

## SEASONAL VARIATION IN NUTRIENT RETENTION DURING INUNDATION OF A SHORT-HYDROPERIOD FLOODPLAIN<sup>†</sup>

GREGORY B. NOE\* and CLIFF R. HUPP

*U.S. Geological Survey, 430 National Center, Reston, VA 20192, USA*

### ABSTRACT

Floodplains are generally considered to be important locations for nutrient retention or inorganic-to-organic nutrient conversions in riverine ecosystems. However, little is known about nutrient processing in short-hydroperiod floodplains or seasonal variation in floodplain nutrient retention. Therefore, we quantified the net uptake, release or transformation of nitrogen (N), phosphorus (P) and suspended sediment species during brief periods (1–2 days) of overbank flooding through a 250-m floodplain flowpath on the fourth-order Mattawoman Creek, Maryland U.S.A. Sampling occurred during a winter, two spring and a summer flood in this largely forested watershed with low nutrient and sediment loading. Concentrations of  $\text{NO}_3^-$  increased significantly in surface water flowing over the floodplain in three of the four floods, suggesting the floodplain was a source of  $\text{NO}_3^-$ . The upper portion of the floodplain flowpath consistently exported  $\text{NH}_4^+$ , most likely due to the hyporheic flushing of floodplain soil  $\text{NH}_4^+$ , which was then likely nitrified to  $\text{NO}_3^-$  in floodwaters. The floodplain was a sink for particulate organic P (POP) during two floods and particulate organic N and inorganic suspended sediment (ISS) during one flood. Large releases of all dissolved inorganic N and P species occurred following a snowmelt and subsequent cold winter flood. Although there was little consistency in most patterns of nutrient processing among the different floods, this floodplain, characterized by brief inundation, low residence time and low nutrient loading, behaved oppositely from the conceptual model for most floodplains in that it generally exported inorganic nutrients and imported organic nutrients. Published in 2007 by John Wiley & Sons, Ltd.

KEY WORDS: flood; floodplain; nitrogen; nutrient; phosphorus; retention; sediment; wetland

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### INTRODUCTION

Wetlands are generally thought to be important locations for the uptake and transformation of nutrients and sediment in fluvial landscapes (Johnston, 1991; Hupp *et al.*, 2005). However, variation in nutrient biogeochemistry among and within wetland ecosystems can make generalizations difficult. For example, floodplains are frequently thought of as sinks of inorganic nutrients and sources of organic nutrients, in other words nutrient transformers (e.g. Ward, 1989). Most studies of floodplain biogeochemistry have occurred in forested wetlands with long-hydroperiods (week to months of inundation) or permanently inundated water bodies with temporary river connections. These floodplain environments have the long contact times between floodwaters and biota or sediment or the strongly reducing conditions that can facilitate nutrient removal. Studies of long-hydroperiod floodplains have consistently documented decreases in the concentration of  $\text{NO}_3^-$  and increases in dissolved organic N and P during flood pulses; however, floodplains can also either increase or decrease concentrations of  $\text{NH}_4^+$ , particulate N and P and dissolved reactive P (Conner and Day, 1982; Brinson *et al.*, 1983; Yarbrow, 1983; Hamilton and Lewis, 1987; Brunet *et al.*, 1994; Knowlton and Jones, 1997; Sánchez-Pérez *et al.*, 1999; Tockner *et al.*, 1999, 2002; Hein *et al.*, 2003; Valett *et al.*, 2005). This variation in the retention of some nutrient species limits broad generalizations about long-hydroperiod floodplains.

Much less is known about the influence of shorter hydroperiod floodplains on nutrient processing in floodwaters. Short-hydroperiod floodplains situated on low-order streams are abundant and could be cumulatively important to water quality maintenance in watersheds, despite their narrower width (Brinson, 1993). Many studies have

\*Correspondence to: Gregory B. Noe, U.S. Geological Survey, 430 National Center, Reston, VA 20192, USA. E-mail: gnoe@usgs.gov

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examined how riparian zones along low-order streams decrease nutrient concentrations along groundwater flowpaths, but fewer have studied flowpaths of surface water from uplands (Lowrance, 1998). Even less information is available on riparian retention of nutrients from upstream surface water during overbank flooding, even though nutrient loading rates may be great during these short periods. The brief duration of surface water inundation, higher water velocities and resulting low residence time may constrain the ability of short-hydroperiod floodplains to change the concentration of reactive elements in surface floodwaters. Temporary inundation may also be insufficient to deplete dissolved oxygen and establish strongly reducing conditions. Alternatively, dynamic fluctuations between reducing and oxidizing environments associated with flashy flooding could stimulate coupled mineralization–nitrification–denitrification and thereby lead to decreasing N concentrations in floodwaters. It is likely that short-hydroperiod floodplains vary more in their influence on nutrient concentrations in floodwaters compared to longer hydroperiod floodplains.

Few studies have examined seasonal variation in floodplain nutrient processing regardless of hydroperiod length. The timing of flood pulses with respect to seasonal trends in biology and hydrology could influence floodplain biogeochemistry. Changes in biotic activity associated with seasonal climate can affect productivity (Junk *et al.*, 1989), decomposition (Brinson *et al.*, 1981) and nutrient processing in floodplains (Brinson *et al.*, 1983; Tockner *et al.*, 2000). In addition, seasonal variation in the characteristics of flood pulses and groundwater exchange is likely to affect nutrient loading and thereby influence floodplain nutrient cycling. Seasonal variation in floodplain function has implications for downstream ecosystems. For example, the limiting nutrient for primary production changes seasonally in many coastal water bodies (Conley, 1999). Seasonal differences in N versus P retention by floodplains could play an important role in controlling the productivity of downstream estuarine ecosystems.

Here we present the results of a study designed to document seasonal patterns of changes in nitrogen and phosphorus concentrations during overbank flooding of a short-hydroperiod floodplain ecosystem. The monitored floodplain was located on Mattawoman Creek, located in the Coastal Plain of Maryland in a largely forested watershed that has a relatively high channel gradient for the Coastal Plain and incurs relatively low nutrient loading. Surface water was sampled repeatedly during most or all of time that overbank flooding occurred at multiple locations along a floodplain flowpath during a winter flood, two spring floods in different years and a summer flood. Changes in concentrations of nitrogen, phosphorus and suspended sediment species were evaluated along the longitudinal floodplain flowpath to quantitatively determine whether the floodplain was a net sink, source or transformer of nutrients during each flood.

## METHODS

### *Site description*

The Mattawoman Creek is a fourth-order tributary to the tidal Potomac River, located in Maryland roughly 50 km south of Washington, DC, U.S.A. (Figure 1). The 244-km<sup>2</sup> watershed is largely forested (63%), with some urban (23%) and agricultural (14%) land use (Maryland Department of Natural Resources, 1997). The river has a broad, 1-km wide floodplain on Quaternary lowland alluvial deposits in the valley bottom with geologically controlled pinch points that substantially reduce floodplain breadth over short reaches. The bottomland hardwood forest on the floodplain has both Zone IV and V (drier) floodplain plant communities (Wharton *et al.*, 1982) dominated by *Quercus* spp., *Acer rubrum* and *Asimina triloba* with a patchy herbaceous layer. The research floodplain segment is located in the lower watershed immediately downstream from a pinch point with an adjacent USGS river gauge (38° 36' N, 77° 03' W; near Pomonkey, MD, period of record from November 1949 to September 1972 and from January 2001 to present).

Three sampling stations were located along a 250-m floodplain flowpath that begins at a crevasse splay, transitions into a floodplain slough and then forms a channel before reentering the main river channel (Figure 1). The 'upstream' floodplain station is positioned 25 m into the floodplain from the crevasse splay. The 'midstream' floodplain station is located 150-m downgradient from the upstream station and immediately below the transition from small rivulet channels coming from the upstream location into a broader, 20-m wide floodplain slough. The 'downstream' floodplain station is located 100-m downgradient from the midstream station in a 5-m wide floodplain channel that reenters the main channel of Mattawoman Creek.

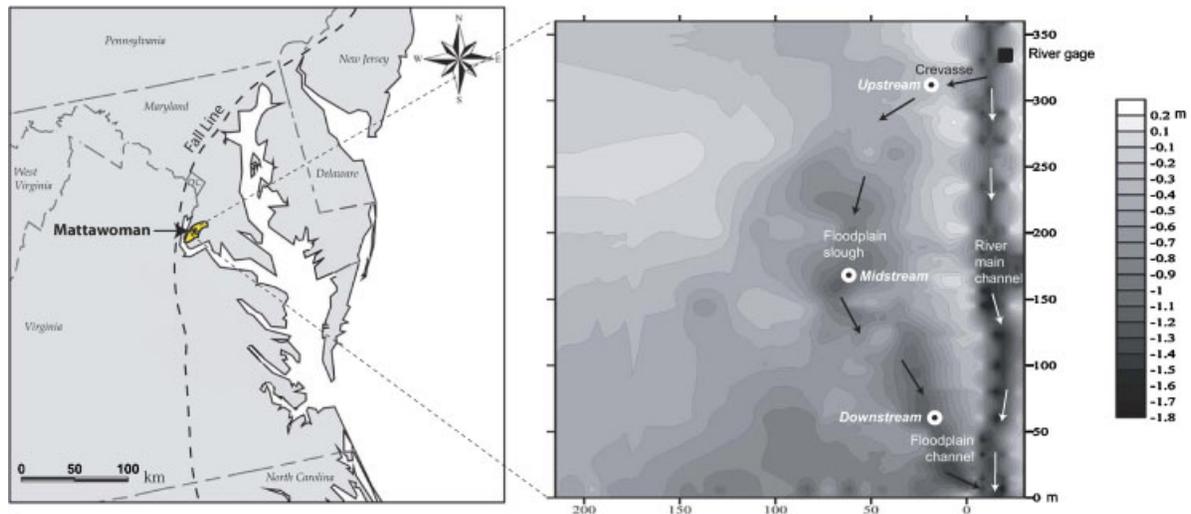


Figure 1. Map of the location of the Mattawoman watershed in the mid-Atlantic region of the U.S.A. Inset map shows the soil elevation (contour plot spatially interpolated from survey points) and layout of the research floodplain including the crevasse, floodplain slough and floodplain channel with their corresponding sampling stations (Upstream, Midstream and Downstream, respectively) as well as the main channel and USGS river gauge. Arrows in the inset indicate flow directions during flood events. This figure is available in colour online at [www.interscience.wiley.com/journal/rra](http://www.interscience.wiley.com/journal/rra)

Mean annual and peak streamflow in the Mattawoman Creek is  $1.4$  and  $57.1 \text{ m}^3 \text{ sec}^{-1}$ , respectively, and discharge drops to zero some summers. Overbank flow at the crevasse splay begins at  $11.3 \text{ m}^3 \text{ sec}^{-1}$  (400 CFS); daily mean channel discharge above this level occurs on average 7 days per year (range: 0–22 days) but this statistic underestimates the frequency of flooding events shorter than 1 day. Floods occur most frequently from December through April. During the course of the study we observed that flooding frequently begins by backfilling through the downstream floodplain channel up to the floodplain slough, followed by overbank flooding from upstream if the main channel rises sufficiently to overtop the crevasse in the natural levee. Observations of water velocity during two floods indicate that residence time of water in the floodplain flowpath is roughly 45 min.

#### Sample collection and analysis

Samples (0.9 L) of surface water were collected with an ISCO autosampler located at each station that was programmed to collect every 1 hr (February 2004, beginning of April 2004 floods) or 2 hr (end of April 2004 flood, September 2004 and May 2005 floods) after overbank flooding began. Not all floods were sampled; instead, we chose to sample four floods that had overbank flooding and occurred in the seasons of winter, summer and spring (twice). Autosamplers were automatically triggered by resistance element actuators that detected the presence of surface water and then sampled 24 times into separate bottles or until surface water dropped below the height of the actuator. Actuators were initially set at 20, 50 and 40 cm above the soil surface at the upstream, midstream and downstream stations, respectively. Actuator height at the upstream station was changed to 10 cm prior to the September 2004 flood. The different heights were intended to account for soil elevation differences among sites and to initiate sampling at all stations at the same time once the upstream station was inundated. Intake lines were positioned at the same height as the actuators. The autosamplers were programmed to purge their sample lines three times before every sample collection. Samples were retrieved from the autosamplers as soon as possible, from 0 to 48 hr after the last sample was collected by the autosampler. New bottles were installed in the middle of the April 2004 flood. ISCO bottles were processed immediately in the field (February 2004) or stored on ice and processed upon return to the laboratory (all other floods). Storage conditions inside autosamplers were dark and generally cold (except September 2004), minimizing the potential for post-collection nutrient fractionation. Every ISCO bottle was split into 60-ml filtered ( $0.45 \mu\text{m}$  Pall PES filter) and unfiltered nutrient subsamples, and the remaining water

was processed for suspended sediment concentrations. Nutrient subsample bottles were frozen until analysis. Grab samples of surface water, when present, were taken from each floodplain station, field filtered and frozen until analysis. Nutrient concentrations during the April 2004 flood were similar in grab samples and ISCO samples collected at the same time as the grab samples but filtered and frozen 48 hr later.

Concentrations of P and N species in the unfiltered and filtered surface water samples were measured. Particulate (total—dissolved) and dissolved forms of reactive, acid hydrolysable and organic P were measured, as were ammonium, nitrate, nitrite, dissolved organic N and particulate organic N. Total P (TP) and N were measured by digesting subsamples with alkaline persulphate in an autoclave for 1 hr (Patton and Kryskalla, 2003) and measuring the resulting orthophosphate and nitrate. Digestions included water blanks and glycerophosphate and glycine checks to determine digestion efficiency. Acid-hydrolysable P (AHP) was measured by weak acid thermal digestion, using a variant of APHA Method 4500-P (Eaton *et al.*, 1995) that used a final concentration of 0.11 M H<sub>2</sub>SO<sub>4</sub> and heating in an autoclave at 121°C for 30 min, followed by measurement of orthophosphate concentrations. Acid hydrolysis of filtered samples digests inorganic condensed phosphates (Eaton *et al.*, 1995) and some labile organic phosphorus (Maher and Woo, 1998). It is likely that acid hydrolysis of unfiltered samples also digests P adsorbed to fine mineral particles. Preliminary tests indicated that glycerophosphate was not digested by this acid hydrolysis method. Finally, reactive P concentrations in unfiltered and filtered samples were measured as orthophosphate. The AHP fractions were calculated as the difference between acid hydrolysable (which includes reactive P) and reactive P. The organic P fractions were calculated as the difference between TP and AHP + reactive P. Nitrite, nitrate, ammonium and molybdate-reactive orthophosphate concentrations were measured colorimetrically using standard methods by an Astoria-Pacific segmented flow autoanalyser.

Suspended sediment concentrations were quantified on subsets of the ISCO samples starting with the April 2004 flood. Water remaining after subsampling for nutrient analyses was filtered through a 0.7 µm glass fibre filter (Whatman GF/C) and the filtrate volume was measured. Filters with accumulated sediment were then dried at 60°C to constant mass. Inorganic and organic (total—inorganic) suspended sediment concentrations were determined by weighing filters before and after combustion at 400°C for 16 hr (Nelson and Sommers, 1996). The specific conductivity of the filtrate was also measured using a conductivity meter.

Our approach for determining if the floodplain was a sink or source of each analyte was to compare paired changes in concentrations between the floodplain stations over the duration of each flood. A statistically significant decrease in concentration along the flowpath (e.g. upstream to midstream station) over the duration of the sampling was interpreted as net ecosystem uptake of that analyte. A significant increase along the flowpath was considered net ecosystem release. Concentrations were compared only for time periods when overbank flooding occurred (the upstream station was collecting samples) and not during backfilling of the floodplain. It is unlikely that we sampled the same parcel of water as it moved downgradient through the floodplain. However, repeatedly sampling over the duration of the floods ensured a rigorous characterization of net changes in nutrient and sediment concentrations as water flowed through the floodplain. Changes in concentrations between stations for each analyte were tested with nonparametric paired comparisons tests (Wilcoxon Signed Ranks Tests), with  $\alpha = 0.05$ , using SPSS 13.0. The samples were paired by the time of sampling, accounting for flow so that sampling times at upstream stations were paired with sampling times occurring later downstream. For example, a sample collected at 08:37 at the upstream station was paired with the 08:54 sample and not the 07:54 sample at the midstream station. The number of pairings ( $n$ ) varied with each flood (February 2004: 21; April 2004: 26; September 2004: 8 and May 2005: 23). Differences in mean concentrations and per cent change between stations were calculated for each parameter during the time period of overbank flooding for each flood event.

## RESULTS

### *NO<sub>3</sub><sup>-</sup> example*

Changes in surface water concentrations of NO<sub>3</sub><sup>-</sup>, a nutrient species of broad interest, provide an example of some of the patterns observed during inundation of the Mattawoman floodplain. This section will describe NO<sub>3</sub><sup>-</sup> patterns and climatic and hydrologic conditions in detail for each flood. The results for the other analytes will be described later. The first flood to be sampled occurred 6–7 February 2004 as a result of a large rainfall and

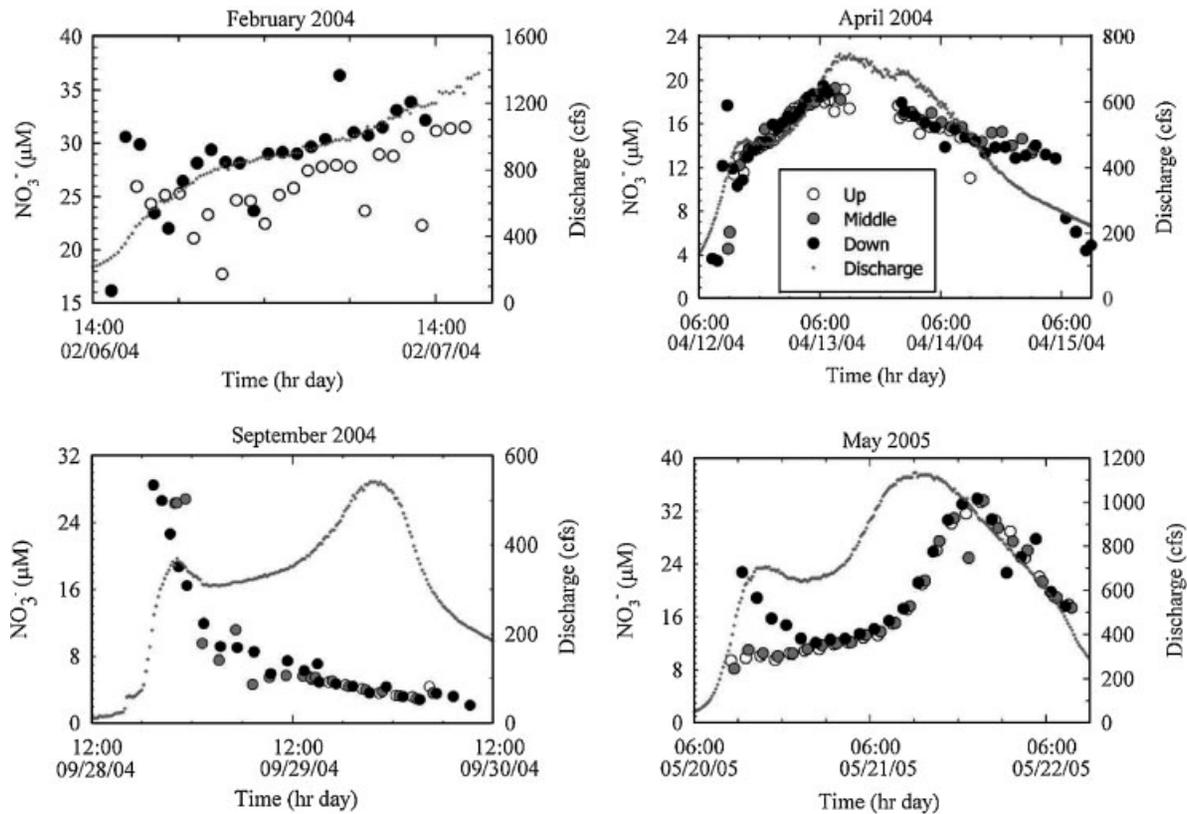


Figure 2. Nitrate concentrations at the different floodplain stations, and main channel discharge, over the duration of four different flood events

snowmelt. Water in the main channel at the USGS gauge was very cold, on average  $1^{\circ}\text{C}$  over the 2-day duration of overbank flooding, and a thin surface layer of ice was present on floodwater in the upper floodplain. The greatest channel discharge occurred during this flood compared to the other sampled floods (Figure 2). Sampling on the floodplain occurred only at the upstream and downstream stations, and only on the rising limb of this February 2004 flood. Nitrate concentrations were significantly greater at the downstream compared to upstream floodplain station (Table I). Over the duration of sampling, floodwater leaving the floodplain had 16% higher  $\text{NO}_3^-$  concentrations than water entering the floodplain. Nitrate concentrations at the downstream station exceeded concentrations at the upstream station at nearly all sampling times and the differences were larger during the beginning of the flood (Figure 2). Therefore, this 250-m floodplain flowpath was a net source of  $\text{NO}_3^-$  to surface water during the rising limb of the February 2004 flood.

The 12–15 April 2004 flood was warmer (average water temperature:  $9^{\circ}\text{C}$ ) than the February 2004 flood and occurred after the emergence of spring ephemeral herbaceous vegetation. Overbank flooding lasted 2 days. Concentrations of  $\text{NO}_3^-$  increased significantly as floodwater flowed between the upstream and downstream floodplain stations. However, the magnitude of the increase was smaller than the February 2004 flood (Table I). The largest increases in  $\text{NO}_3^-$  concentrations occurred between the upstream and midstream stations around peak discharge (Figure 2). Nitrate concentrations were also lower at the downstream compared to midstream stations after discharge decreased below bank full in the main channel and water stagnated in the lower half of the floodplain.

Overbank flooding was brief ( $<1$  day) during the 29–30 September 2004 flood, although a lengthy period of backfilling of the floodplain preceded overbank flow (Figure 2). Water temperature was warm ( $20^{\circ}\text{C}$ ) during this summer flood and woody vegetation was fully leaved. Nitrate concentrations were not significantly different

Table 1. Summary of changes in nutrient and sediment concentrations and conductivity along the floodplain flowpath (Upstream–Downstream station) during four different overbank flooding events (mean water temperature in parentheses)

	6–7 February 2004 (1°C)			12–15 April 2004 (9°C)			29–30 September 2004 (20°C)			20–22 May 2005 (14°C)		
	Concentration change	(%) change	<i>p</i>	Concentration change	(%) change	<i>p</i>	Concentration change	(%) change	<i>p</i>	Concentration change	(%) change	<i>p</i>
NO <sub>2</sub> <sup>-</sup> (μM)	-0.14	-29	0.014	0.00	0	0.804	0.11	33	0.069	0.05	8	0.236
NO <sub>3</sub> <sup>-</sup> (μM)	-4.16	-16	<0.001	-0.37	-2	0.007	0.21	5	0.123	-2.15	-12	0.024
NH <sub>4</sub> <sup>+</sup> (μM)	-0.91	-9	0.002	0.33	8	0.018	-0.46	-21	0.484	-0.34	-6	0.236
DON (μM)	-1.48	-16	0.131	-0.94	-4	0.091	1.89	8	0.093	2.99	12	0.004
PON (μM)	0.58	7	0.455	3.39	25	0.017	1.10	7	0.161	-4.10	-27	0.055
TN (μM)	-4.15	-8	0.131	2.25	4	0.170	2.86	6	0.036	-3.55	-5	0.078
DRP (μM)	-0.13	-63	0.007	-0.02	-9	0.102	-0.02	-7	0.401	0.01	5	0.484
DAHPP (μM)	-0.11	-192	0.037	-0.04	-27	0.602	-0.03	-36	0.182	0.03	15	0.287
DOP (μM)	-0.07	-134	0.825	0.01	5	0.898	0.02	10	0.498	-0.01	-5	0.704
PRP (μM)	-0.05	-49	0.396	-0.02	-13	0.932	0.01	3	0.833	-0.02	-11	0.378
PAHP (μM)	-0.03	-5	0.917	0.05	5	0.162	0.03	2	0.889	0.16	11	0.563
POP (μM)	-0.20	-92	0.232	0.13	32	0.031	0.21	85	0.018	-0.34	-74	0.140
TP (μM)	-0.51	-41	0.004	0.17	9	0.006	0.26	10	0.069	-0.19	-8	0.315
ISS (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	4.31	27	0.012	-2.24	-14	0.612	-2.42	-10	0.959
OSS (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	0.55	12	0.058	-0.50	-17	0.498	3.43	38	0.285
TSS (mg L <sup>-1</sup> )	n.d.	n.d.	n.d.	2.45	14	0.208	-2.77	-15	0.499	1.01	3	0.333
Conductivity (μU)	2.20	1	0.741	-3.28	-3	<0.001	-1.88	-2	0.012	3.30	4	0.626

Absolute concentration change, per cent change and the *p*-value of Wilcoxon Signed Ranks comparison tests are listed for each parameter. Positive changes in parameter concentrations indicate ecosystem uptake from surface floodwater, negative numbers indicate ecosystem release to surface floodwater. Statistically significant changes in concentrations are listed in bold. n.d., no data; dissolved < 0.45 μm; particulate > 0.45 μm; DON, dissolved organic N; PON, particulate organic N; TN, total N; DRP, dissolved reactive P; DAHP, dissolved acid-hydrolysable P; DOP, dissolved organic P; PRP, particulate reactive P; PAHP, particulate acid-hydrolysable P; POP, particulate organic P; TP, total P; ISS, inorganic suspended sediment; OSS, organic suspended sediment; TSS, total suspended sediment.

between the upstream and downstream floodplain stations, although average concentrations were slightly lower downstream (Table I). This summer flood highlights the large changes in nutrient concentrations that sometimes occurred during backfilling as water flowed from the downstream to midstream floodplain stations. At the midstream station,  $\text{NO}_3^-$  concentrations were initially high as the floodplain became inundated, quickly decreased to intermediate values as backfilling continued and then remained consistently low after overbank flow from the upstream station commenced (Figure 2).

Floodwater during the second spring flood, from 20–22 May 2005, was warmer ( $14^\circ\text{C}$ ) and had slightly greater discharge than the first spring flood in April 2004 (Figure 2). Overbank flooding lasted 2 days. Nitrate concentrations were much higher, nearly double, at the downstream compared to upstream and midstream floodplain stations during the beginning of overbank flow. Nitrate concentrations remained slightly higher downstream during the middle of the flood up to peak discharge. Overall,  $\text{NO}_3^-$  concentrations increased 12% as floodwater flowed over the floodplain (Table I).

#### *General trends for each flood*

The winter snowmelt flood in February 2004 was characterized by large releases of dissolved inorganic nutrients by the floodplain. Concentrations of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , dissolved reactive phosphate (DRP), dissolved acid-hydrolysable phosphate (DAHP) and TP were all significantly higher at the downstream compared to upstream floodplain station (Table I). Concentrations of DAHP nearly doubled from the upstream to downstream stations, while concentrations of DRP increased 63%,  $\text{NO}_2^-$  increased 29%,  $\text{NO}_3^-$  increased 16% and  $\text{NH}_4^+$  increased 9%. Thus, surface water was enriched in dissolved inorganic N and P as it travelled through the floodplain. Total N concentrations did not significantly change. The conductivity of surface water did not change across the floodplain, suggesting that other parcels of water did not enter the surface water on the floodplain.

The Mattawoman floodplain was a transformer of inorganic N and sink for particulate nutrients during the first spring flood in April 2004. Over the entire 250-m floodplain flowpath,  $\text{NO}_3^-$  concentrations increased by nearly the same concentration as  $\text{NH}_4^+$  concentrations decreased, roughly  $0.35\ \mu\text{M}$  (Table I). Particulate N and particulate organic P (POP) concentrations decreased by 25 and 32%, respectively, and inorganic suspended sediment (ISS) concentrations decreased 27%. Particulate N decreased  $3.4\ \mu\text{M}$ , 10 times larger than the change in DIN species. Conductivity of the surface water increased slightly, 3%, as it moved down the floodplain, suggesting an interaction between surface floodwater entering the floodplain with other water parcels having higher conductivity. In addition to these whole-floodplain patterns, the upper and lower portions of the floodplain flowpath behaved differently than each other. Nitrate and  $\text{NH}_4^+$  concentrations and conductivity increased by 5, 13 and 3%, respectively from the upstream to midstream floodplain stations. The increases in N concentrations were larger than the increase in conductivity, suggesting that the cause was floodplain biogeochemical reactions and not only the mixing of different water parcels. From the midstream to downstream stations,  $\text{NH}_4^+$ , particulate acid-hydrolysable P (PAHP), POP and ISS concentrations all decreased. Therefore, the upper floodplain segment was a source of nutrients whereas the lower floodplain segment was a sink of nutrients during the spring 2004 flood.

The floodplain influenced the surface water chemistry of floodwater to a lesser degree during the summer September 2004 flood. Only TN and POP concentrations significantly changed along the entire floodplain flowpath, decreasing slightly, 6%, for TN and decreasing greatly, 85%, for POP (Table I). Individual N species did not significantly change, but most of the change in TN was a result of DON and PON concentrations. This was the only flood in which average  $\text{NO}_3^-$  concentrations decreased from the upstream to downstream stations, but not statistically significantly. Conductivity increased by 2% during the flood, similar to the April 2004 flood. The upper floodplain segment was again a source of  $\text{NH}_4^+$  (60% increase) and conductivity (1% increase) as well as a sink for DRP (14% decrease). The increase in  $\text{NH}_4^+$  concentrations was consequently not likely due to hydrologic mixing. The lower floodplain segment was a sink for PON and  $\text{NO}_2^-$ .

The Mattawoman floodplain was again a source of  $\text{NO}_3^-$  during the second spring flood of May 2005 (Table I). Concentrations of DON changed for the first time, decreasing 12% from the upstream to downstream stations. Within the upper floodplain segment, the floodplain was a source of  $\text{NH}_4^+$  and a sink for organic suspended sediment. The lower floodplain was a source of  $\text{NO}_3^-$  (12% increase) and sink of  $\text{NH}_4^+$  (10% decrease), DON (11% decrease) and conductivity (4% decrease).

The floodplain exhibited consistent spatial trends in  $\text{NH}_4^+$  concentrations across many of the floods. Concentrations of  $\text{NH}_4^+$  increased between the upstream and midstream stations for each flood that the midstream station was sampled. For two of these three floods, the largest pulse of  $\text{NH}_4^+$  concentrations at the midstream station occurred at the beginning of overbank flow from the upstream station. In addition,  $\text{NH}_4^+$  concentrations at each station were always highest at the beginning of a flood.

#### *N and P fractionation*

The importance of  $\text{NO}_3^-$  to the N pool in floodwater changed seasonally, decreasing from winter to spring to summer (Table II). The contribution of DON and PON increased concurrently. Dissolved organic N was the largest species of N except during the winter flood. The particulate N fraction was at most 33% of TN and dissolved forms dominated N pools during floods. Nitrite and  $\text{NH}_4^+$  were relatively small fractions of N. Total N concentrations, however, remained similar during all four floods. Nitrogen speciation generally did not change meaningfully (>5% change in percentage of TN) as water flowed through the floodplain. However, the importance of DON decreased 6% and PON increased 5% as floodwater flowed between the upstream and downstream stations during the May 2005 flood.

TP concentrations in floodwater increased over the duration of the study, although the relative size of the different P species did not change meaningfully among the different floods (Table II). The PAHP fraction was the majority, or nearly the majority, of P during every flood. Dissolved forms of P were cumulatively at most 26% of the P pool and the particulate forms dominated P speciation. However, the relative size of the DRP fraction was elevated during the snowmelt flood in February 2004. The relative importance of PAHP and POP to TP pools entering and leaving the floodplain flowpath changed, in opposite directions, by more than 5% for nearly every flood. For example, PAHP constituted 54% of TP in water entering the floodplain, and decreased to 40% of TP as floodwater left the floodplain during the February 2004 flood. The directionality of changes of PAHP and POP were not predictable by the seasonality of flooding. Concentrations of PAHP increased and POP decreased during the February 2004 and May 2005 floods, whereas PAHP decreased and POP increased during the April 2004 and September 2004 floods. However, the changes in PAHP concentrations were never statistically significant indicating the high variation in PAHP concentrations during flooding. In summary, the Mattawoman floodplain has a large but variable influence on particulate P fractionation.

Table II. Variation in the fractionation of nitrogen (N) and phosphorus (P) species and total N (TN) and total P (TP) concentrations at the upstream and downstream floodplain stations during four different floods

	Upstream				Downstream			
	February 2004	April 2004	September 2004	May 2005	February 2004	April 2004	September 2004	May 2005
% $\text{NO}_2^-$	0.9	0.4	0.7	0.9	1.1	0.4	0.5	0.8
% $\text{NO}_3^-$	48.3	27.5	9.0	28.3	52.0	29.3	9.1	30.0
% $\text{NH}_4^+$	18.3	7.7	4.8	8.2	18.6	7.4	6.1	8.2
%DON	17.6	40.8	52.5	39.0	18.9	44.2	51.6	32.6
%PON	15.7	24.0	33.0	23.6	13.6	18.7	32.6	28.4
TN ( $\mu\text{M}$ )	53.3	56.4	45.9	64.6	57.4	54.1	43.0	68.2
%DRP	16.9	9.1	11.1	11.4	19.4	10.9	13.3	10.0
%DAHP	4.7	7.2	3.7	7.3	9.7	10.0	5.6	5.8
%DOP	4.3	9.8	7.7	5.3	7.2	10.2	7.7	5.1
%PRP	8.6	6.0	12.2	7.9	9.0	7.5	13.3	8.1
%PAHP	53.8	47.5	69.1	60.8	39.9	49.4	76.1	50.3
%POP	17.7	21.5	9.7	18.8	24.1	16.0	1.6	30.3
TP ( $\mu\text{M}$ )	1.24	1.87	2.52	2.45	1.75	1.70	2.26	2.63

Fractionation is presented as the average per cent of TN or TP over the duration of an individual flooding event.

## DISCUSSION

This short-hydroperiod floodplain flowpath (1–3 days per flood) located in a relatively undisturbed watershed was never a sink for  $\text{NO}_3^-$  or DRP in surface floodwaters. In fact, it was often a source of these readily bioavailable nutrients. The floodplain was occasionally a sink for particulate organic N and P, and was also a transformer of inorganic N species during some floods. Thus, the Mattawoman floodplain behaved oppositely from many longer hydroperiod floodplains that are sinks for inorganic nutrients and sources of organic nutrients (Conner and Day, 1982; Yarbrow, 1983; Hamilton and Lewis, 1987; Ward, 1989; Knowlton and Jones, 1997; Valett *et al.*, 2005). Although only statistically significant in one instance each, TN and TP concentrations increased as floodwaters moved over the floodplain during two floods, and decreased during two other floods. This floodplain ecosystem behaved largely unpredictably with respect to nutrient processing during different flooding events—except that it often exported inorganic N and P. Although the seasonality of flood pulses has been incorporated into conceptual models of floodplain ecosystems (Junk *et al.*, 1989; Tockner *et al.*, 2000), little detailed empirical data exist on the temporal variation in floodplain nutrient retention. We will attempt to demonstrate that these patterns of ecosystem nutrient processing (inorganic release, organic uptake and high variability) on the Mattawoman floodplain are likely due to the low residence time ( $\sim 45$  min) of floodwaters on the floodplain, brief periods of flooding and relatively low nutrient concentrations in floodwaters.

It is difficult to assign causal mechanisms to the observed patterns in nutrient and sediment concentrations without corresponding process rate measurements. Nonetheless, it is possible to speculate on the processes that led to the observed patterns. Strong inference can be derived, in part, from comparing different portions of the floodplain flowpath. The upper portion of the floodplain exhibited different nutrient processing than the lower portion of the floodplain flowpath. The upper flowpath was more often a source of nutrient species, whereas the lower flowpath was typically a nutrient and sediment sink. The likely cause of this difference in behaviour is the change in geomorphology, and resulting hydrology, from the crevasse splay to floodplain slough. The floodplain broadens substantially through the study reach and the slope in soil surface elevation decreased once the flowpath entered the slough (Figure 1). Therefore, surface water velocities likely decreased from the upper to lower floodplain flowpath. As we will show in detail next, this geomorphic change on the floodplain likely resulted in hyporheic discharge in the upper floodplain and particle settling in the lower floodplain.

*Dissolved inorganic N*

The hyporheic flushing of subsurface porewater rich in  $\text{NH}_4^+$  into surface floodwaters is consistent with the observed increases in  $\text{NH}_4^+$  concentrations over the upper floodplain flowpath during every flood. Conductivity increased concurrently with  $\text{NH}_4^+$  concentrations in the upper floodplain for two of the three floods, but the per cent change in conductivity was always much less than the per cent change in  $\text{NH}_4^+$  concentrations. In addition, pulses of  $\text{NH}_4^+$  release were largest during the initiation of overbank flooding and decreased over the duration of each flood. This suggests that floodwater entered surficial soils in the floodplain near the crevasse splay and natural levee, flushed porewater rich in  $\text{NH}_4^+$  and then was discharged back into surface waters upstream of the floodplain slough. Discharge of deeper groundwater flowpaths rich in  $\text{NH}_4^+$  would likely have changed surface water conductivity to a similar degree as  $\text{NH}_4^+$ . Another source of  $\text{NH}_4^+$  is the mineralization of organic N during flooding. However, the observed increases in  $\text{NH}_4^+$  were never concurrent with changes in either DON or PON concentrations during floods. Ammonium in surficial soils likely builds up between floods through the mineralization of autochthonous and allochthonous sources of DON and PON, and then is exported during inundation.

Concentrations of  $\text{NO}_3^-$  increased significantly as surface water flowed over the Mattawoman floodplain during three out of the four floods. Increases in  $\text{NO}_3^-$  concentrations in surface water could be caused by two processes: nitrification or flushing of  $\text{NO}_3^-$  from soil porewater. Nitrate can accumulate in floodplain soils during dry periods and then be flushed out during rainfall and flooding (Bechtold *et al.*, 2003). However, it was unlikely that the gain in  $\text{NO}_3^-$  on the Mattawoman floodplain was derived from mixing with subsurface waters. The consistent export of  $\text{NH}_4^+$  from the subsurface suggests that porewater was reduced, preventing nitrification, and  $\text{NO}_3^-$  likely was not present. Nitrification more likely accounts for the increased surface water  $\text{NO}_3^-$  during the two spring floods. Similar amounts of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were removed and released, respectively, to floodwaters over the entire floodplain flowpath during the April 2004 flood. However,  $\text{NH}_4^+$  concentrations increased over the upper floodplain

as subsurface water discharged into surface floodwaters. Therefore, the gross  $\text{NH}_4^+$  release rate would have to be greater than the measured net  $\text{NH}_4^+$  release rate to account for the loss of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  due to nitrification. Stronger evidence for nitrification exists for the May 2005 flood. In that flood,  $\text{NH}_4^+$  concentration increases in the upper floodplain were followed by  $\text{NH}_4^+$  decreases and  $\text{NO}_3^-$  increases in the lower floodplain flowpath. This spatial pattern suggests that  $\text{NH}_4^+$  exported from subsurface waters was later nitrified into  $\text{NO}_3^-$ . To summarize, this floodplain also behaved as an inorganic N transformer during some floods. Nitrification has been shown to be an important component of N cycling in other floodplains as well. Strauss *et al.* (2004) demonstrated that nitrification produced a similar amount of  $\text{NO}_3^-$  as was consumed by denitrification and that nitrification was controlled by temperature and oxygen availability.

#### *Particulate nutrients*

Particulate nutrients were retained by the floodplain during a subset of the overbank flooding events. Particle retention by the floodplain resulted in large decreases in nutrient concentrations when it occurred. Concentrations of inorganic suspended solids, POP and particulate organic N each decreased significantly, 27, 32 and 25%, respectively, as floodwater flowed over the floodplain flowpath in April 2004. POP also decreased 85% during the September 2004 flood. Retention of POP over the entire flowpath occurred during the two floods with relatively low discharge, whereas POP increased (but not statistically significantly) during high discharge floods. Therefore, flood energy most likely controls particle retention by influencing the balance between settling and scouring of material from the floodplain. In contrast, Steiger and Gurnell (2002) observed greater riparian sedimentation rates during higher discharge floods largely due to the inundation of larger proportions of the riparian zone during larger floods.

Particulate P species cumulatively decreased from 83 to 81% of TP from upstream to downstream floodplain stations, respectively, averaged across all floods. This small change in particulate versus dissolved P fractionation, despite large decreases in POP concentrations, was due to the dominance of PAHP fractions that never significantly changed in concentration. The majority of suspended sediment was inorganic (mean = 77% inorganic). If PAHP was largely associated with suspended mineral sediment such as silt and clay, and POP was associated with refractory organic detritus, it is likely that PAHP particles were smaller than POP particles. The lower settling rates of PAHP could explain the lack of significant changes in PAHP concentrations in this study. The particulate N fraction decreased slightly from 24 to 23% of TN. This small change in TN fractionation, despite some large changes in PON concentrations, resulted from the dominance of dissolved forms of N in floodwater. To summarize, the Mattawoman floodplain episodically retained large proportions of the particulate organic N and P in floodwaters entering the floodplain, but had a small influence on overall particulate versus dissolved fractionation due to the small proportion in particulate form (N) or the nonreactivity of the dominant particulate form (P).

In contrast to the observed changes in particulate nutrient and sediment concentrations in floodwater, sedimentation rates on the Mattawoman floodplain surface are low relative to floodplains on other rivers. Mean net sedimentation rates on other Coastal Plain rivers tributary to the Chesapeake Bay range between 1.5 and 3.0  $\text{mm yr}^{-1}$  (Hupp *et al.*, 2005). The overall site net sedimentation rate on this Mattawoman floodplain is about 0.05  $\text{mm yr}^{-1}$  (Hupp, unpublished data). However, local deposition rates are typically higher along floodplain flowpaths (Hupp *et al.*, 2005); in this case 1.6  $\text{mm yr}^{-1}$  near the upper floodplain station and 3.5  $\text{mm yr}^{-1}$  below the middle floodplain station. This downgradient increase in sedimentation rates is concordant with the more frequent retention of suspended sediment and particulate nutrients in the lower floodplain flowpath. These relatively low sedimentation rates also support the idea that the particulate organic nutrients occasionally retained during flooding on the Mattawoman floodplain are mineralized between floods. Other floodplains in the watershed of the Chesapeake Bay have high N and P accumulation rates associated with sediment accumulation that are a function of watershed loading rates and channel-floodplain hydraulic connectivity (Noe and Hupp, 2005).

#### *Generality of findings*

The large nutrient export by the Mattawoman floodplain during the winter flood may be typical of the behaviour of cold-temperate floodplains but not other Coastal Plain floodplains. The research floodplain is located at the northern limit of the extensive Coastal Plain of the southeastern U.S.A. The large release of all measured dissolved inorganic nitrogen and phosphorus species during the cold February 2004 flood was most likely due to the freezing

of the floodplain soils prior to inundation, the resulting microbial and root lysis and subsequent flushing of released nutrients into surface floodwaters. Large pulses of nutrients are released from soils following soil freezing (Deluca *et al.*, 1992; Fitzhugh *et al.*, 2001) and can be subsequently transported in streams (Fitzhugh *et al.*, 2003).

Many floodplain and riparian studies have focused on high nutrient concentration systems, where they are effective sinks for particulate and inorganic nutrients (Peterjohn and Correll, 1984). In low concentration watersheds, the riparian zone can be a nutrient source or sink depending on redox conditions (Mulholland, 1992). The Mattawoman Creek is relatively oligotrophic and sediment poor due to its mostly forested watershed and Coastal Plain geomorphology. Mean concentrations of constituents entering the floodplain flowpath (during flooding) were 55  $\mu\text{M}$  TN, 2.0  $\mu\text{M}$  TP and 23  $\text{mg L}^{-1}$  TSS. These values are typical of uncontaminated rivers and streams and much lower than contaminated rivers (Meybeck, 1982). The low concentrations of reactive nutrients may have led to the variable sink and source status of the floodplain during inundation, possibly by limiting reactive substrate availability to microorganisms and maintaining oxygen availability by limiting ecosystem metabolism, or limiting concentration dependent adsorption processes. The highly pulsed flooding may have also contributed to the varying nutrient retention. The soils of the research site are well drained between flooding events and the overbank flooding events sampled in this study lasted under 3 days (although backwater can persist slightly longer). Therefore, reducing environments are not likely long lasting or strongly limited by electron acceptors. This could explain the lack of  $\text{NO}_3^-$  uptake by the floodplain during overbank inundation in any of the floods. Similarly, pulsed  $\text{NO}_3^-$  loading supported less denitrification activity than riparian soils receiving constant  $\text{NO}_3^-$  inputs (Casey *et al.*, 2001). We did observe  $\text{NO}_3^-$  removal by the lower floodplain when backfilling occurred before overbank flooding or when overbank floodwater pooled during flood recession. Water velocity was much slower during these backwater filling or pooling events, likely supporting a denitrification or biotic uptake of  $\text{NO}_3^-$ . Research on additional short-hydroperiod floodplains is necessary to quantify intra- and inter-floodplain variation in nutrient retention in order to fully test the hypothesis that short-hydroperiod floodplains exhibit more variation in their influence on nutrient concentrations in floodwaters as a result of fluctuating redox associated with the duration of inundation compared to longer hydroperiod floodplains.

The observed temporal variation in ecosystem material retention has important implications for watershed transport processes and downstream ecosystems. Most nutrient loading in rivers occurs during high discharge flooding (House *et al.*, 1997). In addition, river channels have very low nutrient retention rates compared to low-order stream channels (Alexander *et al.*, 2000). Consequently, floodplain wetlands represent one of the last locations in hydroscares where meaningful nutrient retention may occur before nutrient loads are discharged to coastal water bodies that may be sensitive to eutrophication. Although overbank flooding is infrequent, the Mattawoman floodplain and other floodplains on low-order rivers are hydrologically connected to the river channel when discharge and nutrient loading is high. Floodplains on lower order rivers also have significant length and area, despite narrower width, due to the greater abundance of lower order compared to higher order rivers (Brinson, 1993). Temporal variation in ecosystem nutrient retention on the Mattawoman Creek floodplain demonstrates that floodplains are not uniformly sinks (or sources) of nutrients. These findings complicate the model of floodplains as consistent nutrient sinks in watersheds that reduce nutrient delivery to coastal waterbodies. The results of this research suggest that a nuanced view of floodplain ecosystem biogeochemistry is needed. Variation in floodplain function should be incorporated into watershed models of nutrient transport (e.g. Linker *et al.*, 2000) and watershed restoration planning (e.g. Mitsch *et al.*, 2001).

We developed a conceptual model of the multiple processes that control nutrient retention by floodplains based on a synthesis of the literature (Figure 3). These broad processes include climate, nutrient availability in the floodplain, the upstream nutrient loading rate, flood hydrology and river-floodplain geomorphology. These processes interactively control features within floodplains including biotic activity, water velocity and floodplain inundation, which in turn influence redox, nutrient loading rates to the floodplain and the hydraulic residence time on the floodplain. Finally, biotic processing and the balance between deposition and erosion are the ultimate factors determining if a floodplain is a sink, source or transformer of nutrients through storage and cycling of carbon, N and P. The behaviour of the Mattawoman floodplain ecosystem clearly demonstrates the importance of several of these mechanisms. Climate had a large influence on temporal variation in nutrient retention likely through variation in biotic metabolism. The brief periods of floodplain inundation also influenced the redox status of floodplain soils, limiting nutrient retention. In addition, the change in nutrient and sediment retention patterns between the upper

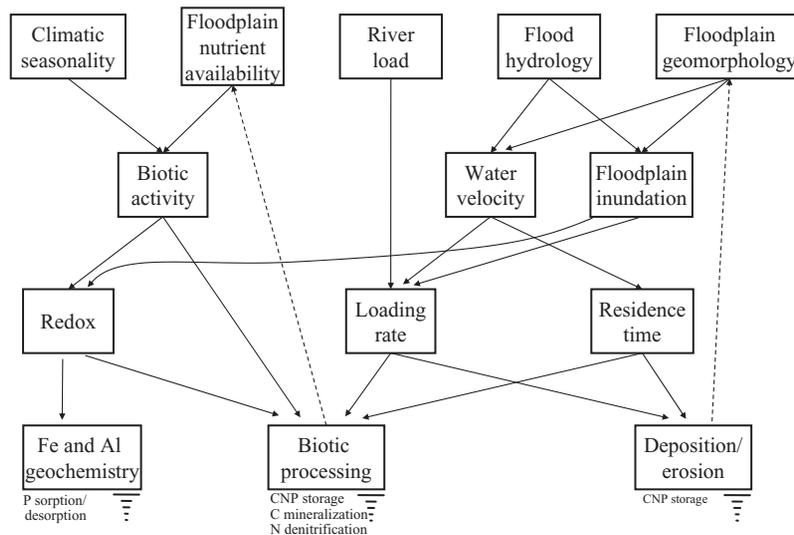


Figure 3. Conceptual model of the hydrologic, geomorphic, climatic and biotic factors influencing the processes in floodplains that determine nutrient retention. Solid lines indicate direct influence, dashed lines indicate indirect feedbacks

and lower portions of the floodplain flowpath highlights the role of floodplain geomorphology. Finally, differences in flood hydrology among overbank flooding events likely influenced patterns of particulate nutrient deposition to sediments. The observed patterns in nutrient and sediment processing by the Mattawoman floodplain indicate that climate and seasonality, geomorphology and surface–subsurface hydrologic exchange all influenced nutrient retention in this floodplain. Models of floodplain nutrient biogeochemistry need to account for the multiple processes that control the loading rate of material to floodplains and subsequent processing rates of this material.

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