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Review Paper

The importance of the riparian zone and in-stream processes in nitrate attenuation in undisturbed and agricultural watersheds – A review of the scientific literature

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SUMMARY

We reviewed published studies from primarily glaciated regions in the United States, Canada, and Europe of the (1) transport of nitrate from terrestrial ecosystems to aquatic ecosystems, (2) attenuation of nitrate in the riparian zone of undisturbed and agricultural watersheds, (3) processes contributing to nitrate attenuation in riparian zones, (4) variation in the attenuation of nitrate in the riparian zone, and (5) importance of in-stream and hyporheic processes for nitrate attenuation in the stream channel. Our objectives were to synthesize the results of these studies and suggest methodologies to (1) monitor regional trends in nitrate concentration in undisturbed 1st order watersheds and (2) reduce nitrate loads in streams draining agricultural watersheds.

Our review reveals that undisturbed headwater watersheds have been shown to be very retentive of nitrogen, but the importance of biogeochemical and hydrological riparian zone processes in retaining nitrogen in these watersheds has not been demonstrated as it has for agricultural watersheds. An understanding of the role of the riparian zone in nitrate attenuation in undisturbed watersheds is crucial because these watersheds are increasingly subject to stressors, such as changes in land use and climate, wildfire, and increases in atmospheric nitrogen deposition.

In general, understanding processes controlling the concentration and flux of nitrate is critical to identifying and mapping the vulnerability of watersheds to water quality changes due to a variety of stressors. In undisturbed and agricultural watersheds we propose that understanding the importance of riparian zone processes in 2nd order and larger watersheds is critical. Research is needed that addresses the relative importance of how the following sources of nitrate along any given stream reach might change as watersheds increase in size and with flow: (1) inputs upstream from the reach, (2) tributary inflow, (3) water derived from the riparian zone, (4) groundwater from outside the riparian zone (intermediate or regional sources), and (5) in-stream (hyporheic) processes.

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1. Introduction

During the last 20 years recognition of the influence of riparian zone processes on water quality has led to a growing interest in the use of riparian buffer zones along river corridors to mitigate the effects of non-point source pollution (Hill, 1996). The use of riparian zones as water-quality management tools results primarily from studies of agricultural watersheds, where large reductions in the concentrations of nitrate, suspended sediment, and, to a lesser degree, phosphorus, have been observed as water flows through riparian zones. Undisturbed headwater streams have been shown to be very retentive of nitrogen, sometimes exporting less than one-half of the input of dissolved inorganic nitrogen (Likens et al., 1977; Peterson et al., 2001). The importance of the riparian zone in the attenuation of nitrate in undisturbed watersheds, however, is largely unknown.

Understanding how hydrological and biogeochemical processes in the riparian zone and in the stream channel (hyporheic zone) control the concentrations of nitrate in undisturbed watersheds is crucial because these watersheds are increasingly subjected to stressors such as changes in land use and climate, wildfire, and increases in atmospheric deposition of nitrate (Landers et al., 2008). Therefore, understanding the processes controlling the concentration and flux of nitrate is critical to identifying and mapping watersheds vulnerable to stresses and predicting the effects of these stresses on water quality. There is also a need to better understand how these processes control the concentrations of nitrate in agricultural watersheds to better manage riparian zones as buffer zones to reduce nitrate loads in streams.

In this paper, the use of the terms "watershed", "basin", "streamflow", and "discharge", follow the usage of the author(s) of the papers included in this literature review. The term hyporheic zone refers to the subsurface zone, where stream water flows through segments of its adjacent bed and banks and is characterized by the mixing of stream water and groundwater (Triska et al., 1993; Winter et al., 1998; Hill and Lymburner, 1998) (Fig. 1).

This review provides a summary of published research primarily from glaciated regions in the United States, Canada, and Europe that demonstrates the importance of biogeochemical and hydrological processes in the riparian zone and in the stream channel on stream nitrate concentration in undisturbed and agricultural watersheds. These watersheds vary in size from small headwater watersheds to large rivers such as the Mississippi. Our purpose is to suggest methodologies to (1) monitor regional trends in nitrate concentration in undisturbed 1st order watersheds and (2) reduce nitrate loads in streams draining agricultural watersheds.

2. Transport of nitrate from terrestrial ecosystems to aquatic ecosystems

Riparian zones in any watershed can be a net source or a net sink of nitrate depending on the flow path of water draining to the stream. Measurements of stream chemistry over short (individual storms and snowmelt) and longer (seasonal and year-to-year monitoring) time scales have shown that temporal and spatial variations in nitrate concentration result from temporal changes in flow paths.

In undisturbed forested watersheds, evidence that riparian zones serve as a source of nitrate is observed when increases in stream nitrate above base flow concentrations occur during snowmelt and/or rainfall events. Peaks in nitrate concentration usually occur before peaks in stream discharge (Denning et al., 1991; Stottlemyer and Troendle, 1992; Hill, 1993; Creed and Band, 1998; Ohrui and Mitchell, 1998; Correll et al., 1999; Hill et al., 1999; Campbell et al., 2000; Coats and Goldman, 2001; Bechtold et al., 2003). Similar increases in nitrate have also been measured in streams draining mixed land use and agricultural watersheds (Schnabel, 1986; Schnabel et al., 1993; Correll et al., 1999; Kalkhoff et al., 2000; Royer et al., 2004). This temporal behavior is a "flushing effect" when a water table rises to the soil surface with subsequent mobilization of nutrients stored near or at the soil surface (Creed et al., 1996; Creed and Band, 1998). When saturated throughflow is deep below the soil surface, nitrogen accumulates in the soil, resulting in small export of nitrogen into adjacent waters. As saturated throughflow rises, nitrogen is flushed from the soil to the stream. As saturated throughflow intersects the soil surface, nitrogen formed in the highly bioactive surface of the soil is flushed resulting in large export of nitrogen into adjacent waters.

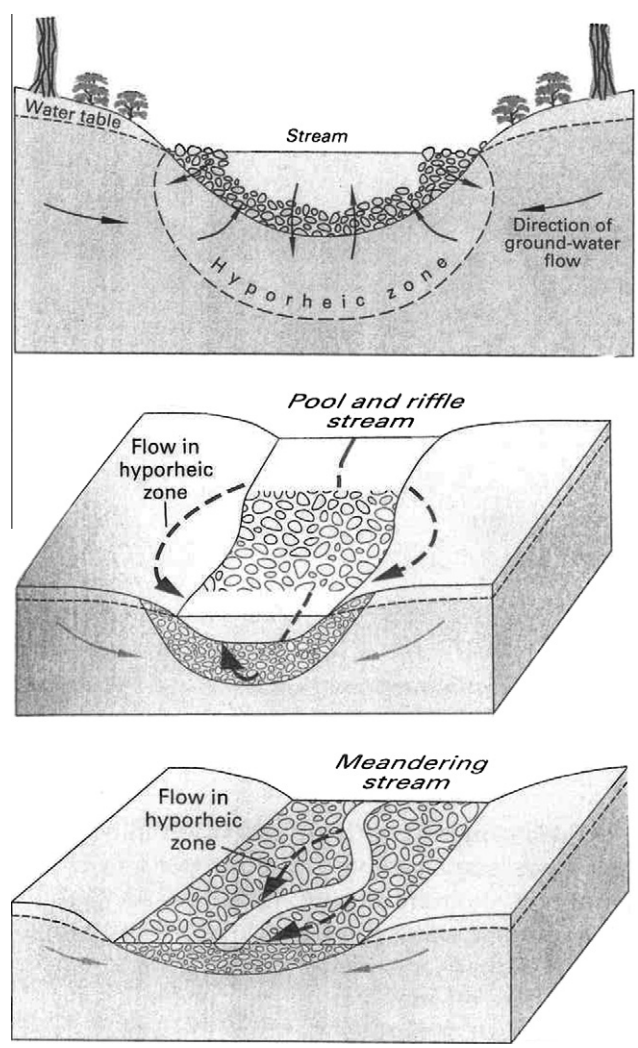

Fig. 1. Examples of stream hyporheic zones (from Winter et al., 1998).

Riparian zones function as net sources of nitrate during high flows because the rising water table that flushes nitrate occurs primarily in the riparian zone (Dunne and Black, 1970a,b; Freeze, 1972a,b; Engman, 1974; Dunne et al., 1975; Pearce et al., 1986; Sklash et al., 1986; Pionke et al., 1988; Abdul and Gillham, 1989).

Nitrate is also delivered to streams by groundwater (Freeze and Cherry, 1979; Creed et al., 1996). Nitrate is very water soluble and does not adsorb to soil to any significant degree (Johnson, 1992). Therefore, any nitrate that is dissolved in precipitation or irrigation water that infiltrates the upper soil horizons and is not taken up by vegetation or microbes will migrate with water that percolates into the water table.

3. Attenuation of nitrate in the riparian zone

Nitrate attenuation in groundwater occurs in the riparian zones of undisturbed headwater watersheds (McDowell et al., 1992; Campbell et al., 2000; Sueker et al., 2001; Sickman et al., 2003), agricultural watersheds (Peterjohn and Correll, 1984; Schnabel, 1986; Pinay and Decamps, 1988; Cooper, 1990; Jordan et al., 1993; Hill, 1996), and watersheds with varied land uses (Hedin et al., 1998; Ostrom et al., 2002). Although low concentrations of nitrate have been reported in riparian-zone groundwater in undisturbed headwater watersheds, the overwhelming majority of such observations have been reported for agricultural watersheds. Using data from several papers, Hill (1996) calculated percent removal of nitrate in groundwater traversing the riparian zone in 20 watersheds by comparing the nitrate concentration of groundwater upgradient from the riparian zone with that of groundwater at the riparian zone/stream interface. He found that in 14 riparian zones nitrate removal was greater than 90%, and that nitrate removal in all 20 watersheds ranged from 65% to 100%.

4. Processes contributing to nitrate attenuation in riparian zones

The reduction in nitrate in groundwater flowing through the riparian zone in agricultural watersheds has been attributed to denitrification, uptake by vegetation, and immobilization by microorganisms (Pinay and Decamps, 1988; Cooper, 1990; Simmons et al., 1992; Pinay et al., 1993, 2000; Groffman et al., 1993; Hanson et al., 1994; Nelson et al., 1995; Lowrance et al., 1995; Devito et al., 2000). Plant uptake and microbial immobilization represent only temporary storage as the nitrogen will be returned to the ecosystem upon death and subsequent decomposition. In contrast, denitrification represents a nitrate sink. Denitrification is the biochemical reduction of oxidized nitrogen anions, nitrate and nitrite, to N_2 gas with concomitant oxidation of organic matter (Wetzel, 2001),

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O \quad (1)$$

Measurable rates of denitrification occur only in the presence of soil organic matter and under low-oxygen conditions, and rates are also controlled by spatial and temporal variability in groundwater nitrate concentrations (Pinay and Decamps, 1988; Cooper, 1990; Pinay et al., 1993, 2000; Lowrance et al., 1995; Jacinthe et al., 1998; Hedin et al., 1998; Devito et al., 2000; Clément et al., 2002; Ostrom et al., 2002; Puckett and Cowdery, 2002; Hill et al., 2004; Grimaldi et al., 2004).

Studies of denitrification in soil cores (Jacinthe et al., 1998), in situ, plot-scale field studies (Clément et al., 2002; Hill et al., 2004), and in a transect of groundwater wells across a riparian zone (Puckett and Cowdery, 2002) have shown that (1) there are strong vertical gradients of potential and actual rates of denitrification in a soil profile, with the highest rates occurring in the upper soil layer corresponding to the highest amounts of soil organic carbon, and (2) low rates of denitrification occurred at depth in all seasons. These observations show that even small amounts of soil organic carbon can support denitrification and cause measurable decreases in nitrate concentration in groundwater. Riparian zone hydrology may control denitrification through the interaction of groundwater with soil organic matter, so that negligible nitrate attenuation occurs in deep groundwater, but as the groundwater moves upward through the riparian zone 100% attenuation occurs (Devito et al., 2000).

Bedrock geology can also be a factor in nitrate attenuation because certain minerals can promote denitrification by serving as electron donors. Although organic carbon is the common electron donor in the denitrification reaction, other reduced species such as ferrous iron in pyrite (FeS_2) and silicate minerals such as pyroxenes and amphiboles can also serve as electron donors (Puckett and Cowdery, 2002). In the absence of oxygen, nitrate reduction coupled with the oxidation of sulfur in pyrite can occur in a reaction mediated by the bacterium *Thiobacillus denitrificans* (Grimaldi et al., 2004):

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O \quad (2)$$

Studies of spatial variations in denitrifications rates have reported that the highest rates of denitrification occur at the upslope edge of the riparian zone, and the lowest rates occur near the soil–stream interface (Pinay and Decamps, 1988; Cooper, 1990; Simmons et al., 1992; Pinay et al., 1993). This is attributed to the low concentrations of nitrate in the groundwater adjacent to the soil–stream interface, due to denitrification upslope of the soil–stream interface. When measured across a slope from ridge-top (watershed divide) to the soil–stream interface, higher rates of denitrification occur in the soil–stream interface relative to upslope (Groffman et al., 1993; Hanson et al., 1994; Nelson et al., 1995; Burt et al., 1999). Groffman et al. (1993) attributed the consistently higher levels of denitrification in a poorly drained toe-slope position compared to a well-drained ridge top position to differences in the immobilization of N by microbes at the two sites. In the well-drained landscape position, there was a large amount of microbial immobilization; as a result there was little denitrification (or nitrification). In the poorly drained site there was little microbial immobilization; as a result $^{15}NH_4^+$ availability to nitrifiers was high, and rates of nitrification were high. Therefore, there was an accumulation of nitrate in the poorly drained soil. This accumulation of nitrate, along with high soil moisture, fostered high denitrification N losses.

Studies of denitrification rates have shown that nitrate attenuation occurs throughout the year but the relative contribution of different attenuation mechanisms may vary and denitrification may not always be the dominant process (Pinay and Decamps, 1988; Simmons et al., 1992; Pinay et al., 1993; Groffman et al., 1993; Hanson et al., 1994; Nelson et al., 1995). During the growing season, plant uptake, denitrification, and microbial immobilization may contribute to nitrate attenuation, but during the dormant season attenuation was likely the result solely of microbial processes.

Although most studies of nitrate attenuation have occurred in agricultural watersheds, there is evidence that riparian zone processes also cause temporal variability of nitrate concentrations in streams draining high-elevation, undisturbed watersheds (McDowell et al., 1992; Campbell et al., 2000; Sueker et al., 2001; Sickman et al., 2003). In high-elevation watersheds in Colorado and Nevada (USA), stream nitrate concentrations typically peak just before or at the peak of spring snowmelt, decline throughout the summer, and rise slightly over the winter. This is caused by relative differences in the rates of nitrification, denitrification, microbial immobilization, and plant uptake. Nitrification is the most

important process early in the spring, followed by a dominance of denitrification later in the spring, then microbial immobilization and plant uptake become more important in summer and fall with a return to dominance by denitrification and microbial immobilization in winter (Williams et al., 1996; Brooks et al., 1996, 1998; Lipson et al., 1999; Sickman et al., 2003). In the early spring freeze/thaw cycles favor nitrification, while in later spring the saturation of soils with meltwater and the relatively high levels of nitrate favor denitrification.

The reduction in groundwater nitrate concentrations across riparian zones in agricultural watersheds and low nitrate concentrations in the riparian zones of high-elevation watersheds (Sueker et al., 2001; Sickman et al., 2003) supports the hypothesis that the decline in-stream nitrate concentrations in summer and autumn in undisturbed headwater watersheds is due to nitrate-attenuation processes in the riparian zone.

5. Variation in the attenuation of nitrate in the riparian zone

Nitrate attenuation in groundwater traversing the riparian zone varies in its effectiveness as a function of riparian-zone (buffer) width. Mayer et al. (2005) found that 50%, 75%, and 90% removal efficiencies occur in buffers approximately 3 m, 28 m, and 112 m wide respectively. This variability is due to two factors, which will be discussed in detail: variation in the position of the riparian zone with respect to local, intermediate, and regional groundwater flow systems, and variation of the hydrogeologic properties among riparian zones. By comparison, differences in the capacity of various types of vegetation to attenuate nitrate is relatively small.

5.1. Variation in nitrate attenuation capacities of riparian zones due to differences in the location of the riparian zone with respect to local, Intermediate, and regional groundwater sources

Hill (1996) cautions against the assumption that nitrate attenuation always occurs in riparian zones, noting that the position of the riparian zone in relation to local and regional groundwater flow systems is important. Differences in the recharge location and water residence time of the flow systems may produce contrasts in water chemistry. For example, low concentrations of nitrate in riparian-zone groundwater in a small headwater catchment may reflect originally low nitrate concentrations in a regional groundwater flow system (Hill, 1990; Puckett et al., 2002).

Even within a local groundwater flow system in small, undisturbed headwater watersheds, groundwater flow paths can be complex and differences in groundwater residence time among flow paths can be responsible for variations in the concentration of nitrate in streams during periods of base flow. Burns et al. (1998) found that the source of nitrate in two streams in the Catskill Mountains of New York, USA, during base flow was groundwater derived from two sources; a shallow-flow system within the till and soil and a deep flow system within bedrock fractures and bedding planes that discharges as perennial springs. In the shallow-flow system, as biological activity increases during the growing season, nitrate concentrations can decline to near zero, whereas in the deep flow system, water moves below the root zone before entering the stream channel or discharging at the surface at a spring and thus maintains nitrate concentrations of ~20 μmol/L throughout the growing season.

5.2. Variation in nitrate attenuation capacities of riparian zones due to differences in hydrogeologic properties

Another cause of variation in nitrate attenuation in groundwater-traversing riparian zones is spatial variation in hydrogeologic properties within and among riparian zones (Warwick and Hill, 1988; Vought et al., 1994; Hill, 1996; Burt et al., 1999; Rosenblatt et al., 2001; Gold et al., 2001; Wigington et al., 2003; Vidon and Hill, 2004).

Hill (1996) observed that riparian zones that effectively remove nitrate have similar hydrogeologic settings, with shallow subsurface flow caused by permeable surface soils and sediments that are underlain at a depth of 1–4 m by an impermeable layer. In this setting, small amounts of groundwater follow shallow, horizontal flow paths that increase water residence time and contact with vegetation roots and organic-rich riparian soils. Riparian zones have less effect on nitrate transport where groundwater has little interaction with vegetation and sediments because flow occurs mainly across the surface or at depth. If shallow aquicludes are absent in riparian zones, the thicker surficial aquifer allows groundwater to follow deeper, longer flow paths bypassing riparian vegetation and soils (Warwick and Hill, 1988; Vought et al., 1994; Mayer et al., 2005).

Thus on a floodplain permeable alluvium favors subsurface flow, providing opportunity for both denitrification and uptake (Burt et al., 1999). Impermeable alluvium tends to deflect influent groundwater through aquifers below the floodplain or across the floodplain surface; in either case, the buffering capacity of the floodplain is greatly reduced.

Rosenblatt et al. (2001) and Gold et al. (2001) found that in glaciated watersheds in Rhode Island (Figs. 2 and 3) sites with hydric soils (Fig. 2A) had groundwater nitrate removal rates greater than 80%, whereas sites with nonhydric soils (Fig. 2B), which have steeper slopes and a greater depth to the water table had nitrate removal rates less than 30%. Riparian zones with high groundwater nitrate-removal capacity had both >10 m width of hydric soil and an absence of groundwater seeps causing a slow rate of groundwater flow and leads to lengthy residence times in biologically active soils with high nitrate-transformation rates. In contrast nitrate removal was restricted where there was minimal hydric soil width or rapid flow across the riparian zone occurred due to the presence of seeps, where groundwater emerges onto the ground surface and bypasses the biologically active zone of riparian soils (Fig. 3).

Baker et al. (2001) found that land use/land cover (LU/LC) data were of limited value compared to hydrologic conditions for explaining nutrient exports because, although LU/LC maps identify location and areal extent of wetlands, they assume that all wetlands have the same magnitude and direction of influence on nutrient export.

Landscape hydrogeologic characteristics (upland aquifer size, riparian-sediment lithology, and topography) also influence groundwater nitrate removal. A study of stream riparian sites on glacial till and outwash landscapes in southern Ontario, Canada showed a mean nitrate-removal efficiency of >90% for seven of eight sites (Vidon and Hill, 2004). This removal occurred within the first 15 m of the riparian zone at sites with loamy sand and sandy loam soils overlying a shallow confining layer at 1–2 m. However, at sites with more conductive sand and cobble sediments the width required for 90% nitrate removal ranged from >25 m to a maximum of 176 m at a site with a confining layer of 6 m.

The greater distance required for nitrate attenuation at riparian sites with sand and gravel was partly related to hydraulic conductivity. In highly permeable coarse sediments, shorter residence times of groundwater in contact with aquifer sediments may restrict the development of anaerobic conditions and decrease the amount of nitrate removed. Also, very coarse grained sediments frequently contain only small amounts of organic matter, which limits denitrification.

Although nitrate attenuation in groundwater occurs in riparian zones, the degree to which this attenuation affects stream con-

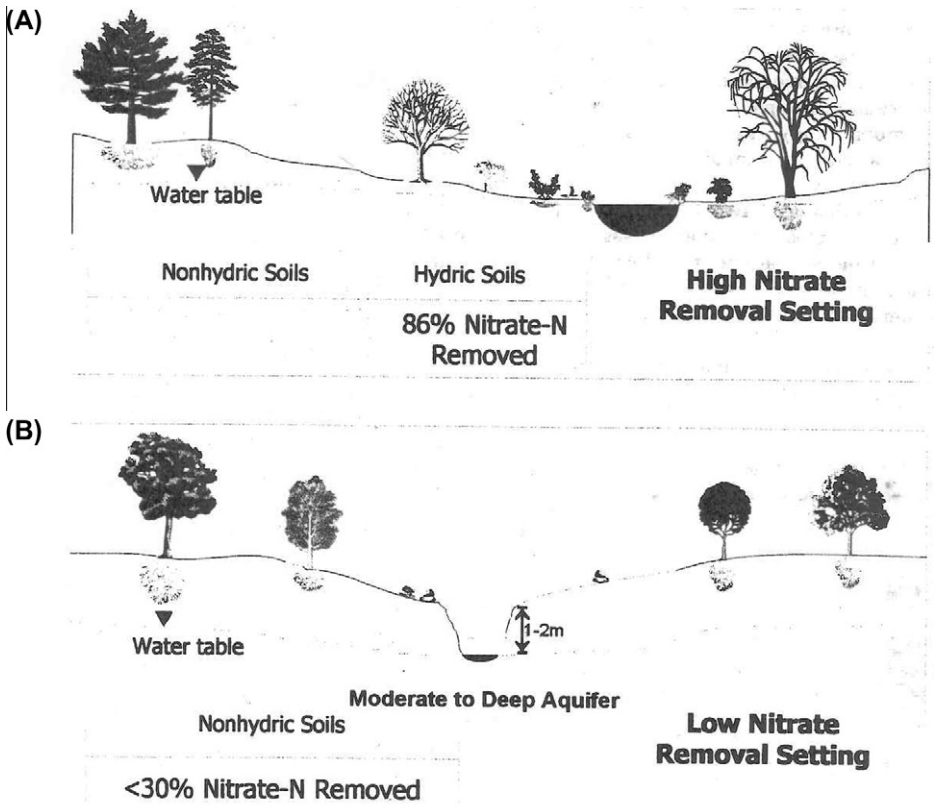

Fig. 2. Examples of high and low nitrate attenuation capacities of riparian zones. In sites with hydric soils (A), ground water nitrate-N removal greater than 80% was noted. In contrast, in sites with steeper slopes and greater depth to water table (B), nonhydric soils occurred and ground water nitrate-N removal was less than 30%. (From Gold et al., 2001. Reprinted with permission from Wiley-Blackwell Publishing.)

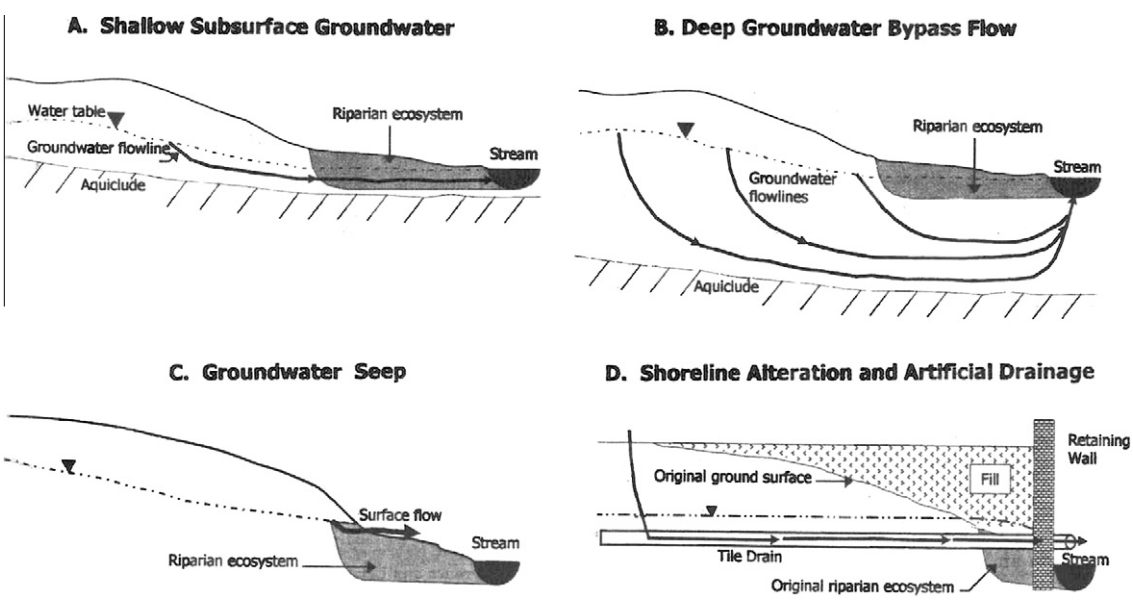

Fig. 3. Other examples of high and low nitrate attenuation capacities of riparian zones. Ground water flow paths through riparian areas can control the delivery of nitrate-enriched ground water to streams. (A) Substantial interaction of ground water with biologically active zone in shallow aquifers. (B) Direct upwelling to streams in deep aquifers. (C) Bypass flow due to surface seeps. (D) Bypass flow due to dilling and articifical drainage. (From Gold et al., 2001. Reprinted with permission from Wiley-Blackwell Publishing.)

centrations and loads has to be assessed on a watershed scale (Wigington et al., 2003; Vidon and Hill, 2004). A riparian zone may have a high nitrate-removal efficiency based on the decline in concentration of nitrate, but if nitrate fluxes to the stream are very small stream concentrations and loads will be minimally affected. Conversely, some riparian zones may have a lower capacity to reduce nitrate concentrations but receive high loads of nitrate throughout the year. When considered at the watershed scale, these

riparian zones with a lower nitrate-removal capacity may actually exert a greater influence on stream concentrations and loads.

5.3. Effect of vegetation on the nitrate attenuation capacities of riparian zones

Reports of the differences in the ability of different types of vegetation to reduce nitrate concentrations in groundwater in the riparian zone have been contradictory, but overall the differences are small. Reports of higher rates of denitrification under pastures than in cropped soils (Clément et al., 2002; Weier et al., 1993; Lensi et al., 1995) were contradicted by Bijay-Singh et al. (1989). Clément et al. (2002) found no significant difference in actual rates of denitrification among three vegetation types (forest, understorey vegetation, and grass), because each vegetation type provides enough organic carbon for the denitrifying bacteria. Topography of the stream valley, rather than vegetation type, was regarded as the controlling factor on denitrification in the riparian zone. Studies by Martin et al. (1999) on woody and grassy vegetation in southern Ontario, Canada and by Sabater et al. (2003) on a range of riparian zones in seven European countries demonstrated that vegetation type was not a dominant factor in the attenuation of nitrate or dissolved inorganic nitrogen.

In central North America Lyons et al. (2000) found that wooded areas are generally better than grassy areas in removing nitrate from groundwater, because the deeper root systems of trees and shrubs allow them to take up nitrogen from a greater volume of subsurface water. However, several studies cited by Lyons et al. (2000) found the reverse; grass was found to remove more nitrogen than woody vegetation.

Mayer et al. (2005) summarized many studies of nitrate attenuation in riparian zones and found that nitrogen-removal effectiveness was significantly lower in grass riparian zones relative to forest, forested wetland, and wetland and that forests were slightly, but significantly, more effective than the other vegetation types.

6. Attenuation of nitrate in the stream channel

Any nitrate that is not removed in the riparian zone and enters the stream channel can be attenuated by various abiotic and biotic processes occurring mainly on sediments and biofilms covering submerged surfaces within the stream channel (Peterson et al., 2001; Kemp and Dodds, 2002). Abiotic processes include passive hydrologic storage in pools, side channels, and subsurface interstices (pore waters), and dilution by groundwater (Triska et al., 1989a). Biotic processes include uptake by stream organisms and transformation by denitrification. Passive hydrologic storage, although temporary, can play an important role in nitrogen cycling in streams as its longer residence time enhances the possibility of subsequent biotic uptake or transformation (Triska et al., 1989a,b; Wondzell and Swanson, 1996a,b).

Many studies have investigated the cycling of nitrogen in the hyporheic zone (Triska et al., 1989a,b, 1993; Wondzell and Swanson, 1996a,b; McMahon and Böhlke, 1996; Holmes et al., 1996; Alexander et al., 2000; Martin et al., 2001; Peterson et al., 2001; Kemp and Dodds, 2002; Hall and Tank, 2003; Royer et al., 2004) (Fig. 4). Results have shown that in-stream attenuation of nitrate is most efficient in small headwater streams during low flows, is least efficient at high flows in streams of all sizes, and is practically negligible at all flows in large streams, such as the lower reach of the Mississippi River. The effectiveness of nitrate attenuation within the hyporheic zone decreases at high flows because increasing discharge dramatically decreases the absolute and relative amount of hydraulic retention (decreases the size of the hyporheic zone) and thus minimizes the contribution of interstitial processes to nitrogen retention (Hill, 1988; Valett et al., 1996).

However, significant nitrogen uptake in the hyporheic zone has not been measured in all studies. In a fourth-order mountain stream in Oregon, USA the ability of the stream to retain nitrate was minimal in the fall, especially during early fall storms, because periphyton uptake was low due to reduced rates of primary production, and because the increase in water velocity and stream discharge during storms resulted in shorter residence times within the stream channel and higher ratios of water volume to wetted perimeter (Wondzell and Swanson, 1996a,b).

Hill and Lymburner (1998) measured minor nitrogen retention in the hyporheic zone in two streams near Toronto, Canada. Little retention of nitrate occurred because the hyporheic zone was spatially restricted by large groundwater flows in coarse gravels with high hydraulic conductivities.

Given that most work on the hyporheic zone has been conducted at the level of a stream reach (tens to hundreds of meters), it is logical to ask about the importance of hyporheic processes in nitrate attenuation at other spatial scales. Stanford and Ward

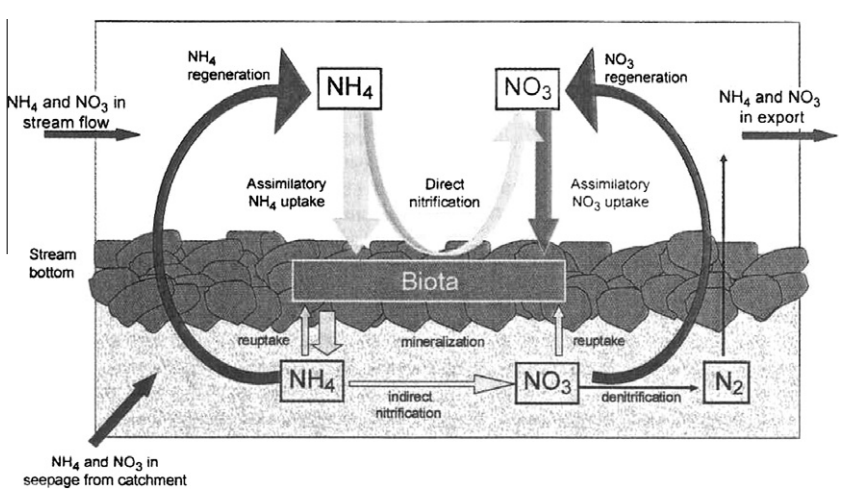

Fig. 4. Conceptual model of dissolved inorganic nitrogen dynamics in headwater stream ecosystems. NH_4 and NO_3 enter the stream reach via stream flow and lateral seepage. NH_4 removal is due to uptake by primary producers, bacteria, and fungi plus direct nitrification. Indirect nitrification is the conversion of NH_4 mineralized from organic matter to NO_3. NO_3 removal from the water is primarily via assimilation by biota and denitrification on the channel bottom. Regeneration is the release of NH_4 and NO_3 from the stream bottom back to the water column and is the net result of several interacting processes, including mineralization, indirect nitrification, denitrification, and reuptake by organisms. NO_3 and NH_4 remaining in the water are exported downstream. (From Peterson et al., 2001. Reprinted with permission from AAAS.)

(1993) hypothesized the existence of a hyporheic corridor from the headwaters to the mouth of alluvial rivers such as the Flathead River in Montana, USA. The expansive floodplains of such rivers are characterized by high volume hyporheic flow because saturated alluvium occurs to some extent beneath and lateral to the active channel from headwaters to river mouth. Longitudinal linkages will vary with the floodplain size, because the size of the hyporheic zone is determined by porosity and relative volume (head) of water recharging the groundwater zone from the channel, or the channel from the aquifer. Thus, the existence of hyporheic zones in larger rivers in certain geomorphic settings indicates that nitrate attenuation by abiotic and biotic processes in the stream channel is possible.

That nitrate attenuation can occur within the hyporheic zone over long distances was demonstrated by McMahon and Böhlke (1996) who showed that denitrification and mixing with river water in the floodplain and streambed sediments substantially reduced groundwater nitrate concentrations between recharge and discharge areas along a 7.5-km segment of the South Platte River in Colorado, USA.

6.1. Denitrification in the stream channel

Studies of denitrification in stream channels have shown that denitrification within stream sediments removes only a small amount of nitrate in the water column, usually less than 5% of nitrogen exports (Holmes et al., 1996; Martin et al., 2001; Kemp and Dodds, 2002; Bechtold et al., 2003; Royer et al., 2004; Inwood et al., 2005). A consistent finding of these studies is that denitrification rates increase as nitrate concentration increases, but the increase is negligible relative to the increase in nitrate concentration. As a result, denitrification cannot increase to compensate for the increased nitrogen loading.

The seasonal variation of in-stream denitrification has only a small effect on in-stream nitrate concentrations (Royer et al., 2004). During spring, increases in discharge lead to increases in both nitrate concentrations and water depth, which reduce the ability of denitrification in the streambed to affect nitrate load. During late summer, the streambed is effective at removing nitrate from the water column but discharge and nitrate concentrations are low. As a result, annually most nitrate is exported downstream rather than denitrified.

Alexander et al. (2000) and Panno et al. (2006) showed that a rapid decline in denitrification occurs with increasing channel size as in-stream loss processes become progressively less effective with increases in channel depth, because channel depth is a measure of the volume of stream water available for processing by a unit area of benthic sediment. Thus, nitrogen removal by denitrification and settling decreases in deeper channels where less contact and exchange of stream waters occurs with the benthic sediment.

7. Research needs

Undisturbed headwater watersheds are very retentive of nitrogen and based on the results of this review, summarized in Table 1, we propose that the causes of the nitrate retention are primarily processes occurring in the riparian zone. Furthermore, the response of streams to changes in non-point source nitrate loads is a function of the nitrate attenuation capacity of the riparian zone. This leads us to conclude that it is possible to use the nitrate attenuation capacities of riparian zones in undisturbed first- and possibility second-order headwater watersheds in areas such as the Rocky Mountains of Colorado to (1) estimate seasonal variations in nitrate concentrations, (2) monitor long-term trends in-stream nitrate concentrations, and (3) predict the response of watersheds to changes in atmospheric deposition of nitrate by classifying and mapping the nitrate attenuation capacity of riparian zones.

We suggest the following procedure to develop the capability for this kind of regional stream nitrate chemistry analysis:

(1) Use topographic, soils, and bedrock maps as an initial screening to classify riparian zones according to their nitrate attenuation capacity. Four suggested classifications are given in Table 2.
(2) Select several watersheds throughout the region of interest that represent the variety of nitrate attenuation capacities of riparian zones in the region.
(3) Sample these watersheds once during a high-flow period, such as during snowmelt, and once during a summer/fall base flow period, which will bracket the seasonal differences in nitrate concentration.

Differences in nitrate concentration among the riparian-zone classifications should be greater than the seasonal differences

Table 1
Summary of nitrogen attenuation processes in the riparian zone and stream channel.

Process or Location	Essential Points
Denitrification	(1) Is the reduction of NO_3^- to N_2 (2) Proceeds by oxidation of soil organic matter under reducing (low oxygen) conditions (3) Rate is fastest in fine-grained sediments and in the upper soil layer, in both cases because of the high organic carbon content (4) Greatest rates occur at the upslope edge of the riparian zone, where high concentrations of nitrate in groundwater occur (5) Minerals, such as pyrite, can also reduce nitrate but it is likely to be a relatively minor influence relative to reduction by organic matter
Riparian zone	(1) Can be a source of nitrate due to the flushing effect during rainstorms and snowmelt (2) However, nitrate concentrations are generally attenuated due to the processes of denitrification, uptake by vegetation, and immobilization by microorganisms (3) The effectiveness of nitrate attenuation varies according to the hydrogeological conditions. Shallow subsurface flow and long residence times in permeable soil/sediments above an impermeable layer allow maximum interaction with soil organic matter and greatest nitrate removal. Rapid shallow groundwater flow through coarse, highly permeable sediments, or flow through soil/sediments with low organic matter content, or deep groundwater flow, or flow across the surface allows relatively little nitrate attenuation (4) Differences in the nitrate attenuation capacity of different types of riparian vegetation are small (5) Nitrate flux as well as nitrate-removal efficiency need to be taken into account
Stream channel	(1) Nitrate removal in the stream channel is a relatively minor process that occurs mostly in the hyporheic zone, where streamwater flows through its bed and mixes with groundwater (2) Nitrate removal is most efficient in small streams at low flows due to the longer residence times (3) In agricultural watersheds, denitrification in the stream channel will increase in response to increases in nitrate loading but the increase in denitrification is negligible relative to the increase in nitrate concentration

Table 2
Examples of the relative differences in the nitrate attenuation capacity of riparian zones.

Riparian zone topography	Riparian zone hydrology	Relative nitrate attenuation capacity	
		High flow	Low flow
Wide or glaciated U-shaped valley	Shallow impermeable layer (1–4 m) allowing most groundwater to flow through soil containing organic matter; groundwater has a relatively long residence time (Figs. 2a and 3a)	Moderate	High
Wide or glaciated U-shaped valley	Impermeable layer present at depth allowing for a moderate to deep aquifer to develop in which most groundwater flow bypasses the soil layers containing organic matter (Figs. 2b and 3b)	Moderate to low	Low
Narrow V-shaped valley	Most likely riparian zones of this type will possess limited soil development, relatively small amounts of soil organic matter, and relatively short groundwater residence time	Low to none	Low to none
Wide or glaciated U-shaped valley or V-shaped valley	Shallow impermeable layer leading to saturation most of the year causing groundwater to discharge as springs flowing across the riparian zone (Fig. 3c)	Low to none	Moderate to low

within a given riparian-zone classification scheme. Thus, the measured concentrations of nitrate should cluster into groups for each type of riparian zone. If this type of clustering occurs, any stream that was not sampled can be assumed to have similar seasonal variations and similar long-term trends in nitrate concentrations, and respond in a similar fashion to increases in atmospheric deposition of nitrate as other streams in a given riparian-zone classification scheme.

In order to assess the sensitivity of 2nd order and larger undisturbed watersheds to increases in atmospheric deposition of nitrate, it will also be necessary to determine how the relative importance of the following sources of nitrate change as watersheds increase in size and flow (base flow as opposed to snowmelt runoff, for example):

- Inputs upstream from the reach (water flowing into the reach above the upstream boundary of the reach).
- Tributary inflow.
- Water derived from the riparian zone (groundwater and storm and snowmelt runoff).
- Groundwater from outside the riparian zone (intermediate or regional sources).
- In-stream and hyporheic processes.

In agricultural watersheds we propose a general scheme for modification of the location of fertilizer application so that the natural attenuation capacity of riparian zones can reduce nitrate loads to streams draining these watersheds. We suggest that nitrate attenuation strategies be focused mostly in riparian zones in 1st order streams. We make this assertion for the following reasons:

- Small streams (10 m in width or less) often make up to 85% of the total stream length within a watershed and collect most of the water and dissolved nutrients, including nitrogen, from the adjacent terrestrial ecosystem (Peterson et al., 2001; Alexander et al., 2007).
- In-stream nitrate-attenuation processes alone are not sufficient to reduce nitrate loads in streams draining agricultural watersheds. Our review has shown that nitrate attenuation in agricultural watersheds occurs primarily in stream riparian zones.
- Groundwater flow will most likely be from a local source in smaller watersheds, i.e. it discharges into the stream from the riparian zone. Therefore, if the riparian zone can effectively attenuate nitrate in groundwater, it will reduce nitrate loads to the stream. Also, in-stream attenuation of nitrate is most effective in small streams, especially under baseflow conditions. Thus, the combination of in-stream and riparian zone attenuation processes operate at maximum efficiency in watersheds this size.

At a minimum we propose that fertilizer application be disallowed in areas within any riparian zone that produce runoff during rain and snowmelt, because overland flow and subsurface runoff from the riparian zone have a major effect on stream chemistry in watersheds this size. Also the effectiveness of in-stream nitrate attenuation in the riparian zone decreases during high flows. One approach would be to identify and map runoff generating areas in riparian zones using a terrain-based hydrologic model such as TOPMODEL (http://smig.usgs.gov/SMIC/model_pages/topmodel.html) which utilizes digital terrain and elevation data to compute flow direction and accumulation across a landscape.

To reduce base flow loads of nitrate it is important to reduce total discharge of nitrate in groundwater, not just nitrate concentration. Therefore, we propose the following. Reaches of riparian zones through which large groundwater nitrate fluxes are discharging into the stream must be identified by collecting water samples and measuring streamflow during a period of low flow such as late summer or early fall. Instantaneous nitrate loads can be calculated for each reach and those reaches with the highest nitrate loading can be targeted for modification of fertilizer application. In such areas fertilizer application should be begin at some distance from the stream/riparian zone interface (in addition to keeping the runoff generating areas free of fertilizer) to allow for complete or nearly complete nitrate attenuation within the riparian zone. Vidon and Hill (2004) and Mayer et al. (2005) give the distances required for effective nitrate removal in a variety of hydrogeological environments.

As in undisturbed headwater watersheds it is necessary to understand how, in 2nd order and larger agricultural watersheds, the relative importance of the flux of nitrate emanating from different sources changes as watersheds increase in size and flow. In 1st order watersheds the riparian zone is the major factor in the delivery and attenuation of nitrate to streams but as watersheds increase in size, the importance of the riparian zone in controlling nitrate loads in streams will decrease. As channel size increases, along any given stretch of river, the input of groundwater following a deep flowpath that bypasses the riparian zone and water flowing into the reach from upstream become more important than water traversing the riparian zone and in-stream processes in controlling stream nitrate loads. The location in any watershed where the influence of riparian zone processes in controlling stream nitrate loads decreases needs to be identified.

Thus, research is needed on the natural attenuation capacity of riparian zones in order to identify (1) the location in a stream/river at which riparian zone processes cease to exert a significant influence on stream nitrate concentrations in both undisturbed and agricultural watersheds, (2) the amount of land that needs to be taken out of production in 1st order agricultural watersheds to reduce stream nitrate loads to a given level, and (3) whether or not land in 2nd order and larger agricultural watersheds also need to be taken out of production to reduce stream nitrate loads. The four scenarios presented in Table 2 for undisturbed watersheds are simplistic and do not describe all of the possible combinations of riparian zone topography and hydrology, but by understanding the

various potential nitrate attenuation capacities of riparian zones in a given region, it should be possible to make the three predictions described above.

References

Abdul, A.S., Gillham, R.W., 1989. Field studies of the effects of the capillary fringe on streamflow generation. J. Hydrol. 112, 1–18.

Alexander, R.B., Smith, R.A., Schwarz, G.E., 2000. Effect of channel size on the delivery of nitrogen to the Gulf of Mexico. Nature 403, 758–761.

Alexander, R.B., Boyer, E.W., Smith, R.A., Schwarz, G.E., Moore, R.B., 2007. The role of headwater streams in downstream water quality. JAWRA 43 (1), 41–59.

Baker, M.E., Wiley, M.J., Seelbach, P.W., 2001. GIS-based hydrologic modeling of riparian areas: implications for stream water quality. J. Am. Water Resour. Assoc. 37 (6), 1615–1628.

Bechtold, J.S., Edwards, R.T., Naiman, R.J., 2003. Biotic versus hydrologic control over seasonal nitrate leaching in a floodplain forest. Biogeochemistry 63, 53–72.

Bijay-Singh, J.C., Ryden, J.C., Whitehead, D.C., 1989. Denitrification potential and actual rates of denitrification in soils under long term grassland and arable cropping. Soil Biol. Biochem. 21, 897–901.

Brooks, P.D., Williams, M.W., Schmidt, S.K., 1996. Microbial activity under alpine snowpacks, Niwot Ridge, Colorado. Biogeochemistry 32, 93–113.

Brooks, P.D., Williams, M.W., Schmidt, S.K., 1998. Inorganic nitrogen and microbial biomass dynamics before and during spring snowmelt. Biogeochemistry 43, 1–15.

Burns, D.A., Murdoch, P.S., Lawrence, G.B., 1998. Effect of groundwater springs on nitrate concentrations during summer in Catskill Mountain streams. Water Resour. Res. 34 (8), 1987–1996.

Burt, T.P., Matchett, L.S., Goulding, W.T., Webster, C.P., Haycock, N.E., 1999. Denitrification in riparian buffer zones: the role of floodplain hydrology. Hydrol. Process. 13, 1451–1463.

Campbell, D.H., Baron, J.S., Tonnessen, K.A., Brooks, P.D., Schuster, P.F., 2000. Controls on nitrogen flux in alpine/subalpine watersheds of Colorado. Water Resour. Res. 36 (1), 37–47.

Clément, J.C., Pinay, G., Marmonier, P., 2002. Seasonal dynamics of denitrification along topohydrosequences in three different riparian wetlands. J. Environ. Qual. 31, 1025–1037.

Coats, R.N., Goldman, C.R., 2001. Patterns of nitrogen transport in streams of the Lake Tahoe basin, California-Nevada. Water Resour. Res. 37 (2), 405–415.

Cooper, A.B., 1990. Nitrate depletion in the riparian zone and stream channel of a small headwater catchment. Hydrobiologia 202, 13–26.

Correll, D.L., Jordan, T.E., Weller, D.E., 1999. Transport of nitrogen and phosphorus from Rhode River watersheds during storm events. Water Resour. Res. 35 (8), 2513–2521.

Creed, I.F., Band, L.E., 1998. Export of nitrogen from catchments within a temperate forest: evidence for a unifying mechanism regulated by variable source area dynamics. Water Resour. Res. 34 (11), 3105–3120.

Creed, I.F., Band, L.E., Foster, N.W., Morrison, I.K., Nicolson, J.A., Semkin, R.S., Jeffries, D.S., 1996. Regulation of nitrate-N release from temperate forests: a test of the N flushing hypothesis. Water Resour. Res. 32 (11), 3337–3354.

Denning, A.S., Baron, J., Mast, M.A., Arthur, M., 1991. Hydrologic pathways and chemical composition of runoff during snowmelt in Loch Vale watershed, Rocky Mountain National Park, Colorado, USA. Water Air Soil Pollut. 59, 107–123.

Devito, K.J., Fitzgerald, D., Hill, A.R., Aravena, R., 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. J. Environ. Qual. 29, 1075–1084.

Dunne, T., Black, R.D., 1970a. An experimental investigation of runoff production in permeable soils. Water Resour. Res. 6 (2), 478–490.

Dunne, T., Black, R.D., 1970b. Partial area contributions to storm runoff in a small New England watershed. Water Resour. Res. 6 (5), 1296–1311.

Dunne, T., Moore, T.R., Taylor, C.H., 1975. Recognition and prediction of runoff-producing zones in humid regions. Bull. Hydrol. Sci., 305–327.

Engman, E.T., 1974. Partial area hydrology and its application to water resources. Water Resour. Bull. 10 (3), 512–521.

Freeze, R.A., 1972a. Role of subsurface flow in generating surface runoff 1. Base flow contributions to channel flow. Water Resour. Res. 8 (3), 609–623.

Freeze, R.A., 1972b. Role of subsurface flow in generating surface runoff 2. Upstream source areas. Water Resour. Res. 8 (5), 1272–1283.

Freeze, R.A., Cherry, J.A., 1979. Groundwater. Prentice-Hall, Inc., Englewood Cliffs. 604 p.

Gold, A.J., Groffman, P.M., Addy, K., Kellogg, D.Q., Stolt, M., Rosenblatt, A.E., 2001. Landscape attributes as controls on groundwater nitrate removal capacity of riparian zones. J. Am. Water Resour. Assoc. 37 (6), 1457–1464.

Grimaldi, C., Viaud, V., Massa, F., Carteaux, L., Derosch, S., Regeard, A., Fauvel, Y., Gilliet, N., Rouault, F., 2004. Stream nitrate variations explained by ground water head fluctuations in a pyrite-bearing aquifer. J. Environ. Qual. 33, 994–1001.

Groffman, P.M., Zak, D.R., Christensen, S., Mosier, A., Tiedje, J.M., 1993. Early spring nitrogen dynamics in a temperate forest landscape. Ecology 74 (5), 1579–1585.

Hall Jr., R.O., Tank, J.L., 2003. Ecosystem metabolism controls nitrogen uptake in streams in Grnad teton Natioanl Park, Wyoming. Limnol. Oceanogr. 48 (3), 1120–1128.

Hanson, G.C., Groffman, P.M., Gold, A.J., 1994. Denitrification in riparian wetlands receiving high and low groundwater nitrate inputs. J. Environ. Qual. 23, 917–922.

Hedin, L.O., von Fischer, J.C., Ostrom, N.E., Kennedy, B.P., Brown, M.G., Robertson, G.P., 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil–stream interfaces. Ecology 79 (2), 684–703.

Hill, A.R., 1988. Factors influencing nitrate depletion in a rural stream. Hydrobiologia 160, 111–122.

Hill, A.R., 1990. Ground water flow paths in relation to nitrogen chemistry in the near-stream zone. Hydrobiologia 206, 39–52.

Hill, A.R., 1993. Nitrogen dynamics of storm runoff in the riparian zone of a forested watershed. Biogeochemistry 20, 19–44.

Hill, A.R., 1996. Nitrate removal in stream riparian zones. J. Environ. Qual. 25, 743–755.

Hill, A.R., Lymburner, D.J., 1998. Hyporheic zone chemistry and stream–subsurface exchange in two groundwater-fed streams. Can. J. Fish. Aquat. Sci. 55, 495–506.

Hill, A.R., Kemp, W.A., Buttle, J.M., Goodyear, D., 1999. Nitrogen chemistry of subsurface storm runoff on forested Canadian Shield hillslopes. Water Resour. Res. 35 (3), 811–821.

Hill, A.R., Vidon, G.F., Langat, J., 2004. Denitrification potential in relation to lithology in five headwater riparian zones. J. Environ. Qual. 33, 911–919.

Holmes, R.M., Jones, J.B.Jr., Fisher, S.G., Grimm, N.B., 1996. Denitrification in a nitrogen-limited stream ecosystem. Biogeochemistry 33, 125–146.

Inwood, S.E., Tank, J.L., Bernot, M.J., 2005. Patterns of denitrification associated with land use in 9 midwestern headwater streams. J. N. Am. Benthol. Soc. 24 (2), 227–245.

Jacinthe, P.A., Groffman, P.M., Gold, A.J., Mosier, A., 1998. Patchiness in microbial nitrogen transformations in groundwater in a riparian forest. J. Environ. Qual. 27, 156–164.

Johnson, D.W., 1992. Nitrogen retention in forest soils. J. Environ. Qual. 21, 1–12.

Jordan, T.E., Correll, D.L., Weller, D.E., 1993. Nutrient interception by a riparian forest receiving inputs from adjacent cropland. J. Environ. Qual. 22, 467–473.

Kalkhoff, S.J., Barnes, K.K., Becher, K.D., Savoca, M.E., Schnoebelen, D.J., Sadorf, E.M., Porter, S.D., and Sullivan, D.J., 2000. Water Quality in the Eastern Iowa Basins, Iowa and Minnesota, 1996–98. US Geological Survey Circular 1210, 37 p.

Kemp, M.J., Dodds, W.K., 2002. Comparisons of nitrification and denitrification in prairie and agriculturally influenced streams. Ecol. Appl. 12 (4), 998–1009.

Landers, D.H., Simonich, S.L., Jaffe, D.A., Geiser, L.H., Campbell, D.H., Schwindt, A.R., Schreck, C.B., Kent, M.L., Hafner, W.D., Taylor, H.E., Hageman, K.J., Usenko, S., Ackerman, L.K., Schrlau, J.E., Rose, N.L., Blett, T.F., Erway, M.M. 2008. The Fate, Transport, and Ecological Impacts of Airborne Contaminants in Western National Parks (USA). EPA/600/R-07/138. US Environmental Protection Agency, Office of Research and Development, NHEERL, Western Ecology Division, Corvallis, Oregon.

Lensi, R., Clays-Josserand, A., Jocteur-Monrozier, L., 1995. Denitrifyers and denitrifying activity in size fractions of a mollisol under permanent pasture and continuous cultivation. Soil Biol. Biochem. 27, 61–69.

Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S., Johnson, N.M., 1977. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York. 146 p.

Lipson, D.A., Schmidt, S.K., Monson, R.K., 1999. Links between microbial population dynamics and nitrogen availability in an alpine ecosystem. Ecology 80 (5), 1623–1631.

Lowrance, R., Vellidis, G., Hubbard, R.K., 1995. Denitrification in a restored riparian forest wetland. J. Environ. Qual. 24, 808–815.

Lyons, J., Trimble, S.W., Paine, L.K., 2000. Grass versus trees: managing riparian areas to benefit streams of central North America. J. Am. Water Resour. Assoc. 36 (4), 919–930.

Martin, T.L., Kaushik, N.K., Whiteley, H.R., Cook, S., Nduhiu, J.W., 1999. Groundwater nitrate concentrations in the riparian zones of two southern Ontario streams. Can. Water Resour. J. 24 (2), 125–138.

Martin, L.A., Mulholland, P.J., Webster, J.R., Valett, H.M., 2001. Denitrification potential in sediments of headwater streams in the southern Appalachian Mountains, USA. J. N. Am. Benthol. Soc. 20 (4), 505–519.

Mayer, P.M., Reynolds Jr., S.K., Canfield, T.J., McCutchen, M.D., 2005. Riparian Buffer Width, Vegetative Cover, and Nitrogen Removal Effectiveness: A Review of Current Science and Regulations. EPA/600/R-05/118.

McDowell, W.H., Bowden, W.B., Asbury, C.E., 1992. Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: subsurface solute patterns. Biogeochemistry 18, 53–75.

McMahon, P.B., Böhlke, J.K., 1996. Denitrification and mixing in a stream-aquifer system: effects on nitrate loading to surface water. J. Hydrol. 186, 105–128.

Nelson, W.M., Gold, A.J., Groffman, P.M., 1995. Spatial and temporal variation in groundwater nitrate removal in a riparian forest. J. Environ. Qual. 24, 691–699.

Ohrui, K., Mitchell, M.J., 1998. Stream water chemistry in Japanese forested watersheds and its variability on a small regional scale. Water Resour. Res. 34 (6), 1553–1561.

Ostrom, N.E., Hedin, L.O., Fischer, J.C., Robertson, G.P., 2002. Nitrogen transformations and nitrate removal at a soil–stream interface: a stable isotope approach. Ecol. Appl. 12 (4), 1027–1043.

Panno, S.V., Hackley, K.C., Kelly, W.R., Hwang, H.-H., 2006. Isotopic evidence of nitrate sources and denitrification in the Mississippi River, Illinois. J. Environ. Qual. V. 35, 495–504.

Pearce, A.J., Stewart, M.K., Sklash, M.G., 1986. Storm runoff generation in humid headwater catchments 1. Where does the water come from? Water Resour. Res. 22 (8), 1263–1272.

Peterjohn, W.T., Correll, D.L., 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. Ecology 65 (5), 1466–1475.
Peterson, B.J., Wollheim, W.M., Mulholland, P.J., Webster, J.R., Meyer, J.L., Tank, J.L., Marti, E., Bowden, W.B., Valett, M., Hershey, A.E., McDowell, W.H., Dodds, W.K., Hamilton, S.K., Gregory, S., Morrall, D.D., 2001. Control of nitrogen export from watersheds by headwater streams. Science 292, 86–90.
Pinay, G., Decamps, H., 1988. The role of riparian woods in regulating nitrogen fluxes between the alluvial aquifer and surface water: a conceptual model. Regul. River: Res. Manage. 2, 507–516.
Pinay, G., Roques, L., Fabre, A., 1993. Spatial and temporal patterns of denitrification in a riparian forest. J. Appl. Ecol. 30, 581–591.
Pinay, G., Black, V.J., Planty-Tabacchi, A.M., Gumiero, B., Decamps, H., 2000. Geomorphic control of denitrification in large river floodplain soils. Biogeochemistry 50, 163–182.
Pionke, H.B., Hoover, J.R., Schnabel, R.R., Gburek, W.J., Urban, J.B., Rogowski, A.S., 1988. Chemical-hydrologic interactions in the near-stream zone. Water Resour. Res. 24 (7), 1101–1110.
Puckett, L.J., Cowdery, T.K., 2002. Transport and fate of nitrate in a glacial outwash aquifer in relation to ground water age, land use practices, and redox processes. J. Environ. Qual. 31, 782–796.
Puckett, L.J., Cowdery, T.K., McMahon, P.B., Tornes, L.H., Stoner, J.D., 2002. Using chemical, hydrologic, and age dating analysis to delineate redox processes and flow paths in the riparian zone of a glacial outwash aquifer-stream system. Water Resour. Res. 38 (8), 9-1–9-20.
Rosenblatt, A.E., Gold, A.J., Stolt, M.H., Groffman, P.M., Kellogg, D.Q., 2001. Identifying riparian sinks for watershed nitrate using soil surveys. J. Environ. Qual. 30, 1596–1604.
Royer, T.V., Tank, J.L., David, M.B., 2004. Transport and fate of nitrate in headwater agricultural streams in Illinois. J. Environ. Qual. 33, 1296–1304.
Sabater, S., Butturini, A., Clement, J.C., Burt, T., Dowrick, D., Hefting, M., Maître, V., Pinay, G., Postolache, C., Rzepecki, M., Sabater, F., 2003. Nitrogen removal by riparian buffers along a European climatic gradient: patterns and factors of variation. Ecosystems 6, 20–30.
Schnabel, R.R., 1986. Nitrate concentrations in a small stream as affected by chemical and hydrologic interactions in the riparian zone. In: Correll, David L. (Ed.), Watershed Research Perspectives, pp. 263–282.
Schnabel, R.R., Urban, J.B., Gburek, W.J., 1993. Hydrologic controls in nitrate, sulfate, and chloride concentrations. J. Environ. Qual. 22, 589–596.
Sickman, J.O., Leydecker, A., Chang, C.C.Y., Kendall, C., Melack, J.M., Lucero, D.M., Schimel, J., 2003. Mechanisms underlying export of N from high-elevation catchments during seasonal transitions. Biogeochemistry 64, 1–24.
Simmons, R.C., Gold, A.J., Groffman, P.M., 1992. Nitrate dynamics in riparian forests: groundwater studies. J. Environ. Qual. 21, 659–665.
Sklash, M.G., Stewart, M.K., Pearce, A.J., 1986. Storm runoff generation in humid headwater catchments 2. A case study of hillslope and low-order stream response. Water Resour. Res. 22 (8), 1273–1282.
Stanford, J.A., Ward, J.V., 1993. An ecosystem perspective of alluvial rivers: connectivity and the hyporheic corridor. J. N. Am. Benthol. Soc. 12 (1), 48–60.
Stottlemyer, R., Troendle, C.A., 1992. Nutrient concentration patterns in streams draining alpine and subalpine catchments, Fraser Experiemental Forest, Colorado. J. Hydrol. 140, 179–208.
Sueker, J.K., Clow, D.W., Ryan, J.N., Jarrett, R.D., 2001. Effect of basin physical characteristics on solute fluxes in nine alpine/subalpine basins, Colorado, USA. Hydrol. Process. 15, 2749–2769.
Triska, F.J., Kennedy, V.C., Avanzino, R.J., Zellweger, G.W., Bencala, K.E., 1989a. Retention and transport of nutrients in a third-order stream: channel processes. Ecology 70 (6), 1877–1892.
Triska, F.J., Kennedy, V.C., Avanzino, R.J., Zellweger, G.W., Bencala, K.E., 1989b. Retention and transport of nutrients in a third-order stream in northwestern California: hyporheic processes. Ecology 70 (6), 1893–1905.
Triska, F.J., Duff, J.H., Avanzino, R.J., 1993. The role of water exchange between a stream channel and its hyporheic zone in nitrogen cycling at the terrestrial–aquatic interface. Hydrobiologia 251, 167–184.
Valett, H.M., Morrice, J.A., Dahm, C.N., Campana, M.E., 1996. Parent lithology, surface–groundwater exchange, and nitrate retention in headwater streams. Limnol. Oceanogr. 41 (2), 333–345.
Vidon, P.G.F., Hill, A.R., 2004. Landscape controls on nitrate removal in stream riparian zones. Water Resour. Res. 40, W03201.
Vought, L.B.M., Dahl, J., Pedersen, C.L., Lacoursiè, J.O., 1994. Nutrient retention in riparian ecotones. Ambio 23 (6), 342–348.
Warwick, J., Hill, A.R., 1988. Nitrate depletion in the riparian zone of a small woodland stream. Hydrobiologia 157, 231–240.
Weier, K.L., McRae, I.C., Myers, R.J.K., 1993. Denitrification in a clay soil under permanent pasture and annual crop: estimation of potential losses using intact soil cores. Soil Biol. Biochem. 25, 991–997.
Wetzel, R.G., 2001. Limnology – Lake and River Ecosystems. Academic Press, San Francisco. 1006 p.
Wigington, P.J., Griffith, S.M., Field, J.A., Baham, J.E., Horwath, W.R., Owen, J., Davis, J.H., Rain, S.C., Steiner, J.J., 2003. Nitrate removal effectiveness of a riparian buffer along a small agricultural stream in western Oregon. J. Environ. Qual. 32, 162–170.
Williams, M.W., Brooks, P.D., Mosier, A., Tonnessen, K.A., 1996. Mineral nitrogen transformations in and under seasonal snow in a high-elevation catchment in the Rocky Mountains, United States. Water Resour. Res. 32 (10), 3161–3171.
Winter, T.C., Harvey, J.W., Franke, O.L., Alley, W.H., 1998, Ground Water and Surface Water a Single Resource. US Geological Survey Circular 1139, 79 p.
Wondzell, S.M., Swanson, F.J., 1996a. Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream. I: hydrologic processes. J. N. Am. Benthol. Soc. 15 (1), 3–19.
Wondzell, S.M., Swanson, F.J., 1996b. Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream. II: nitrogen cycling. J. N. Am. Benthol. Soc. 15 (1), 20–34.