01 - 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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Abstract
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 under- standing 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, water derived from the riparian zone, (4) groundwater from outside the riparian zone (intermediate or regional sources), and (5) in-stream (hyporheic) processes.

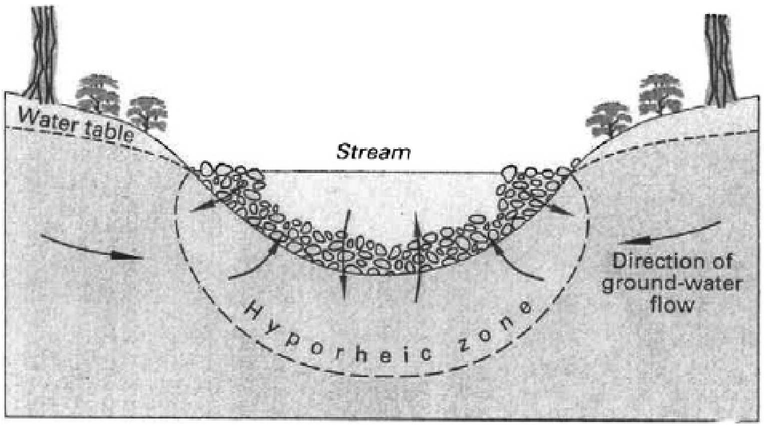
1. INTRODUCTION

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 in- creases 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 water- sheds 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.



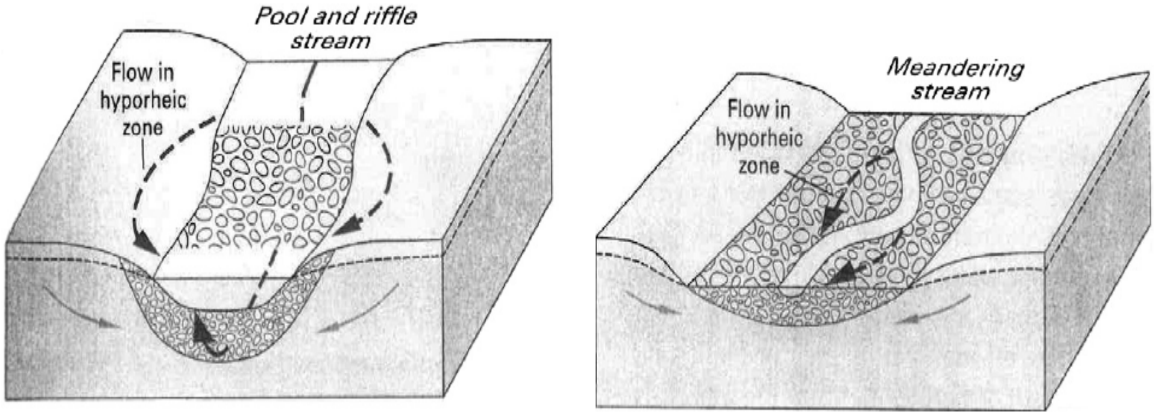


Figure 1: *Examples of stream hyporheic zones (from Winter et al., 1998).*

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 snow-melt 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. 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 N2 gas with concomitant oxidation of organic matter (Wetzel, 2001),

$$5CH_2O + 4NO\text{-}_3 \rightarrow 2N_2 + 4HCO\text{-}_3 + CO_2 + 3H_2O \qquad (1)$$

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 car- bon, 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 sulphur in pyrite can occur in a reaction mediated by the bacterium Thiobacillus denitrificans (Grimaldi et al., 2004):

$$5FeS_2 + 14NO_3- + 4H^+ \rightarrow 7N_2 + SO4_2- + 5Fe_2^+ + 2H_2O \qquad (2)$$

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 15NHþ4 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 favour nitrification, while in later spring the saturation of soils with meltwater and the relatively high levels of nitrate favour denitrification.

The reduction in groundwater nitrate concentrations across riparian zones in agricultural watersheds and low nitrate concentration 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 3m, 28m, and 112m 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 Cats- kill 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 20lmol/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 favours 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.

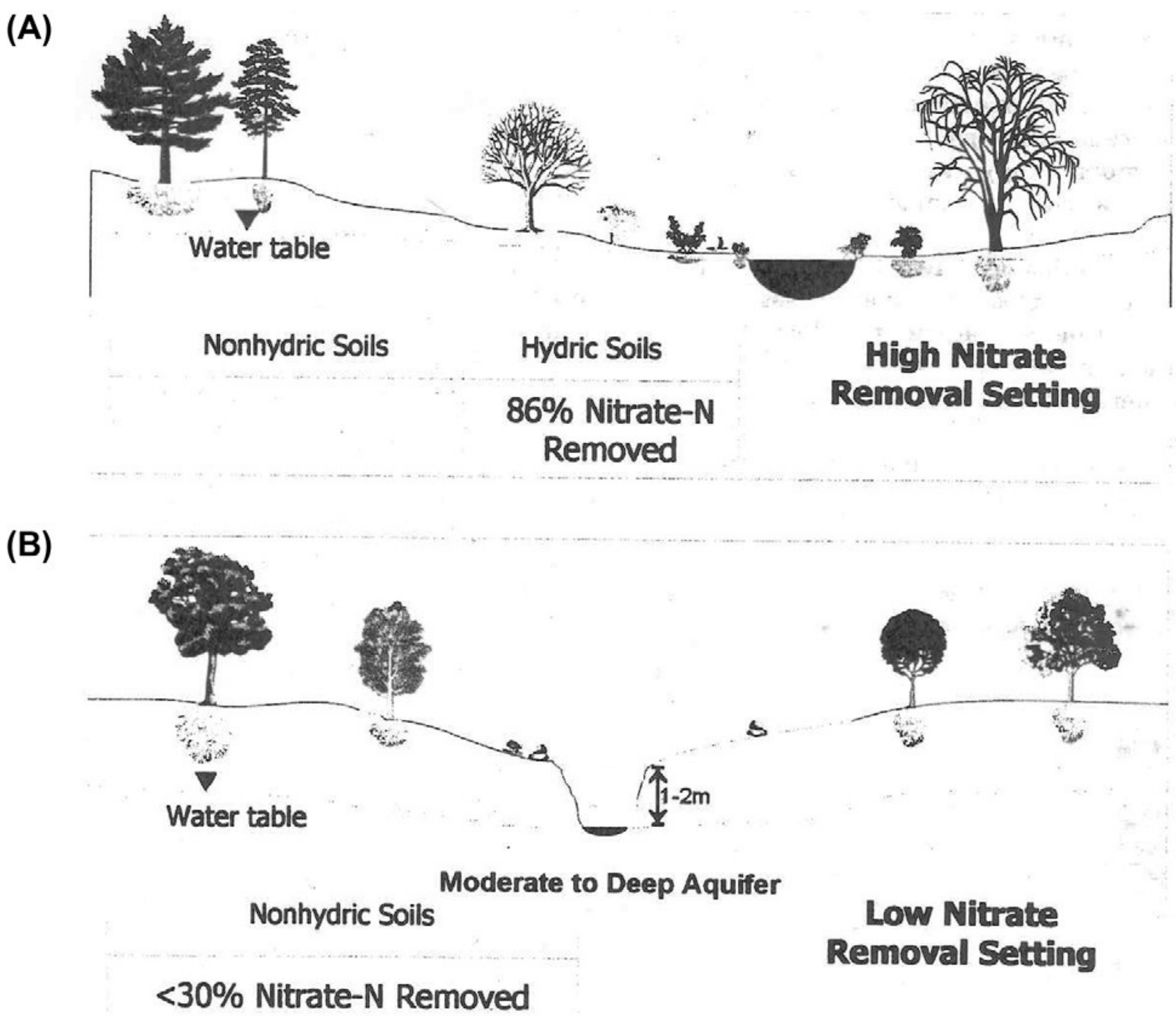


Figure 2: *Examples of high and low nitrate attenuation capacities of riparian zones. In sites with hydric soils (A), ground water nitrate-N removal greater than 80% was noted. In contrast, in sites with steeper slopes and greater depth to water table (B), nonhydric soils occurred and ground water nitrate-N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

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 wet- lands 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.

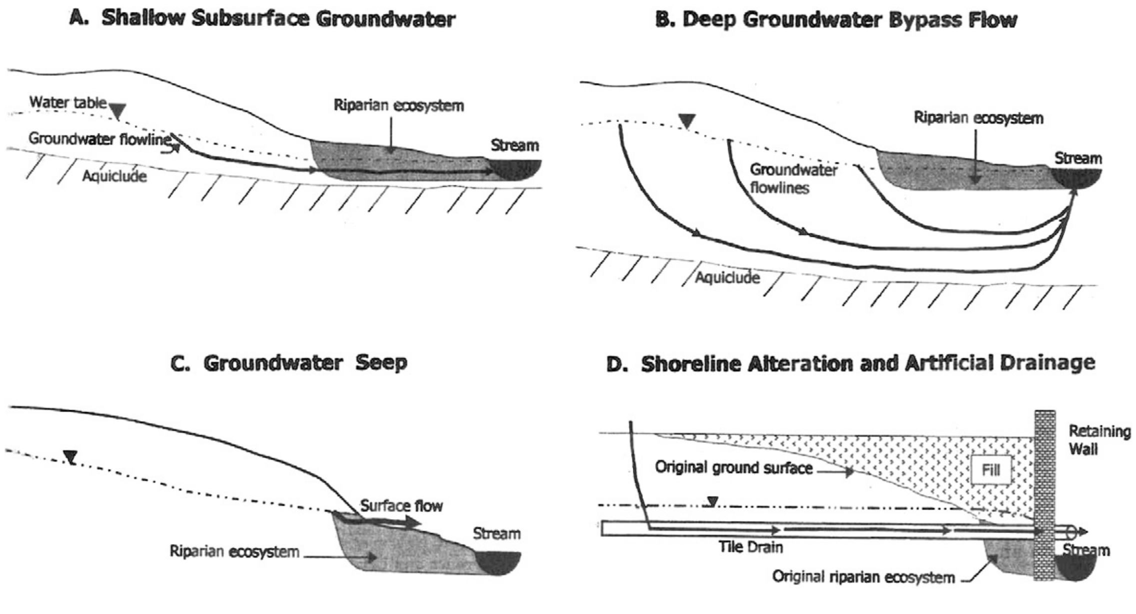


Figure 3: *Other examples of high and low nitrate attenuation capacities of riparian zones. Ground water flow paths through riparian areas can control the delivery of nitrate- enriched ground water to streams. (A) Substantial interaction of ground water with biologically active zone in shallow aquifers.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

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 re- strict 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 concentrations 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 nitro- gen 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.

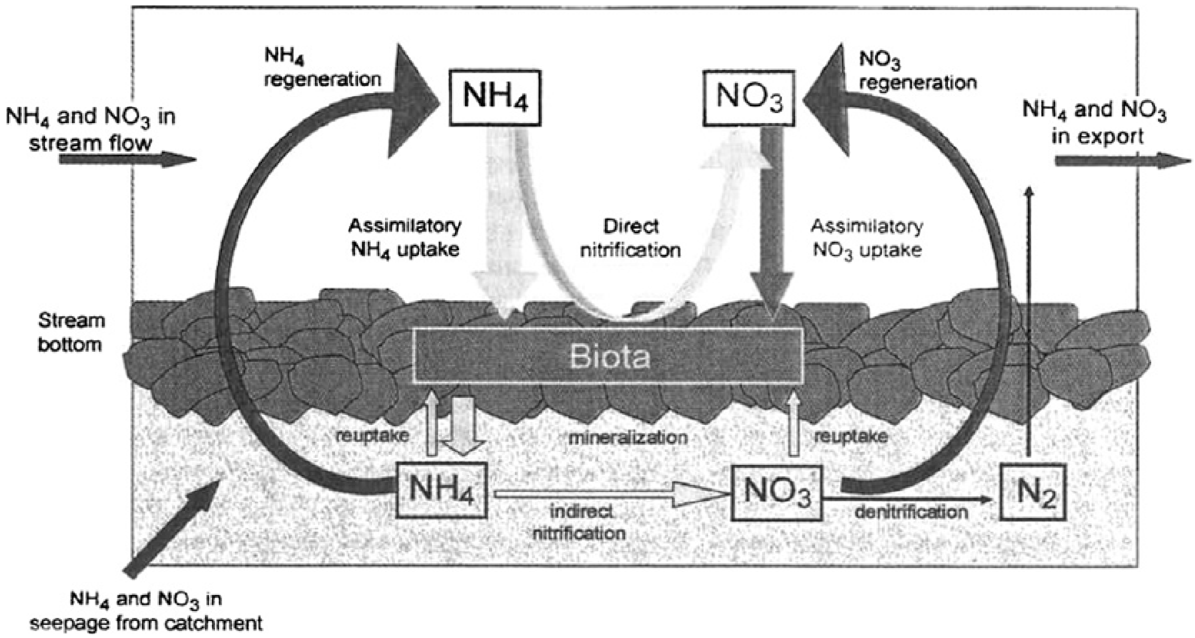


Figure 4: *Conceptual model of dissolved inorganic nitrogen dynamics in headwater stream ecosystems. NH4 and NO3 enter the stream reach via stream flow and lateral seepage. NH4 removal is due to uptake by primary producers, bacteria, and fungi plus direct nitrification. Indirect nitrification is the conversion of NH4 mineralized from organic matter to NO3. NO3 removal from the water is primarily via assimilation by biota and denitrification on the channel bottom. Regeneration is the release of NH4 and NO3 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. NO3 and NH4 remaining in the water are exported downstream. (From Peterson et al., 2001. Reprinted with permission from AAAS.)*

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 (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 nitro- gen 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.

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	6. Can be a source of nitrate due to the flushing effect during rainstorms and snowmelt 7. However, nitrate concentrations are generally attenuated due to the processes of denitrification, uptake by vegetation, and immobilization by microorganisms 8. 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 con- tent, or deep groundwater flow, or flow across the surface allows relatively little nitrate attenuation 9. Differences in the nitrate attenuation capacity of different types of riparian vegetation are small 10. 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

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 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.

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

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 water- sheds. 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 dis- charging 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 water- sheds 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 ta- ken 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.

8. LITERATURE REVIEW UPDATE SUMMARY

Based on the results of our initial literature review we suggest that the natural attenuation capacity of riparian zones is most efficient in areas in which the following conditions are met: (1) the soil contains high levels of organic matter, (2) groundwater is in a local flow system, that is the aquifer is shallow, underlain by at a depth of 1 – 4 m by an impermeable layer, which allows groundwater to come into contact with the upper organic rich soil horizon and the plant rooting zone for most of the year, (3) shallow slopes are present, and (4) little or no groundwater from seeps flows across the surface of the riparian zone. These conditions most likely occur in headwater (1st or possibly 2nd order) watersheds. Also, as stated in our initial literature review small streams (10 m in width or less) often make up to 85% of the total stream length in a watershed and collect most of the water and nitrogen from the adjacent terrestrial ecosystem.

Three major findings of this updated literature review in combination with the result from our initial literature review just described leads us to propose a general approach to maximize the use of riparian buffer zones which will be described subsequently.

This updated literature review has shown that investigations into the width of a riparian buffer zone needed to reduce NO_3- concentrations by a given amount is still a major research topic. Results of these investigations have been somewhat mixed in that some studies report increasing widths of the riparian zone are needed to increase NO_3- removal while other studies report that little or no decrease in NO_3- concentration occurs greater than a certain width, usually 10 - 30 m. One cause of this variation could be that some of these riparian zones are adjacent to higher order streams (≥2nd order) and as such groundwater may be from an intermediate or regional flow system in which most of the groundwater bypasses the riparian zone.

This updated literature review has also shown that riparian zones are now only rarely used as the sole BMP and that the buffering capacity of riparian zones is supplemented by the placement of additional BMPs, such as saturated buffers, denitrification bioreactors and permeable reactive barriers, and artificial wetlands upgradient of the riparian zone.

We have not found any studies that measure NO_3- loads along the length of a stream or river from headwaters to an outlet of a large watershed (≥2nd order). This data can identify the major source or sources of NO_3- from tributaries or along stream reaches between tributaries and would be useful in prioritizing the establishment of riparian buffer zones.

This information leads us to suggest that to optimize the use of riparian buffer zones in any watershed the collection of water quality samples (NO_3- concentration) and the measurement of streamflow should be made from headwaters to the watershed outlet. If such measurements indicate that headwater watersheds are the major source of NO_3- riparian buffer zones only can be established in these areas. If groundwater discharging from stream reaches between tributaries in higher order watersheds (≥ 2nd order) are also contributing significant loads of NO_3-, riparian buffer zones, most likely wider than in the headwaters, should be supplemented with an additional BMP upgradient of the riparian buffer zone.

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10. LITERATURE REVIEW UPDATE

Since the publication of this paper in 2010 a considerable number of papers have been and continued to be published regarding processes occurring in riparian zones that result in the removal of nitrate from runoff derived from agricultural lands. In this updated literature review we selected papers that either discussed topics not included in the original paper or summarized the results of numerous studies. A review of the literature published since 2010 has identified eight major topics that were not discussed in the original paper or have been supplemented by additional studies. These include: (1) a discussion of wetland buffer zones (WBZs) (Pärn et al., 2012) and the effects of harvesting vegetation in wetlands on nitrate removal (Jabłońska et al., 2021), (2) buffer widths needed to reduce nitrate concentrations in agricultural runoff before entering a stream (Sweeney and Newbold, 2014; Valkama et al., 2018; Stutter et al., 2019), (3) enhancement of buffer zone effectiveness through conservation management of agricultural uplands (Vidon et al., 2018; Tomer et al., 2020), (4) models to identify placement of riparian buffer zones (Chandrasoma et al., 2019; Tomer et al., 2020), (5) reducing nitrate leaching from agricultural fields by differences in types of fertilizer and farming techniques (Syswerda et al. 2012), (6) factors affecting rates of denitrification (Uchida et al., 2018; Kreiling et al., 2021), (7) use of $\delta^{15}N\text{-}NO_3$ to qualitatively asses the relative importance of denitrification and plant uptake (Clement et al., 2003) and the use of $\delta^{15}N\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$, and chloride and nitrate concentrations to quantify nitrate removal by denitrification relative to other processes (plant uptake, microbial assimilation, dissimilatory NO_3- reduction to ammonium – DNRA, and anaerobic oxidation (anammox) consuming NO_2- derived from NO_3- or NH_4^+) (Lutz et al., 2020), and (8) managing riparian zones for multiple benefits other than NO3- removal (Sweeney and Newbold, 2014; Vidon et al., 2018; Stutter et al., 2019).

Artificial wetlands or wetland buffer zones (WBZs) are "wetlands located in between the agricultural land and the river that capture nutrient-rich runoff water to reduce loads in surface waters at the water-land interface" (Jabłońska et al., 2021). Jabłońska et al. (2021) state that wetlands retain significantly more nitrogen than rivers and lakes because of lower discharge rates that increase water residence times. An increase in water resident times provide greater opportunities for vegetative uptake and sediment-water contact, which promote retention processes such as denitrification and soil nitrogen accumulation (Jabłońska et al., 2021; Saunders and Kalff, 2001). Increased water residence times in wetlands are due, in part, to the dense stands of aquatic plants in these ecosystems. Retention of N was reported for wetlands below intensively managed agricultural fields in temperate climates by Pärn et al., (2012) who calculated the interquartile range of various nitrogen fluxes from studies indexed by Mander and Mauring (1994) for studies published before 1994 and the ISI Web of Science for the period 1995-2011. They calculated that depending on the amount of rainfall, water use by plants, and soil nitrogen content soil waters in intensive agricultural uplands usually leach between 15 and 70 kg N ha^{-1} $year^{-1}$ with the largest N amounts leaching to groundwater discharge areas. Median surface flow of N from intensive agricultural was calculated as 1.5-12 kg N ha^{-1} $year^{-1}$. The median amount of N discharged to streams from leaching and surface flow combined was reported as 15-75 kg N ha^{-1} $year^{-1}$ from intensively managed catchments with dysfunctional, missing, or non-reported riparian buffers as opposed to 1.5-19 kg N ha^{-1} $year^{-1}$ from extensively managed agricultural fields.

Retention in riparian wetlands was done by comparing the load to these wetlands of 10-270 kg N ha^{-1} $year^{-1}$ with potential extremes up to 6,470 kg N ha^{-1} $year^{-1}$ to the quartile losses that leave these buffers as 1-20 kg N ha^{-1} $year^{-1}$. Median retention ranged between 66 and 89%. Uptake by riparian meadow grasses and herbs normally accumulate 20-70 kg N ha^{-1} $year^{-1}$ while riparian forests take up as much as 30-170 kg N ha^{-1} $year^{-1}$. Retention by wetland plants is generally greatest during the growing season and is low during the period of no growth. Denitrification rates are reported as between 9 and 70 kg N ha^{-1} $year^{-1}$.

Numerous studies that have investigated riparian buffer zone widths needed to reduce NO_3- in groundwater and surface runoff from agricultural lands continues to be published. We present the results of literature reviews by Sweeney and Newbold, (2014); Valkama et al., (2018); and Stutter et al., (2019) who have reviewed a combined total of 92 studies of how NO_3- retention varies as a function of riparian buffer zone width.

Sweeney and Newbold (2014) reviewed 30 studies conducted between 1984 and 2011 to determine the nitrogen removal efficiency of various buffer widths of small streams (≤ 100 km^2 or ~5th order watershed). They developed a relation between subsurface water flux, defined as the subsurface flow into the buffer per unit downstream length of buffer (l/m/day) and buffer width needed for various nitrate removal efficiencies. Subsurface nitrate removal varied inversely with subsurface flow. Median nitrate removal efficiency for sites with a water flux >50 l/m/day was 55% (26-64%) for buffers <40 m wide and 89% (27-99%) for buffers >40 m wide. The relation between nitrate removal efficiency and buffer width when applied to a site with average water flux (125 l/m/day) predicts removal efficiency of 48% for a 30-m buffer, increasing to 90% for a 100-m buffer. Given the wide variation among sites they suggest that effective nitrate removal at the watershed scale probably requires buffers that are at least 30 m wide, and that the likelihood of high removal efficiency increases in buffers wider than 30 m. Sweeney and Newbold (2014) also reviewed two studies of nitrate removal in surface runoff and suggest that a width of 20-30 m should be reasonable effective for removal of nitrate from surface runoff.

Valkama et al. (2018) performed a global weighted meta-analysis on 46 studies conducted between 1980 and 2017. The major findings were that buffer zones reduced NO_3-N by 33% in surface runoff and by 70% in groundwater compared with controls with no buffer zone, but narrow buffer zones (<10m) reduced the NO_3-N and total N concentrations as well as wider buffer zones did, however, there was enormous variation in the data. The main source of variation in the buffer zone capacity to reduce nitrate concentrations in surface runoff and in groundwater was the initial N concentrations discharging from the source of pollution and the capacity increased with increasing N concentrations. For example, with increasing N concentration from 0.1 to 25 mg L^-, the N retention of surface runoff increased from 8 to 45% and of groundwater from 60 to 85%. The main mechanism of N removal in surface runoff is uptake by plants but the N removal efficiency in surface runoff decreased with buffer zone age. Young forest stands, bushes and wet grasslands achieved the most intensive nutrient removal due to intensive uptake by plants as they were in an active growth phase.

Stutter et al. (2019) synthesized 16 new primary studies and review papers to provide the latest insight into riparian management. In contrast to the results present in Valkama et al. (2018), Stutter et al. (2019) present the results of studies by Dal Ferro et al. (2019) and Jaynes and Isenhart (2019) that did support increasing NO_3- reduction effectiveness with buffer zone width. These studies possibly identified minimum sizes, below ~5m where N reduction became negligible compared with input loads. Hènault-Ethier et al. (2019) found no significant difference in the buffering capacity for N. P. or K between 3-m-wide riparian zones planted with willow (Salix spp.) and riparian zones with naturally regenerated herbaceous cover. The buffering ability of the riparian buffer zones was strongly affected by season, with the highest buffering occurring when water entering the zone had the highest nitrate concentrations (immediately after sowing and fertilize application). Hènault-Ethier et al. (2019) concluded that narrow riparian buffer zones (~3m) were insufficient to protect streams from excess nutrients.

A recent concept that has appeared in the literature to enhance the buffering capacity of riparian zones is the coupling of upland and riparian conservation consisting of multiple practices placed in series along water flow paths known as integrated management strategies (Vidon et al., 2018; Stutter et al., 2019; Tomer et al., 2020). Vidon et al. (2018) state that riparian zones are now only rarely used as the sole BMP and these additional practices include stream restoration, subsurface drainage, two-stage ditches, beaver dam analogues, denitrification bioreactors and permeable reactive barriers, artificial wetlands, and short rotation forestry (SRF) crops.

Vidon et al. (2018) state that subsurface drains have been removed in some areas but they continue to be installed in many areas around the world including the US Midwest, where poorly drained soils limit crop yields. Although tile drainage reduce erosion and increase crop yields, the tile drains allow NO_3- rich subsurface flow to bypass riparian zones. One practice that appears to be popular to force water from tile drains to flow directly onto the riparian zone as opposed to below, allowing for N removal to occur, are saturated buffers (Vidon et al., 2018; Chandrasoma et al., 2019; Tomer et al., 2020). According to Tomer et al., 2020 "Saturated buffers comprise a water level control gate and a distribution pipe that are installed within the riparian zone; the gate is used to divert a portion of tile drainage from direct outfall, to be conveyed along the distribution pipe and discharged into riparian soils. Plant species in the riparian buffer should be tolerant of wet soil conditions. Properly designed and implemented, this practice raises the water table in the riparian zone to within 0.3 to 0.6 m (1 to 2ft) of the surface, where soil C is available to effectively facilitate denitrification". Stutter et al. (2019) report the results of a study by Jaynes and Isenhart (2019) that showed that all six sites of their SRBs were effective in removing NO_3 from the tile drainage entering the SRB. Annual N removal effectiveness ranged from 8 to 84%. This corresponds to an average removal rate of 40 mg N m^{-3} d^{-1} (range 4-164 mg N m^{-3} d^{-1}).

Models to locate the placement of saturated buffers in a watershed are described in Chandrasoma et al., (2019) and Tomer et al., (2020). Chandrasoma et al., (2019) used a GIS-based approach using publicly available data to map the placement of saturated buffers along 37,760 km of streams (75,520 km of stream banks) in the Midwest of the United States (states of Illinois, Iowa and Ohio). The modeling showed that 3.85 million ha of drained land has the potential to drain to a saturated buffer resulting in a 5-10% overall tile drainage N load reduction. Tomer et al., (2020) describe the use of the Agricultural Conservation Planning Framework (ACPF) Version 3 ArcGIS toolbox to identify areas where riparian soils are locations for the placement of saturated buffers where riparian soils contain adequate carbon levels and where discharged water is likely to raise the water table.

Other BMPs used upgradient of riparian zones are various types of bioreactors and permeable reactive barriers (Schipper et al., 2010; Addy et al., 2016) and edge of the field wetlands (Kovacic et al., 2000; Díaz et al., 2012). A review of other similar studies is provided in Gold et al. (2013). Figure 2a in Vidon et al. (2019) show that the water quality benefit of these techniques occurs mostly within the wetland or bioreactor. While not placed upgradient of riparian zones, planting of SRF crops (willows and poplars) in the riparian zone is a common practice in the United Kingdom, Germany, Sweden, and the United States (Vidon et al., 2019). The benefit of planting SRF crops is that they can be harvested frequently and immediately processed for commercial use, thus providing an economic benefit to the farmer, and they do not require fertilization, shade out weeds, and provide wildlife habitat (Vidon et al., 2019).

As noted in the study by Pärn et al. (2012) wetland buffer zones can be an effective BMP in reducing nitrate loads to streams. Although plant uptake is an important process in removing nitrate from groundwater nitrogen taken up by plants can be released back after the plant's death at the end of the growing season. A study of the effect of vegetation harvesting and removal in a wetland buffer zone along a small river in Poland revealed that moving and removal of riparian vegetation can result in permanent removal of NO_3- (Jabłońska et al., 2021).

Similar to the use of these various techniques upgradient of the riparian zone to enhance N removal in the riparian zone is the use of different types of fertilizers and farming techniques to reduce nitrate leaching to groundwater from agricultural fields. Syswerda et al. (2012) combined measured nitrate concentrations with modeled soil water drainage to provide estimates of nitrate lost by leaching over 11 years from nine replicated cropped and unmanaged fields in southwest Michigan, USA. The fields include four annual corn–soybean–winter wheat rotations under conventional, no-till, reduced-input, and organic/biologically-based management, two perennial cropping systems that include alfalfa and hybrid poplar trees, and three unmanaged successional communities including an early successional community analogous to a cellulosic biofuel system as well as a mature deciduous forest. The organic, alfalfa, and unmanaged systems received no synthetic, manure, or compost nitrogen. Among annual crops, average nitrate losses differed significantly ($p < 0.05$) and followed the order conventional

(62.3 ± 9.5 kg N ha^{-1} yr^{-1}) > no-till (41.3 ± 3.0) > reduced-input (24.3 ± 0.7) > organic (19.0 ± 0.8) management. Among perennial and unmanaged fields, nitrate loss followed the pattern alfalfa (12.8 ± 1.8 kg N ha^{-1} yr^{-1}) = deciduous forest (11.0 ± 4.2) >> early successional (1.1 ± 0.4) = mid-successional (0.9 ± 0.4) > poplar (<0.01±0.007 kg N ha^{-1} yr^{-1}) systems. Findings suggest that nitrate loss in annual row crops could be significantly mitigated by the adoption of no-till, cover crops, and greater reliance on biologically based inputs, and in biofuel systems by the production of cellulosic rather than grain-based feedstocks.

Studies of processes controlling the rates of denitrification continue to be published and support the findings of the initial literature review that rates of denitrification are positively correlated with soil organic carbon and surface and groundwater nitrate concentrations. Groh et al. (2019) in a study of denitrification rates in saturated riparian buffers found that high groundwater levels and the age of vegetation influenced the rates of denitrification. They recommend promoting high groundwater levels to use the entire soil column, especially the topsoil (0-20 cm), for removal of NO_3- in SRBs, where denitrification rates were greatest (median = 3.7 – 14.1mg N m^{-3} d^{-1}). Denitrification rates measured on 20-year-old riparian buffers explained 48 and 77% of the total NO_3- removed but only 8 and 36% for the SRBs established on the 3-year-old riparian buffer and 4% in SRBs on new established buffers.

Kreiling et al. (2021) measured denitrification rates in stream sediments from 28 sites along the Fox River, in Wisconsin, USA in early May, late June, and early August in 2018. Denitrification rates were found to be strongly correlated to surface water nitrate concentrations. Ambient denitrification rates ranged from 0 to 13.23 µg N cm^{-1} h^{-1}, but median rates were only 0.60 µg N cm^{-1} h^{-1}. In May denitrification rate decreased as the percentage of riparian forest cover increased but this relationship was not observed in other seasons. It was hypothesized that this was the period of greatest connectivity between the watershed and in-stream processing and during this period the riparian forest may have been limiting NO_3- export to the stream from agricultural areas. Indicating that that riparian forest cover indirectly decreased denitrification rates by reducing the concentrations of dissolved nutrients entering the stream.

Uchida et al. (2018) also found that dentification in riverbank soils collected from eight sites along the Shibetsu River in Japan increased with increased concentrations of organic carbon and nitrate. Denitrification rates of soil samples amended with glucose-carbon and NO_3-$^{-}$N ranged from 4.73 to 181 µg-N-kg^{-1} h^{-1} and were higher than samples that were not amended with glucose-carbon and NO_3-$^{-}$N.

A topic not covered in the initial publication of this paper is the use of $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 isotopes to distinguish NO_3- removal from groundwater as a result of denitrification and uptake by plants. Clément et al. (2003) showed how $\delta^{15}N$-NO_3 isotopes can be used in a qualitative manner to distinguish decreases in NO_3- concentration caused by denitrification relative to plant uptake. Clément et al. (2003) collected groundwater, river water, and vegetation samples in a riparian ecosystem along the Petit Hermitage Stream, a fourth order stream in western France. They state that if "plant uptake alone is responsible for nitrate retention along a riparian flow path, isotopic composition of the remaining nitrate would remain essentially unchanged. If both denitrification and plant uptake contribute to nitrate retention along riparian flow paths, isotopic composition of residual nitrate would become progressively enriched and the overlying vegetation would reflect the isotopic composition of its increasingly enriched source. Alternatively, if denitrification was the only process involved, the isotopic composition of residual nitrate would become progressively enriched while plant isotopic composition would remain unchanged with a different $\delta^{15}N$, its nitrogen source not being influenced by denitrification."

Lutz et al. (2019) analyzed nitrate concentration and $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 isotope data in riparian groundwater along a 2-km stream section of the Selke River in Central Germany to determine the extent of denitrification and transient nitrate removal by additional processes associated with negligible isotope fractionation (plant uptake and microbial assimilation). The catchment area upstream of the field site was 200 km2 with most of the upstream catchment being forest but land use was agricultural at and slightly upstream of the sampling site. Nitrate concentrations were as follows: distant groundwater (65.3 ± 36.5 mg L^{-1}), intermediate groundwater (15.5 ± 10.4 mg L^{-1}), near groundwater (8.5 ± 4.9 mg L^{-1}), and river (7.6 ± 4.6 mg L^{-1}). Lutz et al. (2019) stated that "Based on the nitrogen isotope data of nitrate, the simulations suggest a mean removal of up to 28% by additional processes and only about 9% by denitrification. Nitrate removal from riparian groundwater by additional processes exceeded denitrification particularly in winter and at larger distance from the river, underlining the role of the river as organic carbon source. This was because dissolved organic carbon concentrations in the river were more than twice as high as in distant groundwater. This highlights that nitrate consumption by additional processes predominates at the field site, implying that a substantial fraction of agricultural nitrogen input is not permanently removed but rather retained in the riparian zone."

Using median values per sampling date in the near groundwater the relative contribution of denitrification to overall NO_3- removal ranged from 4.2% to 61.3% (mean of 23.8% ± 16.2%) and from 4.9% to 100% (mean of 16.2% ± 19.9%) in the intermediate groundwater. At the two-groundwater sampling transects denitrification was substantially larger during summer than winter, whereas nitrate removal by additional processes were comparable in summer and winter. During summer denitrification was at a similar level as additional processes, whereas it was largely exceeded by additional processes during winter. At the two-groundwater sampling transects denitrification was greatest at the downstream transect relative to the upstream one. The downstream transect had the most river inflow. Denitrification in the river was considered negligible.

Although the concentration of nitrate in the river was nearly the same as that in the near groundwater it was not possible to determine if the low NO_3- concentration in the river was the result of low NO_3-groundwater entering the river along the study reach or if groundwater inflow was small enough to not affect the NO_3- concentration derived from upstream sources. The relative contribution of groundwater inflow relative to upstream sources (headwater tributaries, for example) along higher stream order reaches is a much-needed area of research to allow optimal placement of riparian buffer zones and other BMPs.

In recent years emphasis has been placed on the management of riparian zones for other water quality concerns besides NO_3- (Sweeney and Newbold, 2014; Vidon et al., 2018; Stutter et al., 2019). Sweeney and Newbold (2014) recommend that overall buffers ≥30 m wide are needed to protect the physical, chemical, and biological integrity of small streams. This includes preventing or reducing sediment erosion, stream bank stabilization, and modification of stream temperature and inputs of large woody debris to protect or enhance aquatic habitats. Vidon et al. (2019) note that only recently has the fate and transport of soluble reactive P (SRP), Hg, emerging contaminants, and greenhouse gas fluxes (N_2O, CO_2, and CH_4) been examined in riparian zones. Riparian zones can function as hot spots of methylmercury production when dominated by Hg-rich wet organic soils and do not provide consistent benefits to SRP removal or GHG emissions. They suggest using easily accessible digital environmental datasets to simulate and scale up riparian functions beyond removal to include SRP, TP, and GHG dynamics. Stutter et al. (2019) state that despite the significant number of studies on the functioning of riparian buffers, research gaps remain, particularly in relation to "(i) the capture and retention of soluble P and N in subsurface flows through buffers, (ii) the utilization of captured nutrients, (iii) the impact of buffer design and management on terrestrial and aquatic habitats and species, and (iv) the effect of buffers (saturated) on greenhouse gas emissions and the potential for pollution swapping".

In Ireland the Agricultural and Food Development Authority (Teagasc) is actively working with farmers throughout the country to establish riparian buffer zones and their website contains much information on how riparian buffer zones should be established (www.teagasc.ie/water-quality). One example of such a publication can be found at: Teagasc launches factsheet on how to establish a riparian buffer zone on your farm - Agriland.ie. A publication describing the identification, design, and management of native riparian woodlands can be found at: www.woodlandsofireland.com/sites/default/files/No. 4 - Riparian Woodlands.pdf

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