.6 mg L^{-1}; 0.006–21.5 mg L^{-1}) and Christina River (mean 7.1 ± 7.5 mg L^{-1}; 0.5–30.6 mg L^{-1}). These concentrations were significantly ($p < 0.001$) greater than stream water values at both sites (0.06 ± 0.08 and 0.05 ± 0.06 mg L^{-1} for Chiques Creek and Christina River, respectively). In contrast, elevated groundwater ammonium-N concentrations were depleted in the downstream wells (Figures 2 and 3). For both sites, the near-stream berm wells (W1) had some of the highest ammonium-N concentrations across the transects (Figures 2 and 3). At Chiques Creek, the W1 berm wells at transects T1, T2, and T3 had mean values of 7.4 ± 5.6, 3.7 ± 4.4, and 3.0 ± 1.7 mg L^{-1}, respectively, while at Christina River near-stream berm wells T2W1 and T1W1 had mean concentrations of 17.7 ± 8.5 and 3.1 ± 1.3 mg L^{-1}, respectively (Table 1). TN values for the sampling locations are also included in Figures 2 and 3 to indicate that inorganic N concentrations contributed to a large fraction of the TN values.

3.4. Molar Ratios for DOC:Nitrate-N and Fe:Nitrate-N

Molar DOC:nitrate-N concentrations for upstream groundwater wells at Christina River (mean 879 ± 883; range 15–3,692) were significantly ($p < 0.001$) greater than the corresponding values for Chiques Creek (mean 198 ± 369; 0.2–2,908). Stream water DOC:nitrate-N ratios for both sites were lower than groundwater values (mean 5.6 ± 3.1 and 0.7 ± 0.3 for Christina River and Chiques Creek, respectively). Fe:nitrate-N molar ratios followed an identical trend with high values for upstream groundwater wells at Christina River (mean 589 ± 895; range 1–3,788) and Chiques Creek (mean 13 ± 41; range 0–341) and low values for stream water (mean 0.09 ± 0.05 and 0.03 ± 0.01 for Christina River and Chiques Creek, respectively). Within the sites, the near-stream berm W1 wells with elevated ammonium-N concentrations also had high DOC:nitrate-N and Fe:nitrate-N ratios.

3.5. Na^+, Fe, Ammonium-N, Nitrate-N, and %C Concentrations in Upstream Riparian Soils

Similar to the large difference in upstream groundwater Na^+ concentration between Christina River and Chiques Creek, there was a significant difference in soil M3-Na concentrations (mean 293 ± 180 and 38 ± 25 mg kg^{-1} for Christina River and Chiques Creek, respectively) (Figure 4). In contrast, the M3-Fe for the two sites were not significantly different (means of 586 ± 191 and 536 ± 238 mg kg^{-1} for Christina River and Chiques Creek, respectively). Total soil Fe contents were also determined for the two sites for selected samples using the EPA 3051 method (mean 26,395 and 28,088 mg kg^{-1} for Christina River and Chiques Creek, respectively), and also did not yield any differences between the two sites (data not shown). M3-Fe values for both sites increased with soil depth (Figure 4) and the M3-Fe concentrations at Chiques Creek wells W1 and W2 exceeded the well W3 values.

Similar to M3-Fe, KCl-extracted ammonium-N concentrations for upstream riparian soils increased with soil depth (Figure 4) but were not different between the two sites (Christina River: mean: 63 ± 84, range: 0.11–456 mg kg^{-1}; Chiques Creek: mean 53 ± 60, range: 0.19–233 mg kg^{-1}). While the soil ammonium-N concentrations were elevated, they do not follow the pattern of significant differences in upstream groundwater ammonium-N concentrations for the two sites. Contrary to ammonium-N, riparian soil-bound nitrate-N concentrations were very low and declined rapidly with soil depth for both sites (Figure 4; mean of 1.2 ± 1.9 and 3.1 ± 6.2 mg kg^{-1} for Christina River and Chiques Creek, respectively). Percent C varied between 0.2% and 6% for the two sites with higher values in sediments closer to the stream, for example, W1 versus W3 for Chiques Creek (Figure 4).

3.6. Relationships Between Upstream Groundwater Concentrations

Multi-linear regression analysis for groundwater concentrations at Chiques Creek indicated that ammonium concentrations for near stream (W1 wells) were explained by DOC and ORP values ($R^2 = 0.70$, $p < 0.001$; Figure 5) with DOC being the strongest predictor ($R^2 = 0.60$, $p < 0.001$). In contrast, Christina River groundwater ammonium-N concentrations were explained by DO, DOC, Fe, and Na^+ ($R^2 = 0.88$ and 0.76, $p < 0.001$; Figure 5) with Fe (well T2W1, $R^2 = 0.77$, $p < 0.001$) and Na^+ (all other wells, $R^2 = 0.69$, $p < 0.001$) being the strongest predictors. These relationships indicate that different electron donors and drivers regulated ammonium-N for the two sites; DOC for Chiques Creek; and Fe and Na^+ for the salt-affected Christina River site.

4. Discussion

Results did not support our primary hypothesis of low N concentrations in riparian groundwaters because of denitrification removal, but rather, lent support to the alternate hypothesis of ammonium-N accumulation under reducing soil conditions. These results suggest that milldam sediment, topography (berm and swale), and hydrologic legacies have a strong influence on the redox and biogeochemical environment with subsequent consequences for

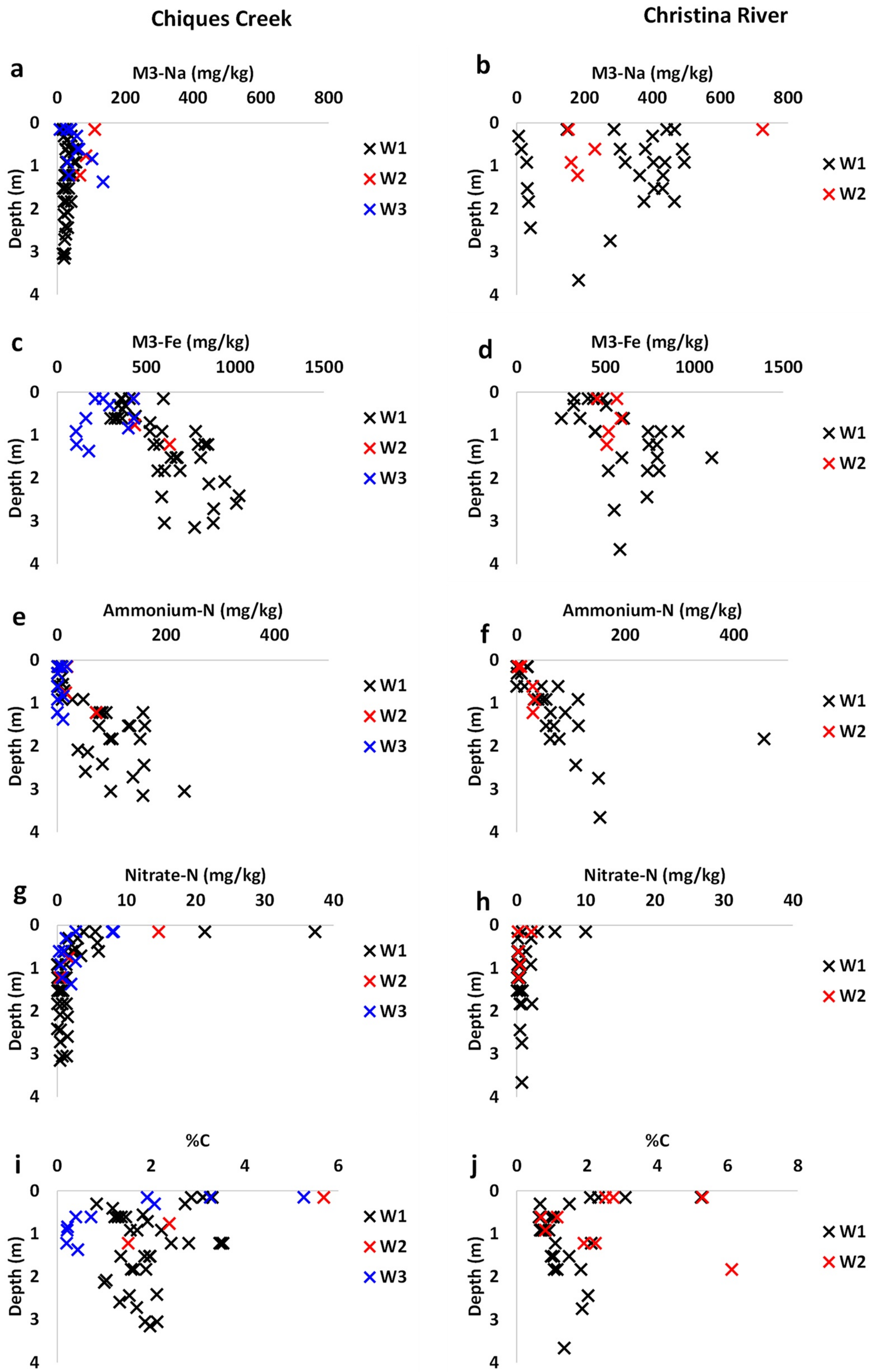

Figure 4. Riparian sediment concentrations at Chiques Creek and Christina River well sites for (a and b) Mehlich-3 extractable sodium (Na); (c and d) Mehlich-3 extractable iron (Fe); (e and f) ammonium-N; (g and h) nitrate-N concentrations; and (i and j) %C values for multiple depths. All values except %C are in mg/kg.

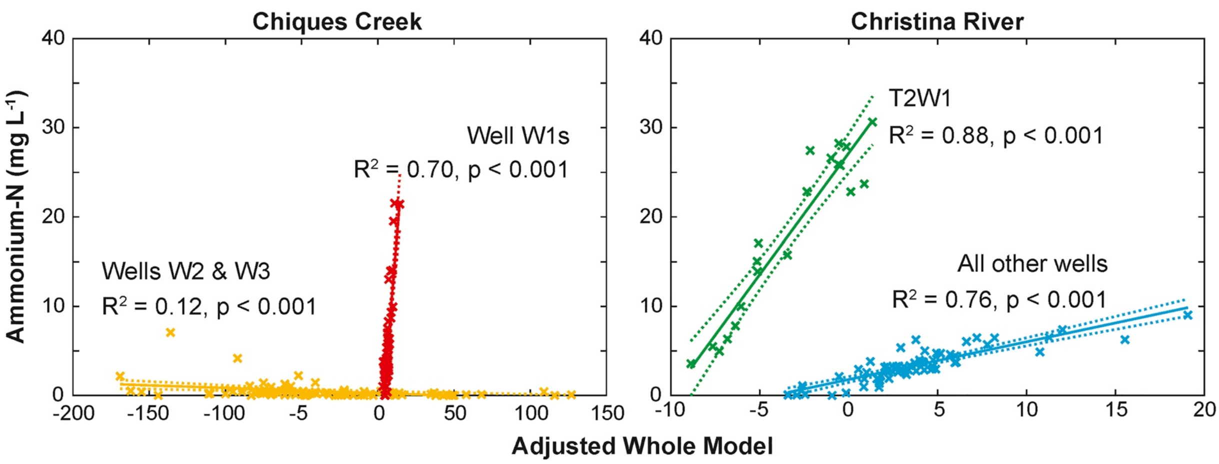

Figure 5. Multiple linear regression between groundwater ammonium-N (*y*-axis) and other variables (*x*-axis) for Chiques Creek (left) and Christina River (right). For Chiques Creek the variables included were DOC and oxidation reduction potential (ORP), while for Christina River the selected variables were dissolved oxygen (DO), DOC, Fe, and Na^+. For Chiques Creek, the W1 wells (red x's) were grouped together because of their elevated ammonium concentrations and indicated a strong relationship with DOC. At Christina River, berm well T2W1 (green x's) displayed very different and elevated ammonium and Fe concentrations compared to other wells (blue x's) and was separated. This well (T2W1) indicated a strong influence of dissolved Fe on ammonium-N concentrations while the other wells had a greater influence of Na^+.

N concentrations in riparian zones. Road salt inputs could further amplify and/or complicate these biogeochemical and N responses. The elevated ammonium-N concentrations in riparian groundwaters and soils upstream of the milldams were associated with multiple factors including: organic rich silt and clay sediments, stagnant and poorly mixed groundwater conditions, persistent reducing soil conditions, and redox and salt mediated changes in Fe and DOC electron donors. These drivers likely facilitated the ammonium-N production through ammonification and/or DNRA. We discuss these drivers for riparian N using a conceptual model (Figure 6) and evaluate the broader environmental implications of milldam and salt legacies for N dynamics.

4.1. Nitrate-N and Ammonium-N Concentrations Along the Riparian Transect—Key Drivers, Processes, and Conceptual Model

4.1.1. Comparisons and Significance of Ammonium-N Concentrations

Ammonium-N concentrations for near-stream groundwaters (wells W1) at Christina River and Chiques Creek were considerably greater than stream water and groundwater concentrations at the upland edge (wells W3, Figures 2 and 3), suggesting the absence of an external anthropogenic source and supporting internal production of ammonium-N. Ammonium-N concentrations for both groundwaters and soils at our sites are high compared to those reported previously for riparian zones, wetlands, and riverbank filtration sites (selected studies in Table 2). Ammonium-N concentrations for soils at our sites (0–456 mg kg^{-1}) were also much higher than those reported in literature for reducing soil conditions (Table 2). The primary mechanisms responsible for the ammonium concentrations are also reported in Table 2.

4.1.2. Role of Riparian Sediment Characteristics

Sediment characteristics exert a first-order control that shapes riparian hydrology, redox, and biogeochemical conditions. These controls occur through soil texture (% sand, silt, and clay), clay type, and/or organic matter content. Organic matter in the sediments directly contributes to ammonium-N through mineralization (Hill, 2011). Riparian sediments upstream of the dams at the Chiques Creek and Christina River sites had high contents of clay and silts (>90%) and % C. These observations are similar to others that have reported fine sediment accumulation upstream of the dams (Liro, 2019; Lu et al., 2022; Lucas-Borja et al., 2021). The high clay contents affected the hydraulic conductivity, residence time of water, and mixing potential (described below) of groundwaters with potential consequences for ammonium production. The clay type in the Piedmont region is predominantly kaolinite which could explain the elevated dissolved groundwater concentrations of ammonium and could also be vulnerable to Na^+ displacement associated with road salts (Buss et al., 2004; Costa & Cleaves, 1984).

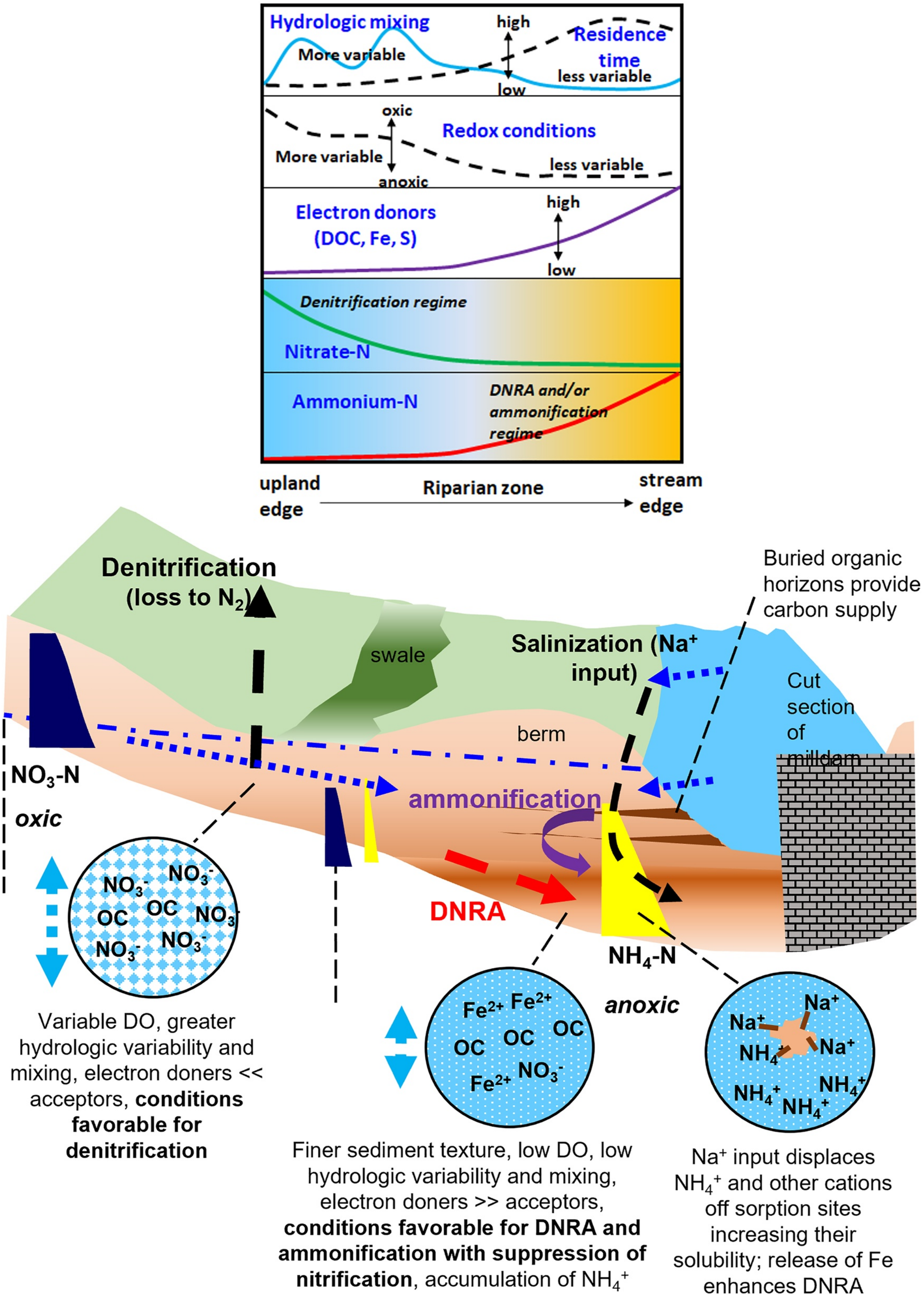
Hydrologic mixing
More variable
high
Residence time
less variable
low
oxic
Redox conditions
More variable
less variable
anoxic
Electron donors (DOC, Fe, S)
high
low
Denitrification regime
Nitrate-N
Ammonium-N
DNRA and/or ammonification regime
upland edge
Riparian zone
stream edge
Denitrification (loss to N2)
Buried organic horizons provide carbon supply
swale
Salinization (Na+ input)
Cut section of milldam
berm
NO3-N
oxic
ammonification
DNRA
NH4-N
anoxic
Variable DO, greater hydrologic variability and mixing, electron doners << acceptors, conditions favorable for denitrification
Finer sediment texture, low DO, low hydrologic variability and mixing, electron doners >> acceptors, conditions favorable for DNRA and ammonification with suppression of nitrification, accumulation of NH4+
Na+ input displaces NH4+ and other cations off sorption sites increasing their solubility; release of Fe enhances DNRA

Figure 6.

Version of record at: https://doi.org/10.1029/2022JG007138

Table 2
Comparisons of Groundwater and Soil Ammonium-N Concentrations From This Study Against Previous Studies

Reference	Study focus and location	Ammonium-N concentration	Explanation for ammonium-N
This study	Milldam influence on upstream riparian groundwater N; mid-Atlantic US (Delaware and Pennsylvania)	Chiques Creek riparian groundwater: 0.006–21.5 mg L^{-1}; soil: 0.19–233 mg kg^{-1}; Christina River riparian groundwater: 0.5–30.6 mg L^{-1}; soil: 0.11–456 mg kg^{-1}	Poorly mixed groundwaters; organic-rich anoxic riparian sediments; ammonification and/or DNRA
Duval and Hill (2007)	Riparian sediments subject to stream water seepage; Toronto, Ontario, Canada	2–5 mg/L with local values >10 mg L^{-1} in summer riparian groundwaters	Anaerobic soils; likely due to ammonification
Chen et al. (2022)	Riverbank filtration, Second Songhua River, China	Average groundwater: 0.65–2.54 mg L^{-1}	DNRA and/or mineralization in anoxic soils
Liang et al. (2020)	Riverbank filtration, Yangtze River basin, China	Groundwater: 0–17 mg L^{-1}	DNRA in anoxic riparian soils
Covatti and Grischek (2021)	Review of 40 worldwide sites for riverbank filtration	0.1–1.7 mg/L (median 0.6 mg L^{-1})	Various surface and groundwater sources; ammonification and DNRA
Zhao et al. (2021)	Influence of redox gradients for ammonium-N; West Dongting Lake wetlands, China	Li riparian groundwater: 0.63–5.6 mg L^{-1}; Yuan riparian: 0.48–2.3 mg L^{-1}	Ammonification and/or DNRA under anoxic soil conditions
Reverey et al. (2018)	Kettle hole sediments, Brandenburg, Germany	Most stable center (A) ~20–30 mg kg^{-1}	DNRA in anoxic soils
Doussan et al. (1998)	Riverbank filtration site, Seine River, France	Groundwater ~7–20 mg L^{-1}	Ammonification in anoxic conditions

Riparian sediments at our sites contained buried organic layers and material which were thicker closer to the dam; similar observation have been reported elsewhere in the mid-Atlantic region (Lutgen et al., 2020; Mattern et al., 2020; Merritts et al., 2011). Respiration of this buried organic C also likely contributed to anoxic hot spots favorable for N reduction (Wallace & Soltanian, 2021). We hypothesize that the thickness, degradability (e.g., Gurwick, Groffman, et al., 2008; Gurwick, McCorkle, et al., 2008; Jantti et al., 2022), and spatial distribution (vertical, longitudinal, and transverse) of the buried organic C determined ammonification and the balance of the N reductive processes along the riparian transect (conceptual model Figure 6). High sediment organic C concentrations closer to the riparian-stream edge likely favored greater accumulation of ammonium-N via ammonification and DNRA (elaborated on below in the section on electron donors).

4.1.3. Hydrologic Controls of N Dynamics

Low hydraulic conductivities of fine-grained sediments along with long water travel/residence times that enhance DO removal and create anoxic or hypoxic environments have been shown to favor ammonium accumulation (Covatti & Grischek, 2021). Ammonium production by DNRA is particularly favored by stagnant or poorly mixed hydrologic conditions that encourage persistent or long durations of hypoxia (Jantti et al., 2021; Palacin-Lizarbe et al., 2019; Reverey et al., 2018). In contrast, denitrification N removal has been reported to be enhanced by hydrologic variability and alternating oxic-anoxic soil conditions that allow for aerobic production of nitrate by nitrification that is subsequently denitrified under anaerobic conditions (Bernard-Jannin et al., 2017; Guo et al., 2014; Peralta et al., 2013; Shi et al., 2020; Tomasek et al., 2019; Ye et al., 2017). Jantti et al. (2021) reported that soil denitrification capacity was almost completely lost and DNRA dominated in estuarine soils when hypoxia lasted for several months. Additionally, differences in hydrologic variation directly influence microbial community composition, with less variable conditions being preferred by DNRA and sulfate reducing bacteria (Chen et al., 2021).

Figure 6. Conceptual model highlighting the changing concentrations of nitrate-N and ammonium-N and the key responsible processes of denitrification, ammonification, suppression of nitrification, and DNRA along a milldam affected riparian transect from the upland to the stream edge. The model highlights a potential regime shift (upland to the stream edge) between nitrate removal by denitrification to ammonium accumulation due to ammonification, suppression of nitrification, and/or increase in DNRA driven by variations in: hydrologic mixing and residence time, redox conditions, sediment lithology, and the biogeochemical balance of electron donors (DOC and Fe) and acceptors (nitrate-N). The nitrate-N and ammonium-N pools in the riparian zone are indicated by blue and yellow trapezoids, respectively in the lower graphic. The influence of sodium input on the sorbed ammonium-N pool and DNRA is also indicated with potential increase in groundwater ammonium concentrations. The blue dashed arrows indicates groundwater and stream water movement.

The hydraulic conductivity for near-stream berm sediments (in the vicinity of the berm W1 wells) was low at our sites and there was minimal groundwater level variations and mixing (Sherman et al., 2022). In contrast, upslope wells (W2 and W3) displayed greater water level variation and mixing during storms (Sherman et al., 2022). We propose that this hydrologic variability (or lack thereof) was a key regulator of N concentrations along the riparian transect (Figure 6). High hydrologic variability at the upland-riparian edge (wells W2–W3) facilitated alternating oxic-anoxic conditions that encouraged denitrification removal of nitrate-N, resulting in sharp declines in nitrate-N concentrations through the riparian zone. In contrast, the longer groundwater residence times, poor mixing, and hypoxic waters closer to the stream edge promoted ammonium accumulation via ammonification, suppression of nitrification, and/or DNRA (conceptual model in Figure 6).

4.1.4. Balance of Electron Donors and Acceptors for N Reduction

The hydrologic controls on N reduction were further regulated by the availability of electron donors. Ammonium production via DNRA is regulated by the balance of electron acceptors (nitrate-N) and donors (organic C, reduced Fe, and sulfide; Burgin & Hamilton, 2007; Pandey et al., 2020; Rutting et al., 2011). High concentrations of nitrate-N vis-à-vis organic C favor denitrification, while high ratios of soil C:N (>12 Wei et al., 2022; S. Yin et al., 1998) and DOC:nitrate-N (>10–15, Chen et al., 2022) and Fe (or sulfide):nitrate-N favor DNRA (Chen et al., 2022; Robertson & Thamdrup, 2017). Under a high C to nitrate-N ratio, DNRA has an advantage over denitrification since more electrons (eight vs. five) can be transferred per mole of nitrate-N and the potential free energy per mole nitrate-N is higher for DNRA than denitrification (Tiedje, 1982). Reductive dissolution of iron oxides in anaerobic soils releases Fe which further increases the electron donor:nitrate-N ratio. Availability of Fe could shift the nitrate-N reductive balance in favor of DNRA while simultaneously suppressing denitrification (Cojean et al., 2020; Robertson & Thamdrup, 2017).

Groundwater concentrations of DOC measured at Chiques Creek and Christina River were high and the molar ratios of DOC:nitrate-N for both sites exceeded the DNRA molar concentration threshold of 10–15 by a substantial amount. Similarly, average riparian soil C:N ratios for Chiques Creek and Christina River (11 and 15, respectively), were close to or more than the threshold reported for DNRA. Multi-linear regression analysis (Figure 5) for Chiques Creek identified DOC as a key predictor for groundwater ammonium concentrations and wells with elevated ammonium concentrations also had high DOC (Figure 2). However, some of the swale wells (e.g., T3W2 and T3W3 at Chiques Creek, Figure 2) that had the highest DOC concentrations and DOC:nitrate-N ratios did not have high ammonium concentrations. We speculate that increased groundwater mixing (Sherman et al., 2022) and more variable ORP and DO conditions at these swale well (T3:W2, W3) locations likely reduced the potential for ammonium production and accumulation. This suggests that DOC:nitrate-N ratios alone cannot determine ammonium concentrations and additional factors come into play (as highlighted in Figure 6).

Compared to Chiques Creek, groundwater DOC and Fe concentrations at Christina River were much higher (Figure 3). At this site, both DOC and dissolved Fe were correlated with groundwater ammonium concentrations, but Fe was the stronger predictor (Figure 5). It is possible that weathered amorphous iron oxides associated with Iron Hill gabbro rocks at the Christina River coupled with reducing soil conditions and road salt input (described below) could have contributed to the elevated solution Fe concentrations at this site. Redox conditions in fine sediments associated with dams could also alter the forms/speciation and solubility of Fe (Lu et al., 2022). Irrespective of the reason, the strong relationships between dissolved ammonium and Fe concentrations (Figure 5), and the high ammonium values for well T2W1 suggest that chemolithotrophic DNRA (Robertson & Thamdrup, 2017) was likely an important driver of groundwater ammonium-N at the Christina River site.

Integrating the observations for Chiques Creek and Christina River, reducing riparian soil conditions closer to the stream edge result in progressive increase of electron donors (DOC and Fe) from the upland edge to the stream with a simultaneous decrease in nitrate-N (electron acceptor) concentrations. We propose that this shift in electron donor to acceptor balance along the riparian transect shifts the reductive N regime from a denitrification dominant system to one where DNRA and ammonium production becomes increasingly pronounced (as highlighted in the conceptual model in Figure 6).

4.1.5. Salt Effects on Riparian N

The Christina River riparian site was strongly influenced by road salt runoff inputs from Interstate 95 and had elevated Na^+ concentrations in both riparian groundwaters and soils (Figures 3 and 4). Road-salt salinization can alter the reducing soil environment and N processing in a myriad of ways (Herbert et al., 2015). Sodium inputs have been reported to have a dispersive effect on high clay soils resulting in reduced hydraulic conductivity, reduced solubility, and diffusion of oxygen, and more negative redox conditions that favor DNRA (Herbert et al., 2015).

Sodium can also displace Fe^{2+} off sorption surfaces (Baldwin et al., 2006) and increase the reduction of iron oxides, resulting in increased availability of Fe^{2+} for DNRA (Weston et al., 2010). In addition, increases in sulfide concentrations linked to salinity may enhance DNRA and depress denitrification (Murphy et al., 2020; Neubauer et al., 2018). Salinization could also directly increase the concentration of ammonium-N in groundwaters through displacement off soil sorption surfaces by Na^+ (Ardon et al., 2013; Weismann et al., 2021; Weston et al., 2010). While the soil-bound ammonium concentrations for the two sites were not different (Figure 4), the groundwater ammonium values were much higher for Christina River (Figure 3). The elevated groundwater ammonium-N could be attributed to multiple possibilities: (a) increased ammonification and simultaneous suppression of nitrification due to salinization (e.g., Joye & Hollibaugh, 1995; Noe et al., 2013, respectively); (b) increased ammonium production due to salinization enhanced DNRA with suppression of denitrification; and/or (c) increased displacement of sorbed ammonium by Na^+ ions. The strong relationships between ammonium-N, dissolved Fe, and Na^+ (Figure 5) support the potential for all of these mechanisms and the elevated Na^+ for Christina River soils clearly suggests that ammonium-N displacement by Na^+ could be occurring as indicated in Figure 6. We should however, recognize that given the many positive and negative feedbacks, a linear relationship between Na^+ and ammonium-N concentrations should not be expected (Weissman et al., 2021).

4.2. Environmental Implications of Milldam Alteration of Riparian N

Results from this study raise important environmental concerns about milldam effects on riparian N processing and buffering capacity and the eventual fate of ammonium-N accumulated in riparian soils upstream of these dams. Our observations suggest that hydrologic and biogeochemical conditions associated with milldams could not only decrease denitrification N removal in riparian zones but also increase ammonium-N through ammonification, depression of nitrification, and/or DNRA. Salinization of these milldam riparian soils could further amplify these processes. This would result in a decrease in riparian buffering capacity suggesting that milldams provide an ecosystem disservice (as opposed to ecosystem services provided by denitrification). This detrimental water quality influence of milldams on riparian zones has not been recognized before and is a new insight. Beyond milldams, such conditions and the conceptual model of Figure 6 could also extend to other landscape elements including hydrologically disconnected wetlands and/or kettle hole sediments in agricultural or rural regions (Reverey et al., 2018) and stagnant and isolated wetlands and/or stormwater basins in urban areas (Kinsman-Costello et al., 2022; Palta et al., 2017).

Our observations reveal that there appears to be a redox tipping or transitional point before which variable reducing conditions may favor denitrification and nitrate removal, but after which persistent reducing conditions could favor DNRA/ammonification and will lead to ammonium accumulation (Figure 6). Recognizing these two contrasting reducing regimes, one potential management option for such N retention hot spots would be to enhance hydrologic connectivity, redox variability, and groundwater mixing while still maintaining some level of anaerobic conditions. The shift toward variable oxic-anoxic conditions would likely move the stagnant and reducing regime favoring DNRA to a more dynamic one favoring coupled nitrification-denitrification processes which could help permanently remove excess ammonium-N. In our settings, milldam removals could provide such a condition where the stagnant hydrologic regime is replaced by a more naturally dynamic groundwater regime which would encourage denitrification over DNRA.

4.3. Caveats and Future Considerations

This study was limited to only two milldams and both study sites were located in the Piedmont physiographic province. Legacy sediments for these sites contained high amounts of silt and clay that created a hydrologic and redox environment favorable for ammonium-N production and accumulation via ammonification and/or DNRA. It is very likely that the same favorable environment may not exist in the more porous and oxygenated sandy soils. Thus, in coarse-grained landscapes (e.g., Coastal Plain with sandy soils), milldams may not necessarily create the extreme reducing conditions and subsequent N effects as reported in this study. Thus, additional studies should be conducted for such and other settings to develop more generalized recommendations.

This study did not investigate the relative amounts of ammonium-N production from ammonification and/or DNRA or the relative rates of denitrification and DNRA under reducing soil conditions. This is an important knowledge gap (Burgin & Hamilton, 2007; Pandey et al., 2020) and we intend to address it in upcoming new investigations at these existing study sites. Sediment size distribution could also directly alter/affect the microbial habitat and communities (e.g., Chen et al., 2021; Li et al., 2020) and should be investigated with its consequences for the DNRA-denitrification dichotomy. Beyond the concentration ratios (e.g., DOC:nitrate-N), the DNRA-denitrification partitioning is also likely influenced by the quality/lability of DOC (Jantti et al., 2022), which needs additional evaluation. The quality of DOC provided by historic, relict buried horizons (e.g., Gurwick, Groffman, et al., 2008; Gurwick, McCorkle, et al., 2008) would likely be less labile and more humic (Myneni, 2019) compared to that from contemporary, surficial organic horizons and could differentially affect the DNRA-denitrification competition (e.g., Jantti et al., 2022). Similarly, the forms, speciation, and bioavailability of Fe could differ with sediment depth in the reducing soil conditions associated with milldams (Lu et al., 2022) and needs further investigating with regard to N cycling (Li et al., 2012).

5. Conclusions

This study provided two novel insights into the potential effects of milldams and road salt salinization on riparian N processing and buffering capacity. The first insight is that sediment (organic-rich sediments with high clays and silts) and hydrologic (stagnant and poorly mixed groundwaters) legacies of milldams result in increased ammonium-N in riparian groundwaters and near-stream sediments. We characterized this using a novel conceptual model that described the change in N concentrations and dominant forms (nitrate to ammonium) as a function of the reducing gradient along the riparian transect. Second, road salt salinization can further alter riparian biogeochemical conditions and increase the concentrations of ammonium-N in groundwaters and sediments. Both of these effects, individually and jointly, reduce the effectiveness of riparian zones in buffering N above milldams.

This work underscores that anthropogenic legacies and their synergistic effects need to be considered in watershed assessment and management plans and policies. Currently, the existence of milldams and their impacts are not accounted for while designing and implementing riparian buffers to meet specific regulatory N load reductions and targets (e.g., total maximum daily load programs). Similarly, riparian zones that are subject to road salt salinization could be more vulnerable and will have to be given greater attention for their (in)ability to buffer N loadings in watersheds. While a lot of attention is rightly given to watershed nitrate-N legacies (Basu et al., 2022; Van Meter et al., 2018), elevated ammonium-N legacies in stream banks are not well recognized and considered. Given our results, elevated ammonium-N sediment concentrations will have to be considered in N loadings and scenario analyses post-milldam removals. Implicitly, our study suggests that milldam removals could potentially benefit riparian N buffering through introduction of a more variable and dynamic hydrologic regime that enhances denitrification and prevents accumulation of ammonium.

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Data Availability Statement

All water and soil chemistry data used in this manuscript is posted on Hydroshare and is publicly available via: http://www.hydroshare.org/resource/cf97ad62cee24892bbfeb16e25956372.

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