

Hydrogeologic controls on the transport and fate of nitrate in ground water beneath riparian buffer zones: results from thirteen studies across the United States

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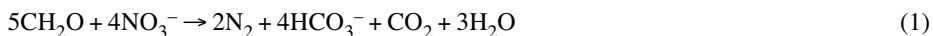
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Abstract During the last two decades there has been growing interest in the capacity of riparian buffer zones to remove nitrate from ground waters moving through them. Riparian zone sediments often contain organic carbon, which favors formation of reducing conditions that can lead to removal of nitrate through denitrification. Over the past decade the National Water Quality Assessment (NAWQA) Program has investigated the transport and fate of nitrate in ground and surface waters in study areas across the United States. In these studies riparian zone efficiency in removing nitrate varied widely as a result of variations in hydrogeologic factors. These factors include (1) denitrification in the up-gradient aquifer due to the presence of organic carbon or other electron donors, (2) long residence times (>50 years) along ground-water flow paths allowing even slow reactions to completely remove nitrate, (3) dilution of nitrate enriched waters with older water having little nitrate, (4) bypassing of riparian zones due to extensive use of drains and ditches, and (5) movement of ground water along deep flow paths below reducing zones. By developing a better understanding of the hydrogeologic settings in which riparian buffer zones are likely to be inefficient we can develop improved nutrient management plans.

Keywords Ground water; hydrogeology; hyporheic zone; nitrate; riparian buffer zones

Introduction

Over the last two decades, there has been growing interest in the use of riparian buffer zones along river corridors to mitigate the effects of nonpoint-source pollution on water quality (Hill, 1996), particularly their ability to remove contaminants from ground water before it enters surface-water bodies (Groffman *et al.*, 1992; Haycock *et al.*, 1993; Gilliam, 1994; Jansson *et al.*, 1994; Hill, 1996). The ability of riparian buffer zones to remove pollutants, particularly nitrate (NO_3^-), from ground water is related primarily to the presence of reducing conditions in the organic-rich, saturated sediments that commonly occur in riparian buffer zones. Nitrate removal in riparian buffer zones is important because (1) it poses human and ecosystem health risks (Mueller *et al.*, 1995), (2) it is the most common nonpoint-source pollutant (Mueller *et al.*, 1995), and (3) it is mobile in ground and surface water (Mueller *et al.*, 1995). Under reducing conditions nitrate can be converted to N_2O and then N_2 gas by the microbially mediated process of denitrification (Korom, 1992):



Studies of denitrification potential in riparian buffer zones increase our understanding of factors controlling this process and may allow us to predict when, where, and how riparian buffer zones will be effective nonpoint-source pollution controls. Assuming NO_3^- is present, there are three basic requirements for denitrification: (1) a microbial denitrifier population, (2) low concentration of dissolved oxygen (O_2), and (3) a readily available source of C or a reduced inorganic species such as Fe^{2+} , Mn^{2+} , or S^{2-} to serve as an electron donor (Tiedje *et al.*, 1982; Postma *et al.*, 1991; Korom, 1992).

Hill (1996) provided a critical review of the current state of our knowledge concerning

NO_3^- retention by riparian buffer zones. He concluded that previous research had failed to adequately consider hydrogeologic controls on biogeochemical processes and had been conducted in similar settings, making it difficult to extrapolate findings to other areas. These conclusions seem particularly relevant in light of recent studies that have shown (Figure 1) that ground water may flow under riparian zones and discharge to streams without undergoing denitrification (Bohlke and Denver, 1995; Burt *et al.*, 1999), or may take many decades to transit ground-water flow paths before discharging to surface waters (Modica *et al.*, 1997, 1998). Puckett and Cowdery (2002) have shown that even in aquifers low in organic carbon or other potential electron donors, denitrification may remove most if not all NO_3^- given long residence times. They also established that NO_3^- concentrations have increased in ground water over time due to increased use of fertilizer. Puckett *et al.* (2002) demonstrated that ground water discharging in riparian zones can create patterns in ground-water chemistry that may be misinterpreted as decreasing NO_3^- due to biogeochemical processes in the riparian zone. These recent studies pose challenges for researchers investigating biogeochemical processes in riparian buffer zones making it important to understand the hydrogeologic setting and age structure of the ground waters being sampled in order to avoid misinterpreting biogeochemical processes in riparian zones. This paper presents an overview of studies conducted in 13 hydrogeologic settings across the United States (Figure 2) designed to investigate various aspects of hydrologic and biogeochemical processes in riparian zones and at the ground water–surface water interface.

Methods

Study sites (Figure 2) were located throughout the United States as part of the National Water-Quality Assessment (NAWQA) program. Eleven of the 13 sites consisted of unconfined sand and gravel aquifers and their hydrologically connected streams. The remaining 2 sites, in Wisconsin (WMIC) and Indiana (WHIT), consisted of unconfined till aquifers with either sand and gravel lenses or various combinations of clay, sand and gravel; in Wisconsin the streambed consisted of fluvial sand and gravel deposits while in Indiana it was primarily comprised of fluvial sand and gravel over clay and silt similar to the surrounding aquifer. At each site piezometers constructed of 5-cm diameter PVC pipe were installed following standard protocols (Lapham *et al.*, 1995) and sampled according to pro-

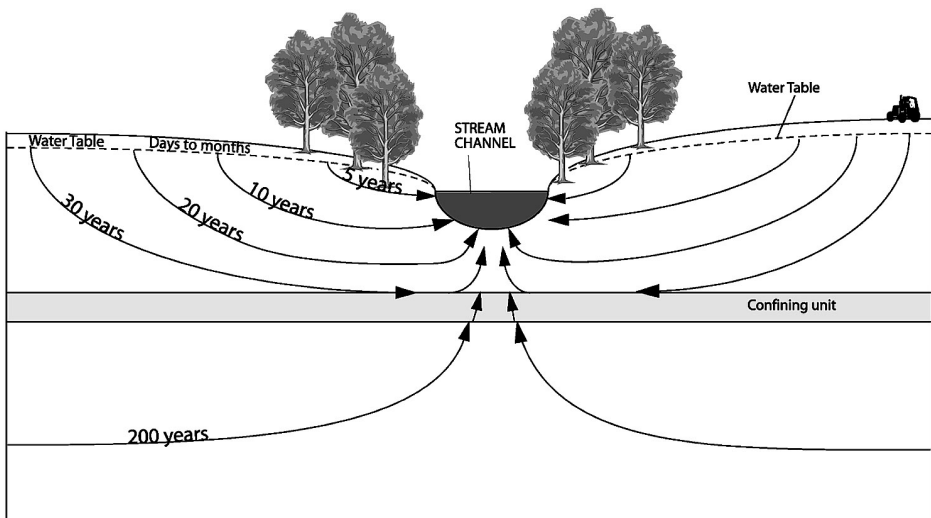


Figure 1 Ground water may take years to decades to centuries to travel from recharge to discharge zones

Table 1 Site names, location, publication reference, and NO₃⁻ concentrations (mg/L) in upland ground water, riparian and hyporheic zone ground water, and stream water

Site	Name	Location/Reference	NO ₃ ⁻ (mg/L) Ground water	Riparian/ Hyporheic zone	Stream
ACFB	Apalachicola, Chattahoochee, Flint River Basins	Lime Creek near Albany, GA (Puckett, 1999)	<0.05–8.8	<0.05–6.1 <0.05–1.6	0.13–1
ALBE	Albemarle Pamlico Drainages	Neuse River Basin near Wilson, NC (Spruill and Galleone, 2000)	10–12 5–15 0.6–5.4 5.6–7.7	11–12 <0.05–0.3 4.5–6.8 <0.05 0.02/0.01	0.6 3.8 0.76 0.46
CONN	Connecticut, Housatonic, and Thames River Basins	Hockanum River, Manchester, CT (Mullaney and Grady, 1997)	3.7	<0.05/2.8	2
LINJ	Long Island New Jersey Coastal Drainages	Cohansey River near Seeley, NJ (Kaufman <i>et al.</i> , 2001)	<0.05– 15.6	0.76–13	3–6
PODL	Potomac Delaware	Chesterville Branch/Morgan Creek near Locust Grove, MD (Bohlke and Denver, 1995)	1.3–16/ 14	2.7–8.6 <0.05–5.3	0.7–10 1.1–8.7
PUGT	Puget Sound Basin	Fishtrap Creek near Abbotsford, BC (Tesoriero <i>et al.</i> , 2000)	<0.05–36	<0.05	1.1–4.3
REDN	Red River of the North Basin	Otter Tail River near Perham, MN (Puckett <i>et al.</i> , 2002)	<0.05–46	<0.05–25	0.07
SANT	Santee River Basin	Cow Castle Creek near Bowman, SC (Puckett, 1999)	<0.05– 28.3	0.4–3.6 0.4–4.5	0.6–3.9
SPLT	South Platte River Basin	South Platte River near Denver, CO (McMahon and Bohlke, 1996)	26	6.6/6.5	4.5
UMIS	Upper Mississippi River Basin	Shingle Creek, Minneapolis, MN (Andrews <i>et al.</i> , 1999)	<0.05–3.1	<0.05	0.11–0.85
WHIT	White River Basin	Sugar Creek near Indianapolis, IN (Fenelon and Moore, 1998)	<0.05	1.1 <0.05	<0.05–9.5
WILL	Willamette Basin	Willamette River near Portland, OR (Hinkle <i>et al.</i> , 2001)	6.6–20	<0.05–5.8	0.25
WMIC	Western Lake Michigan Drainages	North Branch Milwaukee River near Milwaukee, WI (Saad and Thorstenson, 1998)	<0.05–4.3	<0.05–0.09 <0.05–0.12	1.8–2.4

>150 years. Such long travel times are an important factor since these ground waters recharged in a time period before commercial fertilizers were in widespread use. Consequently, when these old ground waters discharge in a riparian zone they will have low NO₃⁻ concentrations, which could be misinterpreted as evidence that denitrification or plant uptake had occurred there.

In most cases, organic carbon was determined to be the dominant electron donor in the denitrification process, however there were exceptions. At the PUGT site, pyrite localized in the riparian sediments also served as the electron donor. Glauconite, a marine clay containing ferrous iron, was determined to be the electron donor at the PODL site. In the CONN study there were no appreciable amounts of electron donors. Consequently, most ground water was oxic and the apparent losses of NO₃⁻ were due to mixing of ground waters of different concentrations and with river water.

At several sites (ACFB, ALBE, LINJ, SPLT, WILL) there were significant losses of NO_3^- as a result of denitrification in the hyporheic zone either as ground water discharged through it or as a result of interactions with stream water. The SPLT site was especially interesting with about 15–30 per cent of the NO_3^- losses attributed to denitrification before ground water reached the stream; then another 70 per cent was lost due to hyporheic interchange and denitrification.

Conclusions

Denitrification was found to occur in almost any hydrogeologic setting where organic carbon or other reduced-phase electron donors were present in sufficient amounts to generate reducing conditions. Conversely, where these potential electron donors were absent or in limited abundance, denitrification was either very slow or insignificant. The net result is that denitrification will occur in any setting where ground water flow paths intersect reducing environments, including up-gradient portions of an aquifer, riparian zones, and hyporheic zones. Even in some hydrogeologic settings where reducing conditions are limited, long residence times of ground water along flow paths may allow sufficient time for even slow reactions to remove most NO_3^- . Long residence time of the order of 50–70 years means that some ground waters may have lower NO_3^- concentrations simply because less NO_3^- was being applied at the time the ground water recharged, further complicating interpretation of riparian zone processes.

The long residence times of ground water may pose an issue for future water quality in that in many areas where fertilizers have been applied for over 50 years it may take that long for ground water to move completely through the aquifer. Consequently, NO_3^- applied in the past may continue to be a problem for many decades to come, even if large-scale fertilizer reductions are implemented.

Another important factor is that any process that allows NO_3^- rich ground water to bypass reducing environments may limit the effectiveness of riparian zones to remove NO_3^- . In some hydrogeologic settings ground-water flow paths may pass below reducing conditions in a riparian zone and discharge NO_3^- rich ground water to streams. In settings where tile drains and ditches are used to drain fields, NO_3^- rich water may also be discharged directly to streams. Even in settings where NO_3^- reaches the surface-water environment, denitrification may still take place in the hyporheic zone.

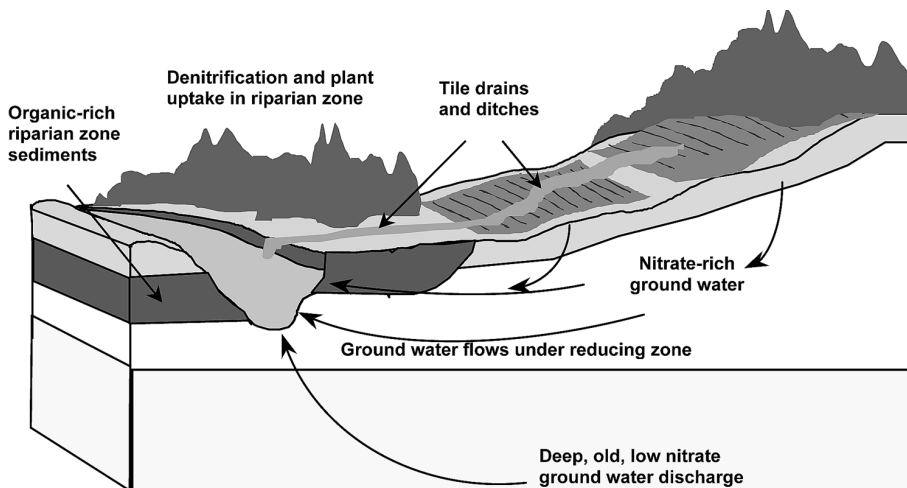


Figure 3 Several factors including the use of tile drains and ditches, and ground water flowing beneath organic-rich riparian sediments, may limit the effectiveness of riparian zones. In addition, discharge of old ground water low in nitrate may give the appearance that denitrification has occurred

These findings point out the importance of developing a complete understanding of the hydrologic flow system in the study area and the up-gradient aquifer in order to be able to distinguish between biogeochemical processes that may be taking place in the riparian buffer zone and those that are controlled instead by processes in other portions of the flow system. More importantly, by developing an understanding of the hydrology and biogeochemistry of both the riparian and up-gradient aquifer and how they interact, we can in the end develop a more accurate capability to predict when and where riparian buffer zones will be most effective in protecting water quality.

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