

Travel time controls the magnitude of nitrate discharge in groundwater bypassing the riparian zone to a stream on Virginia's coastal plain

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Abstract:

Groundwater that bypasses the riparian zone by travelling along deep flow paths may deliver high concentrations of fertilizer-derived NO_3^- to streams, or it may be impacted by the NO_3^- removal process of denitrification in streambed sediments. In a study of a small agricultural catchment on the Atlantic coastal plain of Virginia's eastern shore, we used seepage meters deployed in the streambed to measure specific discharge of groundwater and its solute concentrations for various locations and dates. We used values of Cl^- concentration to discriminate between bypass water recharged distal to the stream and that contained high NO_3^- but low Cl^- concentrations and riparian-influenced water recharged proximal to the stream that contained low NO_3^- and high Cl^- concentrations. The travel time required for bypass water to transit the 30-cm-thick, microbially active denitrifying zone in the streambed determined the extent of NO_3^- removal, and hydraulic conductivity determined travel time through the streambed sediments. At all travel times greater than 2 days, NO_3^- removal was virtually complete. Comparison of the timescales for reaction and transport through the streambed sediments in this system confirmed that the predominant control on nitrate flux was travel time rather than denitrification rate coefficients. We conclude that extensive denitrification can occur in groundwater that bypasses the riparian zone, but a residence time in biologically active streambed sediments sufficient to remove a large fraction of the NO_3^- is only achieved in relatively low-conductivity porous media. Instead of viewing them as separate, the streambed and riparian zone should be considered an integrated NO_3^- removal unit. Copyright © 2011 John Wiley & Sons, Ltd.

KEY WORDS denitrification; bypass; groundwater discharge; travel time; riparian; fertilizer

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INTRODUCTION

Eutrophication is increasingly problematic in coastal zones that are under pressure from high NO_3^- loads that originate in upstream areas (Nixon, 1995). Agricultural nitrogen application often results in leaching of NO_3^- from croplands in coastal plain settings into the groundwater and eventually into streams and thence to coastal bays and lagoons (Denver, 1989; Speiran, 1996; Bachman *et al.*, 1998). In some locations, biological processes such as plant uptake and denitrification by bacteria can remove substantial amounts of NO_3^- from the discharging water as it passes through riparian forests (Lowrance *et al.*, 1984; Lowrance, 1992; Lowrance *et al.*, 1997) or wetlands (Brusch and Nilsson, 1993; Fisher and Acreman, 2004; Ensign *et al.*, 2008). In some cases, NO_3^- -rich water from adjacent agricultural fields may flow to the stream by paths that are too deep to allow interaction with riparian vegetation, a

situation termed 'riparian bypass' (Jacks and Norrstrom, 2004; Wilcox *et al.*, 2006; McCarty *et al.*, 2008; Mills *et al.*, 2008). Where NO_3^- bypasses biologically active riparian areas or where buffers do not exist, it may remain at high concentration as it moves through streambed sediments resulting in appreciable nutrient export to streams (Böhlke and Denver, 1995; Denver *et al.*, 2003; Angier *et al.*, 2005). In other cases, however, the streambed substantially reduces NO_3^- concentrations as the NO_3^- -rich water discharges to the stream (Lee and Hynes, 1978; Jacobs and Gilliam, 1985; Mills *et al.*, 2008).

Willems *et al.* (1997) determined that denitrification rates measured in water-saturated columns of riparian-zone soil were sufficient to remove all NO_3^- present. Similarly, we previously reported that biological activity in stream sediments of Cobb Mill Creek, a low-relief coastal stream that empties into the lagoons of the seaside of Virginia's eastern shore, has the potential to remove all of the NO_3^- from groundwater as it passes through them. Profiles of NO_3^- obtained from numerous sediment cores and with piezometers placed at various depths in the streambed generally showed a strong decline in NO_3^- concentration from 15- to 20 mg NO_3^- -N l^{-1} to levels

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approximately equal to streamwater NO_3^- concentrations ($1\text{--}2 \text{ mg NO}_3^- \text{-N L}^{-1}$). Additionally, profiles of denitrification potential indicate sufficient capacity to remove all of the NO_3^- from the groundwater (Galavotti, 2004; Mills *et al.*, 2008). Experiments conducted by Gu *et al.* (2007) using intact cores of streambed sediment determined that the denitrification was adequate to remove all the NO_3^- contained in the influent water. Nevertheless, despite nitrogen-removal processes active in the shallow subsurface, NO_3^- is present in streams, and Gu *et al.* (2007) speculated that the residence time of discharging water in biologically active sediments of Cobb Mill Creek was inadequate to completely remove the NO_3^- contained therein.

The distribution of groundwater discharge through stream sediments is not uniform (e.g. Chestnut and McDowell, 2000; Conant *et al.*, 2004; Genereux *et al.*, 2008), and reflects the variations in grain size and three-dimensional sedimentary structure that naturally evolve from heterogeneous depositional processes in river channels (e.g. Bridge, 1997). Cardenas and Zlotnik (2003) measured a wide range of hydraulic conductivity values that spanned nearly the entire collection of all measurements made in streambed sediments (Calver, 2001). Nonetheless, they were able to relate the observed heterogeneity in physical properties to predictions based on knowledge of sedimentary processes and streambed structure. Although spatial variations in streambed topography (Rosenberry and Pitlick, 2009) and hydraulic gradient (Kennedy *et al.*, 2009) influence the distribution of groundwater flux through streambeds, water fluxes in gaining streams are generally most strongly influenced by hydraulic conductivity of the bed sediments (Conant *et al.*, 2004; Kennedy *et al.*, 2009).

Whereas hydraulic conductivity is proportional to the magnitude of groundwater flux, it is inversely related to residence time. The presence of groundwater flowpaths with short residence times (correlated with high hydraulic conductivity and with high water flux) has been suggested as an explanation for incomplete NO_3^- removal in streambed sediments that possess sufficient denitrification potential to completely remove all the NO_3^- (Pinay *et al.*, 1995; Willems *et al.*, 1997; Gu *et al.*, 2007; Puckett *et al.*, 2008). For example, Chestnut and McDowell (2000) found locations of high hydraulic conductivity associated with low concentrations of denitrification reaction products, and concluded that less extensive denitrification occurred in groundwater with shorter residence time. On the other hand, Kennedy *et al.* (2009) found the opposite trend in a coastal plain stream in North Carolina, i.e. that areas of high groundwater flux were associated with low NO_3^- concentrations. They hypothesized that these high-flow, low- NO_3^- regions were 'old' groundwater that presumably recharged at a time when fertilizer application to adjacent fields was relatively low, and that streambed denitrification was not the proximate cause for the observed spatial variability. Similarly, in a study of a PCE plume, Conant *et al.* (2004) found that high PCE concentrations were associated with zones of

low hydraulic conductivity (i.e. low flow) and concluded that these were remnants of earlier times when the plume was more concentrated. In this case, groundwater age was also the determining factor for the correlation between hydraulic conductivity and PCE, and not biodegradation parameters *per se*.

Factors other than groundwater discharge rates (and thereby travel times through sediments) may affect spatial variation in nitrate fluxes through the streambed. The amount of organic material in sediments can influence rates of denitrification; for example, Opdyke *et al.* (2006) found a high correlation between denitrification in streambed sediments and benthic organic carbon. Also, there may be more than one source of water providing discharge to the stream, and the solute composition of one source may differ from that of the other body. Kennedy *et al.* (2009) concluded that the lack of symmetry of the concentration of NO_3^- in porewaters of an agricultural stream is a complex outcome of temporally variable N use in the source area and different patterns of fertilizer application on opposite sides of the channel in addition to any variation in degree of denitrification by specific location in the streambed. Adjacent to Cobb Mill Creek, depth profiles of the groundwater composition indicate that NO_3^- content of the shallow groundwater beneath the hillslope adjacent to the stream is lower than the deeper water which is presumed to originate from agricultural fields beyond the hillslope and distal to the stream (Galavotti, 2004). Using those data and additional data collected as part of a later study, Gu *et al.* (2008) developed a two-dimensional hillslope model that showed a low NO_3^- region in the shallow region near the water table. In both studies, low NO_3^- was accompanied by higher concentrations of Cl^- than was found at greater depths.

Multiple possibilities exist, therefore, to explain the presence of NO_3^- in the water of Cobb Mill Creek despite the capacity for biological processes in the sediments to completely remove it. It may be that the residence time in those sediments for some or all of the discharging groundwater is too short to allow removal of all the NO_3^- . A second possibility is that reaction rates vary spatially due to differences in benthic organic carbon and that low-reactivity flowpaths are responsible for nitrate flux to the stream. Alternatively, NO_3^- in the shallow groundwater proximal to the stream may not be removed by any riparian zone process and may constitute the NO_3^- observed in the streamwater. It is also possible that some combination of these processes operates to maintain NO_3^- concentration of $1\text{--}2 \text{ mg NO}_3^- \text{-N l}^{-1}$ in the stream. In order to understand the effect of residence time on NO_3^- discharge from the stream sediments, it is necessary to separate the water travelling through the riparian zone from that bypassing the riparian zone and discharging into the stream sediments largely unchanged from its regional composition. We examined the possibility that the differing concentrations of Cl^- that were observed might serve to identify the water masses. We were then able to examine the effects

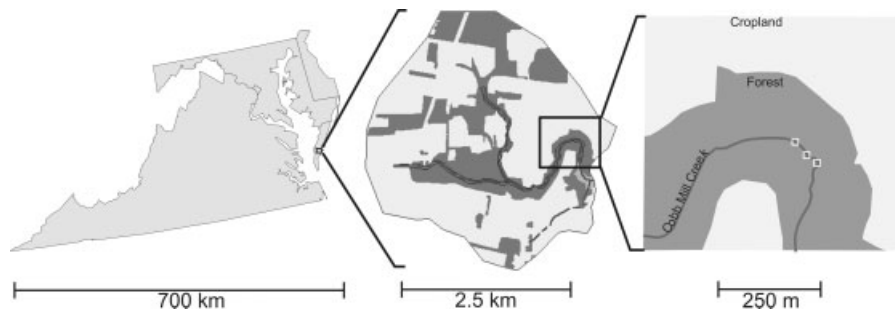


Figure 1. Location of Cobb Mill Creek and its watershed on Virginia's Eastern Shore. Light coloured areas in the centre and right panels indicate land under cultivation whereas the darker colored areas are forest, including riparian forest. The three reaches investigated and mapped in this report are indicated by the three squares in the rightmost panel

of residence time in streambed sediments on removal of the NO_3^- from the so-called bypass water. In the reach of Cobb Mill Creek studied here, almost all the NO_3^- transported to the stream in bypass water travelled through flowpaths with short residence times (<about two days) in the biologically active sediments, whereas water with longer residence times contained little or no NO_3^- . The results, then, suggest that hydrological conditions in the streambed play a dominant role in controlling the extent of NO_3^- removal in this system.

METHODS

Site description

The Cobb Mill Creek catchment is approximately 19 km north of the mouth of Chesapeake Bay on the eastern shore of Virginia, which is the southernmost portion of the Delmarva Peninsula that encompasses the eastern shores of Delaware, Maryland, and Virginia (Figure 1). The area under examination is located at 37.2910°N and 75.9290°W , and various details of the site, including specifications of wells and piezometers, have been provided elsewhere (Gu *et al.*, 2008; Mills *et al.*, 2008). The watershed is 4.96 km^2 and has low topographic relief ranging from sea level to a maximum of about 12.5 m. Cobb Mill Creek discharges eastward into Oyster Harbor, a component of the system of lagoons that is situated between the Peninsula and a chain of offshore barrier islands, and these lagoons exchange water with the Atlantic Ocean.

Overall, approximately 50% of Virginia's Eastern Shore is agricultural land, with 80% of agricultural area in row crops (USDA, 2002). Cropland is preferentially situated on well drained soils (Phillips *et al.*, 1993) where NO_3^- fertilizers readily leach to generally aerobic groundwater (Denver *et al.*, 2003). Commercial fertilizer (59%) and manure application (35%) to land make up nearly all the nitrogen load to catchments on the Delmarva (Brakebill and Preston, 1999). Land use in the Cobb Mill Creek catchment is dominated by forests (62%) and agriculture (34%), with the remaining 4% of the land area in residential and other uses.

Agriculturally derived nitrogen has leached to the unconfined Columbia aquifer (Denver, 1989) that supplies flow to the small coastal streams on the eastern shore

of Virginia (Bachman *et al.*, 1998). Nitrate concentrations in the Columbia aquifer often exceed the US EPA primary drinking water standard of $10\text{ mg NO}_3^- \text{N l}^{-1}$ (Denver *et al.*, 2003). The Columbia aquifer is composed of Pleistocene-aged unconsolidated sands (generally 8–30 m thick; (Calver, 1968; Mixon *et al.*, 1989)) with high hydraulic conductivity ($5.53 \times 10^{-3} \pm 1.56 \times 10^{-6}\text{ cm s}^{-1}$; (Hubbard *et al.*, 2001)). The aquifer is generally aerobic and contains little organic matter below the soil zone, resulting in little attenuation of NO_3^- concentrations during transport through the aquifer.

The unabated transport of NO_3^- through the Columbia aquifer leaves the riparian zone and streambed as the final barriers to NO_3^- discharge to streams on the Eastern Shore of Virginia. Owing to the significant depth of the Columbia aquifer, a portion of groundwater bypasses the riparian zone and discharges vertically through the streambed (Böhlke and Denver, 1995; Mills *et al.*, 2008). Hydraulic head measurements distributed across 38 separate occasions of monthly and quarterly sampling in 2001–2006 established the typical vertical upwelling of groundwater beneath the stream and lateral groundwater flow towards the stream in the shallow riparian zone (Flewelling, 2009). Groundwater concentration of about $12\text{ mg NO}_3^- \text{N l}^{-1}$ characterized the groundwater beneath the stream during the study period (Flewelling, 2009), yet streamwater concentration was typically $1.7\text{ mg NO}_3^- \text{N l}^{-1}$. Galavotti (2004) and Gu *et al.* (2007) found that most or all of the NO_3^- in groundwater discharging vertically through the streambed of Cobb Mill Creek could be denitrified within a 30-cm-thick organic-rich layer located directly beneath the sediment surface.

Measurement of groundwater seepage rates and solute concentrations

Seepage meters constructed after the general design of Lee (1977) were used to measure specific discharge of groundwater from the streambed and to collect samples for the determination of Cl^- and $\text{NO}_3^- \text{N}$ concentrations in groundwater seepage. The meters were constructed from 10-cm-diameter steel cans cut to 10 cm in length. The open end of the can was inserted into the streambed. The closed end of the can was fitted with a half-inch-diameter nozzle, through which all groundwater vented

to a latex condom (about 150-ml unstretched volume). Arrays of seepage meters were installed in several different reaches of Cobb Mill Creek during baseflow conditions in the summer of 2006 and 2007. Specific discharge, q (cm d^{-1}), was calculated as the volume of water collected (cm^3) divided by the length of the collection period (d) and divided by the cross-sectional area of the seepage meter (cm^2).

Seepage meters were deployed without condoms 24 h prior to making measurements to allow the remnant streamwater to purge from the seepage meter. At each seepage-meter location, two sequential measurements were made. Specific discharge was measured first using a powder-coated condom. Then, an acid-washed condom was used to collect a water sample for determination of NO_3^- and Cl^- concentrations in seepage water. The powdering of the latex condom prevented the walls from sticking together and was considered helpful for estimating flow rates. Because the powder could contaminate water samples, the acid-washed condom was used to collect seepage water for chemical analysis. Acid washing was done by rinsing each condom thoroughly 3 times with approximately 100 ml of 10% nitric or hydrochloric acid. To ensure removal of all Cl^- or NO_3^- , the condoms were rinsed 3 times with deionized water (DIW), placed in a 2-gallon tank filled with DIW for 1 h and then rinsed an additional 10 times with DIW. Washed condoms were stored in clean Ziploc® bags and used within 48 h after washing.

As discussed below, we identified measurement sites in the streambed that were associated with groundwater that bypasses the shallow riparian soils and discharges upward through a biologically active zone of streambed sediments. For these samples, travel time (t) (equivalent to the residence time of a parcel of water in the biologically active zone) was estimated by dividing the length of the biologically active zone by the average linear pore velocity, q/n where n is the sediment porosity and q was measured using seepage meters.

$$t = \frac{nL}{q} \quad (1)$$

Water samples collected for chemical analysis were centrifuged at approximately $6900 \times g$ for 20 min to remove suspended particles. Analysis of Cl^- and NO_3^- was performed on a Dionex® Ion Chromatograph equipped with a Dionex IonPac AS4A® 4×250 -mm Analytical Column preceded by a Dionex IonPac AG4A-SC® 4×50 -mm Guard Column. All NO_3^- concentration data are expressed as NO_3^- -N.

During 8 sampling events in August and September of 2006 and July and August of 2007, 158 individual seepage samples were collected for specific discharge and a similar number were collected for chemical analysis. The latter samples were transferred from the condoms to clean 25-ml glass vials in the field and stored on ice until returned to the laboratory, where they were refrigerated until analysed. Vials were cleaned with detergent and rinsed 10 times with DIW in the laboratory prior to

sample collection. Anion concentrations in samples were determined in the laboratory within one month of collection. The precision of sample collection with seepage meters was specifically examined by making sequential measurements of both groundwater seepage and NO_3^- concentrations for an array of meters on one of the sampling days. For each measurement, the results of the first and second samplings fell along a 1:1 line yielding a Pearson's correlation coefficient of 0.814 and 0.996 for discharge and NO_3^- , respectively, indicating that making two separate measurements for discharge then NO_3^- concentration did not introduce appreciable error into the results (Flewelling, 2009).

For three sampling events in the summer of 2007, specific discharge from the streambed was mapped. These arrays comprised 86 of the total 158 measurements completed for the entire study. Multiple transects of seepage meters were deployed in three different stream reaches that varied from 2.5 to 4 m in length). The three reaches were each mapped on a different day. Seepage meters in transects were spaced 20 cm apart and the spacing between transects varied from 0.29 to 1.12 m. The discharge and solute concentration data were interpolated onto an evenly spaced 10-cm grid using a cubic spline procedure.

Separating groundwater source components

Chloride concentrations in the shallowest groundwater directly beneath the riparian zone adjacent to the stream are higher than concentrations in upwelling groundwater beneath the streambed at Cobb Mill Creek (Galavotti, 2004; Gu *et al.*, 2008). There may be several causes for these observations; e.g. the riparian hillslope receives no fertilizer applications which may explain low nitrate concentrations, and the vegetation in this area of a very shallow water table may lead to evapoconcentration of chloride. Although speculation about which of several plausible processes gives rise to the observation cannot be easily resolved, the net effect is that shallow, riparian-zone groundwater along Cobb Mill Creek contains higher Cl^- and lower NO_3^- concentrations than does upwelling groundwater beneath the streambed (Figure 5 in Gu *et al.*, 2008). To explain some of our observations about the chemical composition of the groundwater discharging from the stream sediments in the absence of any other way to trace sources, we used the observed difference in Cl^- concentrations as a basis for separating shallow groundwater that originated in the riparian zone from relatively deeper groundwater that bypassed the riparian zone and discharged directly through the streambed sediments, similar to what has been done elsewhere to identify source components in mixed waters (Clement *et al.*, 2003).

We tested the solute data for multimodality in the Cl^- distribution using kernel density estimation (KDE) and a bootstrapping technique (Silverman, 1981; Efron and Tibshirani, 1993). KDE uses a bandwidth parameter to smooth distributions of observed data. Larger bandwidths

lead to more smoothing (fewer modes) and smaller bandwidths lead to less smoothing (more modes). There is a critical bandwidth that defines the break point between a distribution with one mode and a distribution with multiple modes. A bootstrapping technique can be applied to a KDE made with the critical bandwidth to test whether that cutoff point is large or small at a defined level of significance.

Calculation of reaction rate coefficients

In the presence of an excess of organic matter, microbial denitrification is a first-order kinetic process limited only by NO_3^- availability in various environmental settings, including soils (e.g. Starr *et al.*, 1974), constructed wetlands (Gale *et al.*, 1993), and water-saturated sediments (Reddy and Patrick, 1984). Even for an enzyme-catalysed reaction for which a Michaelis-Menten expression would be appropriate, Betlach and Tiedje (1981) pointed out that the reaction follows a simpler first-order rate law when substrate concentration is low. Ocampo *et al.* (2006) asserted that, with an excess of organic carbon present in the riparian zone, the first-order rate law should apply to denitrification in their study system.

Integrating the first-order expression for NO_3^- attenuation leads to a description of exponential decay of NO_3^- concentration over time,

$$N = N_0 e^{-kt} \quad (2)$$

where N_0 is the initial (influent) NO_3^- concentration, N is NO_3^- concentration at time t , i.e. at the time that the water discharges from the sediment surface, and k is the first-order rate coefficient (inverse time). Values for k were calculated from the first-order expression using the (sensibly constant) measured value for groundwater N_0 , measured values of N for each seepage meter, and values of travel time calculated from Equation (1).

RESULTS

Seepage rates and solute concentrations

Specific discharge varied by several orders of magnitude, and ranged from 2.6×10^{-6} to 1×10^{-3} cm s^{-1} , and large variations occurred over small spatial scales in the streambed (Flewelling, 2009). In some cases, specific discharge measurements made 20 cm apart differed by more than an order of magnitude. There tended to be high and low specific discharge regions in the streambed, and those regions tended to be aligned parallel to the direction of flow. In two of the three mapped reaches, the zones having the highest discharge were in the centre of the streambed (Figure 2(a) and (c), located relatively downstream and upstream, respectively), whereas in the third reach (Figure 2(b), located between the other reaches), the areas of highest discharge, although oriented parallel to flow, were located more toward both edges of the stream.

Qualitative comparison of the maps for one mapped array of Cl^- (Figure 3(a)) and NO_3^- (Figure 3(b)) concentrations in groundwater seepage showed that NO_3^- concentrations were low where Cl^- concentrations were high. In detail, areas of the streambed where Cl^- concentrations in seepage were greater than 20 mg l^{-1} corresponded to NO_3^- concentrations less than 2 mg l^{-1} . For chemical data collected from the 3 spatial arrays, the samples with the lowest Cl^- concentrations displayed a range of NO_3^- concentrations but samples with the highest Cl^- concentrations tended to be low in dissolved NO_3^- (Figure 4).

Groundwater source components

A histogram of Cl^- concentration in samples collected from all the seepage meters suggested the presence of several peaks (i.e. modes) in frequency (Figure 5). The KDE test for multimodality in the Cl^- distribution indicated that three modes were significant ($\alpha = 0.05$, $p = 0.014$). Samples with concentrations distributed around the lowest mode were presumed to represent deeper groundwater that is characterized by low concentrations of Cl^- at this site relative to shallower (i.e. potentially riparian-influenced) subsurface water. The upper cutoff value of Cl^- concentration associated with that lowest mode was 20.9 mg l^{-1} (Figure 5) which was consistent with the observation that Cl^- concentrations exceeding 20 mg l^{-1} were associated with low NO_3^- concentrations as would be expected in the riparian water. Thus, samples distributed around the two modes associated with higher Cl^- concentrations were assumed to represent groundwater that originated in or was influenced by processes in the riparian zone.

Relationship between N and q

Separation of all seepage-water samples into the two inferred source-water groups using the 20.9 mg/l Cl^- cutoff showed that there was a relationship between NO_3^- concentrations discharging from the streambed and the inverse of specific discharge for bypass water (Figure 6(a)), in which lower values of q (i.e. higher values of $1/q$) in the sediments are related to lower NO_3^- concentrations. In contrast, no relationship between NO_3^- concentrations and specific discharge was evident for samples categorized as riparian-influenced groundwater (Figure 6(b)).

Travel times for bypass water

To estimate travel times using Equation 1, we need values for the depth of the biologically active zone that the bypass traverses, and for the sediment porosity. Galavotti (2004) and Gu *et al.* (2007) showed that NO_3^- removal occurs over a finite-length scale in the streambed—i.e. the organic-rich zone near the streambed surface. The thickness of that organic-rich zone is fairly constant at 30 cm (Galavotti, 2004; Gu *et al.*, 2007), so a length of flowpath (L) within the streambed sediments where denitrification was concentrated was taken as that

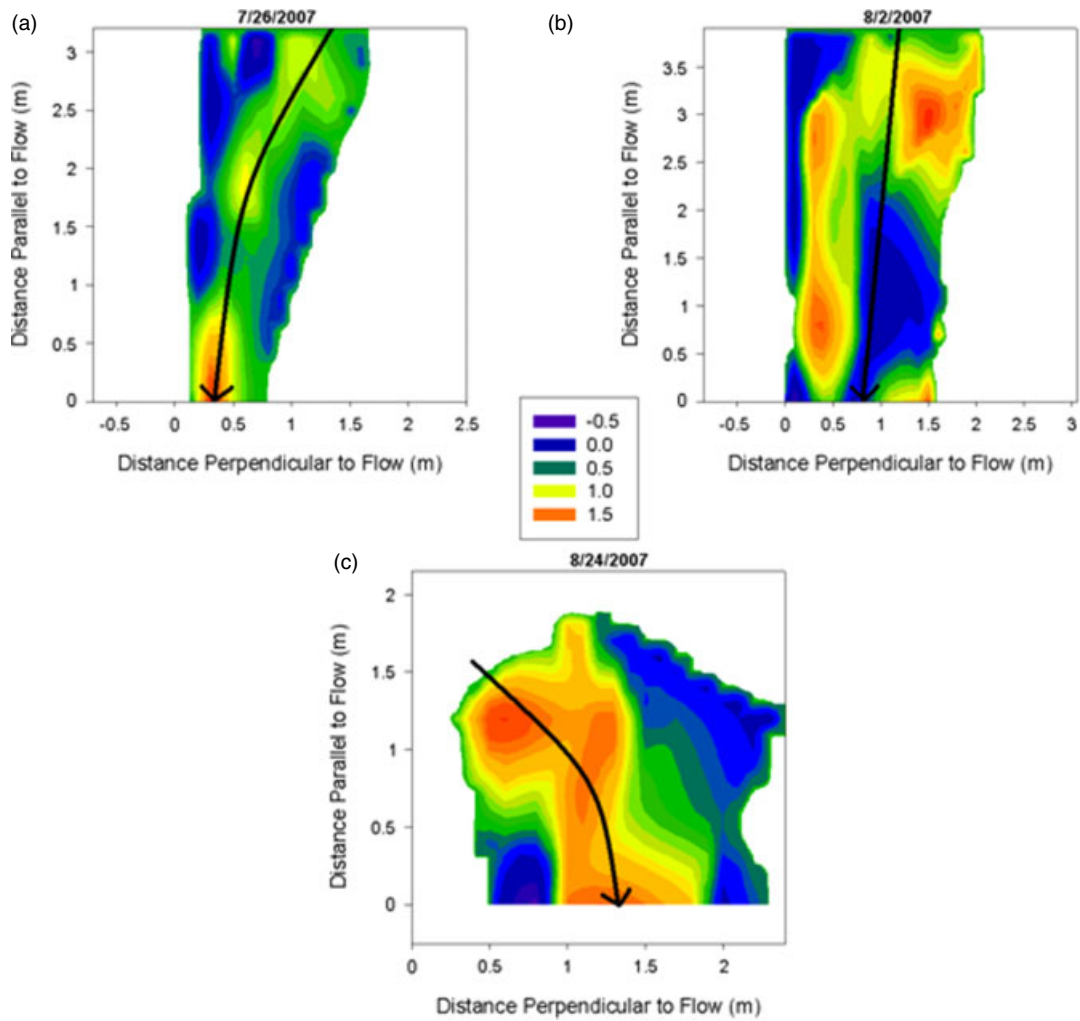


Figure 2. Maps of specific discharge observed in three different stream reaches on three different dates: (a) Site relatively downstream sampled on 7/26/2007; (b) Site in the middle position sampled on 8/2/2007; and (c) Site relatively upstream sampled on 8/24/2007. The large black arrow in each figure indicates the direction of stream flow and the approximate centre of the channel. All maps are in units of the natural logarithm of specific discharge (q) in cm d^{-1}

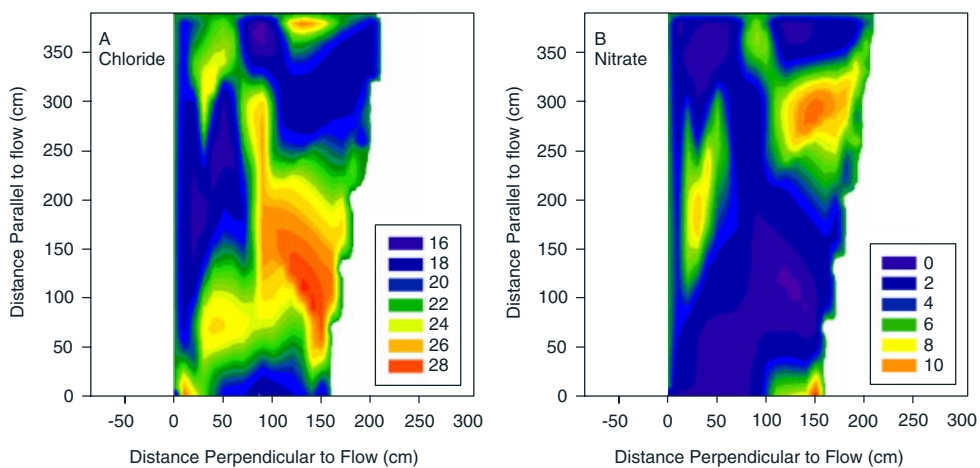


Figure 3. Map of (a) Cl^- concentrations; and (b) NO_3^- concentrations in groundwater seepage from the streambed array deployed in the middle section on 8/02/2007

30-cm value. Porosity (n) for the sandy sediments at our study site was taken to be 0.35. Given that the specific discharge varies over almost three orders of magnitude, slight variations or errors in the fixed values of L and n

that we use are negligible. With these assumptions, the travel times for the bypass pathways range from about 3 h to about 10 days and have an exponential shape (Figure 7).

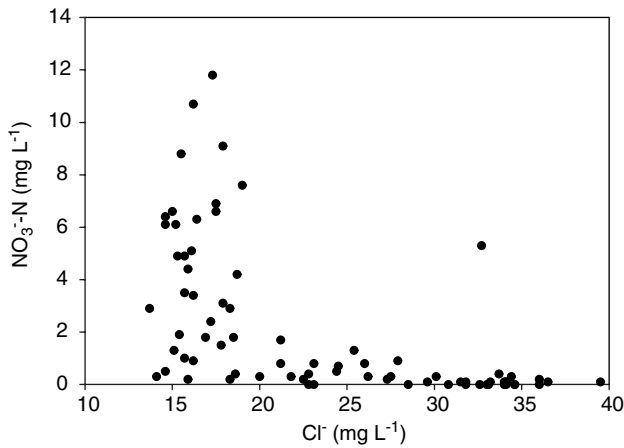


Figure 4. Scatter plot of NO_3^- versus Cl^- concentrations for 75 groundwater seepage samples collected in 2007 from the areas illustrated in Figure 2. Nitrate was undetectable in 19 of the 94 samples collected and values, therefore, were not plotted

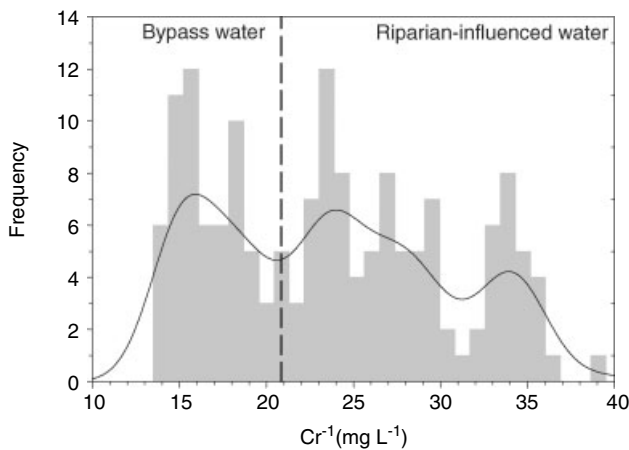


Figure 5. Histogram (bars) and kernel density estimate (KDE, solid line) of the Cl^- concentration in groundwater seepage into Cobb Mill Creek for all 158 samples collected over the field seasons of 2006 and 2007 from transects and from arrays. The vertical dashed line indicates the inferred cutoff between riparian-influenced (at higher Cl^- concentrations) and bypass (at lower Cl^- concentrations) groundwater. Of the total 158 samples, 62 were bypass water and 96 were riparian-influenced water. Nitrate was observed above the analytical detection limit in 57 of the 62 bypass samples and in 78 of the 96 riparian-influenced samples

Reaction rate coefficients

Once travel-time estimates are available, it is straightforward to calculate the first-order reaction rates as

$$k = -\frac{1}{t} \ln \left(\frac{N}{N_0} \right) \tag{3}$$

The initial NO_3^- concentration entering the denitrifying zone, N_0 , was assumed to be a constant $12.2 \text{ mg NO}_3^- \text{ N l}^{-1}$, which was the average NO_3^- concentration in four piezometers that opened 40–80 cm beneath the streambed repeatedly sampled between October 2003 and May 2005 ($12.2 \pm 0.2 \text{ mg NO}_3^- \text{ N l}^{-1}$, $n = 52$) (Flewelling, 2009). The calculated rate coefficients, k , for denitrification in bypass flow average 1.5 d^{-1} and range from about 0.15 d^{-1} to about 7 d^{-1} with the greatest frequency of occurrence for the low values of

rate coefficient and a steadily decreasing frequency of occurrence of high values of rate coefficient (Figure 8).

DISCUSSION

Physical control on seepage

Hydraulic conductivity (K_S) exerts the dominant control on groundwater travel time (i.e. residence time in biogeochemically active zones of the streambed) in this low-gradient hydrogeological system. The potentiometric gradient across the biologically active zone in the sediment into the stream for our study reach is a uniform value of 0.2 m/m (Flewelling, 2009), so q and K_S are in direct proportion. Although we did not measure K_S , it is represented in Figure 2 through its proportionality with q . Confirmation of the importance of physical hydraulic properties of the streambed in determining NO_3^- flux is extensively documented in papers by Kennedy and others in which direct measurements using a falling-head permeameter were recorded (Genereux *et al.*, 2008; Kennedy *et al.*, 2009). They found that NO_3^- concentrations did not vary nearly so much, even considering riparian-zone processes, as specific discharge varied in space and time for a small coastal stream.

Differences in riparian-influenced and bypass water

The occurrence of higher Cl^- concentrations in shallow riparian-zone groundwater relative to deeper groundwater was used as the basis for separating source components. Previous work at Cobb Mill Creek showed that Cl^- concentrations in shallow, riparian-zone groundwater were elevated relative to deeper groundwater (Galavotti, 2004; Gu *et al.*, 2008). Vertical variation of Cl^- with depth in the riparian zone has been characterized in other settings showing lower Cl^- concentrations at depth (Hill *et al.*, 2000). A number of processes can affect the concentration of Cl^- , including evapotranspiration (Claassen and Halm, 1996), plant uptake (Xu *et al.*, 2004), microbial cycling of organic and inorganic chlorine (Bastviken *et al.*, 2006), and infiltration of Cl^- -poor precipitation. These processes may not always have an effect in the same direction and may operate at different temporal and spatial scales; thus, the aggregate effect on groundwater Cl^- concentrations is not obvious. Nevertheless, differences in Cl^- concentrations between deep and shallow groundwater may serve as a useful means of determining the source of water discharging into streams. Even with the relatively wide range in Cl^- concentrations that was observed in groundwater seepage in our study site, we were able to identify distinct modes in the Cl^- distribution (Figure 5) that successfully distinguished water primarily derived from different sources, the important distinction being a low- Cl^- , high- NO_3^- source and another mode (or modes) representing a high Cl^- , low- NO_3^- source.

Because the shallow groundwater adjacent to the stream at Cobb Mill Creek likely recharged close to

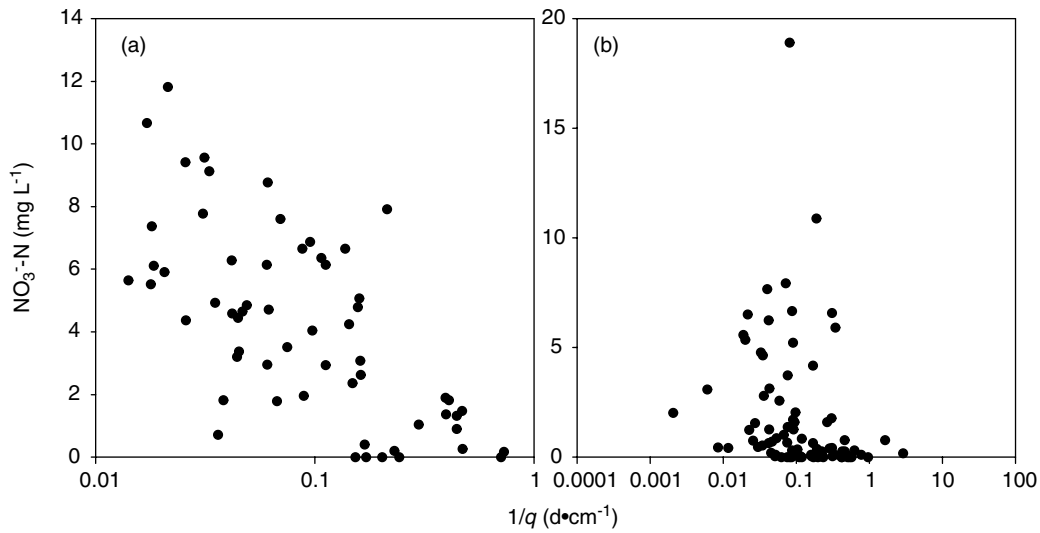


Figure 6. The relationship between NO_3^- concentrations and the inverse of the specific discharge for detected concentrations in (a) the 57 bypass samples; and (b) the 78 riparian-influenced samples for all 158 samples collected over the field seasons of 2006 and 2007 from transects and from arrays (23 samples were non-detect for NO_3^- , and therefore, do not appear in these plots). Note that the abscissas are plotted as the logarithm to facilitate visualisation of the relationships

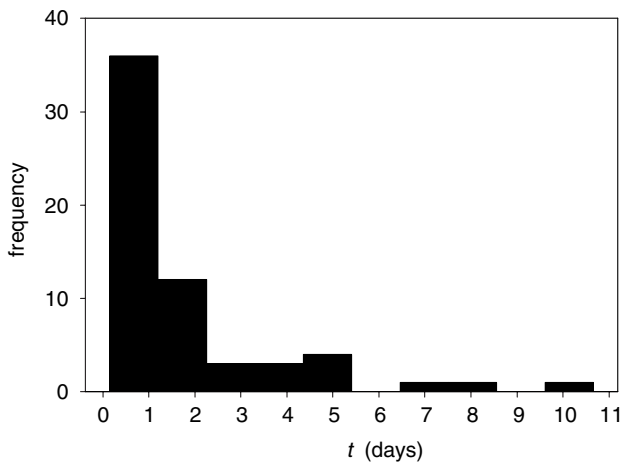


Figure 7. Distribution of travel time (t) through the biologically active zone of the sediments for water that bypasses riparian zone influences and discharges from Cobb Mill Creek sediments

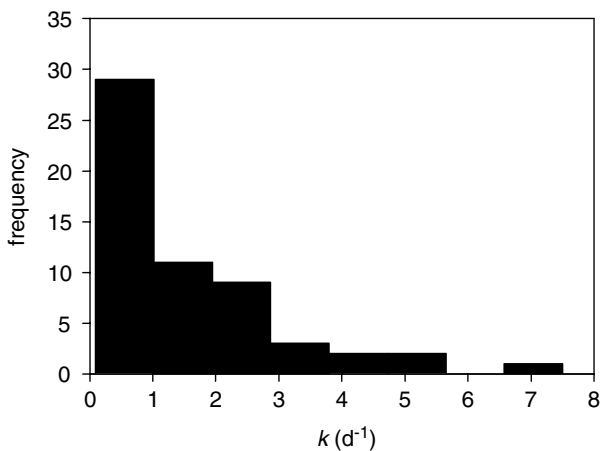


Figure 8. Distribution of rate coefficients, k , for denitrification in seepage water that bypasses riparian zone influences and discharges from Cobb Mill Creek sediments

the stream channel and did not originate from recharge passing through the fertilized agricultural fields (Gu *et al.*, 2008), it is unlikely to contain the large amounts of NO_3^- seen in the deeper groundwater coming from those fields even in the absence of subsurface removal. Furthermore, NO_3^- concentration is likely to be moderated by a suite of microbially mediated N transformations (*viz.* mineralisation, nitrification, and denitrification) and plant interactions (evapotranspiration and plant uptake) during transport through the shallow riparian zone prior to discharging into the stream. A number of authors have pointed to the successful removal of NO_3^- in the riparian subsurface (Lowrance *et al.*, 1984; Lowrance, 1992; Bruschi and Nilsson, 1993; Lowrance *et al.*, 1997; Fisher and Acreman, 2004; Ensign *et al.*, 2008;). Others have pointed to relatively ineffective removal even along significant horizontal distances if organic matter was present in only very localized spots in the heterogeneous subsurface (Jacinthe *et al.*, 1998; Hill *et al.*, 2000). Given the variety of possible influences on NO_3^- concentration in groundwater seepage that originates from shallow riparian flowpaths, it is likely to be very difficult to isolate and analyse specific nitrate-removal mechanisms using our measurements. Consequently, from here on, we focus attention on the results for seepage from bypass flowpaths.

In contrast to the various, often extensive, removal processes acting upon riparian-influenced groundwater, upwelling deeper groundwater that is not influenced by riparian processes (*i.e.* that has bypassed the riparian zone and the processes occurring there and that discharges vertically through the streambed) would be affected mainly by denitrification in the streambed sediments (Gu *et al.*, 2007; Mills *et al.*, 2008). There is evidence in the literature for numerous stream settings where bypass water is the source of the majority of NO_3^- delivered to

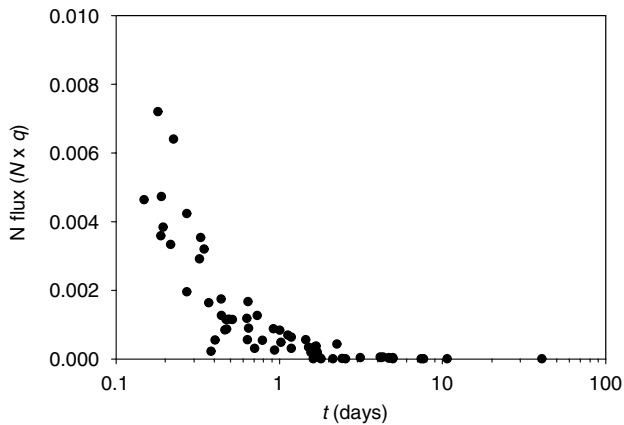


Figure 9. Relationship of NO_3^- flux in seepage water that bypasses riparian zone influences to the travel time through the zone of active denitrification in Cobb Mill Creek sediments

streamwater (Angier *et al.*, 2005; Angier and McCarty, 2008, and citations therein).

Relationship of nitrate flux to travel time in bypass water

Nitrate attenuation in the porewater of the streambed sediments depends upon the residence time of a parcel of groundwater within the biologically active denitrifying zone (Gu *et al.*, 2007; Angier and McCarty, 2008). It is therefore logical to explore the hypothesis that hydraulic residence time is the primary variable controlling removal rates of nitrate in sediments. There is a rather sharp cutoff of nitrate flux ($q \times N$) at a residence time of about 2 days (Figure 9). This result certainly indicates that travel time is an important determinant of nitrate removal, but the role of biogeochemical factors must still be considered.

Biogeochemical factors in denitrification rate

The abundance and lability of organic carbon can affect denitrification rates in streambed sediments, presumably at least in part because reaction rate coefficients may depend on the concentration of the electron donor. Other field studies have found that organic carbon supply is an important factor controlling the location and extent of denitrification in the subsurface (e.g. Hedin *et al.*, 1998; Hill *et al.*, 2000). In Cobb Mill Creek, visual inspection of near-surface sediments and intact sediment cores indicates that terrestrial organic matter (e.g. leaves, sticks, and fine-grained organic particles) is incorporated into the streambed. Galavotti (2004) measured vertical profiles of organic carbon content of the streambed in 31 intact sediment cores from Cobb Mill Creek and found that average organic carbon content decreased exponentially with depth, but was extremely variable. Nonetheless, Gu *et al.* (2007) demonstrated that regardless of a range of linear porewater velocities, the organic matter present in an intact core was capable of sustaining denitrification. There is also potential for organic matter incorporated into the streambed to affect hydraulic conductivity and thereby have an effect that correlates with travel time, but we have only a few isolated measurements at our site that suggest that this might be the case (Gu, 2007) In

addition to the abundance and nature of organic matter present, other factors that may influence the value of the rate coefficients include the temperature of the streambed environment, the size of the active microbial guild, the concentrations of essential nutrients for bacterial growth, and inhibition by toxins and cell exudates.

In our study, the individual values of k determined for each seepage measurement averaged 1.5 d^{-1} and ranged from 0.15 to 7 d^{-1} , and these values represent the total effect of all such factors that are not represented in our presumed first-order rate law which depends only upon NO_3^- concentration (Equation (2)). Depending upon degree of dilution and which of two hillslope sites was examined, Ocampo *et al.* (2006) found rate coefficients resulting from their reactive-transport modelling constrained by field samples ranged from 0.0075 to 0.25 d^{-1} . Applying their approach to other published studies, they determined first-order rate coefficients spanning at least 0.009 to 2.5 d^{-1} . Thus, the bulk of our results fall within the previously reported range of values for this hypothesized rate law, but a handful of the values of k that we estimated are above 2.5 per day. Unlike the strong relationship between nitrate flux and travel time (Figure 9), the nitrate flux and reaction rate coefficients are essentially uncorrelated. Certainly there is a relationship between our calculated values of k and t , but because t is used to calculate k , no sensible inferences can be drawn from such a comparison. To examine the co-effects of travel time and reaction rates, a variable independent of travel time as calculated from specific discharge must be used.

The Damkohler number

The Damkohler number, Da , is the ratio of the timescale for transport to the timescale for reaction, and it is a useful indicator of the relative importance of transport and reaction for the progress of kinetically controlled processes (Domenico and Schwartz, 1998). It is particularly valuable in conflating the variety of influential factors controlling NO_3^- removal, such as the length scale of the system, hydraulic conductivity, head gradient, porosity, and reaction rate coefficient, into an indicative dimensionless result useful in making comparisons among different studies (Ocampo *et al.*, 2006) and for reactive transport modelling (e.g. Gu *et al.*, 2007).

Groundwater travel time through the streambed (t in Equation (1)) is a characteristic timescale for transport, and the reaction rate coefficient (k) is the reciprocal of a characteristic timescale for reaction. The extent of denitrification, therefore, will depend on the relative magnitude of those two characteristic timescales; that ratio is the Damkohler number, Da .

$$Da = kt \quad (4)$$

which, from Equation (3) can be computed directly from the measured concentrations of NO_3^- .

$$Da = -\ln\left(\frac{N}{N_0}\right) \quad (5)$$

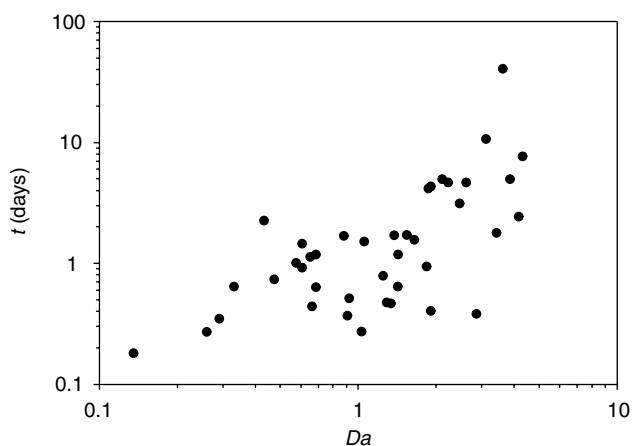


Figure 10. Relationship of Damkohler Number, Da , to the travel time for water bypassing riparian zone influences and discharging through the zone of active denitrification in Cobb Mill Creek sediments

Note that the calculated Damkohler number is independent of specific discharge measurements and, thus, independent of our estimates of travel time.

Damkohler numbers were estimated at all seepage meter locations with Equation (5) using measured NO_3^- concentrations in the sampled seepage water as N . Variability in Da may result from changes in travel times, rate coefficients, or both. The actual value of Da indicates the shifting balance of hydrological *versus* biogeochemical control on NO_3^- export from groundwater. For our site, Da varies as a function of travel time, indicating the strong control that hydrology has on nitrate removal in this stream (Figure 10).

To achieve an appropriate NO_3^- concentration in the stream, Ocampo *et al.* (2006) concluded that Da is a potential tool for prescribing the proper size of a riparian zone for a desired level of NO_3^- removal. This approach worked well for the setting considered by those authors (i.e. shallow perched aquifers or riparian zones above a shallow confining layer and arid-climate grasses vegetating the riparian area), but left them calling for additional work in forested riparian zones. Further, in a setting of thicker unconfined aquifers, significant amounts of water bypass the riparian zone. In some settings, bypass water following longer flowpaths has lower NO_3^- concentration by virtue of the local history of fertilizer use (Böhlke and Denver, 1995; Kennedy *et al.*, 2009), but in other cases, bypass water can contribute the majority of NO_3^- to the stream (Mills *et al.*, 2002; Angier *et al.*, 2005; Angier and McCarty, 2008; McCarty *et al.*, 2008).

Instead of viewing them as separate, the streambed and riparian zone should be considered an integrated NO_3^- removal unit. In addition to plant and microbial NO_3^- removal processes operating in the riparian zone, the riparian vegetation also serves as the source of organic matter to the NO_3^- reducing zone in the streambed of Cobb Mill Creek. Since riparian-influenced and bypass water are the two bodies that determine stream NO_3^- concentration, Da , or the balance between rates of biogeochemical reaction and transport, would need to be optimized along both flowpaths to achieve a desired

NO_3^- concentration in the stream. There is a need to identify more clearly the primary controls on organic matter replenishment in the biologically active zone of the streambed and how riparian zone management may indirectly affect NO_3^- removal in bypass flow.

Our work demonstrated that denitrification in organic-rich streambed sediments is capable of removing NO_3^- from groundwater discharging to streams. While most previous work has focused on the riparian zone (e.g. Hill *et al.*, 2000; Clément *et al.*, 2003; Vidon and Hill, 2004) for active denitrification, we demonstrate the biogeochemical potential for denitrification in bypass water. The shifting balance between biogeochemical and hydrological processes emphasizes the critical role of hydraulic conductivity in determining the magnitude of NO_3^- attenuation through its controls on travel time. Direct measurement of sediment hydraulic properties has confirmed the great spatial variability in hydraulic conductivity (Genereux *et al.*, 2008). Our work captured the seepage water directly and allowed assessment of extent of denitrification. This report of NO_3^- concentration reduction in bypass water expands the realm of limitations on NO_3^- export from contaminated groundwater in agricultural watersheds.

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