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Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology

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Abstract. A better understanding of nitrate removal mechanisms is important for managing the water quality function of stream riparian zones. We examined the linkages between hydrologic flow paths, patterns of electron donors and acceptors and the importance of denitrification as a nitrate removal mechanism in eight riparian zones on glacial till and outwash landscapes in southern Ontario, Canada. Nitrate-N concentrations in shallow groundwater from adjacent cropland declined from levels that were often 10–30 mg L^{-1} near the field-riparian edge to < 1 mg L^{-1} in the riparian zones throughout the year. Chloride data suggest that dilution cannot account for most of this nitrate decline. Despite contrasting hydrogeologic settings, these riparian zones displayed a well-organized pattern of electron donors and acceptors that resulted from the transport of oxic nitrate-rich groundwater to portions of the riparian zones where low DO concentrations and an increase in DOC concentrations were encountered. The natural abundances of d15N and *in situ* acetylene injection to piezometers indicate that denitrification is the primary mechanism of nitrate removal in all of the riparian zones. Our data indicate that effective nitrate removal by denitrification occurs in riparian zones with hydric soils as well as in non-hydric riparian zones and that a shallow water table is not always necessary for efficient nitrate removal by denitrification. The location of 'hot spots' of denitrification within riparian areas can be explained by the influence of key landscape variables such as slope, sediment texture and depth of confining layers on hydrologic pathways that link supplies of electron donors and acceptors.

Introduction

During the past 25 years, there has been considerable interest in the role of stream riparian zones as 'buffers' that reduce the transport of nitrates from terrestrial to aquatic systems (Dosskey 2001). Although nitrate removal effectiveness can vary considerably among riparian zones (Hill 1996; Sabater et al. 2003), many studies have recorded removal efficiencies of greater than 90%, particularly in riparian zones with shallow groundwater flow paths (Peterjohn and Correll 1984; Lowrance 1992; Haycock and Pinay 1993; Jordan et al. 1993; Gilliam 1994). Nitrate removal from groundwater in riparian zones has been attributed mainly to microbiological denitrification and plant uptake (Correll 1997). However, the relative importance of these removal processes remains uncertain in many landscapes (Gilliam et al. 1997).

Conditions required for heterotrophic denitrification include the presence of nitrate, the presence of labile organic matter as an energy source for microbial activity and the absence or low concentration of dissolved oxygen (DO; Korom 1992; Groffman 1994). Several studies indicate that reduced conditions, where DO concentration are $<$2–3 mg L^{-1} and redox potentials are about $+$200 to $+$300 mV, are necessary for denitrification to occur (Gillham and Cherry 1978; Lensi and Chalamet 1982; Cey et al. 1999). Analysis of how supplies of electron donors and acceptors are linked to microbial metabolism can improve our mechanistic understanding of denitrification and other biogeochemical processes in stream riparian zones (Hedin et al. 1998).

Many studies have measured significant denitrification activity in the surface horizon of riparian soils (Cooper 1990; Groffman et al. 1992; Pinay et al. 1993; Clement et al. 2002). Other studies have linked a low or nonexistent potential for denitrification in subsurface riparian sediments to a lack of available organic carbon (Ambus and Lowrance 1991; Groffman et al. 1992; Lowrance 1992; Schnabel et al. 1996; Burt et al. 1999). As a consequence of these patterns of denitrification activity, Gold et al. (2001) have indicated that shallow water tables in riparian areas with hydric soils create conditions favourable for denitrification, whereas in riparian zones with non-hydric soils, nitrate removal is not effective because groundwater nitrate does not interact with organic-rich surface soils. Similarly, Burt et al. (2002) suggest that denitrification occurs mainly during periods of high water table in riparian areas and that in summer the water table often declines below the surface organic horizon limiting denitrification due to a lack of organic matter at depth. Other researchers have also proposed a seasonal shift in nitrate removal mechanisms suggesting that denitrification is most effective in winter when the water table is high, whereas uptake by vegetation and soil microbial biomass might dominate under lower water table conditions during the summer (Simmons et al. 1992; Haycock et al. 1993; Correll 1997). These conclusions regarding denitrification activity in riparian zones emphasize the importance of riparian hydrology and suggest that the role of denitrification may be strongly influenced by the riparian zone hydrogeologic setting which encompasses surface topography, soils and the composition, stratigraphy and hydraulic properties of the underlying geological deposits.

The size and seasonality of hydrologic connections with adjacent uplands influence riparian zone water table fluctuations and the extent of surface saturation with consequent effects on soil redox potential and microbial processes (Roulet 1990; Devito and Hill 1997). The depth of permeable sediments overlying a confining layer in riparian zones can influence hydrologic flow paths (Correll 1997; Lowrance et al. 1997). A confining layer at a shallow depth increases the interaction of groundwater with organic-rich surface soils that may favour rapid nitrate removal by denitrification (Hill 1996; Gold et al. 2001). However, when soils are too permeable, the residence time of water may not be long enough for anoxic conditions to develop (Burt et al. 2002). Topography also affects denitrification. At sites with a relatively flat topography, a low hydraulic gradient can increase the water residence time in the riparian zone and enhance the development of anaerobic conditions necessary for denitrification (Vidon and Hill 2004a). At sites with steeper slopes directly coupled to the channel, research suggests that soil moisture

conditions are unlikely to favour denitrification since the water table is too deep (Burt et al. 2002).

Currently, there are still many gaps in our knowledge of the role of denitrification in the removal of nitrate from subsurface water in riparian zones. Most studies of denitrification have focused on sites with shallow confining layers and only a few studies have examined riparian zones in other landscape hydrogeologic settings. Researchers have also been concerned mainly with measurements of denitrification in near surface riparian soils rather than in the vertical dimension (Martin et al. 1999). Recently, Gold et al. (1998) and Jacinthe et al. (1998) found that denitrification occurred in small patches of organic matter in the C horizon of riparian soils. Hill et al. (2000) also reported the occurrence of denitrification at depth at interfaces between sands and peats or buried channel deposits in a southern Ontario riparian zone. An understanding of controls on 'hot spots' of denitrification and other biogeochemical activity requires knowledge of the role of flow paths in bringing together various reactants (McClain et al. 2003). However, most riparian studies with the exception of Hedin et al. (1998) and Hill et al. (2000) have not examined the interactions between hydrologic flow paths and supplies of electron donors and acceptors. These interactions may vary between riparian zones and can be influenced by landscape setting.

The goal of this study was to examine the influence of contrasting riparian zone hydrogeological settings on (1) the linkages between hydrologic flow paths and patterns of electron donors and acceptors that favour denitrification in riparian areas and (2) on the importance of denitrification as a nitrate removal mechanism. The role of landscape hydrogeologic characteristics as controls on the groundwater nitrate removal effectiveness of riparian zones has been examined in a parallel study (Vidon and Hill 2004b).

Study area

The study sites are located in agricultural catchments in southern Ontario near Toronto (Figure 1). The annual precipitation in the area is 800–900 mm $year^{-1}$ with 120–240 mm falling as snow between December and April (Singer et al. 1997). The mean annual temperature is 7.2 °C with a mean January temperature of −6.7 °C and a mean July temperature of 20.5 °C. There are frequent mid-winter thaws but spring snowmelt in the March–April period is the main runoff period. Lowest stream discharge occurs in July–August when evapotranspiration is highest. During the 2000–2002 study period, rainfall in May and June 2000 was more than two times higher than the 30 year normal for these months whereas the summer of 2001 was the driest recorded in the past 50 years.

The physical characteristics of the study sites are summarized in Table 1. Two of the riparian sites are located on the Eramosa and Speed rivers, 4th and 2nd order streams respectively, that flow in large former glacial meltwater channels, bordered by extensive gravel terraces. The terrain at the speed site is gently sloping and the riparian zone and adjacent upland are underlain by a 3 m thick coarse gravel deposit

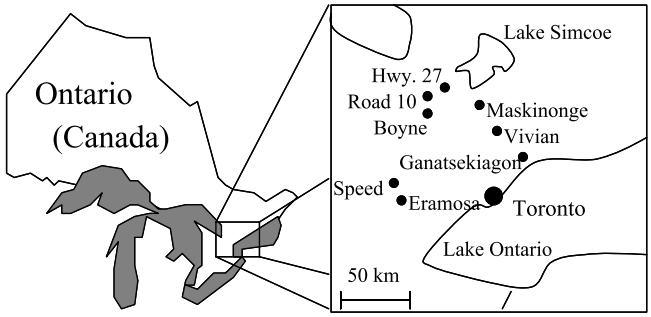


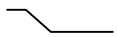
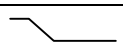
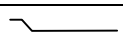
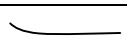
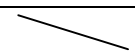
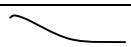
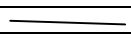
Figure 1. Location of study sites.

(Figure 2(d)). This deposit has hydraulic conductivities of 10^{-4} cm s^{-1} and overlies substrates with low Ks values of 10^{-6} cm s^{-1} that form a confining layer for groundwater flow (Vidon and Hill 2004a). The upland at the Eramosa site is underlain by coarse gravel sediments that are 9–10 m thick along the steep valley slope at the field–riparian perimeter. At the slope base, 2.5 m of loamy sand and coarse gravel (Ks = 10^{-4} cm s^{-1}) thins rapidly downslope where a 1 m thick peat deposit with Ks values of 10^{-5} cm s^{-1} extends towards the river (Figure 2(a)). Beneath the gravel and peat deposits, clay till forms a confining layer throughout the riparian zone (Vidon and Hill 2004a).

The Road 10 and Boyne River riparian sites are located on the Alliston sand plain that forms an unconfined 9–12 m thick aquifer underlain by a thick sequence of silts and clays (Devito et al. 2000). The Boyne River site is located along a 5th order stream in a valley incised approximately 10–12 m below the adjacent upland sand plain surface. Low conductivity peat deposits thicken from 0.5 m at the valley side to 3 m within the riparian area (Devito et al. 2000). Fine sands containing layers of coarse sand and fine gravel with Ks values of 10^{-3} cm s^{-1} occur beneath the peat and are underlain by the regional clay at depths of approximately 6 m (Figure 2(b)). Organic-rich buried channel deposits occurred in the sand layer near the river. The Road 10 site is on a 1st order tributary of the Nottawasaga River and has relatively flat topography. The sediments are mainly sands (Ks = 10^{-3} cm s^{-1}), however a loamy sand layer with lower Ks values of 10^{-5} cm s^{-1} extends across the riparian zone at depths of 1–3 m (Figure 2(c)). Portions of this layer contain relic channel deposit with 2–5% organic matter content (Hill et al. 2004).

The other riparian sites are located on glacial till (Maskinonge, Ganatsekiagon and Hwy. 27) or outwash silt (Vivian). The Maskinonge and Hwy. 27 riparian zones have a concave topography with moderate to steep slopes at the upland perimeter and level terrain near the streams. Soils at the riparian perimeter and in the adjacent upland at the Maskinonge site are loamy sands that extend to a depth of 2 m and have Ks values of 10^{-4} cm s^{-1}. At greater depths, a dense silty sand till restricts subsurface flow (Vidon and Hill 2004a). Within the riparian zone, peats with Ks

Table 1. Site physical characteristics.

	Topography type	Width (m)	Upland permeable sediment depth (m)	Vegetation	Slope gradient
Eramosa river		220	9–10	SW	23.6%/<2%[a] Overall: 5.7%
Boyne river		204	15	SW	38.6%/<2% Overall: 5.2%
Road 10		30	6	H	18.0%/<1% Overall: 5.2%
Speed river		66	2.8–3	H + HW	5.0%/<1% Overall: 2.9%
Maskinonge		45	2	H + HW	13.1%/<1% Overall: 5.1%
Ganatsekiagon		25	1.4	H	Overall: 13.2%
Hwy. 27		33	1.2	H + HW	20.1%/<1-2% Overall: 11.3%
Vivian		37	0.9	H	Overall: 1%

Legend: HW=hardwood; SW=softwood; H=herbaceous.
[a]The first value indicates the gradient of the steepest section of the riparian zone at the upland/riparian boundary and the second indicates the slope gradient of the remaining part of the riparian zone.

values of 10^{-5} and 10^{-6} cm s^{-1} increase in thickness towards the stream (Figure 2(e)).

The Hwy. 27 site is developed on a dense sandy loam till (Ks = 10^{-7} cm s^{-1}) that forms a confining layer at a depth of 1.2 m at the field-riparian zone margin. The soil above the confining layer is a sandy loam (Ks = 10^{-4}–10^{-5} cm s^{-1}) near the field boundary changing to loamy sand and sands near the stream (Figure 2(g)). The Ganatsekiagon site has a slightly convex topography and an average slope of 13.2% that extends to the stream. The soil profile is composed of a coarse sandy ablation till with thin layers of gravel (Ks = 10^{-3} cm s^{-1}) over a dense basal till that restricts subsurface flow to depths < 1.4 m in both the riparian zone and the adjacent upland (Figure 2(f)). The topography at the Vivian site is flat (slope 1%) and an outwash silt forms an aquitard that varies in depth from 0.9 m at the riparian perimeter to 1.4–1.5 m near the stream. The sediment profile above this confining layer in the riparian area is a sandy loam (Ks = 10^{-5} cm s^{-1}) between 0 and 50 cm and a loamy-sand mixed with gravel between 50 and 90 cm (Ks = 10^{-4} cm s^{-1}). Both the Hwy. 27 and Vivian sites contain extensive thin organically-enriched sediment layers (5–21% organic matter content) at depths of 0.5–1.0 m (Hill et al. 2004).

The Boyne and Eramosa riparian zones are forest sites dominated mainly by white cedar (*Thuja occidentalis* L.). The other riparian sites are covered with an herbaceous plant community with scattered shrubs and deciduous trees. All riparian

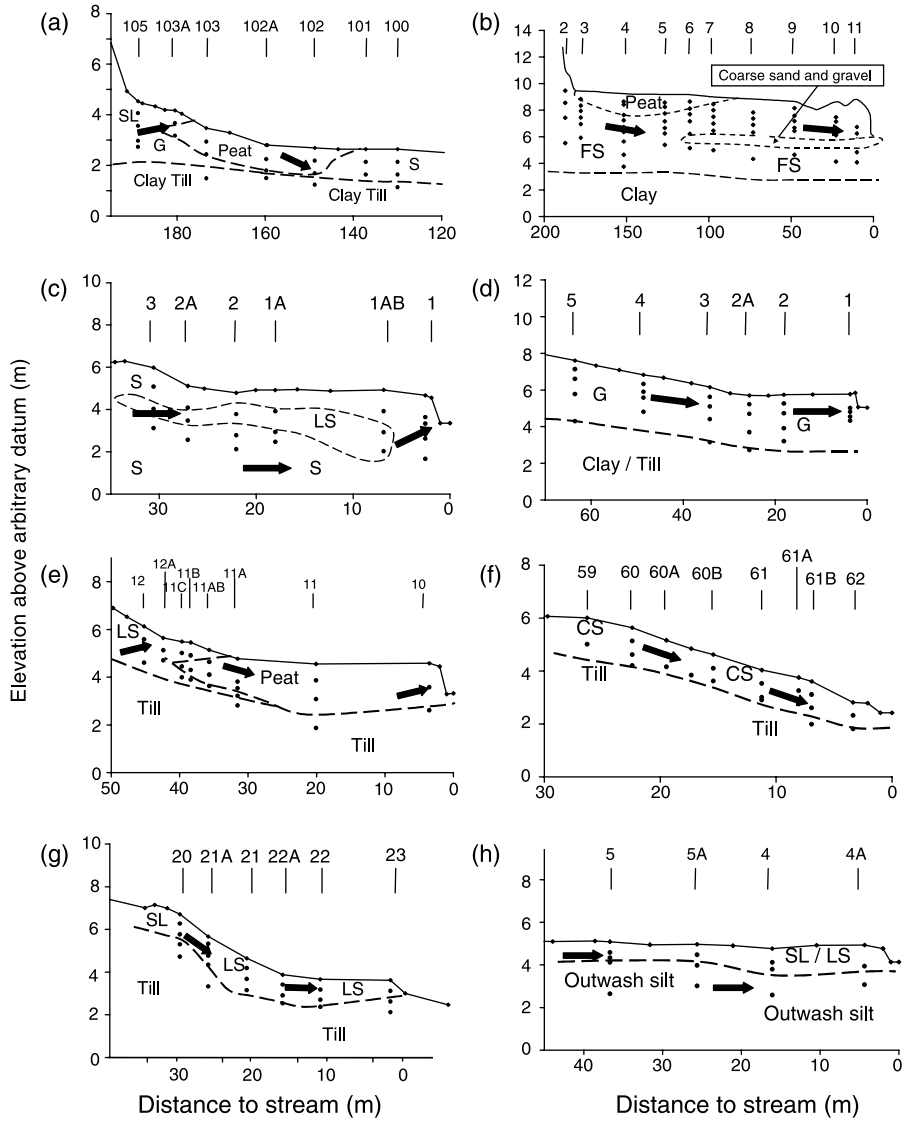


Figure 2. Vertical cross section along the main transect showing riparian lithology. The small flow arrows represent the general direction of flow. Dots represent piezometer slot zones. (a) Eramosa; (b) Boyne; (c) Road 10; (d) Speed; (e) Maskinonge; (f) Ganatsekiagon; (g) Highway 27; (h) Vivian. (SL = Sandy loam; LS = Loamy sand; FS = Fine sand; S = Sand; CS = Coarse sand; G = Gravel).

sites are located downslope from fertilized cropland. The adjacent fields at the Boyne and Road 10 sites are used for potatoes, whereas corn is the main crop at the other riparian zones.

Materials and methods

An extensive network of wells and piezometer nests was installed extending from the field-riparian zone margin to the stream at each riparian site. For most sites, two separate transects of wells and piezometers were installed 20–80 m apart in order to assess variability at the riparian zone scale. Each piezometer nest consisted of piezometers constructed from 1.27 cm ID PVC pipe with 20 cm long slotted ends installed at depth between 0.5 and 5.5 m depending on sites. Groundwater wells (ID 5.1 cm ABS pipe – 1.5 – 2 m long) perforated throughout their length were installed at most piezometer nests and at various other locations within the riparian sites. When necessary, a bentonite clay seal was used to prevent contamination by surface water.

Saturated soil hydraulic conductivities were measured in piezometers and wells using the Hvorslev water recovery method (Freeze and Cherry 1979). Groundwater levels and hydraulic heads were measured at least once a month beginning between March 2000 (Maskinonge, Ganatsekiagon and Vivian sites) and July 2000 (Road 10 and Speed sites) until September 2002. The topography of the riparian zone and of the adjacent upland was surveyed using a total station. Water samples for nitrate and chloride analysis were collected from piezometers at least once a month beginning between March 2000 (Maskinonge, Ganatsekiagon and Vivian sites) and July 2000 (Road 10 and Speed sites) until spring 2002. Nitrate-N and Cl^- concentrations were analysed using standard techniques for automated wet chemistry on a Technicon AutoAnalyzer (Technicon 1977; Environment Canada 1979). The importance of dilution by another water source in decreasing nitrate concentrations along the groundwater flow path was determined using groundwater chloride as a conservative tracer (Altman and Parizek 1995).

DO concentration in groundwater was measured in the field on 3–6 dates during the 2000–2002 study period. Water samples were collected from the piezometers and wells with tygon tubing using a three-way stopcock connected to a syringe to prevent contact with ambient air during pumping. DO was measured with a DO meter by inserting the oxygen probe into the syringe. Dissolved organic carbon (DOC) was measured 2–3 times in all piezometers in 2001 and 2002 depending on sites. For DOC analysis, piezometers were purged and fresh groundwater was withdrawn using a syringe. Samples were filtered in the field through 0.45 µm fibreglass filters and phosphoric acid was added to the sample to bring the pH <2. The samples were stored in the dark in air tight glass vials at 2–3 °C. DOC analyses were performed in the Department of Geography Laboratory at McGill University using a Dorhman high temperature Carbon Analyser.

Riparian groundwater samples for $^{15}N - NO_3^- - N$ stable isotope analysis as an indicator of denitrification activity were obtained from a selection of piezometers and wells at each riparian zone during high water tables in April–June 2001 and April 2002, except at the Vivian site where nitrate concentrations were too low for stable isotope analysis (Karr et al. 2001) and at the Boyne site where $^{15}N - NO_3^- - N$ data have been previously reported (Devito et al. 2000). After collection in the field, samples were filtered and 5–6 drops of mercuric-chloride (HgCl) was added to each 1-L glass flask to inhibit any microbial activity. Isotope

analysis was performed at the Environmental Isotope Laboratory, University of Waterloo. Results are expressed in δ units defined by:

$$\delta^{15}\mathrm{N} = \frac{R_{\mathrm{sample}} - R_{\mathrm{standard}}}{R_{\mathrm{standard}}} \times 1000$$

where R_{sample} and R_{standard} are the $^{15}\mathrm{N}/^{14}\mathrm{N}$ ratios for the sample and standard, respectively. The reference standard is atmospheric nitrogen for $^{15}\mathrm{N}$. Analytical reproducibility of $\delta^{15}\mathrm{N}$ was determined to be about 0.3‰.

Denitrification activity was also determined *in situ* in selected wells and piezometers at the Speed, Ganatsekiagon and Hwy. 27 riparian sites using the acetylene block technique that inhibits the final conversion of N_2O to N_2 gas. The resulting accumulation of N_2O provides evidence of the occurrence of denitrification (Bragan et al. 1997). After one piezometer volume of groundwater was pumped from each piezometer, a fresh gas sample was collected for N_2O analysis prior to acetylene injection. Then 2 L of water were pumped from the piezometers and calcium carbide (CaC_2) was added to produce an acetylene saturated solution. At the Hwy. 27 site, nitrate was added $\left(KNO_3^-\right)$ to compensate for low ambient nitrate concentrations in the piezometers. This amended groundwater was then re-injected slowly over a few hours into the piezometers. Samples of fresh groundwater were then withdrawn 1, 2, 3 and 5 days after injection using syringes and analysed for N_2O in the laboratory with a gas chromatograph equipped with an electron capture detector. Gases were separated with a Poropak Q column using a carrier gas of ultra-high purity (UHP) N_2. All N_2O concentrations were corrected for the amount of N_2O dissolved in water.

Results

Riparian groundwater flow paths and nitrate concentrations

Water input variability and subsurface flow paths at the eight riparian sites have been described in detail by Vidon and Hill (2004a). Briefly, water inputs from the hillslope at the Eramosa and Boyne river sites showed little seasonal variations and the water table remained close to the ground surface throughout the year at both sites. The minimum mean water table height at the Eramosa and Boyne sites was 13 and 50 cm below the ground surface during the study period, respectively. At the slope bottom, seeps and surface streamlets were observed at these two sites throughout the year. At the Eramosa site, water flowed towards the surface at the slope bottom between nests 105 and 103 and parallel to the ground surface on the remaining part of the riparian zone (Figure 2(a)). At the Boyne river site, subsurface flow was mainly parallel to the ground surface across the entire riparian zone although some recharge from surface to deeper sediments occurred between sites 6–8 (Figure 2(b)).

Hillslope discharge was more variable at the Road 10, Speed and Maskinonge sites, nevertheless these sites remained hydrologically connected to uplands

throughout the year. Although the water table was often near the surface at these sites in spring, it dropped to 110–130 cm in the summers of 2000–2002 at the Road 10 site. Minimum mean water table heights at the Speed and Maskinonge sites in the dry summer of 2001 were 137 and 62 cm respectively. Groundwater at the Maskinonge site discharged towards the surface at the slope bottom between nest 12 and 11B creating seeps and surface streamlets that later re-infiltrated into the riparian soil between nest 11B and 11A (Figure 2(e)). At the Speed and Road 10 sites, subsurface flow was mainly parallel to the ground surface throughout the year. Some upward flow near the stream occurred at depths of < 3 m under high water table conditions at the Road 10 site.

Subsurface flows from the adjacent upland ceased in summer and early autumn at the Ganatsekiagon, Hwy. 27 and Vivian sites. Although during high flow periods the water table was within 0.7 m of the ground surface in the three riparian zones, the water table declined below the confining layer at these sites in 2001 and 2002 to minimum elevations of >150 cm (Ganatsekiagon), >200 cm (Hwy. 27) and >250 cm (Vivian).

Groundwater nitrate concentrations shown in Figure 3 are representative of patterns during high water table periods. Although temporal variations during high water table periods were observed, the overall groundwater nitrate patterns at the sites remained similar throughout the 2-year study period for high water table conditions (Vidon and Hill 2004b). Data indicate that a nitrate plume extended from the adjacent cropland into the riparian zone at all sites except Vivian. At this site subsurface NO_3^--N declined from >10 to <1 mg L^{-1} near the field edge before reaching the riparian zone (Figure 3(h)). High groundwater NO_3^--N concentrations declined steeply to <1 mg L^{-1} within a short distance from the riparian perimeter at the Maskinonge and Hwy. 27 sites, whereas elevated nitrate concentrations extended for much greater distances across the riparian area at several other sites.

Groundwater with NO_3^--N concentrations of 20–30 mg L^{-1} at the hillslope base of the Boyne riparian zone flowed at depth in sands beneath peat for a horizontal distance of >150 m before declining to less than 5 mg L^{-1} near the river bank (Figure 3(c)). The NO_3-N concentration at the riparian perimeter varied between 5 and 8 mg L^{-1} at the Speed site and remained high until nests 3 and 2A, where most of the nitrate decline took place between 1 and 3 m of depth (Figure 3(d)). High NO_3^--N concentrations in subsurface flow at the Ganatsekiagon site also only declined to low levels near the stream. Small surface streamlets formed by groundwater emerging at the surface near the upland perimeter at Eramosa, Boyne and Maskinonge sites had elevated nitrate concentrations that extended for varying distances across the riparian area before recharging to underlying soils.

Riparian groundwater nitrate concentrations for a date representative of low water table conditions are shown in Figure 4. Although the nitrate plumes observed at the Boyne, Road 10, Speed and Maskinonge sites in the summer and early autumn generally extended a shorter distance into the riparian zone than in the spring, the spatial pattern of nitrate distribution remained similar (Figures 3 and 4). Nitrate concentration patterns also remained similar throughout the year at the Eramosa site (data not shown). The Ganatsekiagon, Hwy. 27 and Vivian sites

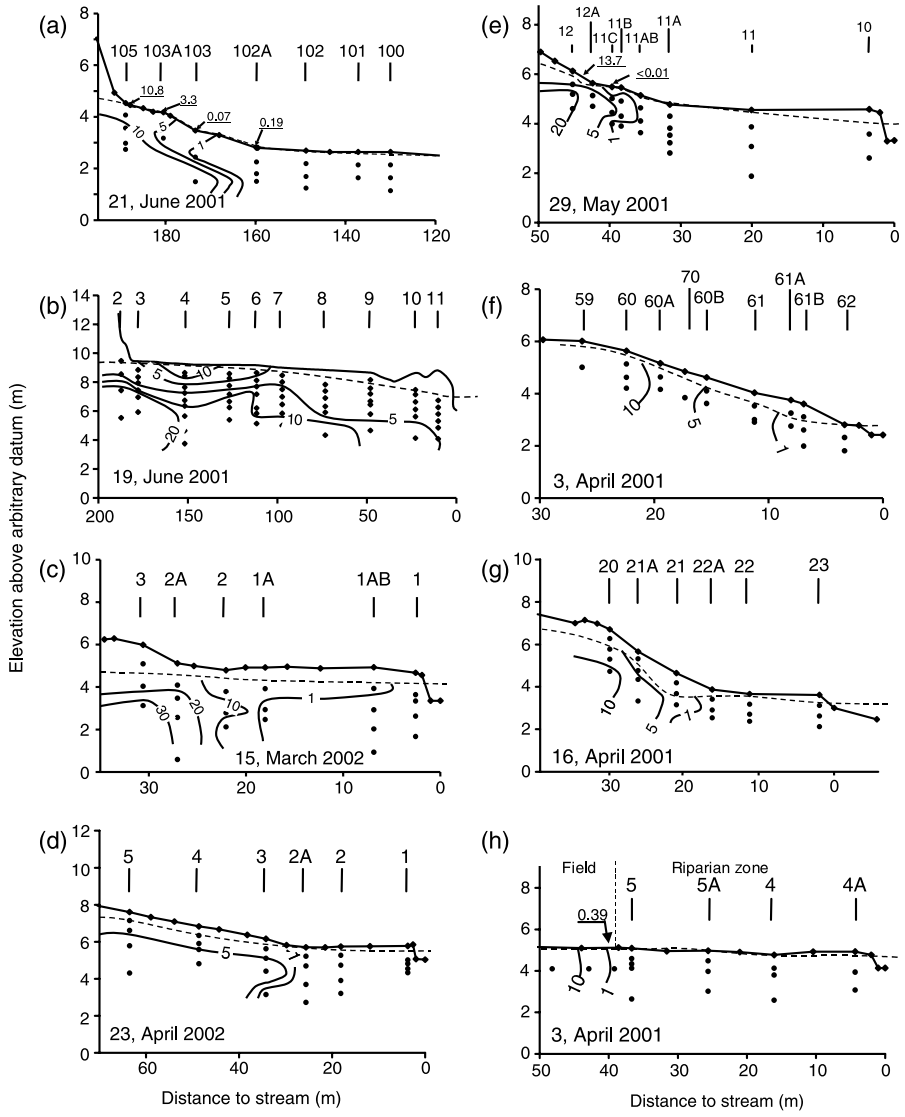


Figure 3. Vertical cross section along the main transect showing NO_3^--N concentration contours (mg L^{-1}) for high water table conditions. Dots represent piezometer slot zones. Arrows indicate the NO_3^--N concentration (mg L^{-1}) in surface streamlets. Dashed line indicates the water table. (a) Eramosa; (b) Boyne; (c) Road 10; (d) Speed; (e) Maskinonge; (f) Ganatsekiagon; (g) Hwy. 27; (h) Vivian.

became hydrologically disconnected from their upland aquifer for most of the summer and early autumn.

Mean Cl^- concentrations in the vertical dimension for piezometer nests along the main groundwater flow path from the riparian perimeter shown in Figure 5 are for

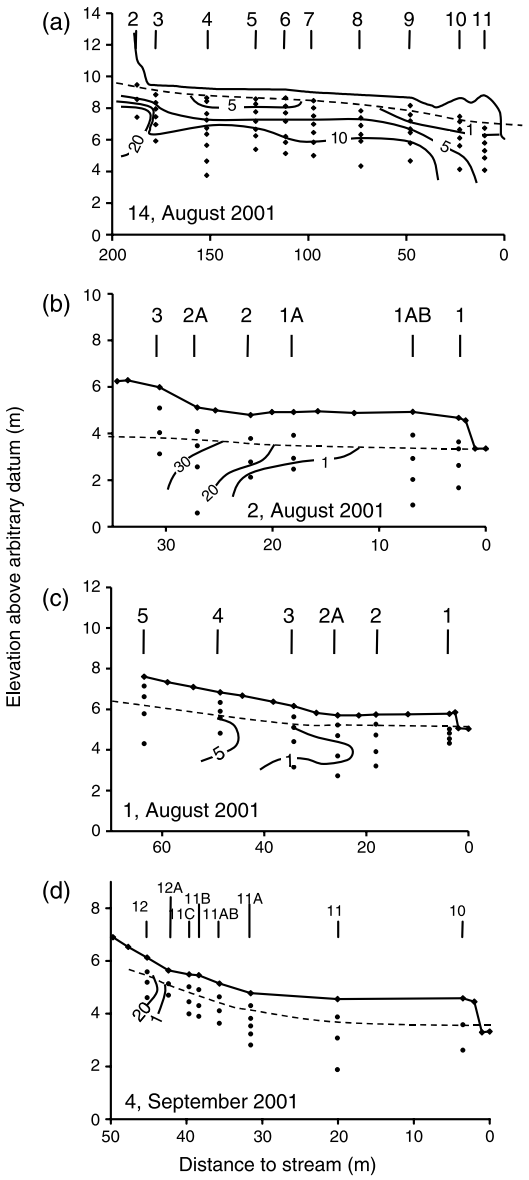


Figure 4. Vertical cross section along the main transect showing NO_3^--N concentration contours (mg L^{-1}) for low water table conditions. Dashed line indicate the water table. Dots represent piezometer slot zones. (a) Boyne; (b) Road 10; (c) Speed; (d) Maskinonge.

the same representative high water table date as the nitrate patterns. At the Speed, Eramosa, Maskinonge, Ganatsekiagon, Hwy. 27 and Vivian sites, chloride concentrations at the riparian perimeter varied between 10 and 30 mg L^{-1} and are

typical of agricultural areas where KCl fertilizer is used. Higher chloride concentrations occurred in groundwater at the Boyne River and Road 10 sites as a result of deicing salts applied on adjacent roads as well as fertilizer use.

Decreases in chloride concentrations were generally small between the field edge, and the piezometer nests that showed a 90% groundwater nitrate decline at Boyne, Road 10, Speed, Eramosa, Hwy. 27 and Maskinonge (Figure 5). At the Ganatsekiagon site, Cl^- concentrations decreased progressively across the riparian zone along the main subsurface flow path from 38 mg L^{-1} at the field edge to 22 mg L^{-1} at the 90% nitrate decrease location in early April 2001 (Figure 5(c)). Similar declines in Cl^- occurred on other sampling dates during high water table conditions. Chloride concentrations at the Vivian site showed contrasting patterns showing little variation along the main subsurface flow path in spring 2002, whereas they dropped significantly from 66 mg L^{-1} in the field to 21 mg L^{-1} at the field edge in April 2001 (Figure 5(d)).

DO and organic carbon concentration patterns

Spatial patterns of DO concentration remained similar throughout the study in the riparian zones. Patterns shown in Figure 6 are means of 3–6 dates in 2000–2002. Subsurface water entering the riparian zones from adjacent fields generally had DO concentrations of 4–9 mg L^{-1}, whereas much lower values were often found within the riparian area (Figure 6). Groundwater DO levels declined to 1–2 mg L^{-1} near the riparian margin at the Eramosa, Vivian and Maskinonge sites. In contrast, these low DO concentrations were restricted to the stream margin at the Ganatsekiagon site. Higher DO concentrations extended for >30 m across the Speed riparian zone and DO values in the Boyne riparian zone were >6 mg L^{-1} at depth in the sands for >100 m from the hillslope (Figure 6(b)).

The spatial distribution of DOC in groundwater within the riparian zones showed well defined patterns at all sites except Ganatsekiagon (Figure 6). DOC levels at the upland margin of the riparian zones were usually <5 mg L^{-1} and low DOC concentrations of <5 mg L^{-1} extended for a considerable distance across the riparian zones at the Speed and Boyne sites. We did not detect high groundwater DOC concentrations in the Ganatsekiagon riparian area. In contrast, considerable areas of the other riparian zones had DOC concentrations that were >5 mg L^{-1} and often ranged from 10 to 20 mg L^{-1} (Figure 6). These elevated DOC values occurred in peat deposits at Eramosa, Boyne and Maskinonge sites, but we also observed higher groundwater DOC values in subsurface organic-rich layers in many of the riparian zones.

$\delta^{15}N$ isotope data and acetylene injections

The $\delta^{15}N$ values in groundwater flowing from cropland generally ranged from +3.8 to +5.5‰ in most of the riparian zones (Figure 7). Groundwater discharging

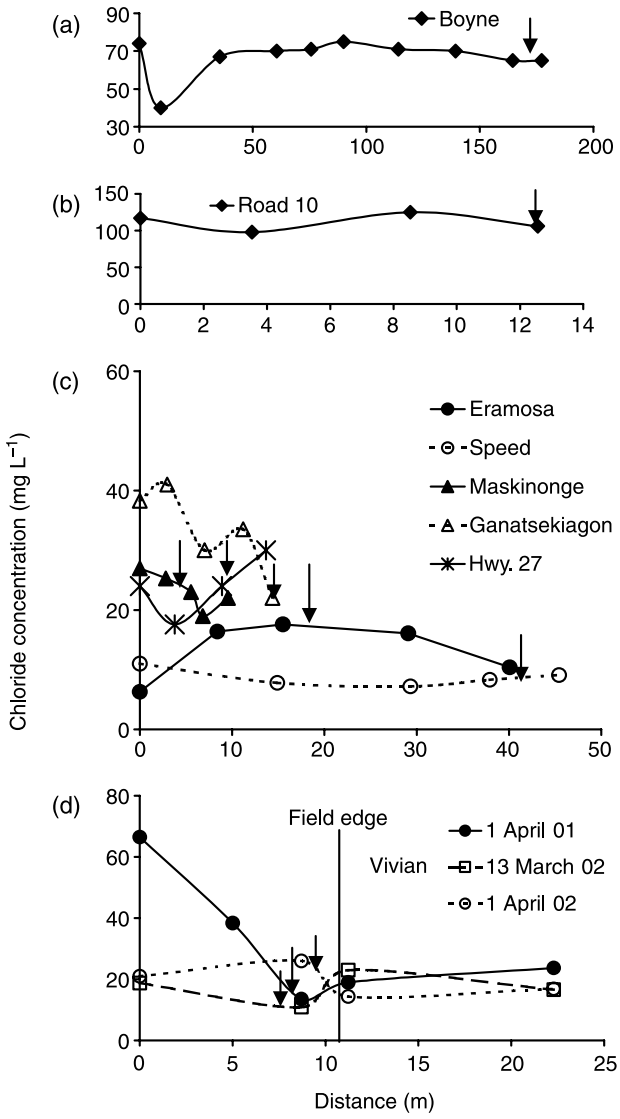


Figure 5. Mean chloride concentrations in piezometers along the main subsurface flow path for high water table conditions in the section of the riparian zones where nitrate is depleted. Black arrows indicate the location where a 90% decline in nitrate concentration is measured. (a) Boyne; (b) Road 10; (c) Eramosa, Speed, Maskinonge, Ganatsekiagon, and Hwy. 27; (d) Vivian.

upwards towards the ground surface near the riparian perimeter showed enriched values of 34.6‰ at Eramosa and 10.5‰ at Maskinonge in conjunction with a large reduction in nitrate concentration (Figures 3 and 7). Elevated $\delta^{15}N$ values were also observed in surface seeps and streamlets in these two riparian zones. A progressive

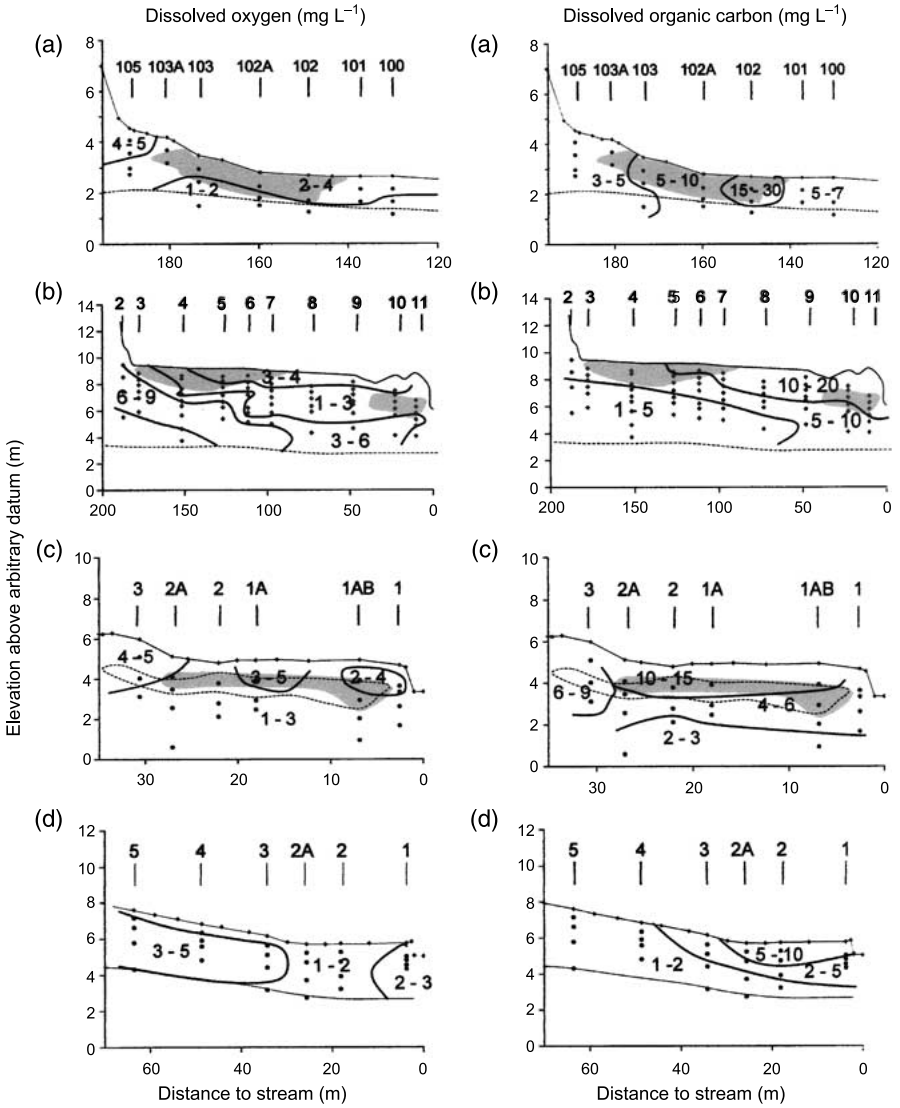


Figure 6. Vertical cross section along the main transect showing DO and DOC concentration contours (mg L^{-1}). DO values are the mean of 3–6 dates and DOC values are the mean of 2–3 dates depending on sites. Dashed lines indicate the confining layer and grey coloured areas indicate organic-rich sediments. (a) Eramosa; (b) Boyne; (c) Road 10; (d) Speed; (e) Maskinonge; (f) Ganatsekiagon; (g) Hwy. 27; (h) Vivian.

$\delta^{15}N$ enrichment from values of 8.5–29.1‰ occurred along the groundwater flow path at the Road 10 site. A similar pattern of high $\delta^{15}N$ values associated with a decrease in groundwater nitrate at the interface between sands and peat or buried

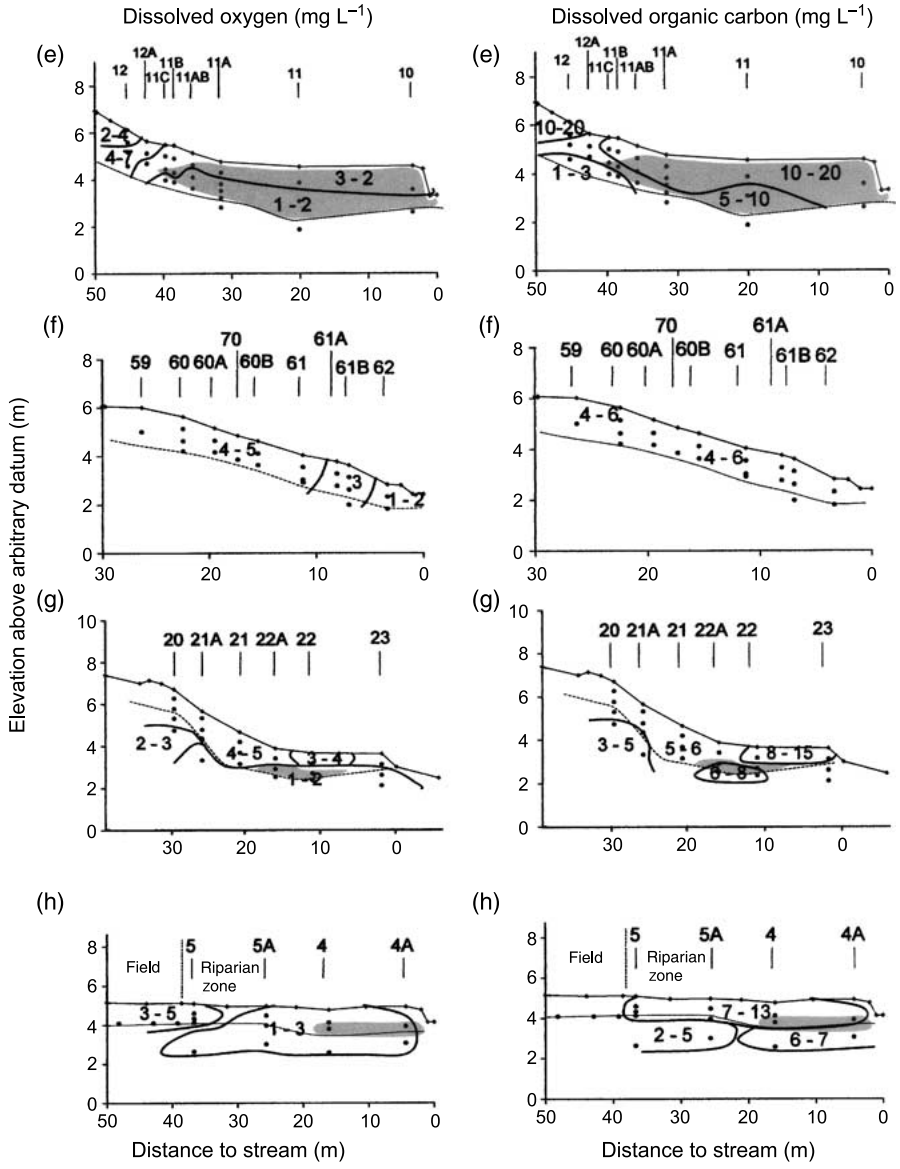


Figure 6. (continued)

channel deposits has been reported by Devito et al. (2000) at the Boyne site (Figure 7(b)).

We did not find evidence of groundwater δ^{15}N isotope enrichment at Ganatsekiagon, where values of δ^{15}N-NO_3^- remained between 14.4 and 12.0‰ along the main subsurface flow path from nest 60 to 61 as NO_3^--N concentrations slowly

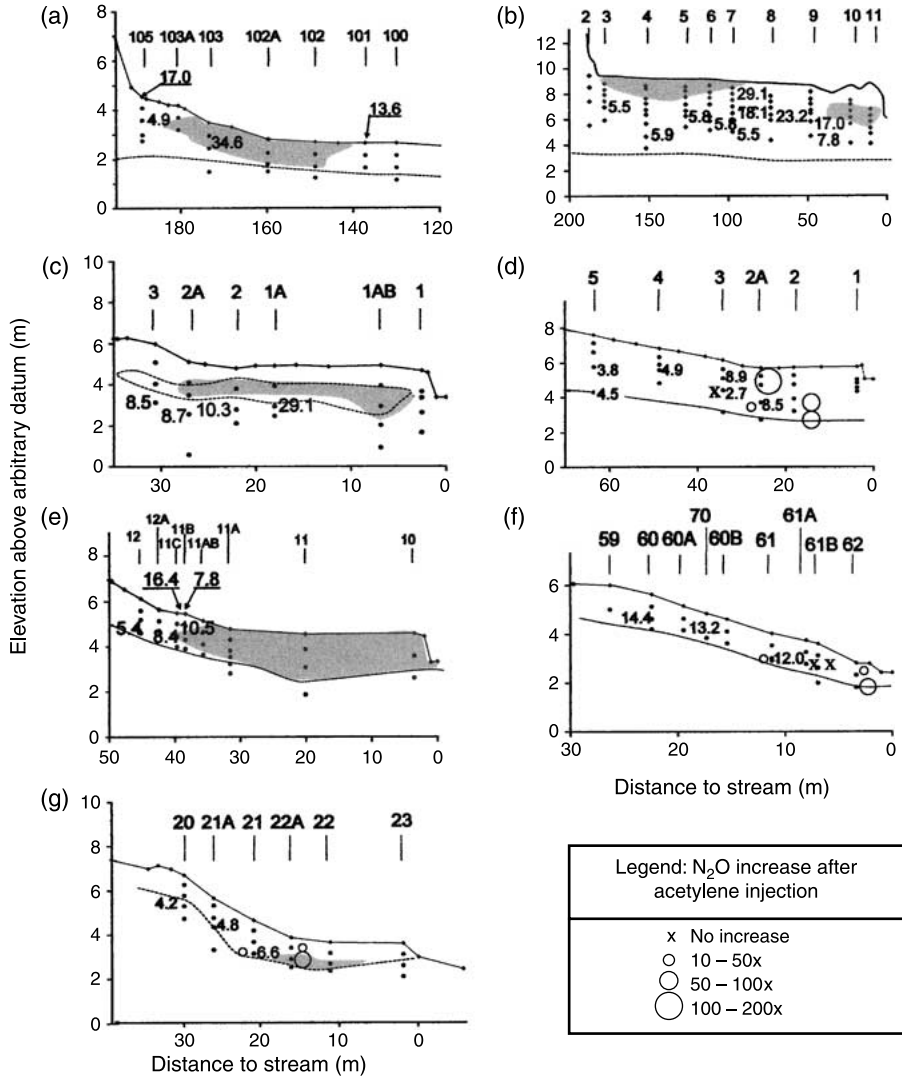


Figure 7. Groundwater $\delta^{15}N$ isotope values along the main transect and maximum increase in nitrous oxide concentrations during a 5 day-period after injection of acetylene into selected piezometers at the Speed, Hwy. 27 and Ganatsekiagon sites. Numbers indicate $\delta^{15}N$ natural isotope abundance of nitrate in piezometers at (a) Eramosa; (b) Boyne; (c) Road 10; (d) Speed; (e) Maskinonge; (g) Hwy. 27 sites. The $\delta^{15}N$ values for the Boyne site were reported by Devito et al. (2000).

decreased from 10.9 to 7.3 mg L^{-1} (Figure 7(f)). A pattern of low $\delta^{15}N$-NO_3^--N values occurred at Speed River from the field perimeter to the mid-point of the riparian zone where a small increase was observed in two piezometers. Little evidence of isotope enrichment was also found at Hwy. 27 where values only rose slightly from 4.2 to 6.6‰ (Figure 7(g)). When all riparian sites were combined

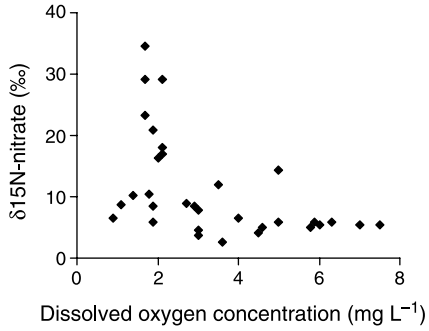


Figure 8. Relationship between groundwater DO concentration (mg L^{-1}) and $\delta^{15}N$-NO_3-N values (‰) for the eight riparian sites.

together, a strong and inverse relationship between groundwater DO and $\delta^{15}N$-NO_3-N values was evident (Figure 8).

Subsurface *in situ* denitrification activity was examined by acetylene blockage in the Speed, Ganatsekiagon and Hwy. 27 riparian zones where $\delta^{15}N$ in NO_3-N did not show clear evidence of strong enrichment. Piezometers and wells selected for acetylene injection were located in areas of the riparian zones where groundwater NO_3^- concentration declined to low levels. Background N_2O concentrations in piezometers before injection at these sites were $<5\,\mu g\,L^{-1}$.

Acetylene additions at the Speed site resulted in N_2O concentrations increases of more than 100 times after 5 days to $420\,\mu g\,L^{-1}$ at nest 2A (1 m). Groundwater N_2O concentrations also increased considerably in nest 2 (1.8 and 2.5 m) and nest 2A (2 m). In contrast, piezometer 3 (1.7 m) showed little response to the acetylene injection (Figures 7(d) and 9(a)). Small increases in N_2O concentration from pre-injection levels were observed at the Ganatsekiagon site in nest 61 (1.1 m) and in the well at nest 62 near the stream. The maximum increase was observed at nest 62 (1 m depth) near the stream where N_2O concentrations increased from 5 to $275\,\mu g\,L^{-1}$ after 3 days. No significant increases in N_2O groundwater concentration were observed in nests 61A and 61B (Figures 7(f) and 9(b)).

At the Hwy. 27 site, NO_3^- was added to the acetylene-saturated groundwater because of low ambient nitrate concentrations. After amendment with KNO_3^-, the NO_3^--N concentration in piezometers increased to a mean value of $9.0\,mg\,L^{-1}$ (range 2.3–19.1) from an average of $0.4\,mg\,L^{-1}$ before amendment. A small increase in N_2O production was observed in nest 21 (1.5 m). Downslope in the riparian zone, a larger N_2O response with peak values of 150 and $180\,\mu g\,L^{-1}$ was observed in nest 22A at depths of 0.5 and 1 m, respectively (Figures 7 (g) and 9(c)).

Most piezometers which showed a large increase in N_2O response to acetylene injection were located in areas where a decline in groundwater NO_3^- concentrations was associated with an increase in DOC and a decrease in DO concentration. This pattern was especially strong at the Speed site where maximum N_2O response occurred in nest 2A (1 m) where DO was 1–2 mg L^{-1} and DOC concentrations

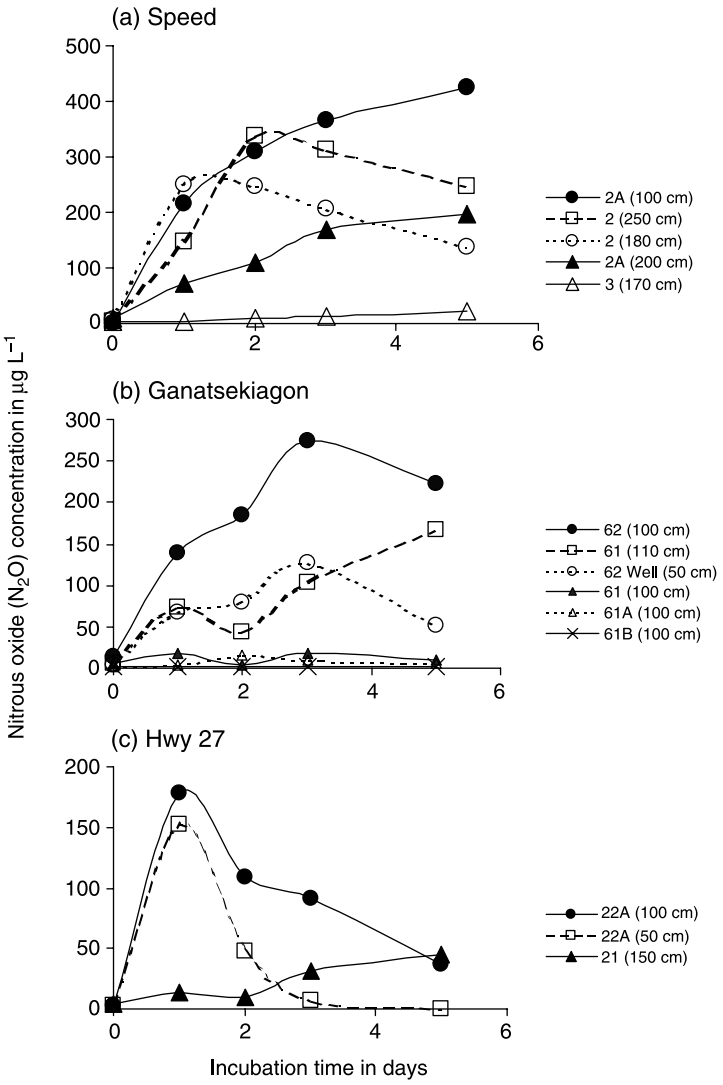


Figure 9. Nitrous oxide concentration in $\mu g\,L^{-1}$ in selected piezometers 1, 2, 3 and 5 days after acetylene injection. (a) Speed; (b) Ganatsekiagon; (c) Hwy. 27.

increased from low values upslope to 5–10 $mg\,L^{-1}$. At the Ganatsekiagon site, groundwater nitrate concentrations decreased gradually downslope and DOC concentrations were relatively stable across the riparian zone, nevertheless the only location that showed a significant N_2O concentration increase was near the stream when DO dropped to 1–2 $mg\,L^{-1}$. The maximum N_2O response at the Hwy. 27 site occurred in nest 22A (1 m) where DO was 1–2 $mg\,L^{-1}$ and DOC increased to 6–

8 mg L^{-1}, whereas in nest 21 (1.5 m) where the N_2O response was weak, DO values were generally >3–4 mg L^{-1}.

Discussion

The results of this study indicate large declines in groundwater NO_3-N concentrations from levels that are often >10 mg L^{-1} at the field-riparian edge to concentrations of <1 mg L^{-1} near the stream channel at most riparian sites. Although there were variations among riparian areas in the distance of the nitrate plume extension towards the stream, a nitrate decline was observed throughout the year in all riparian zones (Figures 3 and 4).

The groundwater chloride data suggest that dilution cannot account for a major portion of the nitrate decrease observed in most of the riparian zones (Figure 5). Mean chloride concentrations along the main subsurface flow path at the Road 10, Speed, Maskinonge and Hwy. 27 sites varied by <25% between the field edge and the location within the riparian zone where a 90% decline in nitrate concentration occurred, suggesting that biological removal was mainly responsible for the nitrate decrease. The initial drop in Cl^- concentration near the slope base in the Boyne riparian zone is due to the mixing of shallow groundwater from unfertilized pastures upslope with deeper chloride-rich groundwater from potato fields on the sand plain (Devito et al. 2000). This local dilution does not affect the general chloride concentration pattern along the groundwater flow path beneath the riparian zone. Dilution was also not important at the Eramosa site where chloride concentrations increased considerably along the groundwater flow path. This pattern was caused by a downslope increase in chloride concentrations in deeper groundwater that discharged towards the riparian surface between nests 105 and 103, although the nitrate concentration of this groundwater input remained constant (Figure 3(a)).

At the Ganatsekiagon site, there was a progressive decrease in Cl^- concentration across the riparian zone indicating that dilution could be partly responsible for the groundwater nitrate decrease observed at this site (Figure 5(c)). However, Cl^- only decreased by 40% in the portion of the riparian zone where a 90% nitrate decline was measured suggesting that biological removal of nitrate was also important in this riparian zone. Chloride concentrations were variable at the Vivian riparian site during high water table periods. Large declines indicate that dilution could account for up to 60% of the nitrate decrease on some dates, whereas minor chloride variations on other dates suggest that dilution was not a factor in the nitrate decline (Figure 5(d)).

Our results indicate that well organized patterns of electron donors and acceptors were present in all riparian zones with oxic subsurface water containing high NO_3^- concentrations entering the riparian zones, whereas areas of low DO and increased DOC associated with low NO_3^- concentration occurred within the riparian zones. These patterns provide strong support for the view that the biogeochemistry of stream riparian zones can be understood by using a thermodynamic perspective that considers how microbial communities interact with supplies of electron donors and acceptors (Hedin et al. 1998).

Spatial patterns of DO and DOC in groundwater indicate the occurrence of biogeochemical conditions favourable for denitrification in all of the riparian areas in this study. Anaerobic conditions (DO $<2\,mg\,L^{-1}$) were often observed at some locations across the riparian zones in conjunction with DOC concentrations of $5\,mg\,L^{-1}$ or higher. Analysis of riparian lithology suggests that these locations are associated with organically-enriched substrates that include peats (Boyne, Eramosa and Maskinonge sites), buried channel deposits (Road 10 and Boyne) and buried soil horizons (Hwy. 27 and Vivian) (Hill et al. 2004). Analysis of the three-dimensional groundwater flow patterns indicates that supplies of nitrate are transported to these locations within the riparian zones creating conditions suitable for denitrification (Groffman 1994; Hedin et al. 1998).

At the Eramosa, Boyne, Speed, Maskinonge and Hwy. 27 sites, the $\delta^{15}N$ values of groundwater entering the riparian zones at the field edge vary between 3.8 and 5.5‰ indicating groundwater derived from agricultural soils and inorganic fertilizers (Wassenaar 1995). Higher $\delta^{15}N$ values between 8.5 and 14.4‰ in groundwater entering the Road 10 and Ganatsekiagon site suggest the use of animal manure fertilizers in the upland field (Kendall and Aravena 2000).

Microbial denitrification produces strong isotopic fractionation that causes any NO_3^- that remains to be progressively enriched in isotopically heavier ^{15}N (Mariotti 1986; Bottcher et al. 1990; Menges et al. 1999). Groundwater nitrate became significantly enriched in ^{15}N-NO_3^- along the main subsurface flow path in the Eramosa, Road 10 and Maskinonge riparian zones indicating that denitrification was occurring actively at these sites. Groundwater nitrate patterns in the Boyne riparian zone measured in the present study in 2000–2002 are similar to the patterns observed by Devito et al. (2000) and Hill et al. (2000) in 1996–1998. The ^{15}N data reported by Devito et al. (2000) show considerable enrichment of residual nitrate in ^{15}N (Figure 7(b)) at piezometer nests where groundwater nitrate patterns measured in June and August 2001 indicate a rapid decline (Figures 3 and 4) suggesting that denitrification continues to occur actively in this riparian zone.

The $\delta^{15}N$ results at the Speed and Hwy. 27 sites showed only a small downslope increase. At the Speed site, groundwater DO concentrations were $3–5\,mg\,L^{-1}$ and DOC were $1–2\,mg\,L^{-1}$ in the first half of the riparian zone suggesting conditions unfavourable for denitrification. An absence of denitrification is consistent with low $\delta^{15}N$ values and minor declines in nitrate concentration in this portion of the riparian zone. An small increase in $\delta^{15}N$ values to 8.2–8.9‰ was found between nests 3 and 2A, where DO dropped to $1–2\,mg\,L^{-1}$ and an increased in DOC values was associated with a sharp decrease in NO_3^- concentration, suggesting that denitrification occurs at this location. At the Hwy. 27 site, $\delta^{15}N$ only increased slightly between nests 20 and 21. Although there was some decline in groundwater nitrate concentrations in this section of the riparian zone, DO concentrations were $4–5\,mg\,L^{-1}$. The $\delta^{15}N$ values in the Ganatsekiagon riparian zone did not increase between nests 60 and 61 suggesting that denitrification did not occur in the upper portion of the riparian zone. This is consistent with the high DO values ($4–5\,mg\,L^{-1}$) and an absence of high DOC concentrations indicating conditions unfavourable to denitrification. When data for all the riparian zones are combined,

it is evident that strongly enriched δ^{15}N-NO_3^- values that indicate significant denitrification only occur in subsurface waters that contained $<2.1\,mg\,L^{-1}$ of DO (Figure 8).

The use of *in situ* acetylene injection confirms the occurrence of considerable denitrification activity in riparian zones where the ^{15}N evidence was not clear. Significant increases in N_2O concentrations after acetylene injection in piezometers were observed at the Speed, Ganatsekiagon and Hwy. 27 sites. These piezometers were located in zones where steep declines in NO_3^- concentration were associated with low DO and an increase in DOC concentration suggesting that the main mechanism for nitrate removal at these locations is denitrification (Figures 7 and 9). Piezometers at Speed and Hwy. 27 that showed a considerable response to acetylene additions were adjacent to locations where the ^{15}N results revealed a small enrichment. Measurements of δ^{15}N and acetylene injections were not carried out at the Vivian site because the site was hydrologically inactive most the year and NO_3^--N concentrations were $<1\,mg\,L^{-1}$ in the riparian zone. However, laboratory measurements in sediment slurries amended with nitrate revealed high denitrification potentials in the extensive buried soil horizon at the Vivian site (Hill et al. 2004). Consequently, results from ^{15}N-isotopes, *in situ* acetylene injection and lab incubations are consistent in suggesting the occurrence of denitrification along groundwater flow paths in all riparian zones.

The role of vegetation uptake in depleting groundwater nitrates was not examined in the present study, and the relative importance of root uptake and denitrification cannot be determined precisely. However, in addition to the strong evidence for denitrification (^{15}N-isotope and acetylene injection data), other types of evidence suggest that vegetation cannot be the main mechanism for nitrate removal. Groundwater nitrate concentration patterns were similar in the spring and the summer for the Boyne, Road 10, Speed and Maskinonge riparian zones (Figures 3 and 4). Small changes in the pattern are probably the result of lower hydraulic gradients and reduced inputs from the adjacent fields in summer rather than the influence of increased nitrate uptake by plants. During the winter when the vegetation is dormant, nitrate patterns showed patterns of decline along groundwater flow paths that were similar to other seasons of the year in these riparian areas (data not shown) although mean monthly air temperatures were -3 to $-7\,^{\circ}C$ and a deep snow cover was often present for several months. Nitrate concentrations patterns also remained similar throughout the year at the Eramosa site. At the Hwy. 27, Ganatsekiagon and Vivian sites, nitrate concentration patterns observed during midwinter thaws were similar to those observed in the spring. In the summer, these sites were hydrologically disconnected from their upland and therefore did not receive any nitrate input from upslope.

Our data also indicate that nitrate removal is often confined to narrow regions of the riparian zone throughout the year particularly at Speed, Eramosa, Boyne and Maskinonge (Figures 3 and 4). Steep changes in nitrate concentration along the main subsurface flow path within a few meters were not related to any change in surface vegetation composition or biomass suggesting that vegetation uptake is not the main mechanism responsible for nitrate removal at these sites.

The results of the present study do not support views of riparian functioning that suggest that denitrification is the main process involved in nitrate removal during the winter when the water table is high, whereas vegetation uptake is the dominant process in the summer when the water table drops (Correll 1997; Burt et al. 2002). We suggest that denitrification can be the primary mechanism for nitrate removal from groundwater in riparian zones in a wide range of landscape hydrogeologic settings. Denitrification was responsible for nitrate removal in the Boyne and Eramosa sites that have hydric soils with shallow water tables sustained by large continuous groundwater inputs from thick upland aquifers. However, it was also the dominant mechanism for nitrate removal in riparian areas with non-hydric soils (Speed, Road 10 and Hwy. 27) where the water table declines to 1 m below the surface in late spring and summer each year.

Although landscape hydrogeology does not limit the occurrence of denitrification to particular riparian sites, it does influence the location of areas of high activity within the riparian environment. Key landscape variables such as topography, permeable sediment depth overlying a confining layer and riparian sediment texture influence the linkages between groundwater flow paths and the supplies of electron donors and acceptors that affect the location of denitrification 'hot spots'.

The occurrence of denitrification hot spots near the riparian perimeter can be linked to upward discharge of groundwater induced by thinning of coarse gravel deposits downslope at the Eramosa site and the presence of low conductivity peat in the Maskinonge riparian zone. This flow path results in the interaction of nitrate-rich groundwater with increased DOC supplies in surface soils creating a narrow zone of enhanced denitrification activity. A similar pattern of denitrification in groundwater discharge at the margin of a Danish riparian fen has been the focus of detailed studies (Blicher-Mathiesen and Hoffman 1999; Hoffman et al. 2000). Other researchers have also reported rapid nitrate depletion in groundwater within a few meters of the upland-riparian margin, although patterns of electron donors and acceptors were not measured (Lowrance 1992; Haycock and Burt 1993; Dhondt et al. 2002).

Considerable depths of coarse textured gravels and sands deficient in organic matter overlie a confining unit at depths of 3 and 6 m in the Speed and Boyne riparian zones, respectively. This riparian lithology permits the lateral transport of an oxic plume of nitrate-rich groundwater beneath surface soils for a considerable distance across the riparian zone before interaction occurs with increased levels of DOC at depth near the channel. In contrast, in riparian zones where a confining layer is absent, nitrate removal may be ineffective as deeper and more vertical flow paths bypass zones of high denitrification activity (Bohlke and Denver 1995; Hedin et al. 1998).

Topography can also affect the location of denitrification hot spots in riparian areas. The removal of nitrate from subsurface water in the field near the riparian margin of the Vivian site may be linked in part to low hydraulic gradient and long water residence times. In contrast, at the sloping Ganatsekiagon site, denitrification was restricted mainly to a small level area near the stream where soil organic matter increased to 5–6% at depths of 35–60 cm and was $>2\%$ at a depth of 80 cm (Hill et al. 2004).

Conclusions

This study indicates the widespread occurrence of well organized patterns of electron donors and acceptors and evidence of denitrification as the primary mechanism for nitrate removal in riparian zones in southern Ontario landscapes with contrasting hydrogeologic characteristics and in locations ranging from headwater 1st order streams to mid-size 4th and 5th order rivers. These results also suggest that the location of 'hot spots' of denitrification within riparian areas can be explained by the influence of key landscape variables such as slope, sediment texture and depth of confining layers on the interaction between hydrologic pathways and supplies of electron donors and acceptors. Three-dimensional spatial patterns of groundwater nitrates in the riparian zones examined in this study do not suggest that vegetation uptake was a dominant nitrate removal mechanism. It may be unnecessary to invoke explanations for nitrate removal that involve seasonal changes in removal mechanisms in riparian areas where organic layers at depth provide a favourable site for denitrification during summer low water table periods.

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References

Altman S.J. and Parizek R.R. 1995. Dilution of nonpoint-source nitrate in groundwater. J. Environ. Qual. 24: 707–718.

Ambus P. and Lowrance R. 1991. Comparison of denitrification in two riparian soils. Soil Sci. Soc. Am. J. 55: 994–997.

Blicher-Mathiesen G. and Hoffman C.C. 1999. Denitrification as a sink for dissolved nitrous oxide in a freshwater riparian fen. J. Environ. Qual. 28: 257–262.

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.

Bottcher J., Strebel O., Voerkelius S. and Schmidt H.L. 1990. Using isotope fractionation of nitrate nitrogen and nitrate oxygen for evaluation of microbial denitrification in a sandy aquifer. J. Hydrol. 114: 413–424.

Bragan R.J., Starr J.L. and Parkin T.B. 1997. Shallow groundwater denitrification rate measurement by acetylene block. J. Environ. Qual. 26: 1531–1538.

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

Burt T.P., Pinay G., Matheson F.E., Haycock N.E., Butturini A., Clement J.C., Danielescu S., Dowrick D.J., Hefting M.M., Hillbricht-Ilkowska A. et al. 2002. Water table fluctuations in the riparian zone: comparative results from a pan-European experiment. J. Hydrol. 265: 129–148.

Cey E.E., Rudolph D.L., Aravena R. and Parkin G. 1999. Role of the riparian zone in controlling the distribution and fate of agricultural nitrogen near a small stream in southern Ontario. J. Contam. Hydrol. 37: 45–67.

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

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

Correll D.L. 1997. Buffer zones and water quality protection: general principles. In: Haycock N.E., Burt T.P., Goulding K.W.T. and Pinay G. (eds) Buffer Zones: Their Processes and Potential in Water Protection. Quest Environmental, pp. 7–20.

Devito K.J. and Hill A.R. 1997. Sulphate dynamics in relation to groundwater–surface water interactions in headwaters wetlands of the Southern Canadian Shield. Hydrol. Process. 11: 485–500.

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

Dhondt K., Boeckx P., Van Cleemput O., Hofman G. and De Troch F. 2002. Seasonal groundwater nitrate dynamics in a riparian buffer zone. Agronomie 22: 747–753.

Dosskey M.G. 2001. Toward quantifying water pollution abatement in response to installing buffers on crop land. Environ. Manage. 28: 577–598.

Environment Canada 1979. Analytical Methods Manual. Inland Water Directorate Water Quality Branch, Ottawa, Canada.

Freeze R.A. and Cherry J.A. 1979. Groundwater. Prentice-Hall, Englewood Cliffs, N.J.

Gillham R.W. and Cherry J.A. 1978. Field evidence of denitrification in shallow groundwater flow systems. Water Pollut. Res. Can. 13: 53–71.

Gilliam J.W. 1994. Riparian wetlands and water quality. J. Environ. Qual. 23: 896–900.

Gilliam J.W., Parsons J.E. and Mikkelsen R.L. 1997. Nitrogen dynamics and buffer zones. In: Haycock N.E., Burt T.P., Goulding K.W.T. and Pinay G. (eds) Buffer Zones: Their Processes and Potential in Water Protection. Quest Environmental, pp. 54–61.

Gold A.J., Jacinthe P.A., Groffman P.M., Wright W.R. and Puffer R.H. 1998. Patchiness in groundwater nitrate removal in a riparian forest. J. Environ. Qual. 27: 146–155.

Gold A.J., Groffman P.M., Addy K., Kellog D.Q., Stolt M. and Rosenblatt M.A.E. 2001. Landscape attributes as controls on ground water nitrate removal capacity of riparian zones. J. Am. Water Resour. Assoc. 37: 1457–1464.

Groffman P.M. 1994. Denitrification in freshwater wetlands. Curr. Topics Wetland Biogeochem. 1: 15–35.

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. and Burt T.P. 1993. Role of floodplain sediments in reducing the nitrate concentration of subsurface run-off. A case study in the Cotswolds, UK. Hydrol. Process. 7: 287–295.

Haycock N.E. and Pinay G. 1993. Groundwater nitrate dynamics in grass and poplar vegetated riparian buffer strips during the winter. J. Environ. Qual. 22: 273–278.

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

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

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

Hill A.R., Devito K., Campagnolo S. and Sanmugadas K. 2000. Subsurface denitrification in a forested riparian zone; interactions between hydrology and supplies of nitrate and organic carbon. Biogeochemistry 51: 193–223.

Hill A.R., Vidon P. and Langat J. 2004. Denitrification potential in relation to lithology in five headwater riparian zones. J. Environ. Qual. 33: 799–804.

Hoffman C.C., Rysgaard S. and Berg P. 2000. Denitrification rates predicted by nitrogen-15 labeled nitrate microcosm studies, *in situ* measurements, and modeling. J. Environ. Qual. 29: 2020–2028.

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

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

Karr J.D., Showers W.J., Gilliam J.W. and Andres A.S. 2001. Tracing nitrate transport and environmental impact from intensive swine farming using delta nitrogen-15. J. Environ. Qual. 30: 1163–1175.

Kendall C. and Aravena R. 2000. Nitrate isotopes in groundwater systems. In: Cook P.G. and Herczeg A.L. (eds) Environmental Tracers in Subsurface Hydrology. Kluwer Academic Publishers, Boston, pp. 261–297.

Korom S.F. 1992. Natural denitrification in the saturated zone: a review. Water Resour. Res. 28: 1657–1668.

Lensi R. and Chalamet A. 1982. Denitrification in waterlogged soils: *in situ* temperature-dependent variations. Soil Biol. Biochem. 14: 51–55.

Lowrance R. 1992. Groundwater nitrate and denitrification in a coastal riparian forest. J. Environ. Qual. 21: 401–405.

Lowrance R., Newbold J.D., Schnabel R.R., Groffman P.M., Denver J.M., Correll D.L., Gilliam J.W., Robinson J.L., Brinsfield R.B., Staver K.S., Lucas W. and Todd A.H. 1997. Water quality functions of riparian forest buffers in Chesapeake Bay watersheds.. Environ. Manage. 21: 687–712.

Mariotti A. 1986. Denitrification in groundwaters, principles and methods for its identification: a review. J. Hydrol. 88: 1–23.

Martin T.L., Kaushik N.K., Trevors J.T. and Whiteley H.R. 1999. Review: denitrification in temperate climate riparian zones. Water Air Soil Pollut. 111: 171–186.

McCLain M.E., Boyer E.W., Dent C.L., Gergel S.E., Grimm N.B., Groffman P.M., Hart S.C., Mcdowell W.H. and Pinay G. 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6: 301–312.

Mengis M., Schiff S.L., Harris M., English M.C., Aravena R., Elgood R.J. and MacLean A. 1999. Multiple geochemical and isotopic approaches for assessing ground water NO_3^- elimination in a riparian zone. Ground Water 37: 448–457.

Peterjohn W.T. and Correll D.L. 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. Ecology 65: 1466–1475.

Pinay G., Rogues L. and Fabre A. 1993. Spatial and temporal patterns of denitrification in a riparian forest. J. Appl. Ecol. 30: 581–591.

Roulet N.T. 1990. Hydrology of a headwater basin wetland: groundwater discharge and wetland maintenance. Hydrol. Process. 4: 387–400.

Sabater S., Butturini A., Clement J., Burt T., Dowrick D., Hefting M., Maitre V., Pinay G., Postolache C., Rzepecki M. and Sabater F. 2003. Nitrogen removal by riparian buffers along a European climatic gradient: patterns and factors of variation. Ecosystems 6: 20–30.

Schnabel R.R., Cornish L.F., Stout W.L. and Shaffer J.A. 1996. Denitrification in a grassed and wooded, valley and ridge, riparian ecotone. J. Environ. Qual. 25: 1230–1235.

Simmons R.C., Gold A.J. and Groffman P.M. 1992. Nitrate dynamics in riparian forests: groundwater studies. J. Environ. Qual. 21: 659–665.

Singer S.N., Cheng C.K. and Scathe M.E. 1997. The hydrogeology of southern Ontario, Hydrogeology of Ontario Series, Report 1. Ministry of Environment and Energy, Toronto.

Technicon 1977. Nitrate and nitrite in water and sea water. Industrial Method 158-71 WIA Technicon Industrial System, Tarrytown, New York.

Vidon P. and Hill A.R. 2004a. Landscape controls on the hydrology of stream riparian zones. J. Hydrol. 292: 210–228.

Vidon P. and Hill A.R. 2004b. Landscape controls on nitrate removal in stream riparian zones. Water Resour. Res. 40, W03201, Doi: 10.1029/2003WR002473.

Wassenaar L.I. 1995. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of ^{15}N and ^{18}O in NO_3^-. Appl. Geochem. 10: 391–405.