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Seasonal Variation in Floodplain Biogeochemical Processing in a Restored Headwater Stream

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Supporting Information

ABSTRACT: Stream and river restoration activities have recently begun to emphasize the enhancement of biogeochemical processing within river networks through the restoration of river-floodplain connectivity. It is generally accepted that this practice removes pollutants such as nitrogen and phosphorus because the increased contact time of nutrient-rich floodwaters with reactive floodplain sediments. Our study examines this assumption in the floodplain of a recently restored, low-order stream through five seasonal experiments. During each experiment, a floodplain slough was artificially inundated for 3 h. Both the net flux of dissolved nutrients and nitrogen uptake rate were measured during each experiment. The slough was typically a source of dissolved phosphorus and dissolved organic matter, a sink of NO_3^-, and variable source/sink of ammonium. NO_3^- uptake rates were relatively high when compared to riverine uptake, especially during the spring and summer experiments. However, when scaled up to the entire 1 km restoration reach with a simple inundation model, less than 0.5−1.5% of the annual NO_3^- load would be removed because of the short duration of river-floodplain connectivity. These results suggest that restoring river-floodplain connectivity is not necessarily an appropriate best management practice for nutrient removal in low-order streams with legacy soil nutrients from past agricultural landuse.

1. INTRODUCTION

Stream and river restoration is a rapidly growing industry within the United States.[1] Largely, this growth is a response to the almost 1 million km of impaired streams across the United States and regulatory measures associated with the Clean Water Act and Endangered Species Act.[2,3] Traditional restoration objectives include streambank stabilization, riparian/instream habitat enhancement, and more recently, a functional lift of the degraded stream ecosystem.[4,5] Here, functional lift refers to enhancing ecosystem function as a whole, not just focusing on a single aspect of restoration (e.g., bank stabilization), to maximize both ecosystem health and services. Creating functional lift within the stream can include restoring hydrologic connectivity between the channel and adjacent landscape.[6] Specifically, connectivity between rivers and their adjacent floodplains provide many ecosystem services such as floodwater storage, increased ecosystem productivity, and increased biogeochemical processing of floodwaters.[7] The latter is of interest in many urban and agricultural watersheds, where water quality impairment is associated with stormwater management and legacy agricultural practices, respectively.[8]

Because of their transitional and dynamic nature, floodplains are hotspots for biogeochemical activity[9,10] and can be both a source and sink of nutrients such as nitrogen (N) and phosphorus (P). In a typical floodplain found in temperate climates, nutrient retention and removal is controlled by a combination of antecedent moisture condition, biogeochemical processing rates, and the residence time of floodwaters within the floodplain (Figure 1).[11,12] During the interflood period, or the time between flood events, floodplain sediments can accumulate dissolved organic matter (DOM),[13] soluble reactive phosphorus (SRP),[14] and ammonium (NH_4^+).[15] Antecedent soil moisture conditions control the export and processing of these constituents once the floodplain is reconnected to the adjacent river channel.[16] If the floodplain is relatively dry prior to inundation, accumulated nutrients can be flushed downstream, where the NH_4^+ is likely transformed to NO_3^- through nitrification[17] and SRP likely spirals downstream through cycles of sorption and desorption with suspended sediments.[18] When the floodplain is inundated prior to hydrologic connection with the river, an area of mixing known as the perirheic zone is established between the existing floodplain water and river water.[19] In many cases, steep redox gradients form across the perirheic zone and at the sediment-water interface, allowing for rapid transformation of reactive solutes through redox

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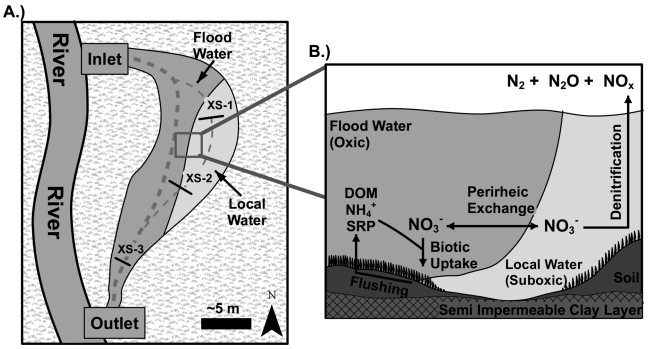

Figure 1. Conceptual model of processes within the experimental floodplain slough. (A) Plan view of the experimental slough highlighting the inlet and outlet structures, the three sampling cross sections (XS-1, XS-2, XS-3), and the mixing zone between floodwater (dark gray area) pumped into the slough and local water (light gray area) likely derived from a combination of groundwater inputs, rainwater, and previous inundation events. Dashed lines represent conceptualized flowpaths: advective flow and transient storage dominated flowpaths, respectively. (B) Cross-sectional view of the inundated floodplain displaying potential mechanisms that control nutrient cycling and retention within the experimental slough.

processes, facilitating the transition of floodwaters to biogeochemically processed floodplain water.[12]

In addition to effects associated with antecedent moisture condition, biotic processing and growing season play an important role in nutrient processing capacity of floodplains.[20,21] Biotic assimilation, or the conversion of inorganic nutrients to organic nutrients, in benthic sediments is typically attributed to algal and vegetative communities in floodplains.[22] In forested floodplain systems where water and/or light are limiting, biotic assimilation can account for less than 10% of added nitrate removal (NO_3^-).[23] In contrast, in highly productive backwater floodplain lakes, assimilation can account for 76% of NO_3^- removal.[24] In both cases, the floodplain is acting as temporary sink of N, which will be available for internal cycling during the interflood period and potentially removed from the floodplain as particulate N through a combination decay processes (e.g., mineralization) and hydrologic export.[25] Seasonal differences in biotic uptake are strongly coupled with seasonal patterns in water availability, temperature, and solar intensity,[21,26] where differences between seasonal processing rates can result in N load reductions ranging from 0.05% to 60%, respectively, within the same floodplain wetland.[27]

Biogeochemical processing is also strongly tied to the residence times of floodwaters,[28,29] or the amount of time floodwaters are contained within a floodplain. In medium to large riverine systems, residence times within floodplains can be long enough to develop conditions ideal for biogeochemical processing.[30] However, in headwater floodplains, short residence times restrict redox dependent processes, such as denitrification,[20] and nutrient export is largely controlled by the balance of biotic uptake and soil flushing processes. This suggests that the variable solute source/sink characteristic observed headwater floodplains[20,31,32] is largely dependent on seasonal variables such as temperature and antecedent soil moisture. The observed variability of biogeochemical processing across studies is inconsistent with recent efforts in the U.S. Mid-Atlantic and Northeast to promote river-floodplain connectivity in restoration projects in order to reduce the downstream flux of nitrogen (N) and phosphorus (P), especially in restoration sites located in headwater catchments. Therefore, our overall objective was to further investigate mechanisms associated with N and P processing in a headwater floodplain over the course of an entire year and to provide the restoration community further guidance to optimize nutrient removal through river-floodplain connectivity. Specifically, the goals of this study were to examine the first flush of dissolved nutrients during the initial wetting of soils; quantify the seasonal variation in source/sink characteristics of the floodplain; and estimate N load reduction associated with river-floodplain connectivity at the reach scale.

2. METHODS

2.1. Site Description. The study site is an abandoned slough within the floodplain of a third-order stream (Stroubles Creek) in the Ridge and Valley physiographic province of southwestern Virginia, U.S.A., and within the Virginia Tech Stream Restoration, Education, and Management Lab (StREAM Lab). The contributing watershed is approximately 15 km^2 which is 84% urban/residential landcover, 13% agriculture, and 3% forest.[33] The contributing area within the stream reach is predominantly row crop agriculture, and the site itself is located along a recently restored (c. 2009) reach of stream. The slough has an approximate surface area of 450 m^2 and the flowpath length approximately 60 m (Figure 1a). Previous to restoration, the channel was severely incised and riparian productivity was altered by agricultural grazing activities.[34] Post-restoration and cattle removal, the site has been inundated 2−3 times a year and is dominated by reed canary grass.

Hydrology within the floodplain slough is largely controlled by both evapotranspiration (ET) and a shallow confining layer of clay. Water sources include periodic inundation from the channel, groundwater, and direct precipitation. Previous modeling studies suggest ET drives seasonal differences in the floodplain water table, where soils are saturated during winter/spring when ET rates are minimal, and the water table is drawn down in the summer when ET rates are high during the growing season.[35] This pattern was experienced during the study period, where soils were saturated from late fall through midsummer (Figure 2), although this pattern was exacerbated by a wetter-than-normal spring and early summer. Further, the shallow clay layer acts as a confining layer, which restricts surface water−groundwater interactions and water loss to the subsurface during the flood experiments. More information about the StREAM Lab and surface water−groundwater interaction at the site can be found at streamlab.bse.vt.edu and in the companion study (Hester et al.),[36] respectively.

2.2. Experimental Design. We conducted five experimental floods over the course of one year to capture seasonal differences in floodplain biogeochemical processes: April 8 (spring), June 29 (early summer), August 30 (late summer), November 11 (fall), and February 7 (winter) across 2013 and 2014. Each experimental flood lasted 3 h to simulate natural overbank flood events, where quasi steady-state flow conditions were achieved in the first 2 h and the third hour was used to conduct a nitrogen uptake experiment. Stream water was pumped into the floodplain slough using a Berkeley B3-ZRMS irrigation pump at a flow rate of approximately 24 $L \cdot s^{-1}$. Inlet and outlet flows were measured using an ultrasonic Fuji M-flow flowmeter and a 7.62 cm parshall flume with an Onset HOBO Pressure Transducer, respectively. We collected water quality

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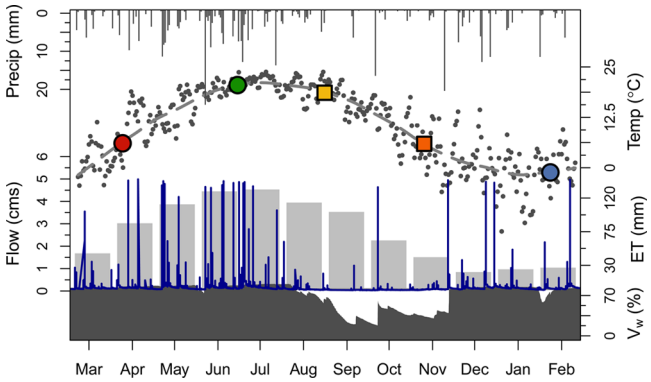

Figure 2. Climatic data measured in the StREAM Lab floodplain. The dark gray area represents the volumetric soil water content (V_w), the blue line is the annual hydrograph (Q), the light gray bars represent monthly evapotranspiration (ET), the dark gray points represent mean daily temperature (temp), dark gray bars represent the rainfall hyetograph (precip), and circles and squares represent the timing of saturated and dry floods, respectively.

samples at the inlet (e.g., the pump) at 30 min intervals and at three locations (XS1, XS2, and XS3) along the centerline of flow in the slough at 15 min intervals (Figure 1a). During the first 15 min after water arrived at each sampling location, we collected samples at 5 min intervals in order to capture the "first flush" phenomena. At hour two of each experiment, we instantaneously added a solution of $NaNO_3$ and NaCl tracers to the inlet of the slough. As the tracer slug moved through the site, we collected samples at 1−3 min intervals at XS2 and XS3. Here, it is important to highlight we pumped streamwater representative of baseflow, not flood flow, into the experimental slough. Because of differences in background solute concentrations and sediment load, some biogeochemical processes (e.g., denitrification) may have altered kinetics and processes associated with sediment deposition (e.g., total phosphorus removal) could not be accurately represented. Further information about sample analysis and handling can be found in the associated Supporting Information.

2.3. Flood Experiment Analyses. We characterized surface water hydraulics using first-arrival and steady-state residence time metrics. The first-arrival time represents the time between the pump starting and the start of water flow at XS3 (e.g., the end of the slough, Figure 1a), while steady-state residence time represents the time from injection of the tracer to the time when the peak of the conservative solute breakthrough curve passed XS3. Note, the tracer occurred at hour two during quasi steady-state flow conditions.

For each experimental flood, we estimated nutrient retention (or export) using a mass balance to examine the source/sink characteristics of the floodplain slough. Inlet flux was calculated using measured flow and solute concentrations at the pump, while outlet flux was calculated using measured flow and solute concentrations at the outlet and XS3, respectfully. Here, we assumed solute concentrations at XS3 represented solute concentrations at the outlet because of the development of concentrated flow and proximity between the two locations.

We estimated NO_3^- uptake using the *Tracer Analysis for Spiraling Curve Characterization* (TASCC) methodology.[37] While this method was designed for stream systems, it has been recently used within alluvial wetlands where advective flow dominates.[38] Essentially, this method utilizes the difference in the breakthrough curves of the conservative (Cl^-) and nonconservative (NO_3^-) tracers to estimate instantaneous spiralling metrics (e.g., Newbold et al.)[39] and also to estimate background spiraling metrics through regression. Here, spiraling metrics refer to kinetic parameters typically used to characterize solute dynamics in streams such as uptake velocity, uptake length, and areal uptake. The calculated areal uptake (U_{tot}, μg N m^{-2} min^{-1}) and uptake velocity (V_{tot}, m min^{-1}) are applied to Michaelis−Menten kinetics model, and relationships are developed between NO_3^- concentrations and spiraling metrics.

To elucidate differences in nitrogen processing across seasons and floodplain location, we compared results from the five TASCC injections. We completed a nonparametric multivariate analysis of variance (NPMANOVA),[40] where the significance of seasonal variables (e.g., season, soil temperature, volumetric water content, and background NO_3^- concentrations), location (e.g., cross section), and interaction between seasonal variables and location were tested. We then used a robust analysis of covariance (robust ANCOVA)[41] in a pairwise fashion to test differences in Michaelis−Menten kinetic models developed for the two cross sections during each event. We completed all calculations with *R Statistical Software*[42] using the Vegan[43] and WRS[44] packages.

2.4. Reach-Scale Modeling. We estimated annual NO_3^- removal for the associated 1 km restoration reach using a simple well mixed-reactor model that incorporated measured areal uptake, a simple inundation model derived from raster analysis, and a synthetic flow record based on regional regression based on USGS gaging data and landuse characteristics. Further model details can be found in the Supporting Information. Here, it is important to highlight the parsimonious and conservative nature of the presented model. Feedbacks between river-floodplain interactions and biogeochemical processing are very complex and at this point, poorly characterized.[12,45,46] However, our model estimates *potential* load reductions utilizing simple measures and provides a rough estimate of biogeochemical processing within the StREAM Lab floodplain. While we acknowledge the uncertainty associated with the resulting load reduction estimates, the estimates provide an approximate characterization of load reductions in low-order floodplains that can be applied to restoration projects in the Mid-Atlantic Ridge and Valley.

3. RESULTS AND DISCUSSION

3.1. Inundation Hydrology. Topography, antecedent moisture conditions, and vegetative roughness controlled inundation hydrology within the floodplain slough. Generally, the flood progression was similar across all five floods: the slough would fill and then begin to drain back into the adjacent stream at the natural outlet point down gradient of XS3 (Figure 1a). When examining the first-arrival times of the experimental floods, two groups are apparent: saturated and dry floods. The spring, early summer, and winter floods all had relatively short first-arrival times (9.5−12.5 min) and were inundated prior to pumping (i.e., saturated floods), whereas the late summer and fall floods had relatively long first-arrival times (>30 min) and the slough was empty prior to the experiment (i.e., dry floods). A discussion of how antecedent moisture and vegetation control surface water-groundwater exchange and water storage in the slough can be found in Hester et al.[36] Similar patterns in flooding have been documented in the Nyack River floodplain in the western US, where individual sloughs were characterized as hydrologic facets[47] and were the scalable unit used to model

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inundation hydrology.[48] However, the filling and overflow of the slough does not entirely characterize water movement within the experimental slough. The lag in conservative tracer signal (Figure 3a), along with visual indicators (e.g., dye tracer and vegetation disturbance), suggest that a mixing zone between the floodwater and local water formed over the course of each saturated flood, potentially indicating multiple surface water flowpaths exist within the slough.

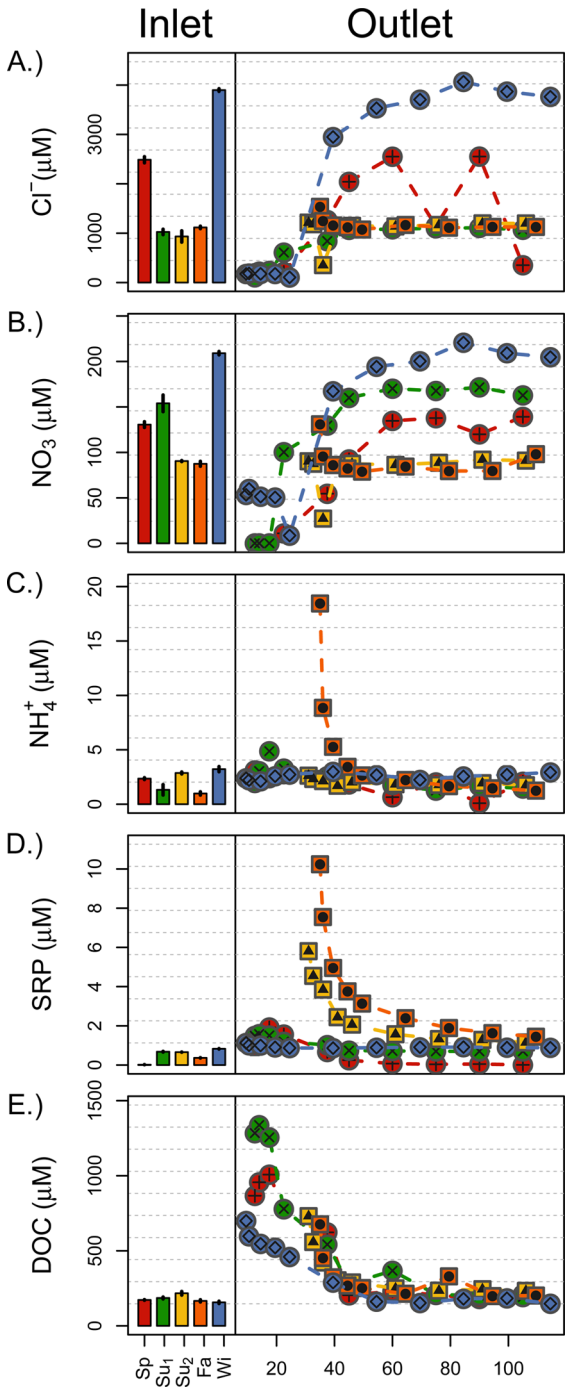

Figure 3. Inlet and outlet concentrations of dissolved reactive constituents during the five inundation experiments. Average inlet concentrations are representative of instream solute concentrations and are shown using bar charts on the left, where error bars represent standard error from the mean. Outlet concentrations from the first 120 min of each flood are displayed on the right. Red (plus sign), green(cross), yellow (triangle), orange (hollow circle), and blue (diamond) are associated with the spring, early summer, late summer, fall, and winter floods, respectively; outer circles and squares denote saturated and dry experimental floods, respectively.

Similar to patterns observed by Mertes[19] in large river systems, inundation hydrology and mixing patterns observed in the floodplain were also controlled by antecedent inundation conditions (e.g., wet vs dry floods). During the saturated floods, two dominant flowpaths were conceptualized (Figure 1a). Flow through the deepest portion of the slough, where local water was present prior to flooding, was largely dominated by transient storage and experienced relatively long residence times. A second primary flowpath formed on the inside of the floodplain slough, which essentially bypassed the existing local water and was dominated by advective transport (Figure 1a). These flowpaths were conceptualized through visual inspection of both dye tracers and vegetation disturbance. During these experimental floods, it took 60−75 min for the slough to become completely mixed as seen in the effluent Cl^- signal (Figure 3a), suggesting the persistence of the perirheic zone at the boundary of the two flowpaths. In contrast, the dry floods displayed relatively uniform effluent signal (Figure 3a) and prolonged first-arrival times (Table 1) because the lack of local water prior to flooding. With the available data, it is unclear if a perirheic zone formed over the course of either dry flood. However, the fall flood had a much longer steady-state residence time, suggesting relatively uniform flow when compared to the late summer flood and could be attributed to greater matting of senescing vegetation within the local water column.[36]

Table 1. Summary of Residence Time Metrics

flood	first-arrival time (min)	steady-state residence time (min)
spring	12.5	28
summer 1	12.5	29
summer 2	31.1	27
fall	35.0	51
winter	9.5	38

Floodplain conductivity of surface waters has been described as a measure of the floodplains ability to route floodwaters and is a function of the storm hydrograph, floodplain topography, and vegetative roughness.[45] However, floodplains exist as a mosaic of habitats[49] and, therefore, experience a heterogeneous distribution of floodplain conductivity. Within the experimental slough, the two conceptualized flowpaths experience differences in vegetation density. Specifically, the deeper portion of the slough has much denser vegetation than the shallow portion, potentially leading to greater mixing and reduced water velocities at the sediment water−interface. Therefore, in addition to a decrease in conductance associated with the perirheic zone, the deeper flowpath could also have decreased conductance because of increased vegetative roughness. As vegetation conditions varied across the five experimental floods, it is likely the relative contribution of the two surficial flowpaths also varied. These differences in inundation hydrology, along with differences in the roughness due plant communities, help explain the difference in biogeochemical processing between the 5 experimental floods.

3.2. Dissolved Organic Matter Export. Floodplains are an important source of DOM to riverine networks.[11] DOC export from the floodplain slough was fairly consistent

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throughout all five floods, where there was a pronounced first flush of DOC during each flood (Figure 3e and 4e). Patterns

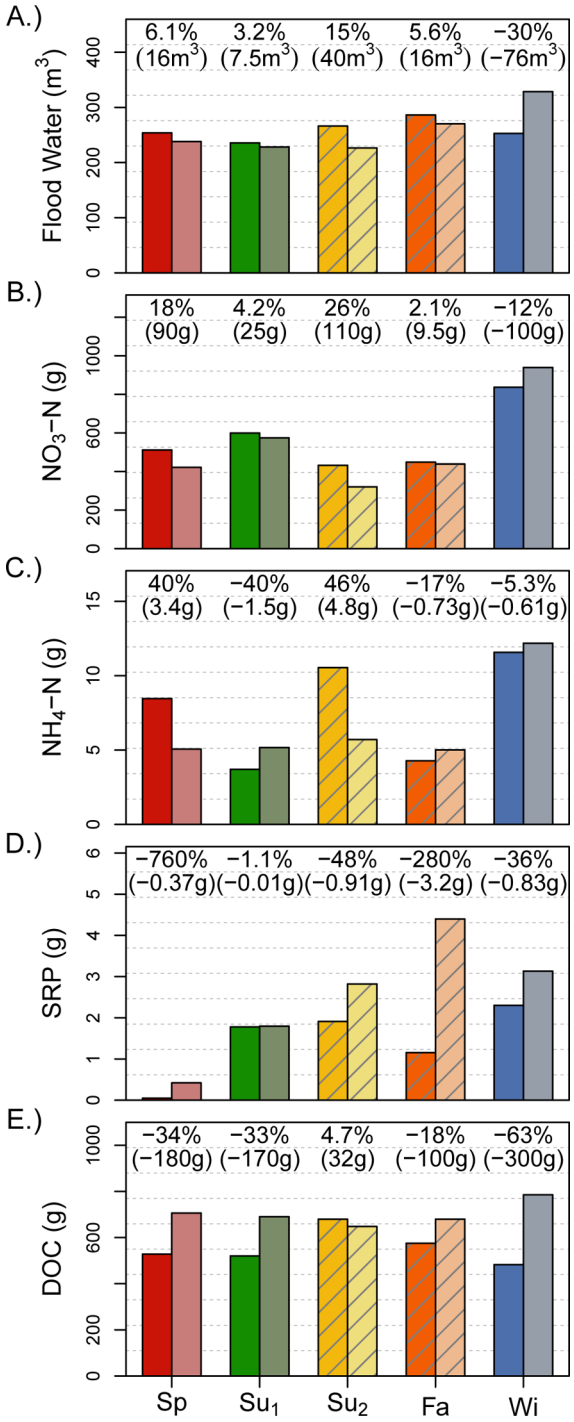

Figure 4. Total load observed at the inlet (dark) and outlet (light) of the floodplain slough during the 5 inundation experiments. Dry floods are denoted by bars with hatching, and both the relative difference (%) and mass difference (g) between the loads is also displayed.

reflective of two distinct processes appear when analyzing the DOC concentration within the floodplain effluent: dilution and flushing. The saturated floods experienced a dilution of DOC, where mixing between streamwater and local water is apparent in the gradual decline in effluent concentration (Figure 3e). In contrast, the dry floods experienced flushing of DOC from the soil surface within the slough,[50] where the signal exhibited a rapid decline in effluent concentration. The experimental slough was a relatively large source of DOC during the saturated floods, where effluent DOC mass was 30−60% greater than the influent mass. However, the dry floods exported relatively little or no DOC. Our results are consistent with other observations of accumulation of DOC in inundated floodplains,[18] and could be attributed to decay of algal biomass[25] and plant material.[13] Because of the dominance of reed canary grass within the study slough, it is likely a dominant source of organic matter and autochthonous nutrients.[51] Further, our results suggest inundation hydrology, and more specifically, antecedent inundation conditions controls DOC export and processing within the experimental slough (Figure 4e).

3.3. Initial Flush of Reactive Solutes. Similar to other studies, the experimental slough was a consistent net source of SRP during each experimental flood. Potential sources of SRP include organic matter, likely derived from reed canary grass decay,[51] nutrient rich sediments and particulate organic matter deposition from previous floods,[14,52] and the legacy of over 100 years of cattle grazing at the site. Possible mechanisms responsible for SRP loss from floodplains include the oxidation of DOM,[53] reduction of iron-phosphate sediment,[54] and desorption of loosely held SRP at the soil surface.[52] However, it is important to note that we did not capture depositional processes during the flood experiments, and thus, were unable to characterize total phosphorus removal and sorption/desportion of SRP associated with newly deposited sediments.

Here, we propose that both hydrologic and biotic processes control SRP export from the slough. In contrast to the DOC signal, the dry floods had relatively large SRP first flushes when compared to the saturated floods (Figure 3 and 4). During the interflood period (e.g., no overbank or artificial flow), organic matter at the soil surface would be available for mineralization and the production of loosely held SRP;[14] thus, this mechanism is likely a dominant source of SRP during the dry floods. While the saturated floods did not experience a strong first flush, they were still net sources of SRP. This is likely attributed to redox conditions that developed during prolonged inundation, where ferrous soils release SRP when reduced,[55] however, thorough analysis of soil chemistry was not conducted across the study slough to identify the persistance of ferrous soils.

In addition to hydrologic control (e.g., dry vs saturated antecedent inundation conditions), SRP loads into and out of the floodplain varied greatly with season (Figure 4d) and are likely linked to biological uptake within the floodplain.[20] During the spring flood, the growing season was just beginning when P is in high demand. Thus, available SRP was likely being utilized for plant biological activity. Plant and microbial uptake has been widely observed in streams and associated riverine wetlands,[56] and periphyton can act as a temporary sink that completely masks P signals.[57] This is a possible explanation of the minimal SRP load experienced within the spring flood, and is in contrast to the fall flood, where much of the plant material was senescing and possibly contributed to the large net export of SRP through mineralization of newly senesced material. Other restored floodplains with legacy nutrients have been shown to be sources of SRP for 20+ years post restoration.[58]

Over the course of the five experimental floods, the slough was a variable source/sink of NH_4^+. During the fall flood, there was an observable first flush of both NH_4^+ and SRP (Figure 3b and c), suggesting elevated mineralization of DOM. However,

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there were no apparent seasonal or hydrologic drivers behind the NH_4^+ signal observed in the other four floods. This is consistent with investigation of other headwater floodplains in both the Mid-Atlantic[20] and upper Mississippi River Valley,[32] where total export varied with season and by event, respectively. NH_4^+ processing within the floodplain environments is relatively complicated because of the lability of NH_4^+, its affinity for sorption, and its tendency to nitrify in oxic environments.[17] Noe et al.[14] examined mineralization rates across a gradient of floodplains in the Mid-Atlantic and found that nitrification was dominant in headwater floodplains while ammonification was dominant in larger river floodplains. While nitrification was not explicitly measured in this study, variability in nitrification rates could explain the variable source/sink pattern experienced within the experimental slough.

3.4. Nitrate Removal. The floodplain was typically a sink of NO_3^-, where net removal ranged from 2% to 26% (Figure 4b). Similar to the DOC effluent signal, perirheic mixing was evident as the NO_3^--rich streamwater mixed with the NO_3^- limited local water during the saturated floods (Figure 3b). When comparing DOC and NO_3^- effluent concentrations, the DOC signal reached equilibrium more quickly, suggesting NO_3^- removal through both biotic uptake and denitrification. Forshay and Stanley[23] observed similar removal of NO_3^- when river water mixed with local water in a backwater floodplain, where rapid NO_3^- loss was attributed to denitrification. Denitrification is a well-documented process within riverine floodplains, with recorded removal rates ranging from undectable[59] to greater than 75%[29] removal of the total riverine NO_3^- load. Denitrification is controlled by the amount of NO_3^- transported into the floodplain,[30] the availability of carbon,[11] and the residence time of floodwaters.[48] In many backwater floodplain associated with large rivers like the Amazon or Danube, denitrification is often limited by the amount of NO_3^- transported into floodplain environment, suggesting limited exchange between channel and floodplain.[60−62] In contrast, in environments where river−floodplain interaction is greater and advective flow dominates in the floodplain, denitrification is often limited by short residence times.[59] This was likely the case in our study slough, where mean residence times ranged from 27 to 51 min (Table 1).

Areal uptake (Figure 5) was a function of both seasonality, and to a lesser extent, heterogeneity of flowpaths within the floodplain. The NPMANOVA model accounted for 52% of variation (R^2 = 0.52, p < 0.001) in the relationship between total areal uptake and NO_3^- concentration across all five tracer experiments at both cross sections. Spatially, sampling location (e.g., XS2 vs XS3) only accounted for 1.7% of the observed variation (p = 0.01). This suggests while sampling location was a statistically significant predictor, it is practically unimportant and the observed nitrate uptake signal was relatively homogeneous at the spatial resolution of our sampling. Therefore, spiraling metrics were calculated using data from both XS2 and XS3. Seasonal variables accounted for 33% of variation (p < 0.001) in the model, where soil moisture, background NO_3^- concentration, and soil temperature account for 15%,10%, and 2.5% of the observed variation (p < 0.001), respectively. Antecedent moisture conditions affect floodwater residence times (e.g., dry vs saturated floods), can limit or enhance biological activity and uptake,[21] and control mechanisms associated with the first flush (e.g., oxidation of organic matter).[16] Additionally, background NO_3^- concentrations have been shown to exert influence on NO_3^- uptake

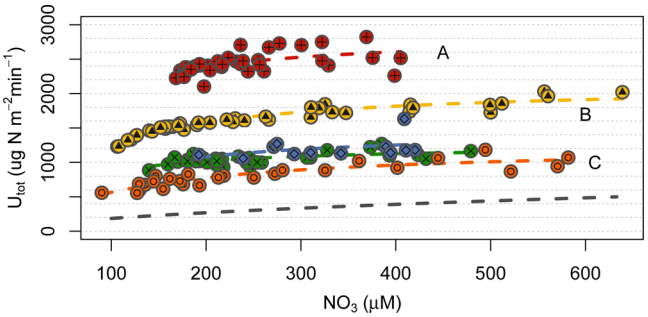

Figure 5. Areal NO_3^- uptake calculated for spring (red, plus sign), early summer (green, cross), late summer (yellow, triangle), fall (orange, circle), and winter (blue, diamond) experimental floods. Points represent individual samples and lines represent Michaelis−Menten Kinetic models developed for each flood, respectively. The black dashed line represents expected total instream uptake based on data taken from the 69 streams across North America in the LINXII study.[65] Statistical differences denoted in Table 2 are displayed using letters A−C.

rates, where higher NO_3^- concentrations typically lead to greater NO_3^- uptake but lower net removal.[63,64] However, because soil moisture and background NO_3^- concentration are confounding variables, it is difficult to isolate their individual effects on the NO_3^- uptake with the available data. For example, the two late summer and fall floods were both dry floods and experiences similar background NO_3^- concentrations. However, the uptake rates were significantly different, suggesting there was a shift in dominant processes affecting export.

Utilizing a Wilcox ANCOVA in a pairwise fashion, the five floods separated into three statistically different groups: (1) spring, (2) late summer, and (3) winter, early summer, and fall (Table 2). Increased biological uptake is expected in the spring and summer and conversely muted uptake in the fall and winter because of seasonal differences in temperature and its effects on the biological communities. However, this pattern is confounded by the low uptake rates experienced in the early summer floods. Potentially, the low uptake rates measured in the early summer flood were related to elevated NH_4^+ export (Figure 4d), where highly labile NH_4^+ satisfied N-demand within the slough and reduced rates of NO_3^- uptake. Similarly, Noe and Hupp[20] did not find seasonal patterns in NO_3^- export from a small floodplain system, suggesting confounding factors, such as nitrification and organic matter availability/lability also controlled the export of NO_3^- from the floodplain.

When compared to typical instream areal NO_3^- uptake,[65] NO_3^- uptake rates were relatively high within the slough during the five experimental floods (Figure 5). In a recent national assessment of instream NO_3^- uptake kinetics, the LINXII study measured total instream NO_3^- uptake using N^{15} additions across 69 different streams in North America. Represented by the dark line in Figure 5, the regression model of LINXII uptake rates is lower than the rates measured across the five experimental floods. This could partially be explained by differences in measurement techniques, where the bulk injection alters instream kinetics because of the large increase in NO_3^- concentrations.[66] Further, the background NO_3^- concentration of the streamwater used to inundate the floodplain (Figure 3) was not necessarily representative of floodwater NO_3^- concentrations. However, the response to the NO_3^- addition was minimal during all five experimental floods

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Table 2. Summary of Spiraling Metrics and Associated Statistics from Tracer Addition

	background uptake length			Michaelis−Menten model			groups
experiment	$S_{w,amb}$ (m)	std error (m)	p-value	U_{max} (μg N m^{-2} min^{-1})	K_m (μg N m^{-2} min^{-1})	p-value	Wilcox ANCOVA
spring	116	21.4	<0.001	2865	39.9	<0.001	A
early summer	258	25.9	<0.001	1256	46.7	<0.001	C
late summer	157	7.9	<0.001	2135	70.2	<0.001	B
fall	319	44.2	<0.001	1255	123	<0.001	C
winter	304	176	0.12	1483	73.9	0.002	C

(e.g., muted rising limbs in the Michaelis−Menten curves), suggesting biogeochemical processing within the floodplain was not limited by NO_3^-, where the current N pool is derived from internal cycling of nutrients and potentially legacy N from the 100+ years of grazing at the site.[51,67] Increased biogeochemical processing within the floodplain can be explained by increased contact between the floodplain soils and floodwater, increase in availability of labile organic matter, and also increase in biological uptake.

3.5. Modeled Load Reductions. Annual and storm NO_3^- load reductions were minimal when measured uptake was extrapolated to the restored floodplain across the synthetic flow record. For individual events, NO_3^- removal ranged from 8.6 to 17.6 kg of NO_3−N removed per storm, or 7.5 to 10.3% removal of the total storm load. However, this resulted in annual removal ranging from 0 to 139 kg of NO_3−N removed, or 0 to 1.5% of the annual load of NO_3^-. Mean individual storm and annual load reductions were 10% and 0.60%, respectively. The relatively simple model is conservative, in that it overestimates inundation time through a rectangular hydrograph, it assumes relatively high NO_3^- concentrations during storm flow (e.g., no dilution affects were accounted for), and the maximum observed areal uptake (spring, 2800 μg N m^{-2} min^{-1}) was used for the estimate of NO_3^- removal. This suggests the restored floodplain is ineffective in removal of instream NO_3^- and can be explained by both limited river-floodplain connectivity and short residence times associated with short-hydroperiod floodplains. Roley et al.[63] found similar load reduction associated with two-stage ditch located in the Midwestern US, where NO_3^- uptake was relatively high but hydrologic connectivity and residence time were relatively low. They went on to conclude that to maximize nitrogen removal, floodplain restoration design should enhance removal of NO_3^- from waters draining to the site (e.g., upslope water). In addition, it is also important to note the modeled stream reach in our study represents a relatively small section of stream, and riparian buffers/wetlands have been shown to remove significant loads of NO_3^- when the entire basin is taken into account.[68] Here, if we assume that 1 km of stream removes 10% of the NO_3^- load for individual storms, then it would take approximately 10 km of restored floodplain to reduce the entire nitrate load being delivered to the StREAM Lab for an average storm. While this is a vast oversimplification of biogeochemical processing of floodwaters within floodplains, it does highlight the importance of the cummulative effects of riparian/floodpalin systems along the stream cooridor.

3.6. Management Implications. Recent efforts by the Chesapeake Bay Program (CBP) have emphasized re-establishing river-floodplain connectivity to improve downstream water quality, essentially making river−floodplain connectivity a best management practice (BMP) for the stream restoration industry in the eastern US.[4,71] Here, we do not want to discount ecosystem services derived from restoration efforts in headwater streams, the water quality benefits (e.g., nutrient retention) riparian zones and floodplains provide by processing upslope water, or even the cumulative influence of floodplains across the river network. However, results from studies in the Upper Midwest,[32] Mid-Atlantic Piedmont,[20,27] and now the Appalachian Ridge and Valley (i.e., this study) show that individual floodplains associated with small to medium size streams can actually be net sources of nutrients. Therefore, these results cumulatively suggest that restoring river−floodplain connectivity is not always an appropriate BMP for nutrient removal, and site specific conditions, such as annual inundation duration and legacy landuse, should be considered when optimizing river−floodplain connectivity for nutrient removal and retention. Potentially, these findings would be most useful during site selection and prioritization phase of restoration design, where multiple objectives and design parameters are often balanced. Further, our results highlight the potential for flushing of reactive SRP from floodplain wetlands, and more specifically, stream−wetland complexes often used for mitigation banking and sediment removal.[69] While these engineered wetlands undoubtedly remove sediment attached P and N through deposition and denitrification,[70] respectively, designers must also balance flushing of allochthonous SRP and other reactive solutes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02426.

Description of climatic data acquisition, sample handling and analysis, and reach scale modeling (PDF)

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Notes

The authors declare no competing financial interest.

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