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Low Transient Storage and Uptake Efficiencies in Seven Agricultural Streams: Implications for Nutrient Demand

Richard W. Sheibley,* John H. Duff, and Anthony J. Tesoriero

Abstract

We used mass load budgets, transient storage modeling, and nutrient spiraling metrics to characterize nitrate (NO_3^-), ammonium (NH_4^+), and inorganic phosphorus (SRP) demand in seven agricultural streams across the United States and to identify in-stream services that may control these conditions. Retention of one or all nutrients was observed in all but one stream, but demand for all nutrients was low relative to the mass in transport. Transient storage metrics (A_s/A, F_{med}^{200}, T_{str}, and q_s) correlated with NO_3^- retention but not NH_4^+ or SRP retention, suggesting in-stream services associated with transient storage and stream water residence time could influence reach-scale NO_3^- demand. However, because the fraction of median reach-scale travel time due to transient storage (F_{med}^{200}) was $\leq$1.2% across the sites, only a relatively small demand for NO_3^- could be generated by transient storage. In contrast, net uptake of nutrients from the water column calculated from nutrient spiraling metrics were not significant at any site because uptake lengths calculated from background nutrient concentrations were statistically insignificant and therefore much longer than the study reaches. These results suggest that low transient storage coupled with high surface water NO_3^- inputs have resulted in uptake efficiencies that are not sufficient to offset groundwater inputs of N. Nutrient retention has been linked to physical and hydrogeologic elements that drive flow through transient storage areas where residence time and biotic contact are maximized; however, our findings indicate that similar mechanisms are unable to generate a significant nutrient demand in these streams relative to the loads.

It is widely understood that humans have dramatically altered the earth's ecosystems through alterations of global biogeochemical cycles (Galloway et al., 1995; Vitousek et al., 1997). In particular, nutrient cycles have been modified through production of N- and P-based fertilizers, cultivation of N-fixing crops, animal waste disposal practices, combustion of fossil fuels, and extensive mining practices (Galloway et al., 1995; Vitousek et al., 1997; Tilman et al., 2001). Agricultural practices have been implicated as the biggest driver of nutrient cycling changes in aquatic ecosystems (Tilman et al., 2001; Bernot et al., 2006; Birgand et al., 2007), and some researchers argue that the dramatic increase in reactive N in the hydrosphere is a more important ecological problem than climate change (Tilman et al., 2001). For example, Tilman et al. (2001) project that N use from future agriculture will increase 1.6 times by 2020, with increases in P and irrigation water reaching 1.4- and 1.3-fold, respectively, during the same time period. Furthermore, with evidence of legacy groundwater pollution (Tesoriero et al., 2013), nutrients that are currently applied to the landscape may not discharge to streams for decades or more. The consequence of this influx of human-derived N and P are dramatic and have led to degradation of drinking water supplies (Burow et al., 2010), eutrophication of aquatic ecosystems (Rabalais et al., 2002), and contributions to global climate change (Groffman et al., 2000).

In agricultural settings only about half of the added fertilizer is captured by crops (Tilman et al., 2001; Puckett et al., 2011), with release of N and P to groundwater, terrestrial, and aquatic ecosystems making up the balance. As a result, the fate and transport of nutrients in agricultural ecosystems has been gaining attention in the past decade (Kemp and Dodds, 2002a; Royer et al., 2004; Bernot et al., 2006; Duff et al., 2008; Mulholland et al., 2008; Puckett et al., 2008, 2011). In particular, there is much interest in how streams process high nutrient loads from agricultural land, and recent studies on agricultural streams have shown that rates of N and P uptake are higher than corresponding reference sites (Bernot et al., 2006; Mulholland et al., 2008). However, the efficiency of NO_3^- uptake is lower in agricultural streams because of higher N concentrations (Mulholland et al., 2008).

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*Corresponding author (sheibley@usgs.gov).

Richard W. Sheibley, U.S. Geological Survey, 934 Broadway, Suite 300, Tacoma, WA 98402; John H. Duff, U.S. Geological Survey, 345 Middlefield Rd., Menlo Park, CA 94019; Anthony J. Tesoriero, U.S. Geological Survey, 2130 SW 5th Ave., Portland, OR 97201. Assigned to Associate Editor Ying Ouyang.

Abbreviations: OTIS-P, one-dimensional transport model with inflow and storage; SRP, inorganic phosphorus.

Innovative best management practices are being implemented to mitigate excessive nutrient loading (Jaynes et al., 2008; Roley et al., 2012; Jaynes and Isenhart, 2014). Nonetheless, understanding the role of riparian and stream processes on nutrients in agricultural settings remains a challenge. For example, variability of nutrient processing in groundwater traversing riparian zones is related to the position of local, intermediate, and regional groundwater flow systems as well as heterogeneous hydrogeologic properties among riparian zones (Ranalli and Macalady, 2010), which are difficult to quantify. Once nutrients reach surface waters, a distinct set of conditions will promote uptake by aquatic plants and microorganisms (Birgand et al., 2007). Therefore, it is important to proactively study the most important factors controlling nutrient retention in agricultural streams and rivers and how best to increase nutrient processing efficiencies.

In a recent study on the fate of nitrate (NO_3^-) in three agricultural basins, Duff et al. (2008) demonstrated that NO_3^- loads were reduced during transport from upland groundwater to nearby streams, but once the excess NO_3^- reached the surface water, it was transported downstream with minimal retention. This tendency for agricultural streams to serve as conduits rather than nutrient processors has also been shown by Royer et al. (2004). This study looks more closely at potential conditions that limit the demand for nutrients in agricultural streams by considering physical, hydrogeologic, and biologic mechanisms that provide these in-stream services. It was designed to identify the presence of reach-scale processes, including hydrologic exchange between surface and groundwater, uptake from surface and groundwater, and nutrient transformations. By identifying the general transport patterns, in-stream hydrodynamics, and nutrient retention efficiencies, specific recommendations can be made for improving the nutrient conditions in agricultural streams.

Materials and Methods

Site Description

Seven study sites were chosen in small, predominantly agricultural watersheds nested inside larger study basins that are being investigated by the USGS's National Water Quality Assessment Program (Fig. 1; Table 1). Sites were chosen to include nationally dominant agricultural systems and to cover a range of hydrologic settings using the hydrologic landscape concept (Capel et al., 2008). Each study was conducted along a subreach of the longer stream during low flow when hydrologic and biological conditions were most likely to maximize N and P retention. Descriptions of these study units and their significance within agricultural systems are provided in detail elsewhere (Capel et al., 2008; Saad, 2008).

Hydrologic Characterization

Travel time, stream discharge, and near-stream groundwater inflow were measured during 72-h tracer injections using well-established tracer-dilution techniques (Stream Solute Workshop, 1990). The injectate consisted of sodium bromide (Br^-) dissolved in ~600 L of native stream water in a plastic stock tank. Bromide was sampled at the base of a mixing reach and at two or three downstream locations, resulting in three or four fixed stations per study reach. Water samples were collected upstream of the injection to correct for background Br^- concentration entering the reach. Three synoptic sampling sweeps were conducted during the Br^- plateau to follow a packet of water from the injection site to the bottom of the reach based on travel times

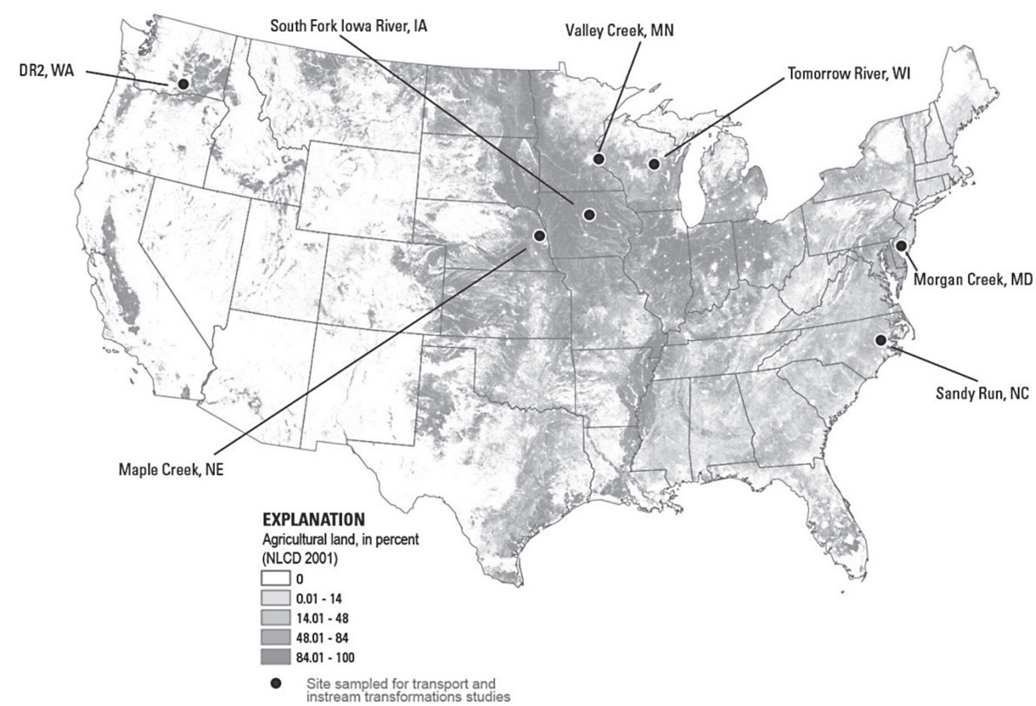

Fig. 1. Location of nitrogen and phosphorus retention studies in agricultural streams. DR2 is located in the Yakima River basin, south-central Washington. Morgan Creek is located in the Chester River Basin, Delmarva Peninsula. Maple Creek is located in the Platte River Basin, eastern Nebraska. Valley Creek is located in the St. Croix River Basin, southeastern Minnesota. South Fork Iowa River is located in central Iowa. Sandy Run is located in the Neuse River Basin, eastern North Carolina. Tomorrow River is located in the Lake Michigan Basin, central Wisconsin. NLCD, National Land Cover Database.

Table 1. Site location and hydrogeologic settings for the study sites.

Site name	Major crops	Study period	Stream order	Reach length	Upstream Q†	Downstream Q	w:d‡
				m	$m^3 s^{-1}$		
DR2 Drain, WA	orchard, vineyard, alfalfa, dairy	Sept. 2003	2	428	0.138	0.145	5
Morgan Creek, MD	corn, soybean	May 2004	2	1145	0.197	0.217	10
Maple Creek, NE	corn, soybean, alfalfa	Sept. 2004	4	1145	0.362	0.408	81
Valley Creek, MN	undeveloped, rural residential, row crop	Sept. 2006	3	1144	0.430	0.449	16
SF Iowa River, IA	corn, soybeans	Sept. 2008	4	1317	0.387	0.400	35
Sandy Run, NC	tobacco, corn, soybeans	Apr. 2009	3	214	0.235	0.235	9
Tomorrow River, WI	corn, alfalfa, dairy	Sept. 2009	1	1041	0.063	0.091	14

† Q, stream discharge.

‡ w:d, width-to-depth ratio of the stream.

derived from preliminary Rhodamine WT slug injections. These sweep samples were used to calculate discharge at each station based on dilution of the Br^- tracer (Stream Solute Workshop, 1990). Continuous, constant-rate injections are an accurate technique for determining longitudinal discharges in stream reaches (Kennedy et al., 1984; Triska et al., 1989; Zellweger et al., 1989; Wagner and Harvey, 1997; Runkel et al., 2013). Uncertainties related to discharge measurements are largely constrained by the analytical precision of Br^- measurements, which are typically less than ±1%.

Within each study reach, a series of small-diameter stainless-steel drivepoints (0.64 cm ID) were installed 0.1 to 1.0 m deep into the streambed to collect subsurface water samples. Approximately 30 drivepoints were spread out to incorporate observed differences in stream velocity, sediment substrate, and stream habitats (riffles, pools, glides) while trying to cover as much of the experimental reach as possible. This approach enabled us to incorporate and characterize the inherent variability of near-stream groundwater throughout each reach. The drivepoints were sampled for Br^- before the start of each tracer injection and again during plateau to calculate the percentage of surface water penetration at the drivepoints using the mass balance method of Triska et al. (1989).

Reach-Scale Nutrient Demand

Retention of N and P was calculated from mass balances determined at each stream during the 72-h tracer injection under background nutrient conditions. Nutrient change (Δmass) was calculated from the upstream nutrient load ($Q_1 \cdot C_1$), the near-stream groundwater load ($Q_{gw} \cdot C_{gw}$), and the downstream nutrient load ($Q_2 \cdot C_2$):

$$\Delta\text{mass} = (Q_1 \cdot C_1) + (Q_{gw} \cdot C_{gw}) - (Q_2 \cdot C_2) \quad [1]$$

where Δmass is the result of biotic (or geochemical) nutrient processing in surface water and near-stream sediment due to nitrification, assimilation by plants and microorganisms, denitrification, and sorption. Changes in nutrient loads are defined as positive for net loss (retention) of nutrient mass and negative for net increase (production) of nutrient mass within the reach. Stream reaches with higher retention have a greater nutrient demand and theoretically a higher capacity for nutrient processing than comparable reaches or streams with lower retention rates.

At five of the seven streams, the nutrient flux from near-stream groundwater ($Q_{gw} \cdot C_{gw}$) was calculated as the change in flow over the reach from tracer dilution times the average nutrient concentration in drivepoints considered groundwater (i.e., drivepoints containing <1% surface water during the Br^- plateau). Approximately 75% of the drivepoints installed in this study contained <1% surface-water Br^-. One exception, DR2, contained a confining layer with fine streambed sediments resulting in diffuse inflows along the margins of the stream banks rather than through the bed (Duff et al., 2008). At DR2, $\underline{C}_{gw}$ was based on estimates from near-stream groundwater wells (Tesoriero et al., 2009). At Morgan Creek, the second exception, inflow through the bed was hindered by a low-permeability clay layer (Puckett et al., 2008), resulting in groundwater discharge through seepage zones at the lateral margins of the near-stream floodplain, which flowed to the stream via small channels or diffuse sheet flow (Duff et al., 2008). The flow-weighted nutrient concentration of all seeps entering the reach was substituted for C_{gw} in Morgan Creek (Duff et al., 2008).

Transient Storage

Transient storage was determined using a one-dimensional transport model with inflow and storage (OTIS-P) (Runkel, 1998), which was fitted to the time series Br^- data that were collected intensively during the rise, plateau, and fall of the tracer at each location during the 72-h injection. Model-fitted transient storage parameters included the dispersion coefficient (D), the storage zone exchange coefficient (α), and the cross-sectional area of the storage zone (A_s) and stream channel (A). The OTIS-P model was run until the solution converged and uncertainty in the modeled parameters was minimized. Parameter uncertainty was minimized two ways to ensure that transient storage metrics calculated from the fitted parameters were statistically different from zero. First, we only accepted model convergences where t-values from fitted parameters (D, α, A_s, A) were >3. The t-value is defined as the estimated value of the fitted parameter divided by its standard deviation; most t-values were much greater than 3. Second, we verified that the 95% confidence interval of each fitted parameter did not cross zero. From these two tests, we ensured that any transient storage metric calculated from the fitted parameters was statistically different from zero.

Model-fitted transient storage parameters were used to calculate the fraction of median travel time due to transient storage (F_{med}^{200}), the turnover length of stream water exchange through transient storage zones (L_s), the main channel residence time (T_{str}), the ratio of the cross-sectional area of the storage zone to the stream channel (A_s/A), the storage exchange flux (q_s), and the depth of the hyporheic zone (d_s). The metrics are primarily derived from the four transient storage parameters (D,

α, A_s, and A), stream velocity (u), and reach length (L) (Table 2). Finally, the Damköhler number (DaI), which is a measure of the reliability that parameter estimates accurately describe transient storage within the study reach, was determined for each site (Wagner and Harvey, 1997). Values of DaI around 1.0 indicate that transient storage zone modeling was accurate for a given study reach (Harvey and Wagner, 2000).

The modeling approach used to calculate transient storage metrics in these seven streams was different from the approach used by Duff et al. (2008). As a result, the A_s/A and F_{med}^{200} for DR2 Drain, Morgan Creek, and Maple Creek in this study differ from those in Duff et al. (2008).

Nutrient Spiraling

Nutrient spiraling theory is based on the concept that nutrients stay in transport in a stream until they reach sites of assimilation or transformation and are taken up by stream biota (Newbold et al., 1981; Stream Solute Workshop, 1990). The most common and easily understood nutrient spiraling metric, uptake length (S_w), is the distance a nutrient molecule is transported in water before it is assimilated or removed from the water column. Uptake length is determined graphically by plotting the change in the natural logarithm of the ratio of nutrient to tracer concentration versus distance downstream (Stream Solute Workshop, 1990). For this study, net uptake lengths were determined by combining background nutrient and elevated Br^- concentrations collected from the sweep samples during the tracer injection plateaus (Marti et al., 1997). If the slope of the change in background nutrient to tracer ratio versus distance was statistically significant, the areal uptake rate (U) and uptake velocity (V_f) for NO_3^-, NH_4^+, and inorganic P (SRP) were computed from stream width, the average nutrient concentration, and discharge in the reach (Stream Solute Workshop, 1990).

Surface and Porewater Sampling

Surface water was collected at each station with an ISCO 2900 water sampler (ISCO Environmental) and by hand. Water was pumped through tubing with a 12-V peristaltic pump and filtered in line (50 mm-diameter, 0.45-μm disposable membrane filters; Advantec MFS, Inc.) into new polyethylene bottles (water samples for total N and P were not filtered). Bottles were prerinsed with filtered sample water before final sample collection. Porewater samples (~30 mL) were collected from drivepoints through in-line filters (50-mm diameter, 0.45-μm disposable membrane filters; Advantec) using a field peristaltic pump (Geopump, Geotech Environmental Equipment, Inc.).

Surface water and porewater samples were analyzed for NO_3^- plus nitrite (NO_2^-) (herein referred to as NO_3^-), NH_4^+, SRP, dissolved organic N, dissolved organic C, total N, total P, chloride (Cl^-), and Br^- using the same analytical methods described in detail in Duff et al. (2008).

Statistical Methods

The statistical significance of the slope of the line used to calculate S_w was tested using a simple linear regression from the change in the natural logarithm of the ratio of nutrient to tracer concentration versus distance downstream. Pearson correlation coefficients were determined to examine the relationship between the retention of NO_3^-, NH_4^+, and SRP and several transient storage metrics (F_{med}^{200}, L_s, T_{str}, A_s/A, q_s). Finally, significant differences between surface water and drivepoint nutrient to chloride ratios were tested using a two-sample t test. Statistical tests were performed using the SAS (SAS Institute, 2009) and Splus (Tibco Software Inc., ver. 8.1) software packages.

Results

Surface and Near-Stream Groundwater Discharge

Discharge along the study reaches increased by 3 to 44% at six of the seven streams and ranged from 90 to 450 L s^{-1} at the downstream end of the reaches (Table 1). Sandy Run did not show any measurable increase over the short 214-m reach. Except at DR2 and Morgan Creek, these increases were mainly due to groundwater discharge through the streambed because sediments were relatively permeable and no tributaries or seeps were observed along the study reaches. At DR2, increase in stream flow was likely a mix of shallow riparian flows, subsurface agricultural return, and irrigation leakage (McCarthy and Johnson, 2009; Tesoriero et al., 2009) rather than true groundwater discharge. At Morgan Creek, true groundwater discharge through seepage zones at the lateral margins of the near-stream floodplain accounted for the flow increases (Duff et al., 2008).

Surface and Near-Stream Groundwater Chemistry

Mean surface water NO_3^- concentrations ranged from 0.1 to 5.2 mg N L^{-1} across all sites (Table 3). Nitrate was the dominant

Table 2. Transient storage zone metrics used in this study.

Parameter description	Equation†	Units	Reference
Fraction of median travel time due to transient storage (F_{med}^{200})	$\left(1-e^{-L(\alpha/u)}\right)\frac{A_s}{A+A_s}$	–	Runkel (2002)
Average distance a molecule travels downstream before entering storage zone (L_s)	u/α	m	Harvey et al. (1996); Harvey and Wagner (2000)
Average time a molecule remains in the main channel before passing into storage zone (T_{str})	$1/\alpha$	h	Harvey and Wagner (2000)
Ratio of storage area to main channel area (A_s/A)	A_s/A	–	Bencala and Walters (1983)
Average water flux through storage zone per unit length of stream (q_s)	αA	L s^{-1} m^{-1}	Harvey et al. (1996); Harvey and Wagner (2000)
Depth of the storage zone (d_s)	A_s/wn	cm	Harvey and Wagner (2000)
Damköhler number (DaI)	$\alpha\frac{(1+A/A_s)L}{u}$	–	Wagner and Harvey (1997)

† L, reach length; n, average sediment porosity; u, advective velocity (Q/A); w, average stream width; and all other parameters defined within the text.

Table 3. Surface water chemistry during intensive field studies.

Site	NO_3–N	NH_4–N	DON†	TN	DOC	SRP	TP
	mg L^{-1}						
DR2 Drain, WA	2.9 ± 0.1 (21)‡	0.02 ± 0.02 (12)	0.35 ± 0.13 (18)	3.2 ± 0.0 (10)	2.8 ± 0.1 (4)	0.08 ± 0.03 (18)	0.33 ± 0.24 (18)
Morgan Creek, MD	2.9 ± 0.2 (36)	0.11 ± 0.05 (36)	0.75 ± 0.31 (16)	3.6 ± 0.2 (12)	5.1 ± 0.6 (4)	0.03 ± 0.01 (16)	0.15 ± 0.02 (16)
Maple Creek, NE	0.8 ± 0.3 (36)	0.01 ± 0.0 (36)	0.72 ± 0.5 (19)	1.7 ± 0.0 (13)	4.9 ± 0.9 (5)	0.01 ± 0.01 (19)	0.10 ± 0.03 (19)
Valley Creek, MN	5.2 ± 0.11 (53)	0.01 ± 0.01 (53)	0.30 ± 0.2 (11)	5.1 ± 0.19 (14)	2.3 ± 0.10 (6)	0.02 ± 0.01 (53)	0.04 ± 0.02 (21)
SF Iowa River, IA	0.69 ± 0.08 (85)	0.02 ± 0.02 (90)	NS§	1.4 ± 0.16 (21)	3.3 ± 0.17 (25)	0.01 ± 0.01 (64)	0.06 ± 0.03 (21)
Sandy Run, NC	0.12 ± 0.03 (34)	0.07 ± 0.02 (50)	1.0 ± 0.05 (34)	1.3 ± 0.09 (27)	20.1 ± 0.75 (31)	0.21 ± 0.02 (50)	0.35 ± 0.02 (27)
Tomorrow River, WI	2.9 ± 0.56 (35)	0.03 ± 0.01 (65)	0.28 ± 0.07 (29)	3.3 ± 0.49 (35)	2.9 ± 0.74 (22)	0.03 ± 0.02 (79)	0.04 ± 0.01 (35)

† DOC, dissolved organic C; DON, dissolved organic N; SRP, inorganic P.

‡ Data are presented as mean ± SD with the number of samples in parentheses.

§ No samples taken.

form of N at most sites, with the exception of Maple Creek, South Fork of the Iowa River, and Sandy Run, where dissolved organic N made up 50% or more of the total N concentrations, in part because NO_3^- levels were relatively low (<0.8 mg N L^{-1}). Ammonium concentrations were low across all sites, with only Morgan Creek having levels >0.1 mg N L^{-1} (Table 3). Similarly, SRP was relatively low across all sites, with only Sandy Run having average concentrations >0.1 mg P L^{-1}. Except for two sites (Sandy Run and Tomorrow River), SRP was a minor fraction of total P concentrations (Table 3), indicating that most P in surface waters was in particulate form. Dissolved organic C was highest in Sandy Run (~20 mg L^{-1}), which was a stream in a poorly drained watershed with a low base flow index and floodplain deposits rich in C (Tesoriero et al., 2005, 2013), with all other sites having concentrations between ~2 and 5 mg L^{-1}. Average surface water temperatures ranged from 12 to 23°C and correlated with sediment temperatures.

Mean near-stream groundwater NO_3^- concentrations ranged from 0.02 mg N L^{-1} at Sandy Run to 6.3 mg N L^{-1} at Morgan Creek (Table 4), with five of the seven sites having near-stream groundwater NO_3^- values higher than corresponding surface water. For NH_4^+ (range, 0.05–0.80 mg N L^{-1}) and SRP (range, 0.01–0.88 mg P L^{-1}), average near-stream groundwater concentrations were higher than corresponding surface water at all sites.

Approximately 25% of the drivepoints across all seven streams received tracer during the surface water Br^- injections, suggesting they were located in sediments hydrologically connected to the stream. At most sites, the mean NO_3^-–N:Cl^- ratio of downwelling drivepoints was lower and significantly different (p < 0.05) than the corresponding surface water NO_3^-–N:Cl^- ratio (Table 5). The exception was at Tomorrow River, which was also the only site with high dissolved oxygen in the downwelling drivepoints (7.7 mg L^{-1}).

Table 4. Near-stream groundwater chemistry during intensive field studies.

Site	NO_3	NH_4	SRP†
	mg N L^{-1}		mg P L^{-1}
DR2 Drain, WA	3.5 ± 1.0 (9)‡	0.05 ± 0.09 (9)	0.14 ± 0.06 (12)
Morgan Creek, MD	6.3 ± 5.8 (26)	0.10 ± 0.21 (26)	0.01 ± 0.01 (26)
Maple Creek, NE	3.2 ± 4.4 (14)	0.16 ± 0.20 (15)	0.13 ± 0.08 (17)
Valley Creek, MN	0.61 ± 1.2 (9)	0.14 ± 0.20 (9)	0.02 ± 0.02 (9)
SF Iowa River, IA	2.9 ± 4.9 (18)	0.11 ± 0.10 (24)	0.02 ± 0.01 (18)
Sandy Run, NC	0.02 ± 0.01 (17)	0.80 ± 0.91 (17)	0.88 ± 0.54 (17)
Tomorrow River, WI	5.3 ± 2.6 (15)	0.08 ± 0.02 (15)	0.15 ± 0.03 (15)

† Inorganic P.

‡ Data are presented as mean ± SD with number of samples in parentheses.

Reach-Scale Nutrient Demand

The largest percentage of the NO_3^- loads entering the study reaches came from upstream (Fig. 2a), ranging from 53% at Tomorrow River to 100% at Sandy Run. The balance of the NO_3^- loads entered the reach in near-stream groundwater and ranged from 0% at Sandy Run to 47% at Tomorrow River. Upstream NH_4^+ loads entering the reaches ranged from 20 to 100% of all inputs into the reaches (Fig. 2b). Similar to NO_3^-, NH_4^+ loads in near-stream groundwater were typically lower than surface water loads entering the reaches except at Valley Creek, where they were 78% of total inputs. Surface water loads contributed over 90% of the total SRP inputs to the reaches at five of the sites (Fig. 2c).

Retention of NO_3^- among the reaches (net loss of mass) occurred at four of the seven sites (DR2, Maple Creek, Morgan Creek, Tomorrow River), with Valley Creek, South Fork of the Iowa River, and Sandy Run having a net increase (production) in mass (Table 6). Retention of NH_4^+ among the reaches was observed at six of the seven sites and for SRP at five of the seven sites. Overall, only three of the seven sites consistently showed retention of all three nutrients (DR2, Maple Creek, and Tomorrow River). In streams showing a net retention, the

Table 5. Comparison of nitrate N:chloride ratios in surface water and downwelling drivepoints.

Site	Surface water	Drivepoints	
	NO_3^-–N:Cl^-†	NO_3^-–N:Cl^-	Median DO‡
			mg L^{-1}
DR2 Drain, WA	NS§	NS	NS
Morgan Creek, MD	0.17 ± 0.01¶	0.00 ± 0.01	NS
Maple Creek, NE	0.08 ± 0.03	0.01 ± 0.01	0.8
Valley Creek, MN	0.27 ± 0.01	0.12 ± 0.12	1.3
SF Iowa River, IA	0.05 ± 0.01	0.03 ± 0.02	0.9
Sandy Run, NC	0.01 ± 0.00	0.00 ± 0.00	0.3
Tomorrow River, WI	0.27 ± 0.04	0.45 ± 0.13	7.7

† Surface water and drivepoint ratios are statistically different at each site (p < 0.05).

‡ Dissolved oxygen.

§ No samples taken.

¶ Values represent mean ± SD.

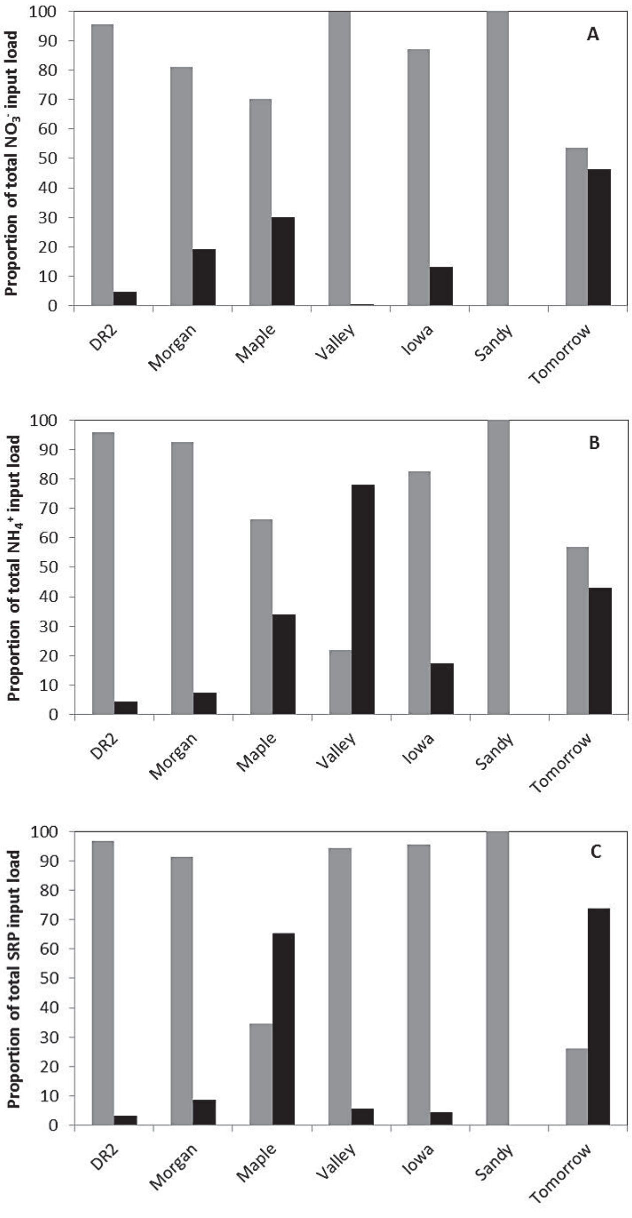

Fig. 2. Proportion of total loads entering each study reach from upstream (gray) and groundwater (black) for (A) NO_3^-, (B) NH_4^+, and (C) inorganic P (SRP).

median retention values as a percent of total inputs for NO_3^-, NH_4^+, and SRP were 6, 28, and 18%, respectively (Table 6).

Transient Storage

Values for *DaI* were between 1 and 10 (Table 7) and were within the range of acceptable values reported in Harvey and Wagner (2000), indicating that our modeling results accurately described transient storage within our reaches. The transient storage metrics (F_{med}^{200}, L_s, T_{str}, A_s/A, and q_s) varied across all sites but in general indicated a relatively small amount of transient storage in the reaches (Table 7). The highest fraction of the median travel due to transient storage (F_{med}^{200}) was 0.012 (1.2%), with an average of 0.004 (0.4%) for all streams. The average distance traveled downstream by a parcel of water before it entered the storage zone (L_s) ranged from about 0.6 to 15.1 km and was much greater than the corresponding reach length at the sites. The average time a conservative tracer remained in the main channel before passing into the storage zone (T_{str}) ranged from 1.3 to 43.1 h, much longer than their respective tracer travel times down the reach. The A_s/A fractions ranged from 0.02 to 0.11, indicating that transient storage cross-sectional areas were less than about 12% (average 6%) of the channel cross-sectional area. Surface water exchange with the storage zone (q_s) ranged from 0.014 to 0.204 L s^{-1} m^{-1} and was roughly equivalent to or higher than reach-normalized groundwater flux through the bed (q_l) (Table 7). The median depth (d_s) of the hyporheic areas was 3.1 cm (range, 1–7 cm) (Table 7). Surface water penetration of the streambed based on the presence of added Br^- was highly variable among and within streams (0–100%), but measurable surface water penetration occurred in ~25% of the drivepoints across the sites.

There was no correlation between nutrient demand and any of the storage metrics when both positive and negative Δmass (retention and production) values were included in the correlation analysis. However, NO_3^- retention (positive values only; $n = 4$) correlated with all transient storage metrics ($p < 0.05$) except L_s (Table 8). Retention of NO_3^- was positively correlated with F_{med}^{200}, A_s/A, and q_s and negatively correlated with T_{str}. There was no significant correlation between NH_4^+ and SRP retention and transient storage metrics ($p > 0.05$) (Table 8).

Nutrient Spiraling

None of the 21 regressions used to calculate nutrient uptake lengths (seven sites each for NO_3^-, NH_4^+, and SRP) was statistically significant, revealing that net uptake of N and P from the water column was minimal and inefficient relative to their surface water loads ($p > 0.05$; data not shown). Although Morgan Creek, Maple Creek, and Sandy Run had positive uptake length values, these values were often much greater than the corresponding reach lengths. For example, the net NO_3^- uptake length at Sandy Run was ~1,700 m, compared with a reach length of 214 m, suggesting that a NO_3^- molecule had to travel approximately eight reach lengths before it was assimilated.

Discussion

Reach-Scale Nutrient Demand

Nutrient losses were present at six of the seven streams (Table 6). Based on the frequency of sites showing a net loss of mass, our sites were more likely to retain NH_4^+ and SRP than NO_3^-. For example, four of seven sites showed a net NO_3^- retention, compared with five for SRP and six for NH_4^+. This has been observed in other studies (Bernot et al., 2006) and is likely because (i) NH_4^+ is more readily taken up by plants and microbes than NO_3^- (Peterson et al., 2001; Kemp and Dodds, 2002b), (ii) P is often a limiting nutrient in freshwater environments (Elwood et al., 1981) and therefore can be in high demand (N:P ratios were >> 16 in six of seven streams), and (iii) NH_4^+ and SRP can sorb to sediments (Triska et al., 1994; Hendricks and White, 2000), which would show up as demand in our mass balances.

For each nutrient, we calculated the amount of reach-scale retention (Δmass) as a percentage of upstream inputs, groundwater inputs, and total inputs for each site where Δmass was positive; median values from these calculations are shown in Table 6. The magnitude of retention as a percentage of total

Table 6. Reach-scale nutrient mass balances.†

Mass loads	DR2 Drain	Morgan Creek	Maple Creek	Valley Creek	Iowa River	Sandy Run	Tomorrow River
Nitrate, mg N s^{-1}							
Upstream	410	536	279	2264	234	30	192
Downstream	412	658	349	2293	293	31	313
Groundwater	24.4	126.3	145.1	11.5	38.2	0.0	147.6
Δmass	22.0	4.7	75.4	−18.5	−20.9	−0.9	26.1
Median retention							
As % of total inputs	6						
As % of upstream inputs	9						
As % of groundwater inputs	35						
Ammonium, mg N s^{-1}							
Upstream	6.21	25.02	14.48	5.16	6.97	15.48	2.77
Downstream	5.80	19.10	16.32	5.39	12.80	11.26	3.00
Groundwater	0.34	2.03	7.36	2.66	1.47	0.00	2.24
Δmass	0.75	7.96	5.52	2.43	−4.37	4.22	2.01
Median retention							
As % of total inputs	28						
As % of upstream inputs	35						
As % of groundwater inputs	91						
Inorganic P, mg P s^{-1}							
Upstream	11.34	5.91	3.11	6.88	4.64	50.18	1.39
Downstream	11.17	7.60	7.47	4.94	26.40	49.95	2.18
Groundwater	0.96	0.23	5.98	0.46	0.20	0.00	4.17
Δmass	1.13	−1.45	1.63	2.40	−21.6	0.23	3.37
Median retention							
As % of total inputs	18						
As % of upstream inputs	35						
As % of groundwater inputs	81						

† Positive values for Δmass indicate retention or loss in the study reach (shaded cells); negative values indicate production within the reach.

Table 7. Summary of OTIS-P output parameters and transient storage metrics.†

Site	Travel time	D	A	A_s	α	F_{med}^{200}	L_s	T_{str}	A_s/A	q_s	q_l†	d_s	DaI
		m s^{-1}	—— m^2 ——		s^{-1}	fraction	km	h	fraction	— L s^{-1} m^{-1} —		cm	
DR2 Drain, WA	0.7	0.52	0.81	0.05	2.81E-05	0.0018	6.2	9.9	0.060	0.023	0.016	7	1.2
Morgan Creek, MD	1.5	1.32	0.95	0.02	1.44E-05	0.0003	15.1	19.3	0.020	0.014	0.017	1	3.8
Maple Creek, NE	1.0	0.99	0.94	0.10	2.18E-04	0.0120	1.6	1.3	0.111	0.204	0.040	3	7.4
Valley Creek, MN	1.2	1.00	1.62	0.08	4.37E-05	0.0016	6.2	6.4	0.052	0.071	0.017	5	3.7
SF Iowa River, IA	4.7	3.89	4.52	0.45	6.45E-06	0.0013	13.5	43.1	0.101	0.029	0.009	7	1.1
Sandy Run, NC	1.2	0.46	4.41	0.15	8.31E-05	0.0089	0.6	3.3	0.034	0.367	0.000	3	10.1
Tomorrow River, WI	2.5	0.44	0.67	0.03	2.52E-05	0.0018	4.6	11.0	0.045	0.017	0.021	2	5.3

† α, storage zone exchange coefficient; A, stream channel; A_s, cross-sectional area of the storage zone; A_s/A, ratio of the cross-sectional area of the storage zone to the stream channel; D, dispersion coefficient; DaI, Damköhler number; d_s, depth of the hyporheic zone; F_{med}^{200}, fraction of median travel time due to transient storage; L_s, turnover length of stream water exchange through transient storage zones; q_l, reach-normalized flux of groundwater through the streambed defined as the change in flow along the reach divided by the reach length;q_s, storage exchange flux; T_{str}, main channel residence time.

Table 8. Correlation coefficients between nutrient retention values and transient storage metrics.

Nutrient retention	Transient storage metrics†									
	F_{med}^{200}		L_s		T_{str}		A_s/A		q_s	
	r^2	p value	r^2	p value	r^2	p value	r^2	p value	r^2	p value
NO_3^- retention	0.98	0.02	−0.82	0.18	−0.95	0.05	0.97	0.03	0.96	0.04
NH_4^+ retention	0.22	0.67	0.43	0.39	0.29	0.58	−0.12	0.82	0.19	0.72
SRP‡ retention	−0.52	0.37	0.51	0.38	0.53	0.36	0.02	0.98	−0.73	0.16

† A_s/A, ratio of the cross-sectional area of the storage zone to the stream channel; d_s, depth of the hyporheic zone; F_{med}^{200}, fraction of median travel time due to transient storage; L_s, turnover length of stream water exchange through transient storage zones; q_s, storage exchange flux; T_{str}, main channel residence time.

‡ Inorganic P.

inputs to the reach (median of upstream and near-stream groundwater inputs for all streams showing demand) was 28% for NH_4^+, 18% for SRP, and 6% for NO_3^- (Table 6). Although retention as a percentage of total inputs was four or five times higher for NH_4^+ than NO_3^-, NH_4^+ inputs were only 3% of the total inorganic N inputs (dissolved inorganic N; median of all seven streams), meaning the largest demand for inorganic N was met with NO_3^- even though a larger percentage of the NH_4^+ pools were exhausted. Overall, the demand for NO_3^- was relatively low compared with the total upstream and near-stream groundwater inputs.

The median reach-scale retention values (Δmass) were ~2 to 4 times higher as a percentage of near-stream groundwater inputs than as a percentage of upstream inputs (Table 6), suggesting that groundwater inputs alone can supply a large proportion of the reach-scale nutrient demand. For NH_4^+ and SRP, near-stream groundwater loads satisfied 81 to 91% of the median reach-scale demands, whereas for NO_3^- groundwater loads satisfied 35% of the median reach-scale demand. Another way to express these findings is to compare reach-length–normalized rates of NO_3^- retention (calculated from the whole-stream nutrient mass balances) to groundwater NO_3^- inputs (calculated from groundwater nutrient concentrations and discharge rates). For NO_3^-, the reach-scale demand was 0.04 mg N m^{-1} s^{-1} (median of the four streams with retention), and the median NO_3^- input from groundwater was 0.12 mg N m^{-1} s^{-1}. Excess NO_3^- (or other nutrients) in groundwater discharge above the demand generated by sediment processes increases surface water loads, resulting in a downstream accumulation of nutrients.

Duff et al. (2008) estimated that streambed processes potentially retained 45 to 75% of groundwater NO_3^- before discharging into three of the seven streams reported here. Similarly, we found that streambed processes potentially retained 35 to 91% of groundwater NO_3^-, NH_4^+, or SRP before discharging into six of the seven streams. These calculations suggest microbial processes at the sediment surface or in sediments up to 1 m deep contributed to nutrient processing in stream upwelling zones, which comprised about 75% of the drivepoints sampled. We calculated a median hyporheic depth of 3.1 cm using transient storage metrics derived from the OTIS model (Table 7), suggesting that a large percentage of upwelling drivepoints was located in subhyporheic sediments. Although we lack direct evidence of nutrient processing in the subhyporheic zone, Stelzer et al. (2011) reported direct and indirect evidence for NO_3^- reduction by denitrification in streambed sediments up to 70 cm below the bottom of the hyporheic zone, which was ~5 cm deep (Emmons Creek, WI). Stelzer and Bartsch (2012) and Krause et al. (2013) also show the importance of deeper sediments in the removal of NO_3^- from upwelling groundwater.

Evidence that sediment microbial processes could, at least circumstantially, fulfill the stream demand was observed in the NO_3^-–N:Cl^- ratios from downwelling drivepoints. Approximately 25% of the drivepoints across all seven streams received tracer during the surface water Br^- injections, and the majority of these had a lower median NO_3^-–N:Cl^- ratio compared with surface water (Table 5). Chloride is biotically conservative but is affected by evapotranspiration and dilution; therefore, changes in NO_3^- concentrations relative to Cl^- can indicate biotic (or geochemical) NO_3^- retention as surface water moves through the bed. The one exception, Tomorrow River, had high dissolved oxygen concentrations in streambed sediments (median drivepoint dissolved oxygen levels were 7.7 mg L^{-1}, compared with 0.3–1.3 mg L^{-1} at the other sites), suggesting that elevated NO_3^-–N:Cl^- ratios in streambed pore water could have resulted from absence of denitrification and from the presence of nitrification.

Transient Storage

In streams with a NO_3^- demand, the retention values for NO_3^- were significantly (p < 0.05) correlated with F_{med}^{200}, T_{str}, A_s/A, and q_s (Table 8), transient storage metrics that describe conditions that affect transient storage time, residence time in the channel, transient storage volume, and the exchange flux of surface water. Nitrate retention was positively correlated with F_{med}^{200}, indicating that the longer time water spent in storage, the higher the retention in the reach. However, the highest F_{med}^{200} was 1.2%, indicating that surface water exchange with transient storage zones was low overall. An F_{med}^{200} of 1.2% describes water moving downstream with a relatively short residence time and minimal biotic or geochemical contact, limiting plant and bacterial exposure to nutrients relative to the loads in transport, consequently minimizing uptake from the water column. The average F_{med}^{200} of all streams (0.4%) in this study was lower than stream average values elsewhere (Fig. 3), including agricultural and urban sites across the United States. The low F_{med}^{200} observed in our study may be due, in part, to the low stream gradients (slopes range from 0.001 to 0.005).

The variable T_{str} describes the average time a conservative tracer remains in the main channel before passing into the storage zone. The negative correlation between NO_3^- retention and T_{str} (Table 8) shows that the longer a molecule remained in the main channel before passing into storage, the lower the retention. Values of T_{str} were 1 to 16 times longer than the actual travel times of the conservative tracer down the reach, supporting our contention that stream water exchange into and out of the bed was minimal and that hyporheic storage can have little effect on nutrient retention if the channel functions like a pipe. High T_{str} values are consistent with the fact that the relative sizes of the storage zones (A_s/A) were low, ranging from 0.02 to 0.11. For comparison, many high-gradient headwater streams have A_s/A exceeding 1.0 (Bencala et al., 1990; Broshears et al., 1993; Morrice et al., 1997), and the A_s/A values from Morgan Creek and Sandy Run (0.02–0.03) were among the lowest published values among a large range of streams (Runkel, 2002). The low A_s/A indicates these agricultural streams have low transient storage volumes relative to their surface transport volumes and therefore a reduced potential for nutrient cycling and retention.

We saw a positive correlation between NO_3^- retention and the storage exchange flux, q_s, a metric that represents the volume of water per unit length of stream that moves into the storage zone (Table 8). A greater potential for retention at a higher rate of surface water flux through the storage zone is consistent with the potential but limited role of storage exchange in these streams. The short residence times and low storage potentials inferred from these four metrics suggest that NO_3^- retention was limited by physical transport into hyporheic storage zones as much as by biotic or chemical processing in the storage zones. In fact, rates of sediment nitrification and denitrification tend

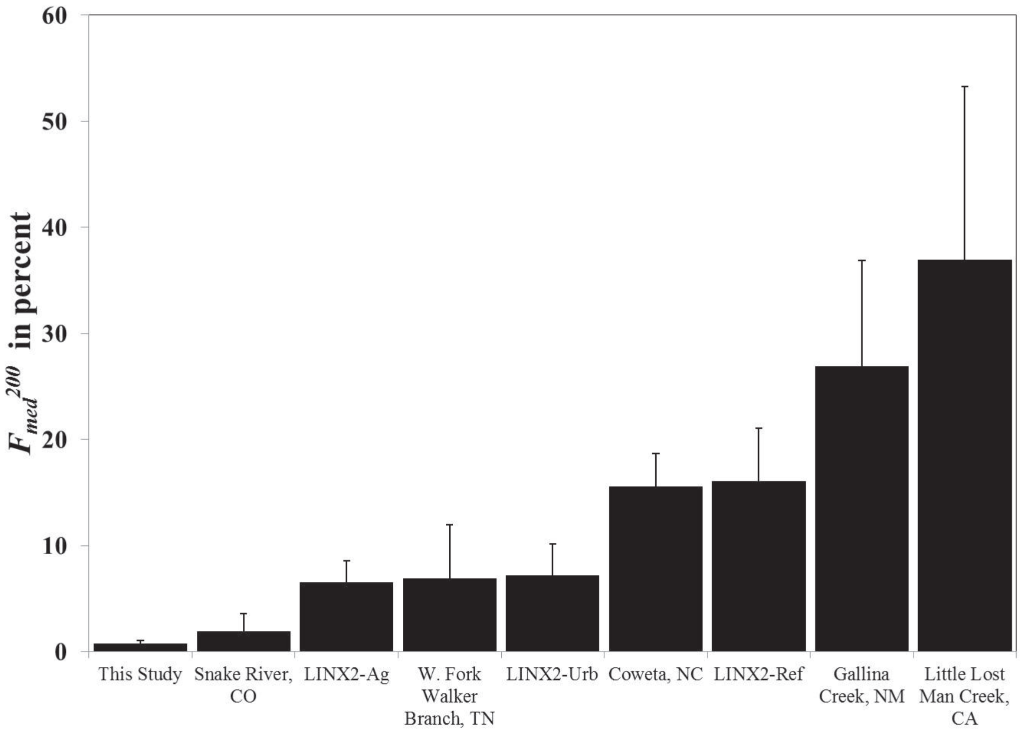

Fig. 3. Comparison of average values of median travel time due to transient storage (F_{med}^{200}) expressed as a percent (±SE) at various streams (Runkel, 2002**; R.W. Sheibley, LINX2, unpublished data) and those from this study. Details of the LINX2 study can be found in Mulholland et al. (2008). Ag, agricultural sites; LINX2, Lotic Intersite Nitrogen eXperiment, phase 2; Ref, reference sites; Urb, urban sites.**

to be higher in agriculturally dominated than in pristine streams (Kemp and Dodds, 2002a; Strauss et al., 2004; Royer et al., 2004; Duff et al., 2008), probably because of the long-term N loading and accumulation in groundwater, organic-rich sediments, and aquatic vegetation commonly present in agricultural drainages. Therefore, although these streams retain the potential to process nutrients, they do not achieve their highest demand supported by sediment processes because surface water nutrients in downstream transport are disconnected from biotically active processing areas.

Based on studies by Baker et al. (2012) and Harvey and Bencala (1993), which have shown positive links between the presence of bed roughness, flow depth, and stream topography on transient storage and surface-subsurface exchange, we speculate that the low slopes and relatively few roughness features (sand waves, cobbles, channel bars, woody debris) we observed in these agricultural reaches fail to produce significant pressure differentials in the streambed that drive flow through storage zones, including hyporheic flow paths. This is consistent with the shallow hyporheic depths calculated from the OTIS model (median, 3.1 cm). Therefore, in addition to physical transport mechanisms that limit NO_3^- movement into storage zones identified from F_{med}^{200}, T_{str}, A_s/A, and q_s metrics, hydrogeologic characteristics (e.g., gradient, discharge, and bed roughness) may also influence surface water exchange with storage zones or the bed and in turn the size of the storage zone.

The facts that (i) NO_3^- retention (but not NH_4^+ or SRP retention) showed significant relationships with transient storage metrics, (ii) that NO_3^- concentrations were 26 to 520 times higher than NH_4^+, and (iii) that NO_3^-–N:Cl^- ratios were lower in the bed than connected surface water suggest that NO_3^- processing may depend, to a greater degree than NH_4^+ or SRP, on surface water exchange with storage zones in the bed rather than surficial interactions with aquatic communities. However, transient storage modeling also suggests that NO_3^- exchange with the bed is very limited, leading us to speculate that physical stream conditions and hydrogeologic transport mechanisms may regulate nutrient processing more than biotic activity.

Nutrient Spiraling

Nutrient uptake lengths (S_w) calculated at all sites were not statistically significant, and, as a result, uptake lengths were much longer than the study reach. In fact, uptake lengths were ~1 to 10 km, or 4 to 9 times longer than the tracer reach lengths except at Sandy Run where, for SRP, it was 47 times longer. Uptake lengths are often <1 km in nonagricultural streams (Valett et al., 1996; Butturini and Sabater, 1998; Marti et al., 1997; Davis and Minshall, 1999; Mulholland et al., 2000; Simon et al., 2005; Lautz and Siegel, 2007).

The nutrient spiraling calculations indicated that uptake of NO_3^- from the water column was negligible between upstream and downstream stations, which would be true if the upstream loads were the only input loads considered in the mass balance. However, factoring groundwater input loads into the mass balance equation results in net retention of nutrients in six of the seven streams. Together, these results suggest that almost all of the retention measured in the reaches could be associated with groundwater inflows through the bed rather than channel surface water moving into and out of hyporheic storage areas. Because surface waters transport high nutrient loads and because retention associated with surface water movement into hyporheic storage areas is low, an important priority for stream management would be to reduce the nutrient uptake lengths or to increase the uptake efficiency or demand of the streams.

The uptake length is the product of the water depth times velocity divided by the uptake efficiency (V_f), which is a measure of the biotic uptake or denitrification rate (U) relative to the concentration and availability of nutrients in the water (Stream Solute Workshop, 1990). A decrease in the water depth, water velocity, or the nutrient concentration will decrease the nutrient load and therefore decrease the uptake length. In addition, a decrease in the nutrient concentration or an increase in the uptake rate will increase the uptake efficiency, which will also decrease the uptake length. Therefore, to improve the nutrient uptake efficiencies, a change in one or all of these factors needs to occur: (i) a reduction in the quantity of nutrients reaching the channel, (ii) a change in physical transport mechanisms that increase residence time and storage potential, and (iii) a change in hydrogeologic stream characteristics (e.g., bed roughness) that influence surface water exchange with surficial and hyporheic storage zones.

Implications for Management Practices

The results of this study suggest that low transient storage coupled with high N inputs have resulted in low uptake efficiencies that are not sufficient to offset groundwater N inputs. Consequently, NO_3^- exports increase along these stream reaches. Nutrient removal efficiencies may be improved by lowering the present-day nutrient inputs, increasing biotic interaction and thereby nutrient uptake efficiencies, and increasing water residence times. Implementation of best management practices that slow water drainage to the channel to lower nutrient loads could include routing it through controlled bioreactors, wetlands, and riparian areas. Two in-stream strategies could be implemented to increase the effectiveness of nutrient processing by sediment microbial communities and aquatic plants, algae, and periphyton: (i) increase the abundance and distribution of uptake sites by restoring streambed features that drive flow through hyporheic flow paths and (ii) manage in-stream habitats to provide optimal conditions for plant and periphyton growth and at the same time entrap surface water in pools and eddies. Improved stream elements could include debris dams, large wood, steps, rocks, sand waves, channel meanders, and channel bars. Additional stream water entering these storage areas and returning to the channel within the reach should increase residence time and nutrient loss. Ultimately, long-term and sustainable improvement of stream function will require altering the impact of human activities on a watershed scale, with the expectation that the complementary and competitive goals of agricultural resource and stream habitat management will need to be balanced to assure improved water quality.

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