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Nitrogen and Phosphorus Attenuation within the Stream Network of a Coastal, Agricultural Watershed

Scott H. Ensign,* Sara K. McMillan, Suzanne P. Thompson, and Michael F. Piehler

ABSTRACT

Streams alter the concentration of nutrients they transport and thereby influence nutrient loading to estuaries downstream; however, the relationship between in-stream uptake, discharge variability, and subsequent nutrient export is poorly understood. In this study, in-stream N and P uptake were examined in the stream network draining a row-crop agricultural operation in coastal North Carolina. The effect of in-stream nutrient uptake on estuarine loading was examined using continuous measurements of watershed nutrient export. From August to December 2003, 52 and 83% of the NH_4^+ and PO_4^{3-} loads were exported during storms while concurrent storm flow volume was 34% of the total. Whole-ecosystem mass transfer velocities (V_f) of NH_4^+ and PO_4^{3-}, measured using short-term additions of inorganic nutrients, ranged from 0.1 to 25 mm min^{-1}. Using a mass balance approach, this in-stream uptake was found to attenuate 65 to 98% of the NH_4^+ flux and 78 to 98% of the PO_4^{3-} flux in small, first-order drainage ditches. For the larger channel downstream, an empirical model based on V_f and discharge was developed to estimate the percentage of the nutrient load retained in-stream. The model predicted that all of the upstream NH_4^+ and PO_4^{3-} load was retained during base flow, while 65 and 37% of the NH_4^+ and PO_4^{3-} load was retained during storms. Remineralization from the streambed (vs. terrestrial sources) was the apparent source of NH_4^+ and PO_4^{3-} to the estuary during base flow. In-stream uptake reduced the dissolved inorganic N to dissolved inorganic P ratio of water exported to the N-limited estuary, thus limiting the potential for estuarine phytoplankton growth.

Nutrient loading poses the most critical pollution threat to coastal waters (Howarth et al., 2002), exemplified by the fact that eutrophication affects 65% of the estuarine area of the USA (Bricker et al., 1999). The ecological impacts of nutrient enrichment to estuaries are driven by riverine processes occurring upstream. For example, throughout the 1980s, dense phytoplankton blooms in the Neuse River, North Carolina, limited the availability of inorganic N to the N-limited estuarine phytoplankton community downstream (Paerl et al., 2004). Following a phosphate detergent ban in 1988, riverine phytoplankton growth and subsequent N uptake decreased, resulting in increased inorganic N delivery to the estuary that stimulated phytoplankton blooms (Paerl et al., 2004). This example illustrates the dependence of estuarine primary productivity on riverine processes following a large alteration of the river's nutrient chemistry (the phosphate load reduction); however, seasonal and intra-annual patterns in nutrient loading to the Neuse River and nutrient export to the estuary are less apparent (Stow et al., 2001). Thus, knowledge of the processes regulating nutrient cycling within river networks is necessary to understand how estuaries are affected by upstream watersheds.

Numerous biogeochemical processes alter the concentration of nutrients during transport through stream networks, resulting in a net decrease of inorganic nutrients as water moves downstream (Peterson et al., 2001; Webster et al., 2003). These in-stream processes were assumed to be responsible for deficits between N and P inputs to rivers and subsequent riverine exports in a study of 100 European river basins (Behrendt and Opitz, 2000). In a study of watershed stream networks in the northeastern USA, it was estimated that 76% of the N entering the stream networks may have been permanently removed via denitrification or temporarily retained through biotic sequestration (Seitzinger et al., 2002). Alteration of nutrient concentrations by riverine processes during transport also changes the timing of nutrient delivery and the quality (coarse vs. fine particulate organic matter and organic vs. inorganic dissolved nutrients) of nutrients exported to downstream ecosystems (Meyer and Likens, 1979; Mulholland, 2004).

Since the introduction of the nutrient spiraling model (Newbold et al., 1981), nutrient retention in streams has been examined at the reach scale, integrating the effects of advective transport, uptake, and remineralization. The distinct advantage of reach-scale experimentation (relative to mesocosm or chamber studies) is that the measurements reflect whole-stream productivity in combination with the geomorphic and hydrologic influences of the channel. Measurements of nutrient spiraling can also be used to quantify the larger role streams play in watershed nutrient transformations. Nutrient spiraling studies have generally not been extended beyond the stream reach to examine temporal dynamics in nutrient loads within the larger stream network, however. An empirical coupling between reach-scale measurements and the larger stream network is required to understand the temporal dynamics of watershed nutrient export and estuarine nutrient loading.

The objective of this study was to determine the effect of in-stream nutrient uptake on nutrient export from an agricultural watershed. Previous research has demonstrated that nutrient export from rivers is dominated by the effect of discharge (Borsuk et al., 2004). Therefore, particular attention was given to discharge variability and the relationship between nutrient uptake and export during storm events and base flow. Uptake of both

Institute of Marine Sciences, University of North Carolina at Chapel Hill, 3431 Arendell Street, Morehead City, NC 28557. Received 9 Sept. 2005. *Corresponding author (ensign@email.unc.edu).

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Abbreviations: DIN, dissolved inorganic nitrogen; DIP, dissolved inorganic phosphorus.

inorganic N and P were investigated since both can affect autotrophic and heterotrophic productivity in streams and estuaries (Mallin et al., 2004; Sundareshwar et al., 2003; Gallo et al., unpublished data, 2004). The results of this study provided insight into the ecological connectivity of a watershed and the downstream estuary.

This study was conducted in a small (8.5-km^2) watershed in coastal North Carolina that drains into the South River estuary, and subsequently the Neuse River estuary (Fig. 1). In response to declining water quality in the Neuse River estuary (Paerl et al., 1998), the North Carolina General Assembly mandated a nutrient management strategy intended to ameliorate degradation of the estuary and provide eventual improvement in water quality (15A NCAC 2B.0232-.0240). The Neuse River Nutrient Sensitive Waters Management Strategy includes rules for wastewater, urban stormwater, agriculture, and general nutrient management (H2O.enr.state.nc.us/nps/neuse.htm; verified 17 Apr. 2006). The enactment of the Neuse Rules has focused attention on the role of N loading from proximal watersheds adjoining the Neuse River estuary where headwater streams enter estuaries with limited time for nutrient transformation and uptake during transport.

MATERIALS AND METHODS

Study Sites

The agricultural streams selected for study drained soybean [*Glycine max* (L.) Merr.] fields on Open Grounds Farm, a 182-km^2 row-crop farm (Fig. 1). The drainage network of this farm consists of a regular arrangement of engineered ditches and canals that are entrenched 1 and 3 m deep, respectively. Field ditches serve as ephemeral, first-order streams in this agricultural network, have an average width of 0.9 m and depth of 0.2 m, and during the time of study were vegetated primarily with false loosestrife (*Ludwigia* sp.). Canals are second- and third-order streams, averaging 2.6 m wide and 0.1 m deep, that collect flow from field ditches and route water to nearby estuaries. Canals were heavily vegetated with small pondweed (*Potamogeton pusillus* L.). Two representative ditches (Ditch A and B) and two canals (Canal A and B) were chosen for this study, all draining into Southwest Creek, a branch of the South River estuary (Fig. 1). The channel sediments in ditches and canals were a coarse- to medium-grained sand covered by varying accumulations of silt. Bed sediments were regularly reworked during floods, which covered or scoured submerged vegetation from the stream bed. No woody debris or other channel obstructions existed in the reaches studied because of annual channel dredging and clearing activities. Transient storage within the stream channels is almost entirely due to the in-channel flow obstruction associated with submerged vegetation, and the fraction of median travel time attributable to transient storage ranges from 0.5 to 3.3% (Ensign and Doyle, 2005). Stream gradients were approximately 0.12%.

Nutrient Load and Flow Monitoring

Flow velocity and depth were monitored continuously in a drainage pipe that routed water from the agricultural watershed into the Southwest Creek estuary (Fig. 2). An area-velocity flow meter was mounted in the outlet end of the drainage pipe and linked to an automated water sampler and data recorder (Model 6712, ISCO, Lincoln, NE). Data were logged at 30-min intervals from August to December 2003. Volumetric flow rates were calculated using the cross-sectional area of the pipe, velocity, and water depth. Stream water samples were collected weekly from the drainage pipe for analysis of NH_4^+, NO_3^-, and PO_4^{3-}. In addition, more frequent automated flow-paced sampling was conducted during storm events.

A graphical base flow separation method that accounted for watershed size was applied to identify the base flow component of total stream flow during storm events (Dingman,

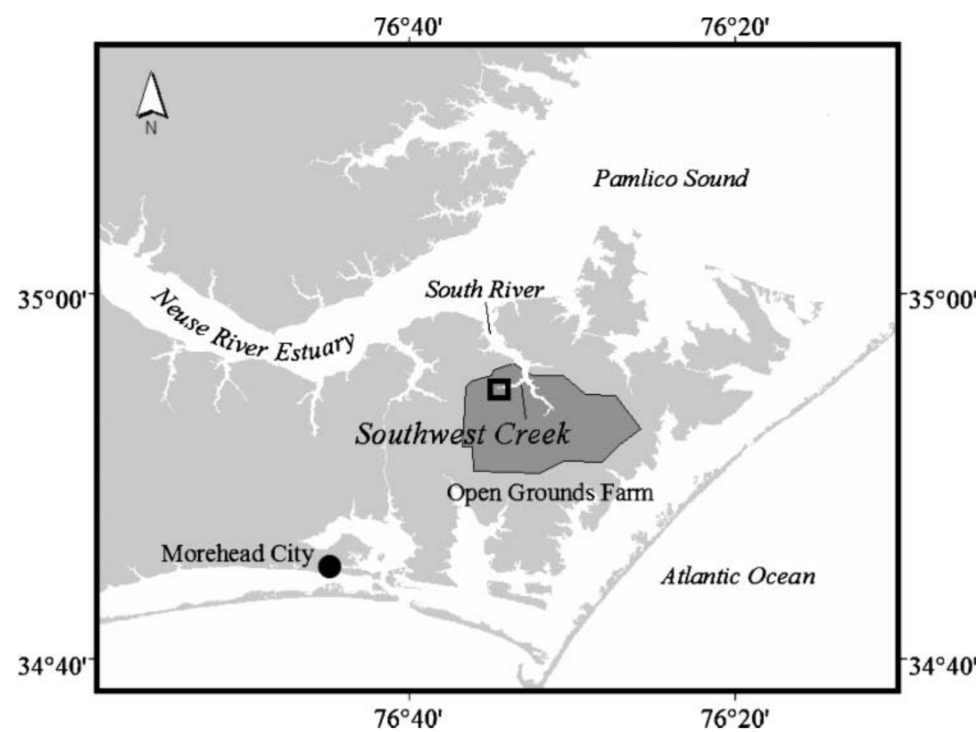

Fig. 1. Location of the study site in eastern North Carolina.

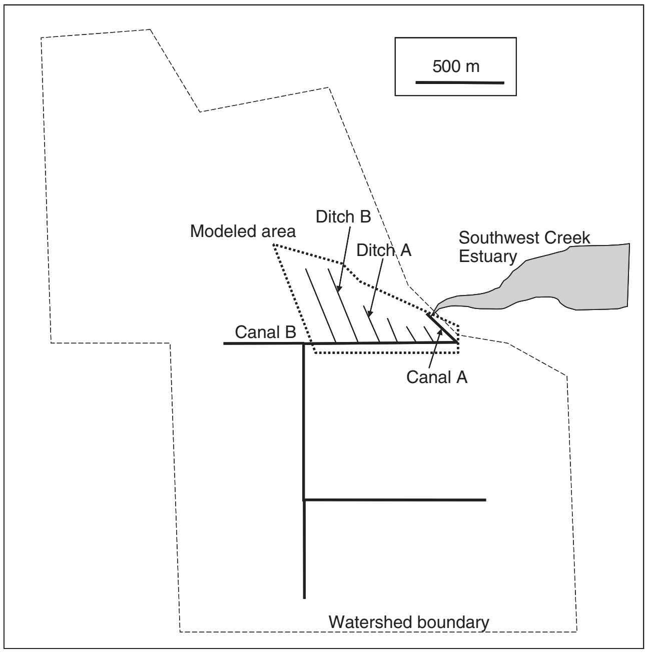

Fig. 2. Planform view of the drainage area of the Southwest Creek watershed, including canals and ditch configuration of the modeled watershed.

1994). A continuous record of nutrient concentrations during storm events was developed by interpolating between observed concentrations during each event. To quantify the nutrient load attributed to groundwater inflow during storm events, the immediately preceding dry weather base flow concentration was applied to the proportion of flow attributed to base flow. A mass balance approach was then used to calculate the resulting storm flow contribution for each event. Base flow nutrient load was calculated using nutrient concentration values from weekly sampling events. Hurricane Isabel made landfall during September 2003, and necessitated the evacuation of instrumentation from the field site. No data were available for 20 d surrounding this event due to high flow conditions that persisted for several weeks and prevented redeployment of instruments.

Nutrient Additions

In-stream nutrient uptake was measured on 10 occasions between August 2003 and January 2004 to examine the range of nutrient uptake exhibited during several seasons. Three experiments were conducted in ditches and six in canals. Short-term nutrient injections were performed using N (NH_4Cl), P (KH_2PO_4), and a conservative tracer (NaCl). A solution of ~230 g NaCl L^{-1} was mixed in the laboratory and amended with N and P in the field just before each injection. The target level of enrichment was two to five times the ambient concentration of NH_4^+ and PO_4^{3-}. A metering pump (Fluid Metering, Syosset, NY) was used at streamside to dispense ~200 mL min^{-1} into the center of the streams. Due to the high injection rate of nutrients that would be required during storm flows, experimentation was limited to base flow periods when discharge was <50 L s^{-1}. Specific conductivity was monitored at the terminus of the stream reach using a conductivity probe and data logger (YSI 600 Series Sonde and Model 650 data logger, Yellow Springs Instruments, Yellow Springs, OH). Discharge was calculated from conservative tracer data collected during the injection (Webster and Ehrman, 1996).

The reach length studied averaged 36 m of ditches and 50 m of canals. Three water sampling stations were located equidistant along the stream reaches, except in January when a fourth station was added. Water column grab samples were collected in triplicate 50-mL polyethylene tubes before solute addition and three times after the conservative tracer reached a plateau concentration at the most downstream sampling station. Water sample collection was accompanied by specific conductivity measurements using a conductivity probe (YSI Model 30, Yellow Spring Instruments) calibrated to an NaCl standard.

Water samples were filtered through 0.7-μm glass fiber filters and frozen until analysis. Concentrations of NH_4^+, NO_3^-, and PO_4^{3-} were measured on a flow injection autoanalyzer (Lachat QuikChem 8000, Lachat Instruments, Milwaukee, WI). Sediment cores 1 cm in diameter were collected in triplicate at each sampling site for analysis of benthic chlorophyll *a* (1 cm deep) and sediment organic matter content (4 cm deep). Water samples collected before solute addition were analyzed for chlorophyll *a* by extracting the glass fiber filter in 90% acetone for 24 h and measuring fluorescence (Turner 700, Turner Designs, Sunnydale, CA) (Welschmeyer, 1994). Sediment chlorophyll *a* was extracted in a solution of 45% methanol, 45% acetone, and 10% water for 24 h, sonicated for 30 s, and fluorescence read as described above. Sediment organic matter content was determined from the percentage difference between dry weight and ash-free dry mass (combustion at 525°C for 4 h).

Calculation of Uptake Metrics from Nutrient Injection Experiments

Nutrient retention was analyzed using the methods outlined by Webster and Ehrman (1996). Nitrogen and P concentrations of samples collected during the injection were normalized using the following formula:

$$C_n = \ln\left(\frac{C - C_b}{T - T_b}\right) \qquad [1]$$

where C_n is the normalized nutrient concentration, C is the observed in-stream concentration, C_b is the background nutrient concentration, and T and T_b are the observed and background tracer concentrations. Assuming nutrient uptake is a first-order rate function of the concentration in the stream, the normalized nutrient concentrations at each sampling site can be modeled as

$$C_x = C_0 \exp(-K_c x) \qquad [2]$$

where C_x is the modeled concentration at distance x downstream from the injection site (C_0), and K_c is the first-order uptake rate coefficient (m^{-1}). The slope of the linear regression of C_n and distance downstream is represented by K_c. The inverse of K_c is defined as the uptake length of a nutrient from the water column, S_w. The mass transfer velocity, V_f, is calculated as

$$V_f = uhK_c \qquad [3]$$

where u is stream flow velocity and h is water column depth.

All nutrient data collected at each sampling point (instead of average values) were used for the linear regression to calculate K_c. The standard error of this regression was propagated through the calculations of V_f by substituting $K_c \pm 1$ standard error for K_c in Eq. [3]. The standard error integrates the two potential sources of error: (i) analytical variance in the replicate samples, and (ii) environmental variability in nutrient uptake along the reach.

The fraction of the nutrient load removed by in-stream processes as a function of the total load transiting field ditches was calculated as

$$f = \frac{V_f C_b a}{(V_f C_b a) + (C_b Q)} \quad [4]$$

where a is channel bottom area (estimated to be 600 m^2) and Q is the volumetric flow rate. As V_f is derived from a short-term nutrient enrichment of the stream, the equation does not account for remineralized nutrient flux from the benthos to the water column.

Modeling Nutrient Uptake within the Stream Network

The importance of in-stream nutrient uptake to attenuation of watershed nutrient export to the estuary was examined by extrapolating the nutrient uptake rates measured in short-term injections during the 5-mo period of study. An empirical model of nutrient retention efficiency (the percentage of the upstream nutrient load entering the stream network that was retained in the channel) was developed using discharge as an independent variable. This percentage was applied to the measured downstream nutrient load to estimate the upstream load to the stream network and the subsequent mass of nutrient retained in-stream for each day.

The spatial configuration of the lower 900-m reach of the stream network (immediately upstream of the watershed outlet to the estuary) was represented in a spreadsheet model programmed to calculate the exponential decline in nutrient concentration at 10-m intervals (Fig. 2). Nutrient uptake was modeled using a modification of Eq. [2] (sensu Doyle et al., 2003):

$$C_s = C_{s-1} \exp\left(\frac{-xV_f}{du}\right) \quad [5]$$

where C_s is the concentration in 10-m stream segment s, C_{s-1} is the concentration in the adjacent upstream segment, x is the distance between the segments (10 m), d is channel depth, and u is stream velocity. The modeled stream network contained six field ditch inputs at 100-m intervals along the canal (see Fig. 2). Field ditch input concentrations were assumed to be identical to the concentration at the upstream boundary of the system, and the six ditches were assigned volumetric inputs of 10, 5, 5, 2, 2, and 2%, respectively, of the head-of-reach discharge based on relative watershed area draining to each ditch and observations of flow during the study. Increased depth and velocity caused by elevated flow conditions were adjusted by the model using "at-a-station" hydraulic geometry relationships tailored to the study site (Leopold and Maddock, 1953). The model was run with discharge ranging from 1 to 2500 L s^{-1} to develop an empirical relationship between the percentage reduction in total nutrient load removed in-stream and discharge. This discharge-specific nutrient attenuation rate was applied to flow and concentration data at the watershed outlet to calculate the mass of nutrient retained within the lower 900 m of the stream network on a 30-min basis from August to December 2003. To evaluate the sensitivity of the model to the variability in V_f, the model was run using the 25th, 50th, and 75th percentile values of V_f for NH_4^+ and PO_4^{3-} that were measured from nutrient injection experiments in canals.

The following assumptions are inherent to the model: First, that a first-order uptake rate approximates the numerous processes contributing to the longitudinal change in nutrient concentration (see Dodds et al., 2002, for discussion of the relationship between nutrient concentration and V_f). Second, that there was no remineralization of nutrients absorbed from the water column. Third, that flow velocity and depth do not change faster than the transport time through the stream reach. Finally, that the concentrations of lateral inputs to the modeled stream reach are the same as the upstream nutrient concentration. Based on these assumptions, the model is intended to estimate the fraction of the upstream, inorganic nutrient load removed during transit through the 900 m of canal before export to Southwest Creek.

RESULTS

The frequency distribution of flow values recorded during the period of study is shown in Fig. 3. The steepness of the curve depicting "All data" reveals the characteristic hydrology of this Coastal Plain watershed: stormwater runoff caused flow rates to increase quickly in response to rainfall events. The flow regime was dominated in time by base flow, with >85% of the 30-min flow values classified as base flow (<200 L s^{-1}). The 5-mo cumulative volumetric discharge from the watershed shows the importance of storm events, however, with 34% due to event flow and 66% due to base flow (Fig. 3 and 4). Further, a high percentage of the inorganic

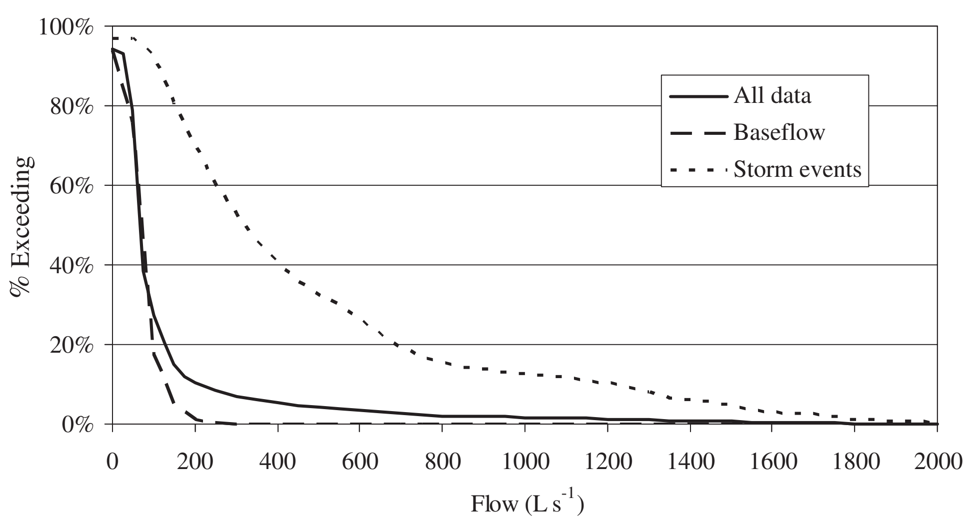

Fig. 3. Frequency distribution of discharge data from the watershed at Southwest Creek, August to December 2003.

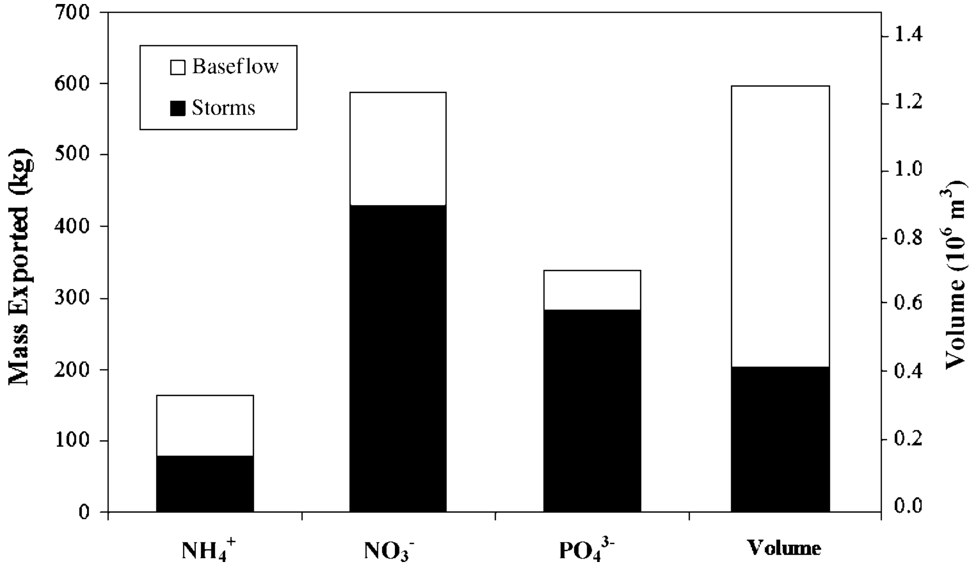

Fig. 4. Distribution of runoff volume and nutrient loads between base flow and storm flow periods, August to December, 2003.

nutrient load occurred during storm events (48, 72, and 83% for NH_4^+, NO_3^-, and PO_4^{3-}, respectively; Fig. 4).

The average discharge of the ditches was 12 L s^{-1}, ranging from 1.1 L s^{-1} during base flow to 61 L s^{-1} during a bankful storm event (Table 1). Discharge in canals averaged 18 L s^{-1}, ranging from 1.8 to 31 L s^{-1}. On average, background NO_3^- and PO_4^{3-} concentrations were substantially higher in the ditches than the canals studied, while background NH_4^+ concentrations were slightly higher in the canals than ditches (Table 1). The nutrient additions increased NH_4^+ two- to 11-fold above the ambient concentrations (with the exception of 27 Aug. 2003). The nutrient additions increased PO_4^{3-} 1.1 to 8 times ambient concentration (Table 1). With the exception of 27 Aug. 2003, all in-stream peak concentrations achieved by the additions were within the range of concentrations observed during storm events in this watershed (0–322 μg L^{-1} NH_4^+ and 0–1395 μg L^{-1} PO_4^{3-}).

Median V_f of NH_4^+ in ditches and canals was 5.2 and 6.7 mm min^{-1}, respectively, with highest values reported on 15 Oct. 2003 (Fig. 5). Median V_f of PO_4^{3-} in ditches and canals was 5.9 mm min^{-1} and 3.2 mm min^{-1}, respectively. The interquartile range of NH_4^+ V_f in canals was 4.1 mm min^{-1} (25th percentile) to 8.8 mm min^{-1} (75th percentile), and 1.0 to 7.2 mm min^{-1} for PO_4^{3-}. Potential error in these uptake measurements was very high in some cases (26 Sept. and 15 Oct. 2003 and 19 Jan. 2004; Fig. 5).

By applying Eq. [4] to the nutrient uptake measured in ditches, in-stream uptake was found to constitute 98, 65, and 94% of the total NH_4^+ load from Ditches A and B on 6 Aug., 24 Sept., and 15 Oct. 2003, respectively. In-stream processes were responsible for retention of 98, 78, and 98% of the total PO_4^{3-} load of Ditches A and B on 6 Aug., 24 Sept., and 15 Oct. 2003, respectively.

The model predictions of nutrient attenuation at a range of discharges are shown in Fig. 6. The fraction of upstream nutrient load retained in the stream network was more sensitive to discharge at low V_f values than at the high V_f values as exhibited by the contrast between the NH_4^+ and PO_4^{3-} model output (Fig. 6). Due to the higher mass transfer velocity of NH_4^+ than PO_4^{3-}, uptake within the stream network was expected to remove nearly 100% of the upstream NH_4^+ load (main channel plus lateral inputs) at discharges $<$100 L s^{-1}. In contrast, PO_4^{3-} removal decreased rapidly as discharge exceeded 50 L s^{-1}. The concentration of NH_4^+ and PO_4^{3-} at the Southwest Creek monitoring site during these base flow periods is presumably a function of mineralization from the streambed, since all upstream nutrient load is predicted to be completely attenuated during transport through the lower 900 m of the canal.

Table 1. Hydrologic, chemical, and biologic conditions of stream reaches used for nutrient enrichment experiments.

Date	Stream name	Discharge	Ambient NH_4^+	ΔNH_4^+	Ambient PO_4^{3-}	ΔPO_4^{3-}	Ambient NO_3^-	Water column chlorophyll *a*	Benthic chlorophyll *a*
		L s^{-1}	μg N L^{-1}		μg P L^{-1}		μg N L^{-1}	μg L^{-1}	μg cm^{-2}
6 Aug. 2003	Ditch A	1.1	51	35	148	19	22	–	–
24 Sept. 2003	Ditch B	2.3	110	49	370	49	70	1.1	8.7
15 Oct. 2003	Ditch B	5.2	42	227	582	22	217	2.2	–
27 Aug. 2003	Canal A	5.1	3	645	113	332	6	5.1	0.9
3 Sept. 2003	Canal A	1.8	15	75	122	142	3	3.3	0.5
15 Sept. 2003	Canal B	1.9	22	209	46	210	4	3.2	1.3
26 Sept. 2003	Canal B	19.3	378	16	144	12	27	1.9	3.8
23 Oct. 2003	Canal B	24.6	81	49	37	85	29	2.7	1.7
19 Jan. 2004	Canal B	31.0	23	153	24	159	33	25.8	–

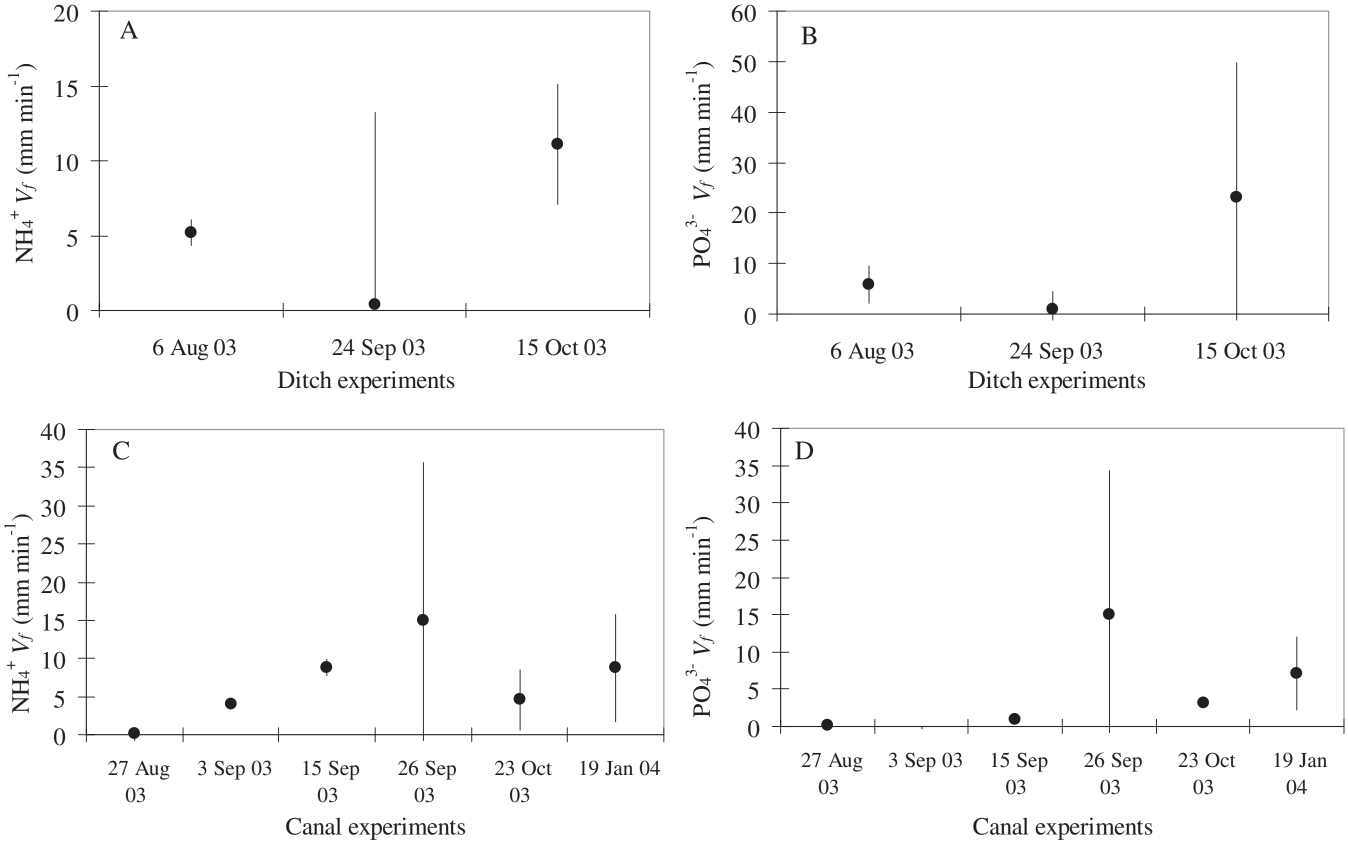

Fig. 5. Mass transfer velocity (V_f) of (A) NH_4^+ in ditches, (B) PO_4^{3-} in ditches, (C) NH_4^+ in canals, and (D) PO_4^{3-} in canals; error bars represent one standard error. No net uptake of PO_4^{3-} was measured on 3 Sept. 2003.

During higher flow, the stream network attenuated a lower proportion of the upstream load (Fig. 6). During the study period, 151 kg of NH_4^+–N were predicted to be removed during storm events, accounting for 64.7% of the total NH_4^+ load to the stream network during storm events (Fig. 7). Using a range in NH_4^+ V_f values, this nutrient retention percentage was predicted to range from 46.0 to 75%. The stream network attenuated 36.6% of the total PO_4^{3-} load during storm events (ranging from 12.5 to 66.1% given the interquartile range in V_f; Fig. 7). This translates into retention of 173 kg P within the stream network and export of 300 kg P during storm events during the 5-mo period.

Due to the higher in-stream attenuation of NH_4^+ than PO_4^{3-}, the molar ratio of dissolved inorganic N to P was predicted to decrease during transit through the lower 900 m of the canal (Fig. 8). The observed DIN (dissolved inorganic N)/DIP (dissolved inorganic P) at the watershed outlet averaged 12, with a value of 27 predicted upstream. During and immediately after storm events, the predicted upstream DIN/DIP ratio decreased substantially, and was similar to the observed values downstream. Nitrate uptake was unknown, and therefore the downstream observed NO_3^- values were used to estimate upstream DIN/DIP. If NO_3^- uptake along the canal system was accounted for, the predicted upstream DIN/DIP in Fig. 8 would be higher. These data demonstrate that in-stream uptake decreases the ratio of DIN/DIP delivered to the estuary, especially during base flow periods.

DISCUSSION

Nutrient Retention and Implications for Estuarine Function

Water exported from this agricultural watershed immediately enters Southwest Creek, an oligohaline tributary of the South River estuary. This 15-km^2 estuarine complex hosts a productive finfish and shellfish fishery that is adversely affected by periodic algal blooms exceeding the North Carolina state standard (40 μg L^{-1}) and consequent low dissolved O_2 in surface and bottom water (Gallo, unpublished data, 2003). Nutrient limitation bioassays conducted in August and November 2003 showed that primary production was enhanced by additions of either NH_4^+ or NO_3^-, and further enhanced by a combination of DIN and PO_4^{3-} (Gallo et al., unpublished data, 2004). Thus, discharge of N and P from the Southwest Creek agricultural watershed can directly influence estuarine ecology, especially given the close proximity (<1 km) of the agricultural drainage to the estuary.

The ephemeral, first-order drainage system removed 65 to 98% of the nutrient load derived from edge-of-field runoff. Gross retention efficiency of inorganic N and P in the lower reaches of the stream network was 100% of the watershed load during base flow periods. The observed concentrations at the watershed outlet during base flow periods were presumably a result of mineralization of organic material within the stream channel.

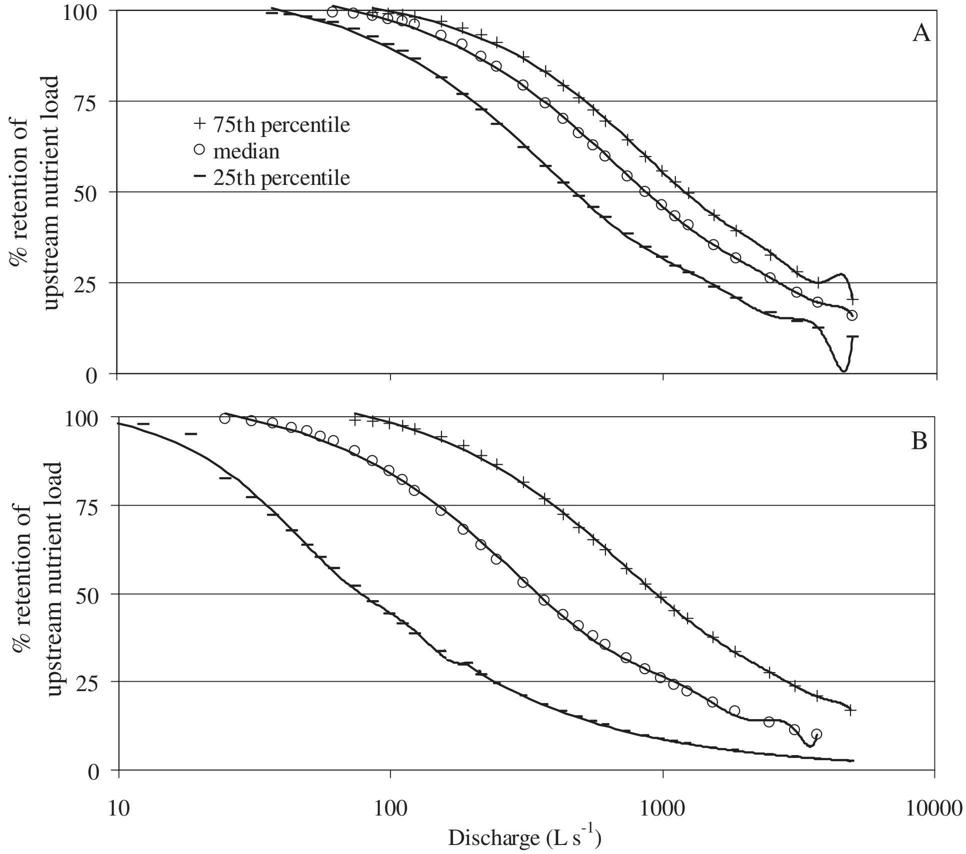

Fig. 6. Empirical relationship between the fraction of the (A) NH_4^+ load, and (B) PO_4^{3-} load retained within the stream network and upstream discharge; lines show a polynomial equation fit to the model output. No measured discharge exceeded 2500 L s^{-1}.

Thus, terrestrial nutrient sources in the watershed are disconnected from the estuary during base flow periods.

In contrast to the nearly complete retention occurring during base flow, only 65 and 37% of NH_4^+ and PO_4^{3-} were retained during storm events duirng the 5-mo period. The lower retention percentage during storms was due to greater flow velocity and increased water column depth resulting from high discharge. A range of V_f values

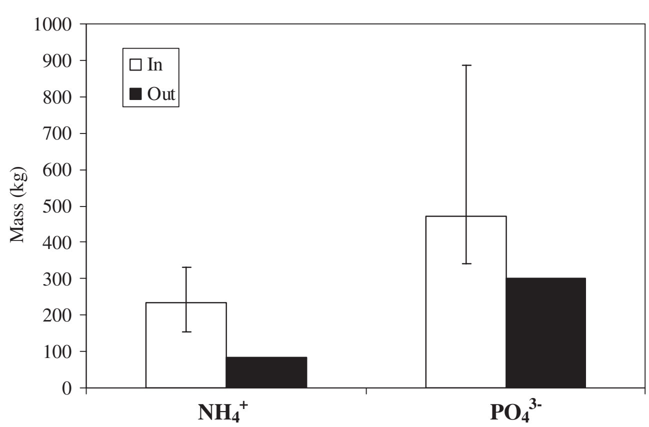

Fig. 7. Cumulative predicted mass of NH_4^+ and PO_4^{3-} entering the modeled stream network (In) and observed values exiting the watershed (Out) during storm events. The bar representing "In" is based on the model simulations using the median V_f (mass transfer velocity) from experimental injections, and error bars represent simulations using V_f values at the 25th and 75th percentile.

were used for both NH_4^+ and PO_4^{3-} to evaluate the potential variability in retention. Even when a lower value of NH_4^+ V_f was used, in-stream uptake still accounted for a 46% reduction in NH_4^+ load during storms; however, when a lower PO_4^{3-} V_f was applied in Eq. [5], PO_4^{3-} retention decreased to only 12.5% of the upstream load. Since the nutrient injection experiments were performed during the daylight hours, the V_f measurements are probably higher than those that occur at night (Marti et al., 1994). Therefore, a value of V_f between the 25th and 50th percentiles may be most appropriate, given the lower uptake that probably occurs at night and the effect of this variability on the net daily uptake.

Examination of the influence of in-stream processes on watershed nutrient export must also consider changes in DIN/DIP that occur within the channel. As demonstrated by the difference in observed downstream nutrient concentrations and model predictions of upstream concentrations, the DIN/DIP ratio of stream water decreased during transport. The higher V_f of NH_4^+ than PO_4^{3-} reduced the DIN/DIP from, on average, >15:1 upstream to <15:1 at the watershed outlet (Fig. 8). If in-stream NO_3^- uptake were accounted for, the decrease in DIN/DIP would be even greater. The phytoplankton community in the Southwest Creek estuary is N limited (Gallo et al., unpublished data, 2004), and this limitation generally occurs at DIN/DIP ratios <15:1 (Rhee, 1978). Hence, on the basis of relative nutrient availability (vs. concentration), the export of low DIN/DIP water from

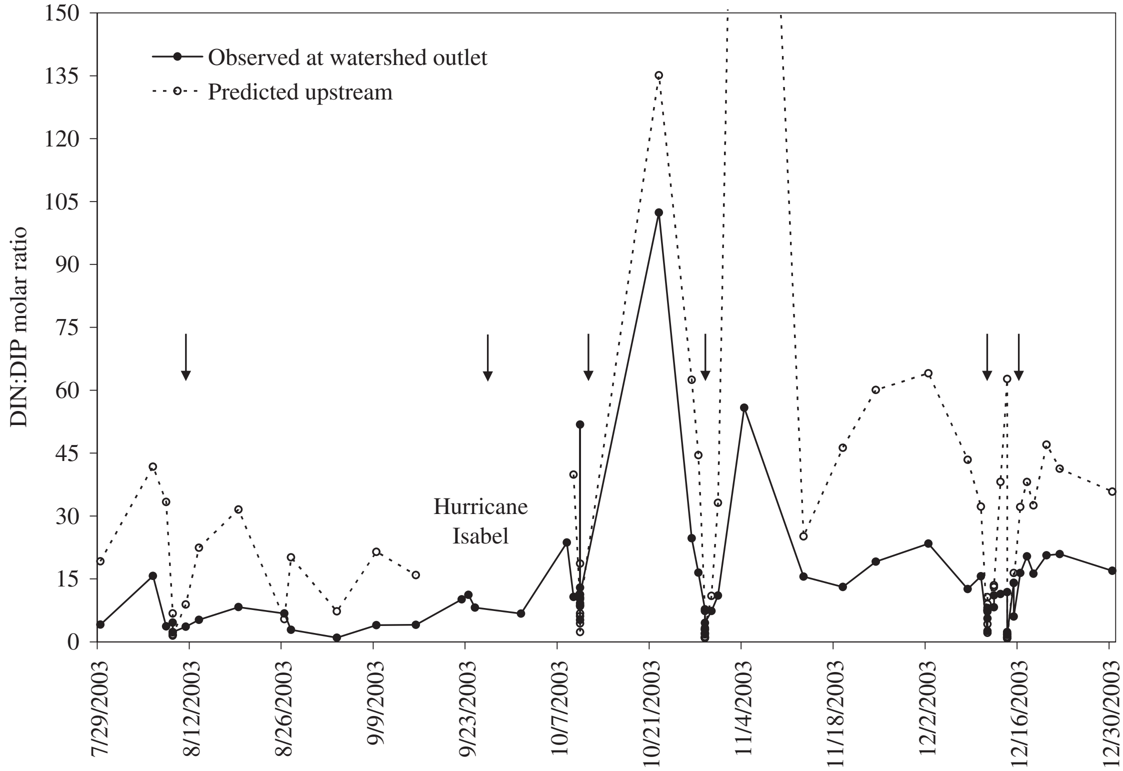

Fig. 8. Dissolved inorganic N/P ratios observed at the watershed outlet upstream of the Southwest Creek estuary. Predicted values are derived from the upstream NH_4^+ and PO_4^{3-} concentrations estimated using the retention model (Eq. [5]) for the lower 900 m of canal; predicted values incorporate the downstream observed NO_3^- values. Arrows indicate storm events.

Southwest Creek would be expected to constrain phytoplankton growth in the estuary downstream.

The gross retention efficiencies reported for the ditches and lower watershed canal system do not imply permanent sequestration of nutrients during an annual period. It is expected that a portion of the ~150 to 170 kg of NH_4^+ and PO_4^{3-} removed in-stream during the 5-mo period considered in this study was eventually remineralized and exported as dissolved or particulate organic matter. A similar agricultural stream in coastal North Carolina was found to provide an annual net uptake of 10 and 8% of the NH_4^+ and PO_4^{3-} load, with concomitant retention of 2 and 9% of the total annual N and P load (Birgand, 2000). Similar N retention but higher P retention was found in a lowland river system in Denmark, where annual net in-stream retention amounted to 1% for total N and 21% of total P flux (Svendsen and Kronvang, 1993). In the Danish river system, high total N and P retention in-stream during low-flow summer conditions (12–16% of N flux and 60–105% of P flux) was balanced by increased particulate export during scouring floods in the winter.

Nutrient Uptake Modeling and Measurement

Two different methods were used to examine the role of in-stream uptake on watershed-scale nutrient flux. First, a mass balance calculation of nutrient flux was made for experiments performed in ditches. Ditches serve as the first-order streams in this watershed and receive all of their inflow via diffuse subsurface flow or overland flow during storm events. Thus, Eq. [4] provides a simple way to compare the nutrient mass removed from the water column to the total flux of nutrients through the channel.

A second modeling technique was used for the lower portion of the watershed's canal system. Continuous discharge and concentration data at the end of the canal allowed development of a model relating nutrient retention to the independent variables discharge and concentration. The model allowed for adjustments of main channel depth and stream velocity (with concomitant changes in V_f, see Eq. [3]) and lateral inputs from ditches along a 900-m length of canal. Essentially, the attenuation coefficient derived from the model is a function of stream velocity and subsequently travel time through the system. Other studies have modeled nutrient uptake as a first-order function of residence time as well. Seitzinger et al. (2002) used water displacement time to model N retention in 16 northeastern U.S. drainage basins, showing 20 to 40% retention in the stream network. Similarly, water travel time from the edge of the field was used to develop annual export coefficients for NO_3^- from an agricultural stream network in North Carolina (Amatya et al., 2003).

The retention efficiencies calculated with both of the methods used above are derived from commonly used metrics of nutrient spiraling, and share the underlying assumptions made in other studies of nutrient spiraling and uptake; however, few studies have extrapolated nutrient uptake values to broader spatial and temporal scales, a process necessary for understanding the role streams play in modulating watershed nutrient flux. Development and application of a nutrient uptake model such as the one in this study is necessary because of the difficulty in measuring uptake during high-discharge periods. Research conducted using isotopic tracers in six Alaskan streams did not find systematic changes in V_f among streams with discharge ranging four orders of magnitude (Wollheim et al., 2001). This supports the use of the model developed in this study in which V_f was independent of discharge, and nutrient retention was modeled as a function of discharge and concentration.

The first-order uptake rate based on V_f is assumed to reflect gross uptake of added nutrients, since injection experiments are performed more quickly than the turnover times of nutrients from the benthos (Dodds et al., 2002). In our study, the limitation of considering gross uptake alone is evident during base flow periods. While the model predicted that upstream nutrient loads will be completely attenuated, the model did not account for the source of nutrients to the stream via mineralization from the benthos. During storm events, the model was adequate to estimate upstream nutrient load attenuation since transport time through the stream reach (<12 h) was probably faster than remineralization of the most active biotic compartments. For example, aufwuchs and fine benthic organic matter (FBOM) in Walker Branch, Tennessee, had P turnover times of 5.6 and 6.9 d, respectively (Newbold et al., 1983), and epilithon and FBOM in Kings Creek, Kansas, had N turnover times of 1.4 and 20 d, respectively (Dodds et al., 2000). In summary, the model used here was effective at estimating the attenuation of the upstream nutrient load, but did not account for uptake of remineralized nutrients from the stream bed. This deficiency was more apparent during base flow than storm flow periods.

This study focused on in-stream processing of NH_4^+ instead of NO_3^-, although research on denitrification and NO_3^- dynamics in this watershed are currently underway. Ammonium accounted for 12 to 47% of the DIN load during the study period, averaging 21% of the total DIN pool. This ratio of NH_4^+/DIN is 2 to 53 times higher than in other agricultural watersheds (Haggard et al., 2001; Royer et al., 2004). The high ratio of NH_4^+ to NO_3^- in the Southwest Creek stream network and the generally higher rates of NH_4^+ uptake than NO_3^- in streams (Webster et al., 2003) demonstrate the importance of NH_4^+ as a N source to riverine biota in this watershed. Furthermore, dramatic increases in riverine NH_4^+ concentrations in eastern North Carolina rivers including the Neuse River and estuary provide incentive to examine how NH_4^+ is transported through streams in this region (Burkholder et al., 2006).

Comparability of Nutrient Uptake Metrics to Other Streams

The nutrient uptake values and variability found in this study are similar to others reported in the literature. The median NH_4^+ V_f from ditches (5.2 mm min^{-1}) is within the interquartile range of first-order streams reported in the literature (1.1–6.1 mm min^{-1}) (Ensign and Doyle, unpublished data, 2006). The PO_4^{3-} V_f of ditches in our study (5.9 mm min^{-1}) is higher than the 75th percentile of first-order streams reported in the literature (5.0 mm min^{-1}) but within the range of reported values (Ensign and Doyle, unpublished data, 2006). The relatively high PO_4^{3-} uptake velocities in our study are probably due to the high primary productivity by epiphytic algae in these unshaded ditches with abundant macrophytes.

The median NH_4^+ V_f of canals in this study (6.7 mm min^{-1}) is within the interquartile range of both second- and third-order streams reported in the literature (2.6–10.9 and 2.4–10.8 mm min^{-1}, respectively; Ensign and Doyle, unpublished data, 2004). Likewise, median PO_4^{3-} V_f values in canals (3.2 mm min^{-1}) were within the interquartile range for second- and third-order streams reported in the literature (1.0–6.9-and 0.9–7.1 mm min^{-1}, respectively; Ensign and Doyle, unpublished data, 2004).

The spatial variability in nutrient retention found in this study is similar to other reach-scale measurements. Due to the heterogeneous biogeochemical nature of streambeds, nutrient retention often differs dramatically across small distances. For example, Macrae et al. (2003) reported an eightfold difference in PO_4^{3-} V_f between two adjacent stream reaches, and Marti and Sabater (1996) found threefold differences in NH_4^+ V_f in adjacent reaches of La Solana Stream, Spain.

As with other studies that use nutrient additions to characterize nutrient spiraling, estimation of ambient V_f in this study is confounded by the temporarily elevated uptake rates that occurred during the addition. Due to the nonlinear relationship between nutrient concentration and biotic uptake, estimation of ambient V_f from nutrient enrichment experiments can result in up to a threefold underestimation of the ambient mass transfer velocity (Dodds et al., 2002). Thus, while the V_f values calculated from field experiments are realistic of rates occurring during storms (when nutrient concentrations are elevated), these data may be lower than the rates occurring at ambient nutrient concentrations. Our rates of modeled nutrient attenuation are therefore conservative during base flow conditions, perhaps by a factor of 3.

This study has stressed the importance of placing nutrient uptake metrics in the context of total watershed nutrient export. Similar studies have been performed using different techniques to measure nutrient uptake. Williams et al. (2004) developed a watershed mass balance for the Ipswich River basin and determined that the stream network retained 9% of the total N entering the river. Mulholland (2004) found that a 300-m reach of Walker Branch, Tennessee, decreased annual NO_3^- and PO_4^{3-} inflow by 20 and 30%, respectively. Several reaches of the Neversink River, New York, were a year-round net sink for NO_3^-, attenuating 3 to 29% of the nutrient load entering them (Burns, 1998). Ammonium and PO_4^{3-} uptake in the Southwest Creek stream network accounted for 65 and 37%, respectively, of storm flow discharge during a 5-mo period.

CONCLUSIONS

The data presented here are of particular importance due to the proximity of this and many other agricultural installations to estuarine waters vulnerable to nutrient-driven algal blooms. This study found that 66% of the volumetric discharge was exported to the estuary during base flow, during which time nutrient regeneration within the stream network itself was the sole source of nutrients, not the terrestrial landscape. Therefore, nutrient management practices in this watershed that focus on preserving or restoring stream ecosystem function within the drainage network will probably improve estuarine water quality.

The agricultural stream network examined in this study was entirely constructed during the development of the Open Grounds Farm, and similar drainage networks constitute a significant portion of the eastern U.S. Coastal Plain. Despite its anthropogenic origin, in-stream uptake of NH_4^+ and PO_4^{3-} in this system was well within the range of data from less impacted streams, indicating that engineered aquatic ecosystems can provide a nutrient uptake function similar to unimpacted streams. The stream network was responsible for considerable nutrient retention of watershed loads despite a lack of coarse woody debris and other flow obstructions, no geomorphic heterogeneity (e.g., meander bends, riffle-pool sequences), and limited hyporheic exchange due to a sandy substrate and very low channel gradients. The ultimate fate of the NH_4^+ and PO_4^{3-} removed from stream water in this system is unknown, however. Further research on the mechanisms of nutrient uptake and the subsequent fate of remineralized N and P are needed to fully evaluate and compare the ecosystem services provided by this agricultural drainage network with more natural stream networks.

While 52% of the NH_4^+ export occurred during base flow, 72 and 83% of the NO_3^- and PO_4^{3-} load occurred during storm events. Even during these high-flow periods, the second-order stream network was estimated to remove 46 to 75% of the NH_4^+ load and 13 to 66% of the PO_4^{3-} load. The first-order streams draining this agricultural watershed had even higher retention efficiencies. Although these data represent gross nutrient uptake (vs. permanent sequestration), they clearly demonstrate how in-stream processes affect temporal patterns in watershed nutrient loading to streams and subsequent export to an estuary. These in-stream processes serve to smooth temporal patterns in N export by reducing peak loads and exporting relatively more NH_4^+ during base flow periods. Nutrient uptake within the stream ecosystem substantially decreased the DIN/DIP ratio, and may have reduced primary productivity in the N-limited estuary downstream.

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