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

L.J. Puckett

U.S. Geological Survey, 413 National Center, Reston 20192 (E-mail: *lpuckett@usgs.gov*)

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):

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O \tag{1}$$
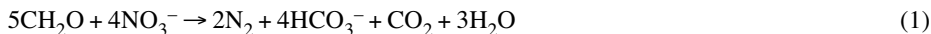
Studies of denitrification potential in riparian buffer zones increase our understanding of factors controlling this process and may allow us to predict when, where, and how riparian buffer zones will be effective nonpoint-source pollution controls. Assuming NO_3^- is present, there are three basic requirements 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-
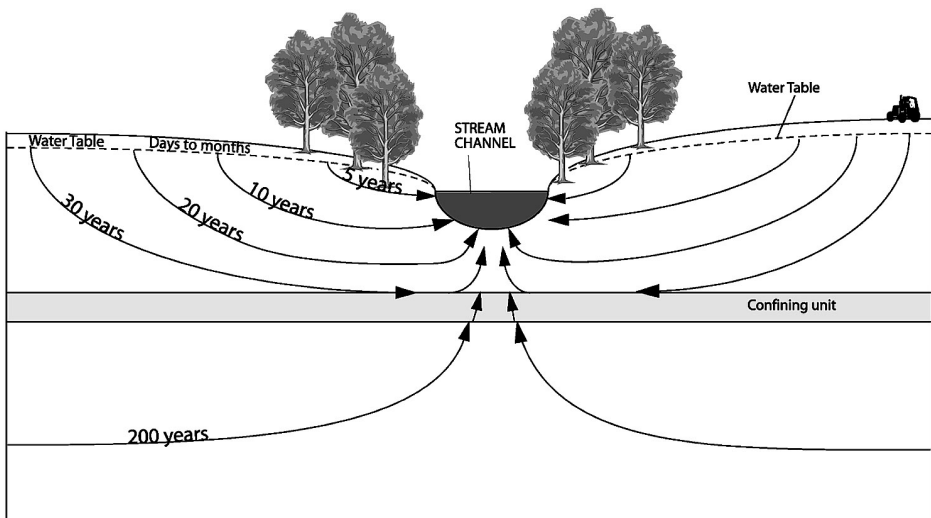

Figure 1 Ground water may take years to decades to centuries to travel from recharge to discharge zones

cedures detailed by Koterba *et al.* (1995). At the UMIS and SANT sites multiport samplers (Delin and Landon, 1996) were used. Hyporheic zone and some riparian zone samples were collected using small drive points of various diameters and stream samples were collected in multiple vertical sections using a depth-integrating sampler. Samples were shipped overnight to the USGS central laboratory in Denver, Colorado for immediate analyses of nutrients, major ions, and DOC. Dissolved oxygen, pH, temperature, conductance, and alkalinity (by incremental titration) were all measured in the field. Ground-water ages were determined at most sites using the chlorofluorocarbon ($CFCl_3$, CF_2Cl_2, and $C_2F_3Cl_3$) dating procedure developed by Busenberg and Plummer (1992); in a few cases tritium age dating was used.

Results and discussion

As can be seen from Table 1, changes in NO_3^- concentrations between the ground water, riparian/hyporheic zones, and the streams varied from almost complete removal at the ALBE, REDN, UMIS, WILL, and WMIC sites to net increases in the case of the WHIT where tile drains and ditches routed shallow ground water from fields directly to streams. Bypassing the riparian zone through the use of ditches and tile drains was also identified as a factor in the SANT study. In several studies (ACFB, ALBE, LINJ, PODL, SANT) the riparian zone was bypassed by ground water traveling beneath the reduced riparian sediments and discharging directly into the stream bed.

At the majority of sites NO_3^- concentrations decreased by about 50–75 percent by the time they reached the stream. In several cases however the reasons for decreases in NO_3^- were not directly related to denitrification and (or) plant uptake in the riparian zone. For example, in the UMIS study NO_3^- removal was attributed to denitrification in buried wetlands scattered in the up-gradient aquifer. These buried wetlands provided the carbon necessary for denitrification, and although dispersed in pockets throughout the aquifer, they were numerous enough to result in widespread denitrification. At the REDN site most NO_3^- was also removed from ground water in the up-gradient aquifer before it reached the riparian zone. In this case, organic carbon dispersed throughout the aquifer in relatively small concentrations served as the electron donor and the 50–70 year residence time allowed sufficient time for complete denitrification. This denitrified ground water flowing along deep flow paths discharged in the riparian zone giving the appearance that denitrification had occurred there.

Long ground-water residence times played another important role in the LINJ, PODL, and REDN studies where maximum travel times along deep flow paths ranged from 50 to
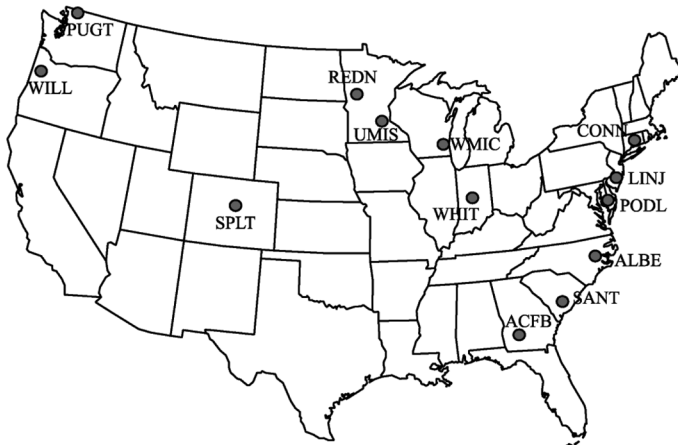

Figure 2 Locations of study sites. Site abbreviations are defined in Table 1

Table 1 Site names, location, publication reference, and NO_3^- 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 et al., 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 et al., 2000)	<0.05–36	<0.05	1.1–4.3
REDN	Red River of the North Basin	Otter Tail River near Perham, MN (Puckett et al., 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 et al., 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 et al., 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 NO_3^- 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 NO_3^- 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.
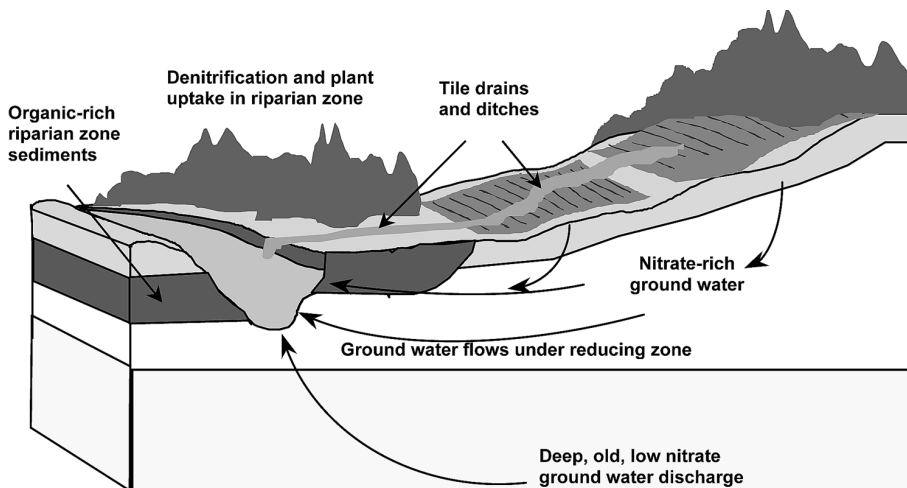

Figure 3 Several factors including the use of tile drains and ditches, and ground water flowing beneath organic-rich riparian sediments, may limit the effectiveness of riparian zones. In addition, discharge of old ground water low in nitrate may give the appearance that denitrification has occurred

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.

References

Andrews, W.J., Stark, J.R., Fong, A.L. and Hanson, P.E. (1999). Ground-water quality along a flowpath in a surficial outwash aquifer in the Upper Mississippi River Basin – The influence of land use. *Hydrol. Sci. Technol.*, **15**, 66–75.

Bohlke, J.K. and Denver, J.M. (1995). Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. *Water Resour. Res.*, **31**, 2319–2339.

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

Busenberg, E. and Plummer, L.N. (1992). Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age-dating tools: The alluvium and terrace system of central Oklahoma. *Water Resour. Res.*, **28**, 2257–2283.

Delin, G.N. and Landon, M.K. (1996). Multiport well design for sampling of ground water at closely spaced vertical intervals. *Ground Water*, **34**, 1098–1104.

Fenelon, J.M. and Moore, R.C. (1998). Transport of agrichemicals to ground and surface water in a small central Indiana watershed. *J. Environ. Qual.*, **27**, 884–894.

Gilliam, J.W. (1994). Riparian wetlands and water quality. *J. Environ. Qual.*, **23**, 896–900.

Groffman, P.M., Gold, A.J. and Simmons, R.C. (1992). Nitrate dynamics in riparian forests: Microbial studies. *J. Environ. Qual.*, **21**, 666–671.

Haycock, N.E., Pinay, G. and Walker, C. (1993). Nitrogen retention in river corridors: European perspectives. *Ambio*, **22**, 340–346.

Hill, A.R. (1996). Nitrate removal in stream riparian zones. *J. Environ. Qual.*, **22**, 743–755.

Hinkle, S.R., Duff, J.H., Triska, F.J., Laenen, A., Gates, E.B., Bencala, K.E., Wentz, D.A. and Silva, S.R. (2001). Linking hyporheic flow and nitrogen cycling near the Willamette River – a large river in Oregon, USA. *J. Hydrol.*, **244**, 157–170.

Jansson, M., Anderson, R., Berggren, H. and Leonardson, L. (1994). Wetlands and lakes as nitrogen traps. *Ambio*, **23**, 320–325.

Kaufman, L.J., Baehr, A.L., Ayers, M.A. and Stackelberg, P.E. (2001). Effects of land use and travel time on the distribution of nitrate in the Kirkwood-Cohansey aquifer system in southern New Jersey, U.S. Geological Survey Water-Resources Investigations Report 01-4117, 49 p.

Korom, S.F. (1992). Natural denitrification in the saturated zone: A review. *Water Resour. Res.*, **28**, 1657–1668.

Koterba, M.T., Wilde, F.D. and Lapham, W.W. (1995). Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program – Collection and documentation of water-quality samples and related data, U.S. Geological Survey Open-File Report 95-399, 113 p.

Lapham, W.W., Wilde, F.D. and Koterba, M.T. (1995). Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program – Selection, installation and documentation of wells, and collection of related data, U.S. Geological Survey Open-File Report 95-398, 69 p.

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

Modica, E., Buxton, H.T. and Plummer, L.N. (1998). Evaluating the source and residence times of groundwater seepage to streams, New Jersey Coastal Plain. *Water Resour. Res.*, **34**, 2792–2810.

Modica, E., Reilly, T.E. and Pollock, D.W. (1997). Patterns and age distribution of ground-water flow to streams. *Ground Water*, **35**, 523–537.

Mueller, D.K., Hamilton, P.A., Helsel, D.R., Hitt, K.J. and Ruddy, B.C. (1995). Nutrients in ground water

and surface water of the United States – An analysis of data through 1992, U.S. Geological Survey Water-Resources Investigation Report 95-4031, 74 p.

Mullaney, J.R. and Grady, S.J. (1997). Hydrogeology and water quality of a surficial aquifer underlying an urban area, Manchester, Connecticut, U.S. Geological Survey Water-Resources Investigations Report 97-4195, 40 p.

Postma, D., Boesen, C., Kristiansen, H. and Larsen, F. (1991). Nitrate reduction in an unconfined aquifer: water chemistry, reduction processes, and geochemical modeling. *Water Resour. Res.*, **27**, 2027–2045.

Puckett, L.J. (1999). The effectiveness of riparian buffer zones in removing nitrate from ground water of the Atlantic Coastal Plain. *Proceedings, 6th Symposium on Wetland Biogeochemistry*, Fort Lauderdale, FL, 7/1999, 50.

Puckett, L.J. and Cowdery, T.K. (2002). Transport and fate of nitrogen in a glacial outwash aquifer in relation to ground-water age, land use practices, and redox processes. *J. Environ. Qual.*, **31**.

Puckett, L.J., Cowdery, T.K., McMahon, P.B., Tornes, L.H. and 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 Resources Research*, **38**(8), 10.1029/2001WR000396, 20 p.

Saad, D.A. and Thorstenson, D.C. (1998). Flow and geochemistry along shallow ground-water flowpaths in an agricultural area in southeastern Wisconsin, U.S. Geological Survey Water-Resources Investigations Report 98-4179, 62 p.

Spruill, T.B. and Galeone, D.R. (2000). Effectiveness of riparian buffers in reducing nitrate-nitrogen concentrations in ground water, Proceedings of the International Conference on Riparian Ecology and Management in Multi-Land Use Watersheds, Portland, OR, 9/2000, 119–124.

Tesoriero, A.J., Liebscher, H. and Cox, S.E. (2000). Mechanism and rate of denitrification in an agricultural watershed: Electron mass balance along groundwater flow paths. *Water Resour. Res.*, **36**, 1545–1559.

Tiedje, J.M., Sexstone, A.J., Myrold, D.D. and Robinson, J.A. (1982). Denitrification: ecological niches, competition and survival. *Antoine van Leeuwenhoek*, **48**, 569–583.