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Influence of base flow stream bank seepage on riparian zone nitrogen biogeochemistry

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Abstract We examined the effect of sustained stream bank seepage during base flow conditions on the pore water nitrogen biogeochemistry of two riparian zones in lowland agricultural areas in southern Ontario, Canada. Nitrate, ammonium and dissolved oxygen concentrations in riparian subsurface water over a two-year period showed well-organized spatial patterns along stream bank seepage flow paths that extended seasonally up to 25 m inland. High levels of dissolved oxygen and NO_3^- in stream inflow were depleted rapidly at the stream bank interface suggesting the occurrence of aerobic microbial respiration followed by denitrification. A zone of NH_4^+ accumulation persisted in more anaerobic sediments inland from the bank margin, although the magnitude and intensity of the pattern varied seasonally. A bromide tracer and NO_3^- co-injection at the stream bank interface indicated that bank seepage occurred along preferential flow paths in a poorly sorted gravel layer in the two riparian zones. Depletion of NO_3^- in relation to co-injected bromide confirmed that the bank margin was a hot spot of biogeochemical activity within the riparian zone. Conceptual models of humid temperate riparian zones have focused on nitrogen biogeochemistry in relation to hillslope to stream hydrologic flow paths. However, our results suggest that sustained stream bank inflow during low flow conditions can exert a dominant control on riparian nitrogen cycling in lowland landscapes where level riparian zones bounded by perennial streams receive limited subsurface inflows from adjacent slopes.

Keywords Nitrogen cycling · Groundwater · Riparian zone · Stream bank seepage · Denitrification · Nitrogen flushing

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Introduction

Stream riparian zones have been a major focus of research in the past two decades because of their role as important landscape ecotones for the regulation of energy and material fluxes between land and aquatic ecosystems (Gregory et al. 1991; Haycock et al. 1997; Naiman and Decamps 1997). Knowledge of hydrology in riparian environments is essential for an understanding of the chemistry. Differences in water residence time and the location of interaction of various surface and subsurface hydrologic flow paths in riparian zones influence element transformations and retention (Hill 1990; Burt 2005). Water table fluctuations and the extent of surface saturation in riparian areas are linked to spatial and temporal patterns of soil redox reactions that regulate biogeochemical processes (Hefting et al. 2004). The dynamics of soil redox potential exert a particularly strong control on nitrogen cycling in riparian soils (Reddy and Patrick 1975 Groffman and Tiedje 1989).

Much of the hydrologic research related to riparian zones has centred on the interactions between hillslopes and riparian zones in headwater forested and agricultural watersheds in humid temperate landscapes (Cirmo and McDonnell 1997; Hill 2000). It has generally been assumed that the riparian water table in these landscapes is controlled mainly by hillslope runoff and the influence of the adjacent stream is restricted to short-lived flood events (Burt et al. 2002). However, studies of riparian zones in Europe have recorded more sustained reversals of hydraulic gradient from the stream inland that were not linked to floods (Haycock and Pinay 1993, Burt et al. 2002). Stream bank seepage into riparian sediments during summer base flows also influenced riparian hydrology in several lowland agricultural areas of southern Ontario, Canada (Vidon and Hill 2004a). Recently, Duval and Hill (2006) have suggested that prolonged periods of stream bank seepage may be a dominant factor controlling hydrology in flat riparian zones along low-order perennial streams, where discharge from adjacent hillslopes is seasonally absent.

Research concerning the role of headwater riparian zones as buffers that regulate water chemistry has focused on surface and groundwater flow paths that transport sediment and solutes from hillslopes through riparian zones to the stream channel (Burt and Haycock 1996; Correll 1997; McGlynn and Siebert 2003). Numerous studies have examined the effectiveness of riparian zones for the removal of nitrates in subsurface flows from upslope landscapes affected by agriculture and other human activities (Hill 1996: Sabater et al. 2003; Vidon and Hill 2004b). The current paradigm of riparian zone nitrogen processing holds that high levels of nitrate in subsurface water from an abutting agricultural field can often be effectively removed during transport through the riparian zone to the stream channel, primarily through the process of denitrification (Cooper 1990; Lowrance 1992; Clement et al. 2003).

Despite this extensive body of research, McClain et al. (2003) have emphasised that a full understanding of the controls on zones of enhanced biogeochemical reaction rates in landscapes and an ability to predict their location requires increased knowledge of biogeochemical transformations associated with different hydrological flow paths in a greater range of landscape settings. The biogeochemistry of riparian zones affected by sustained stream bank seepage has received little attention. The removal of pollutants including nitrates in riverbank infiltration has been studied in areas where drinking water production occurs in alluvial aquifers adjacent to large rivers (Grischek et al. 1998; Hiscock and Grischek 2002). However, the effect of prolonged periods of stream bank seepage during base flow conditions on the nitrogen cycling of headwater valley riparian zones in lowland temperate landscapes has not been previously investigated. Because sustained stream inflow has important controls on riparian zone hydrology (Duval and Hill 2006), we suggest that it also has a considerable effect on riparian zone biogeochemistry. In this study we examine how the spatial and temporal extent of stream inflow and its interaction with hillslope runoff affect subsurface riparian nitrogen dynamics in lowland agricultural landscapes. The spatial pattern of nitrate, ammonium, and dissolved oxygen concentrations collected from piezometer networks were used to investigate the chemistry of the groundwater system at the riparian zone scale. The co-injection of a bromide tracer with nitrate in a plot scale study at the stream bank interface was also used to examine the dynamics of nitrate transport and removal during bank seepage in greater detail.

Study sites

The study was conducted in two riparian sites located in agricultural watersheds north of Toronto in southern Ontario, Canada. This region has an annual precipitation of 800–900 mm year^{-1}, with 120–240 mm falling as snow between December and April (Singer et al. 1997). The stream hydrological regime is characterized by a high water period during snowmelt in March–April and minimum base flows of 10–12 L s^{-1} in July–August. During the study period, temperatures and rainfall were similar to the 30 year normal in summer 2003, whereas the summer of 2004 was cooler and rainfall was 44% higher than normal in July.

One of the riparian sites was located in a gently sloping glacial outwash landscape along Vivian Creek, a second order tributary of the Black River, which flows into Lake Simcoe. The second riparian site, which was relatively flat with a 3–10% slope gradient at the upland perimeter, was located in a glacial till landscape along a second order tributary of West Duffins Creek that flows into Lake Ontario. The vegetation of the two riparian sites was characterized by an herbaceous plant community of grasses and forbs except for the upstream area at Vivian Creek where a stand of Northern white cedar (*Thuja occidentalis* L.) was located.

The soil profile at both sites consisted of a 0.8–1.0 m deep mix of loamy sand and sandy loam. Below this, a poorly sorted gravel layer occurred at both sites, ranging in thickness from 5 cm to 30 cm at Vivian Creek and 30 cm to 75 cm at W. Duffins Creek, where the sediment was coarser than at Vivian Creek (Fig. 1). A 10–15 cm thick organic-rich horizon overlies and grades into this gravel layer near the stream bank at Vivian Creek. Saturated hydraulic conductivities in the gravel layer were highly variable with values measured at 25–30 sites in each riparian zone ranging from 1 cm d^{-1} to >300 cm d^{-1}. The coarse grained layer was underlain by dense till at the W. Duffins Creek site and by outwash silt at the Vivian Creek site, both of which formed an aquitard with low hydraulic conductivities of <0.02 cm d^{-1} beneath the riparian zones (Duval and Hill 2006).

Methods

Within each site, single piezometers were installed at depths of 1–1.2 m in the coarse-grained layer along transects extending from the stream into the riparian zones (Figs. 2 and 3). Piezometers were constructed of narrow diameter PVC pipe with the lowest 20 cm perforated and covered with Nitex mesh to reduce sediment clogging. In addition fully screened ABS wells and nests of piezometers at depths of 0.5–2.0 m were installed at several locations along the field-riparian perimeter and in the riparian zone. Similar hydraulic heads in wells and at various depths in

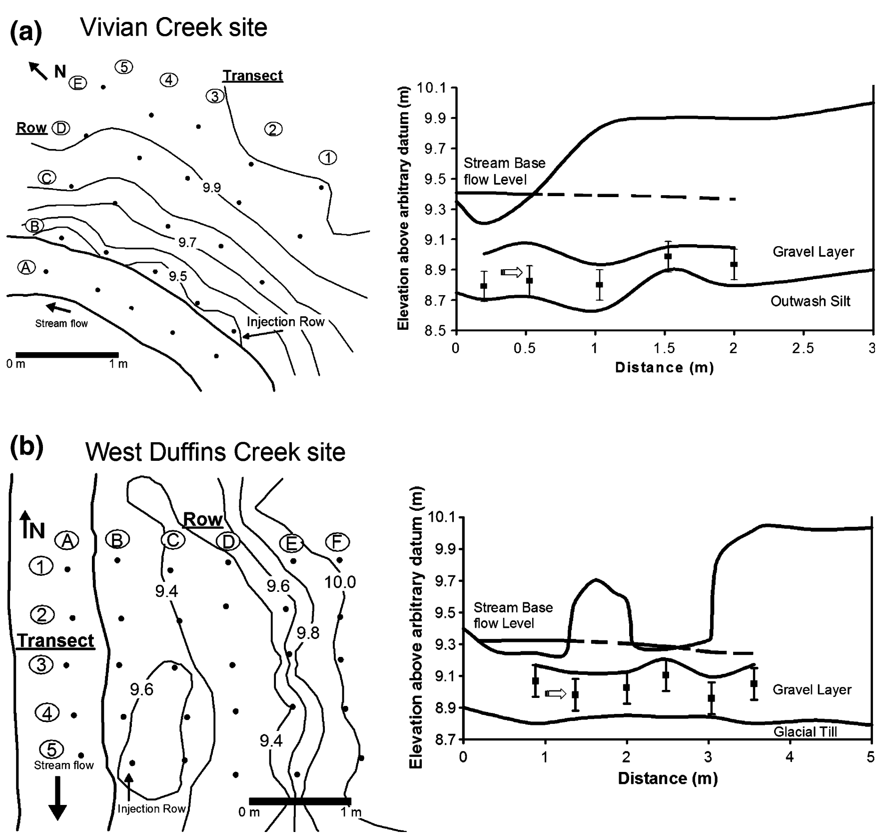

Fig. 1 Topographic maps and cross-section profiles of stream bank plots used in solute injections, with piezometer locations and depths indicated. The arrows in the cross-sections indicate the row of injection piezometers

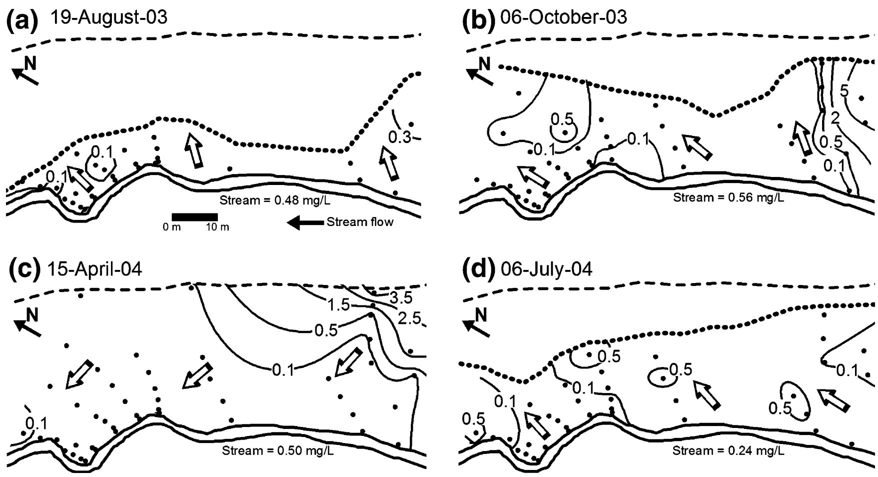

Fig. 2 Seasonal patterns of pore-water nitrate-N concentration within the gravel layer at the Vivian Creek site. Concentration isoline interval is variable. Arrows represent the direction of subsurface flow. The dashed line indicates the riparian zone—agricultural field boundary. The dotted line indicates the area of unsaturated riparian sediments. Piezometer locations indicated by •

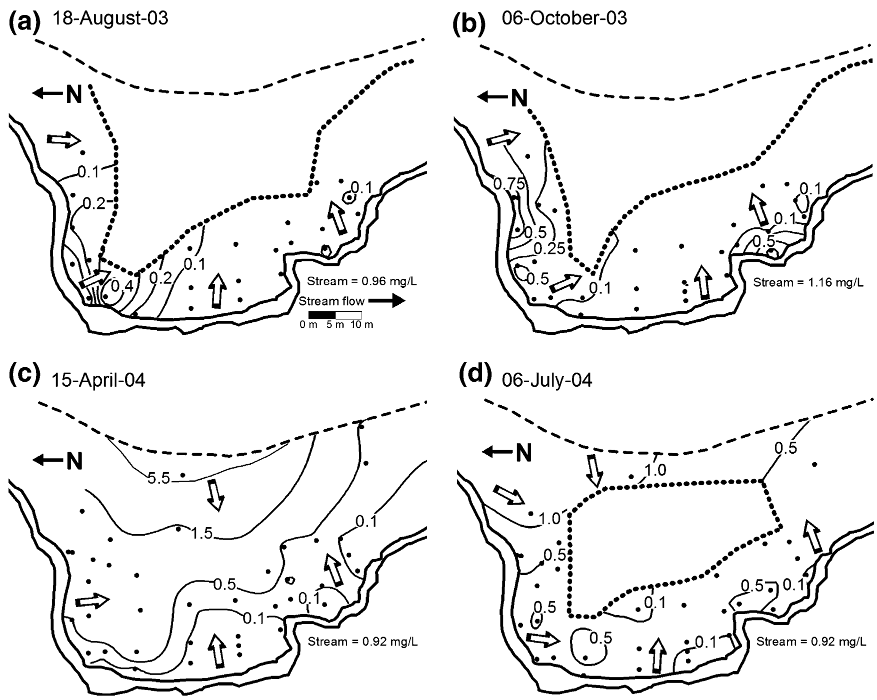

Fig. 3 Seasonal patterns of pore-water nitrate-N concentration within the gravel layer at the West Duffins Creek site. Concentration isoline interval is variable. Arrows represent the direction of subsurface flow. The dashed line indicates the riparian zone—agricultural field boundary. The dotted line indicates the area of unsaturated riparian sediments. Piezometer locations indicated by •

piezometers indicated that vertical hydraulic gradients were very small in both riparian zones.

Groundwater was sampled and hydraulic heads measured at least monthly in April–October 2003 and less frequently in 2004. All piezometers were emptied and allowed to refill before water was sampled. A portable DO meter was used to measure dissolved oxygen in the field. Water samples were collected with Tygon tubing connected to a syringe with a three-way stopcock to prevent contact with the ambient air. The oxygen probe was then inserted directly into the syringe. A second extracted sample was collected and stored in a cooler for transport to the lab for further testing. Samples were placed in the fridge upon return to the lab. Testing for ammonium and nitrate was done through colorimetric determination using a flow-through auto-analyzer using standard procedures (Technicon 1977, 1978). Detection limits for NO_3^--N and NH_4^+-N were 0.003 mg l^{-1}. Topography and the location of wells and piezometers were mapped using a total surveying station. Topographical and dissolved solute contour maps of the riparian sites were produced with Surfer 7 mapping software (Golden Software 1999).

Nitrogen dynamics during bank seepage at the stream channel margin were studied at a plot scale using a co-injection of bromide, a conservative ion, and nitrate. Five rows of piezometers with a 20 cm slot zone were installed in the gravel layer approximately 0.5 m apart in a 25-m^2 grid in both riparian zones near the mid-point of the stream reach (Fig. 1). At this location on West Duffins Creek the margin of the active channel was separated from the bank by a small secondary channel that contained a few centimeters of stagnant water during summer base flows.

Subsurface liquid tracer injections have been reported to alter hydraulic heads around the injection point (Wagner and Bretschko 2002). Instead a small amount of sodium bromide (NaBr) and potassium nitrate (KNO_3) was slowly added as a powder into the row of piezometers at the active channel margin during base flow conditions. The powder was injected with an applied mass NO_3^--N/Br^- ratio of 10% in mid August 2004 at Vivian Creek and a 20% ratio in late September 2004 at W. Duffins Creek. Water from the piezometer grid was sampled at intervals for periods of 10–13 days after injection and the samples were analyzed for bromide (Br^-) using an ion selective electrode (ISE). The probe was cleaned every 5 samples and recalibrated every 30 samples. Sample measurements were repeated during the analysis to check for consistency of values. Background concentrations of porewater Br^- in both plots were <0.3 mg l^{-1} and a value of >1.0 mg l^{-1} was considered to indicate the occurrence of the tracer. Background DO concentrations in subsurface water were <2.5 mg l^{-1} and NO_3^--N concentrations were <0.05 mg l^{-1}. Nitrate depletion was determined by comparing observed nitrate concentrations in piezometers with concentrations predicted from the initial ratio of NO_3^--N and Br^- mass injected.

Results

Riparian subsurface hydrology

The dynamics of riparian groundwater flow is described in detail elsewhere (Duval and Hill 2006). Briefly, during the spring snowmelt period subsurface flow at Vivian Creek occurred in an oblique downvalley direction across the riparian area from the adjoining cropland to the stream. In contrast at W. Duffins Creek hillslope inflow only produced a water table gradient towards the stream in a limited upslope section of the riparian zone. Evapotranspiration reduced hillslope inflow to the two riparian zones by early summer. During this period of water table decline, the stream channel became the hydraulic highpoint in the landscape, producing reach-scale bank seepage at Vivian Creek. Stream inflow to the riparian zone sustained a reversed water table gradient inland for periods of up to four months in summer and autumn at the Vivian Creek site. Stream bank seepage occurred throughout the year at the W. Duffins Creek riparian site where hillslope inflow was restricted by an upslope spur. Despite high evapotranspiration rates in summer, stream inflow maintained a zone of saturated riparian sediments that extended up to 25 m inland.

Water chemistry

Nitrate

During the high water table period in spring, subsurface flows from the adjacent cropland had elevated NO_3^--N concentrations of 2–6 mg l^{-1} near the upland-riparian zone margin, as indicated by the April 2004 data (Figs. 2c and 3c). At Vivian Creek NO_3^--N concentrations elsewhere in the riparian gravel layer were <0.1 mg l^{-1}. Subsurface water with low nitrate levels also occurred in the downstream portion of the W. Duffins Creek riparian area near the channel. In contrast, NO_3^--N concentrations varied between 0.5 mg l^{-1} and 1.0 mg l^{-1} in the upstream portion of the riparian zone inland from the stream channel at this site. Hydraulic gradients and high chloride concentrations indicate that subsurface water in this area originated from the stream channel rather than inflow from the hillslope where chloride concentrations were low (Duval and Hill 2006).

In early summer 2003, the two riparian zones became hydrologically disconnected from the upslope fields. As the water table declined during July and August the area of saturated riparian sediments overlying the confining layer sustained by stream seepage became restricted to a width of 5-10 m at Vivian Creek and approximately 25 m at W. Duffins Creek. Riparian groundwater NO_3^--N concentrations in this zone shown in Fig. 2a and 3a are representative of patterns during July–September 2003. Although stream NO_3^--N levels in summer were usually 0.25–0.5 mg l^{-1} (Vivian Creek) and 0.5–1.2 mg l^{-1} (W. Duffins Creek), concentrations in riparian groundwater were generally at trace levels. Higher NO_3^--N concentrations of 0.1–0.4 mg l^{-1} in a few riparian piezometers suggest the occurrence of localized patches of elevated nitrate in both riparian areas. In the cooler summer of 2004 the two riparian areas had a larger zone of saturated sediments above the confining layer. The riparian area with pore water NO_3^--N concentrations of <0.1 mg l^{-1} in early July 2004 was more restricted than in the previous summer (Figs. 2d and 3d). However, a pattern of localized patches of higher concentration (>0.5 mg l^{-1}) was still evident in both riparian areas.

During autumn, subsurface flows in both riparian areas were still in a stream to field direction but the area of saturated riparian sediments above the confining layer increased with the rising water table. At this time nitrate concentrations in the riparian gravel layer were mainly at trace levels. However, the localized patches of higher nitrate concentrations observed during the summer were more prominent (Figs. 2b and 3b). Pore water NO_3^--N values in several piezometers were >5.0 mg l^{-1} beneath the upstream area of cedars at Vivian Creek, and several locations at W. Duffins Creek had concentrations of 0.5–0.9 mg l^{-1}.

Ammonium

Subsurface water inputs to the riparian area from the upslope agricultural land during the spring had trace level ammonium concentrations at both sites. In contrast, near-stream NH_4^+-N concentrations in riparian subsurface water were elevated at both sites at this time. Near-stream gravel pore water ammonium-N levels of ~1.0 mg l^{-1} in April 2004 at Vivian Creek are representative of patterns observed in spring 2003 and 2004 (Fig. 4c). During this season NH_4^+-N concentrations at W. Duffins Creek in most of the near-stream riparian area were >0.5 mg l^{-1}, with localized patches of 3.0–7.0 mg l^{-1} (Fig. 5c). There was however, an upstream portion of the riparian area near the stream with NH_4^+-N concentrations of <0.1 mg l^{-1}.

During the summer months, with both sites receiving subsurface water through stream seepage, ammonium levels in the riparian pore water increased greatly. In 2003 at Vivian Creek the saturated sediments had NH_4^+-N concentrations 2.0–5.0 mg l^{-1}, with localized patches of >10.0 mg l^{-1} (Fig 4a). During the cooler summer of 2004 however, the NH_4^+–N concentrations were only 1.0–1.6 mg l^{-1} near the stream margin and declined to <0.5 mg l^{-1} inland (Fig 4d). The seasonal increase in NH_4^+-N concentrations at W. Duffins Creek in 2003 and 2004 was less than at Vivian Creek, with levels typically <1.0 mg l^{-1} (Fig. 5a and d). Localized patches of NH_4^+-N concentrations >5.0 mg l^{-1} were still apparent in the summer, however.

In autumn as the saturated zone above the confining layer expanded inland with the rising water table, NH_4^+-N concentrations generally were less than summer values at both sites. Near-stream NH_4^+-N concentrations at Vivian Creek were between

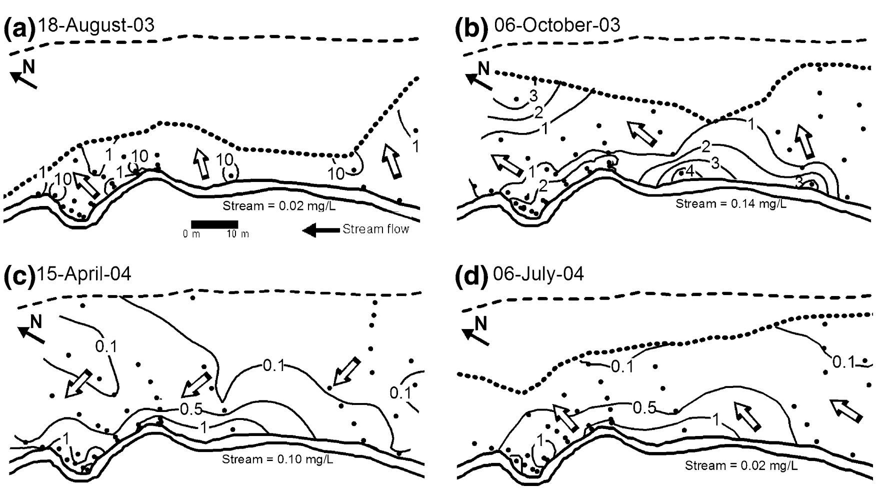

Fig. 4 Seasonal patterns of pore-water ammonium-N concentration within the gravel layer at the Vivian Creek site. Concentration isoline interval is variable. Arrows represent the direction of subsurface flow. The dashed line indicates the riparian zone—agricultural field boundary. The dotted line indicates the area of unsaturated riparian sediments. Piezometer locations indicated by •

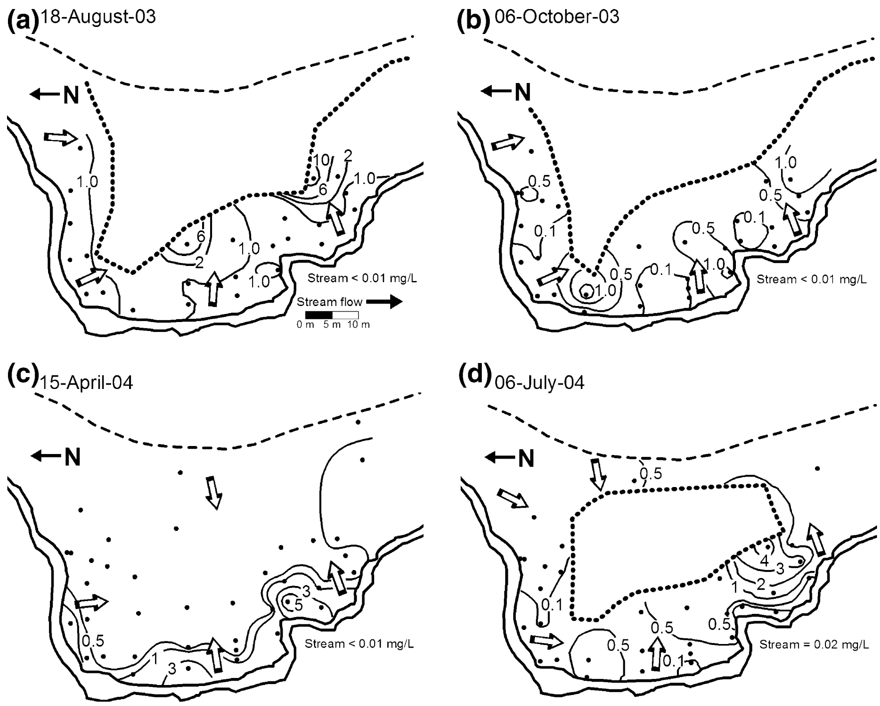

Fig. 5 Seasonal patterns of pore-water ammonium-N concentration within the gravel layer at the West Duffins Creek site. Concentration isoline interval is variable. Arrows represent the direction of subsurface flow. The dashed line indicates the riparian zone—agricultural field boundary. The dotted line indicates the area of unsaturated riparian sediments. Piezometer locations indicated by •

2.0 mg l^{-1} and 5.0 mg l^{-1} in the fall of 2003, with levels generally decreasing inland (Fig. 4b). Ammonium-N concentrations were also reduced in the fall of 2003 at W. Duffins Creek, where much of the riparian zone was again below 0.5 mg l^{-1} (Fig. 5b). There were however, a few locations at this site with NH_4^+-N concentrations >1.0 mg l^{-1}.

Dissolved oxygen

The dissolved oxygen concentration in the pore water of the conductive gravel layer in the two riparian zones varied seasonally in relation to shifts in source water inputs. During the high water table period in spring 2003 and 2004, subsurface flows from the adjacent cropland at Vivian Creek had elevated DO concentrations of 4–5 mg l^{-1} near the upland-riparian zone margin and concentrations declined to <2 mg l^{-1} near the stream (Fig. 6a and d). A similar pattern was found at W. Duffins Creek, although an area of high DO levels also occurred in upstream piezometers near the channel (Fig. 7c).

During late spring and early summer 2003 as the cropland to riparian hydraulic connection declined,

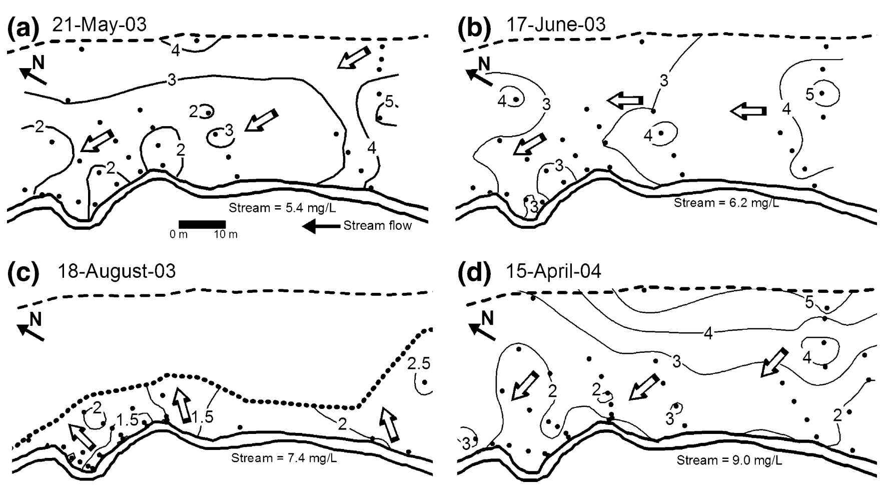

Fig. 6 Seasonal patterns of pore-water dissolved oxygen concentration within the gravel layer at the Vivian Creek site. Concentration isoline interval is variable. Arrows represent the direction of subsurface flow. The dashed line indicates the riparian zone—agricultural field boundary. The dotted line indicates the area of unsaturated riparian sediments. Piezometer locations indicated by •.

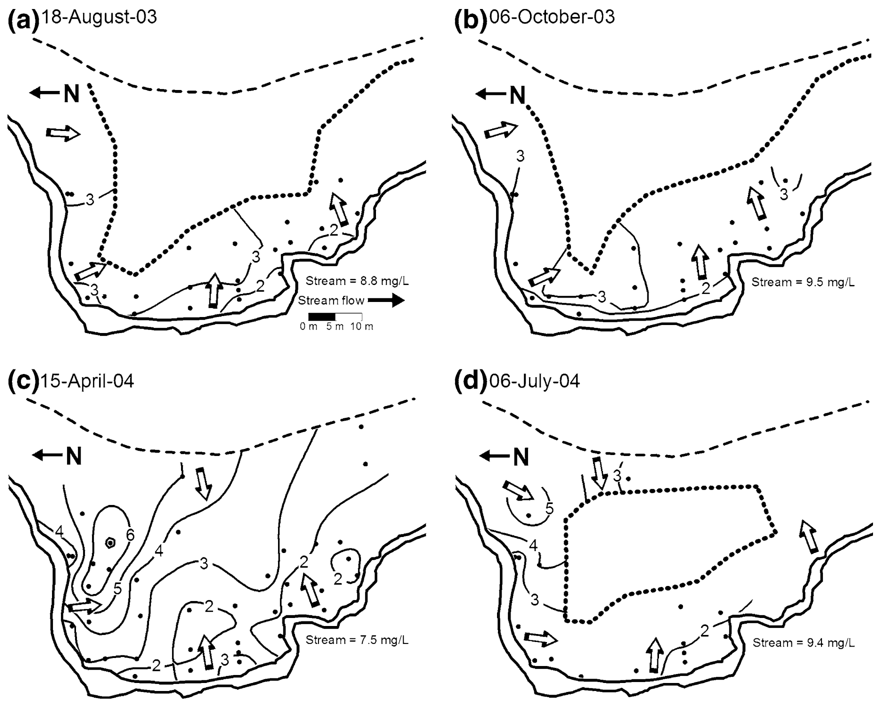

Fig. 7 Seasonal patterns of pore-water dissolved oxygen concentration within the gravel layer at the West Duffins Creek site. Concentration isoline interval is variable. Arrows represent the direction of subsurface flow. The dashed line indicates the riparian zone—agricultural field boundary. The dotted line indicates the area of unsaturated riparian sediments. Piezometer locations indicated by •

the dominant flow direction at Vivian Creek shifted to a down valley direction and DO values became more uniform ranging between 3 and 5 mg l^{-1} (Fig. 6b). At W. Duffins Creek, the pattern in early summer 2003 and 2004 showed elevated DO values of 3–5 mg l^{-1} in the upstream portion of the riparian zone and lower DO concentrations of <2.0 mg l^{-1} in the downstream riparian area in close proximity to the stream (Fig. 7d).

During the summer when stream inflow was the dominant water source, the dissolved oxygen of the pore water of the saturated riparian sediments was low at both sites. By mid summer at Vivian Creek most of the saturated riparian zone had DO concentrations of <2.0 mg l^{-1} (Fig. 6c). Dissolved oxygen concentration was similar at W. Duffins Creek, though the upstream riparian area contained elevated DO concentration of 3.0 mg l^{-1} (Fig 7a). During the autumn as a rising water table extended the zone of saturated riparian sediments further inland, DO concentrations remained similar to summer values (Fig. 7b). At Vivian Creek, DO was only measured along the four downstream piezometer transects in October 2003. Concentrations that ranged between 2.0 mg l^{-1} and 2.5 mg l^{-1} were only slightly greater than summer levels (data not shown).

Solute injections

The bromide/nitrate co-injection experiments at the bank margin of Vivian Creek and W. Duffins Creek were conducted under base flow conditions in mid-August and late September, respectively. Throughout the experiments, no Br^- was detected in the row A piezometers installed in the stream bed at the two sites. Two days after injection at Vivian Creek, Br^- was detected in piezometer 2C although no nitrate was present (data not shown). Elevated Br^- concentrations were detected only in piezometers 2C and 5C in the first row of piezometers adjacent to the injection row after 4 days (Fig. 8a). The tracer had also extended to distances of 1 m and 1.5 m laterally away from the injection points in transect 5. Nitrate-N concentrations increased to 0.52 mg l^{-1} and 0.88 mg l^{-1} in piezometer 2C and 5C, but remained at trace levels in the other piezometers with Br^- in transect 5.

Eight days after injection the pattern had shifted (Fig 8b). Bromide concentrations had declined along transect 5, whereas the upstream portion of the plot contained very high levels of Br^-. Bromide had reached the entire E row of piezometers, with very high values in 2E. Nitrate-N was detected in the

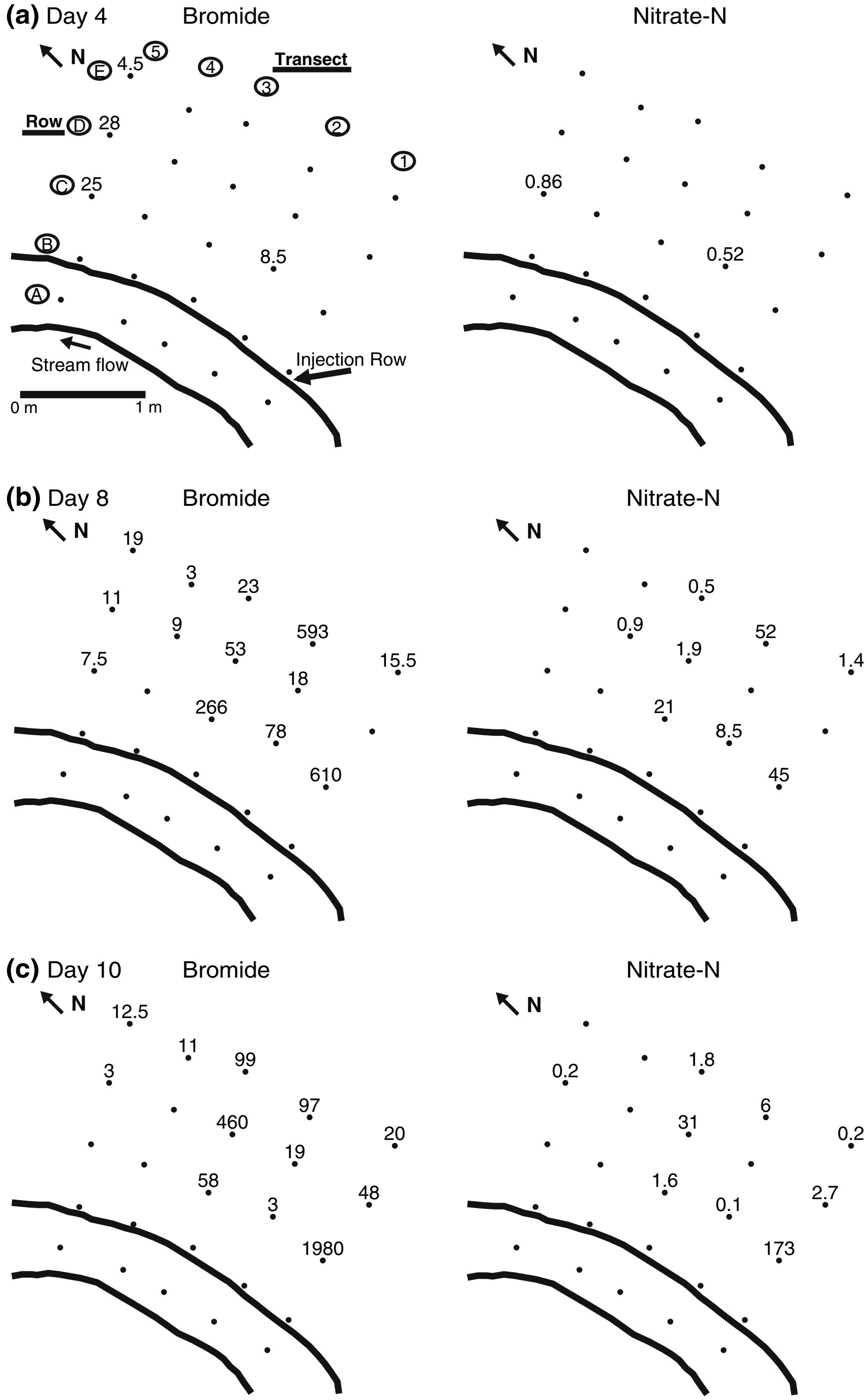

Fig. 8 Bromide tracer movement and nitrate-N concentration in the gravel layer at the Vivian Creek plot during stream base flow in mid-August 2004. Values are in mg l^{-1}. Data are not shown for piezometers with Br^- and NO_3^--N concentrations of <1 mg l^{-1} and <0.1 mg l^{-1}, respectively

piezometers that contained Br^- in most of the upstream piezometers, but transect 5 had no detectable nitrate. Ten days after solute injection the absolute values of Br^- and NO_3^--N had changed but the pattern remained similar to the day eight data. Although very high nitrate concentrations were detected in a few piezometers, concentrations in most piezometers were less than values expected based on the initial ratio of NO_3^--N and Br^- injected (Fig. 8c). Bromide was not observed at piezometer

4C, which was 0.5 m from the injection row during the experiment.

By 3 days after the injection began at W. Duffins Creek two piezometers 0.5 m inland from the injection showed elevated Br^- concentrations with no NO_3^--N detected in either of these locations (Fig. 9a). Six days after injection the Br^- tracer had travelled to two additional piezometers 1 m and 1.5 m inland from the injection row (Fig. 9b). At this time, nitrate concentrations in these piezometers were well below the expected amount based on the bromide concentration. Bromide continued to migrate inland to piezometers 1.5 m from the injection row but by 13 days after injection had not reached piezometers in row F (Fig. 9c). Nitrate-N concentrations in 5 of the 6 piezomters where bromide was detected on day 13 were <0.01 mg l^{-1}, whereas expected concentrations based on the initial ratio of the NO_3^--N and Br^- mass

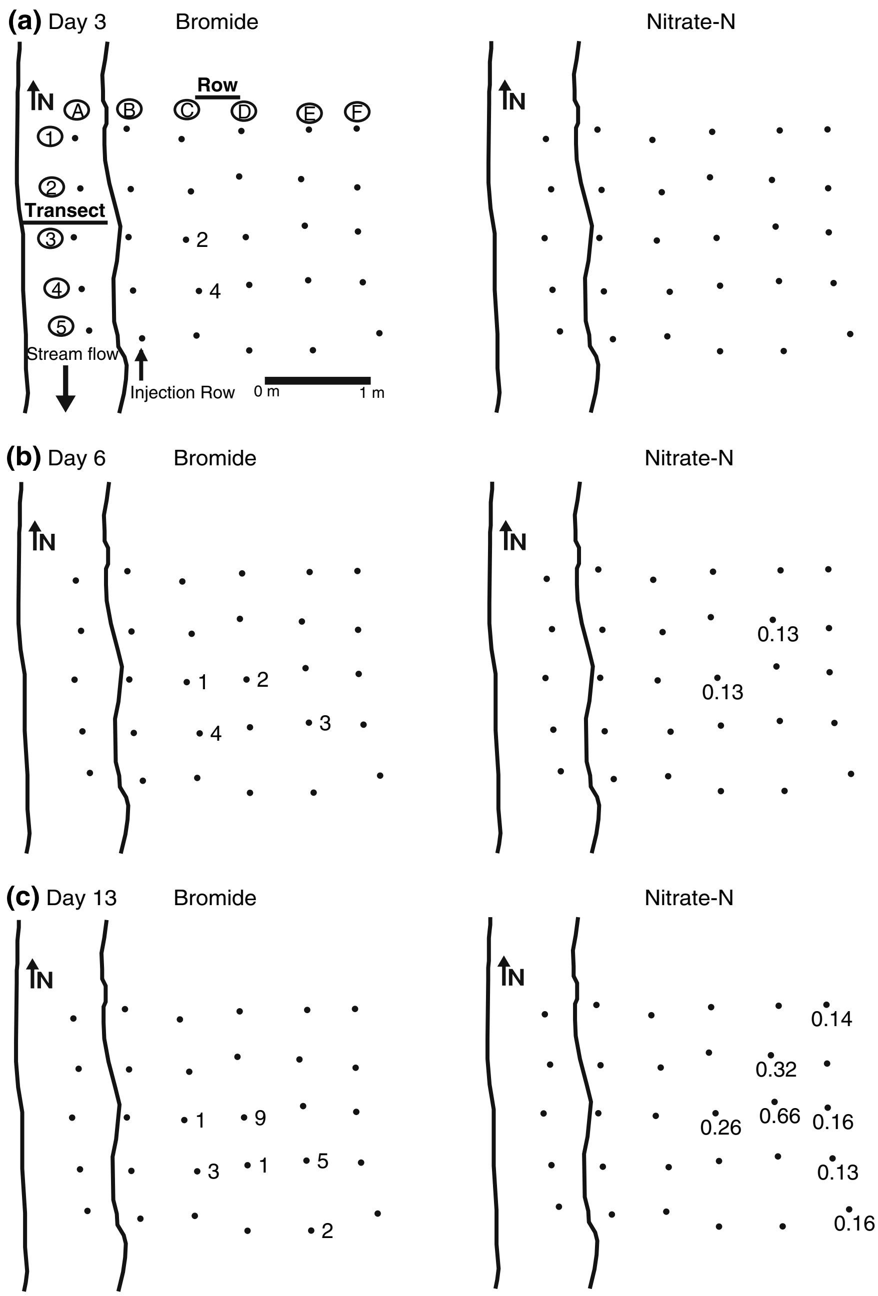

Fig. 9 Bromide tracer movement and nitrate-N concentration in the gravel layer at the West Duffins Creek plot during stream base flow in late-September 2004. Values are in mg l^{-1}. Data are not shown for piezometers with Br^- and NO_3^- -N concentrations of <1 mg l^{-1} and <0.1 mg l^{-1}, respectively

injected were 0.26–1.0 mg l^{-1} (Fig. 9c). Low concentrations of nitrate-N were also detected in some piezometers particularly in row F where bromide was not present on day 13. An absence of precipitation during the experiment resulted in a gradual water table decline to a depth adjacent to the piezometer slot zones in this location that may have induced nitrification in overlying aerated sediment.

Differences at most piezometers between observed and expected NO_3^--N concentration based on the applied NO_3^--N/Br^- ratio indicated removal rates of 70–100% on the first date of exposure to the migrating plume and these rates were sustained throughout the experiment (Tables 1 and 2). Several piezometers showed a low initial rate of nitrate removal that increased to 70–100% upon continued exposure to the injection plume. Nitrate removal rates were <40% at 4 piezometers in the Vivian Creek plot where the injection solution produced very high peak observed NO_3^--N concentrations of 8–173 mg l^{-1} (Fig. 9).

Discussion

Our results indicate that clearly defined horizontal trends in subsurface chemistry at the riparian zone scale are influenced both by hillslope and stream inflow to the two riparian areas. During the spring high water table period, patterns of high DO and nitrate concentrations in subsurface water at the upland perimeter which decline rapidly within the riparian zone reflect the dominant influence of hillslope inflow in these locations. These patterns are similar to those previously reported in many riparian zones where elevated nitrate levels in shallow subsurface flows from cropland are depleted by denitrification and plant uptake over distances of 5–20 m within the riparian zone (Peterjohn and Correll 1984; Simmons et al. 1992; Clement et al. 2002).

The biogeochemistry of a major portion of the riparian zone was influenced by stream bank seepage inland in summer and autumn at Vivian Creek and throughout the year at W. Duffins Creek. The contrast at the stream reach scale between high levels of DO and nitrates in stream flow at both sites and concentrations of DO and NO_3^--N that were often <2.5 mg l^{-1} and <0.1 mg l^{-1} respectively in piezometers several meters inland indicates a strong redox gradient along this flowpath. These patterns suggest the occurrence of aerobic microbial respiration followed by denitrification (Hedin et al. 1998).

Table 1 Observed and expected NO_3^--N concentrations (mg l^{-1}) in streambank plot piezometers at Vivian Creek during an experimental addition of nitrate and bromide

Piezometer	Day 4			Day 8			Day 10		
ID	Exp NO_3^--N	Obs NO_3^--N	NO_3^--N Loss (%)	Exp NO_3^--N	Obs NO_3^--N	NO_3^--N Loss (%)	Exp NO_3^--N	Obs NO_3^--N	NO_3^--N Loss (%)
1C				61	45	25	198	173	13
1D							4.8	2.7	44
1E				1.5	1.4	10	2	0.2	89
2C	0.9	0.5	44	7.8	8.5	0	0.3	0.1	67
2D				1.8	<	100	1.9	<	98
2E				59	52	13	9.7	5.9	39
3C				26	21	20	5.8	1.6	72
3D				5.3	1.8	65	46	31	33
3E				2.3	0.4	80	9.9	1.8	82
4D				0.9	0.8	11			
4E				0.3	<	79	1.1	<	97
5C	2.5	0.8	68	0.8	<	92			
5D	2.8	<	98	1.1	<	96	0.3	0.1	66
5E	0.5	<	94	1.9	<	98	1.2	<	97

< indicates NO_3^--N concentrations <0.1 mg l^{-1}

Table 2 Observed and expected NO_3^--N concentrations (mg l^{-1}) in streambank plot piezometers at W. Duffins Creek during an experimental addition of nitrate and bromide

Piezometer	Day 3			Day 6			Day 13		
ID	Exp NO_3^--N	Obs NO_3^--N	NO_3^--N Loss (%)	Exp NO_3^--N	Obs NO_3^--N	NO_3^--N Loss (%)	Exp NO_3^--N	Obs NO_3^--N	NO_3^--N Loss (%)
3C	0.5	<	100	0.3	<	100	0.3	<	100
3D				0.4	0.1	75	1.8	0.3	86
4C	0.8	<	100	0.8	<	100	0.6	<	100
4D							0.3	<	100
4E				0.6	<	100	1.0	<	100
5E							0.3	<	100

< indicates NO_3^--N concentrations <0.1 mg l^{-1}

The intensity of this gradient is revealed in more detail at the stream bank plot scale. Within 0.25 m of the stream margin at Vivian Creek and approximately 1 m at W. Duffins Creek the stream-origin riparian pore water had DO and NO_3^--N concentrations 70% to 90% less than the stream values.

An exception to the pattern occurred along the upstream transects at W. Duffins Creek during high water table periods, particularly in spring, where NO_3^--N and DO concentrations remained elevated in stream inflow up to 15 m inland (Figs. 3c and 7c). This portion of the riparian zone had higher saturated hydraulic conductivity in the gravel layer, suggesting a shorter residence time for stream-origin water. Additionally, this area generally had a steeper hydraulic gradient inland than the rest of the riparian zone during high water table periods (Duval and Hill 2006) that increased the flux of high DO and nitrate water inland.

During summer and fall when bank seepage maintained a water table gradient inland, localized patches of higher nitrate concentrations occurred in several piezometers up to 10–15 m inland from the stream in the two riparian zones. The water level in these piezometers was either within or just above the perforated slot zone during periods of minimum water table elevation. Thus, seasonal water table drawdown may have resulted in the development of an aerobic environment at or near the depth of the piezometer perforation zone, which would enable nitrifiers to build up nitrate in the sediments. Relatively minor water table increases in elevation brought on by summer precipitation events and a progressive expansion of the area of saturated riparian sediments above the confining layer in the fall season mobilized this accumulated nitrate into the groundwater.

Recharge events that displace nitrate stored in unsaturated riparian sediments to the water table have a potential to accelerate N flushing to the stream (Creed et al. 1996; Butturini et al. 2003; Burns 2005). However, at Vivian Creek, the autumn wet-up rate was slow, and flow was in the stream-to-field direction, eliminating the possibility of the transfer of the localized patches of elevated nitrate to the stream. Burt et al. (2002) found a similar riparian hydrology at a French site; the stream-origin water produced a groundwater ridge that reached the upslope field edge prior to the wet-up of the upslope area. The flowpath direction at Vivian Creek typically does not switch back to the field-to-stream direction until December (Vidon and Hill 2004a). Due to this, as well as the relatively low conductivity of the sediments (<1 m d^{-1}), there is a considerable time lag from autumnal wet up to winter discharge, such that any accumulated nitrate remains in the anaerobic saturated zone for an extended period of time. The residence time of this riparian groundwater is probably sufficient, even with the decreased reaction rates of colder autumn temperatures, for denitrification and/or biologic uptake to remove accumulated nitrate before the water is delivered to the stream.

A prominent feature of the biogeochemical pattern in both riparian zones was the persistence of a zone of high NH_4^+-N concentrations in the riparian gravel layer that extended inland from the bank interface along the stream inflow pathway. DO concentrations in these areas were often <2.5 mg l^{-1} suggesting that ammonium was produced during anaerobic mineralization of organic matter and nitrification was inhibited by the low oxygen levels. Peak concentrations of NH_4^+-N in localized patches were observed in midsummer when increased temperatures probably led to more rapid mineralization.

Ammonium-N concentrations were generally higher in areas within 2–5 m of the stream bank at Vivian Creek, whereas higher concentrations were detected 10–15 m inland at W. Duffins creek. These differences in spatial pattern may be influenced by the occurrence of the buried organic-rich horizon adjacent to the gravel layer near the stream bank at Vivian Creek. Coring did not detect a similar organic layer near the bank along W. Duffins Creek.

Highly organized horizontal trends in subsurface riparian water chemistry that are similar to those measured at Vivian and W. Duffins Creeks have also been found along a first-order stream in southwestern Michigan (Hedin et al. 1998). These patterns in the Michigan stream bank site resulted from the convergence of upwelling deep groundwater with high levels of NO_3^- and a horizontal flow towards the stream of shallow anoxic subsurface water with high levels of electron donors (DOC and NH_4^+). In contrast to the Michigan stream, biogeochemical patterns at the two southern Ontario riparian sites represent a response of the microbial community to a hydrological flow path sustained by stream bank seepage into the riparian zone rather than subsurface flow from the riparian zone to the stream.

The plot-scale injections provide a more detailed perspective of the process of bank seepage inland to the riparian zones and nitrate removal patterns at the stream-bank interface. The plot-scale Br^- injections indicate that bank seepage occurs along preferential flow paths. The Br^- tracer travelled quickly to some piezometers that were distant from the injection points, whereas several piezometers adjacent to the injection points, particularly at W. Duffins Creek did not intercept the tracer. Although the entire stream-bank interface along each stream reach can be viewed as a hot spot of nitrogen processing at the riparian site scale, the preferential flow paths revealed by the injection experiments indicate that localized points at the <1 m scale along the stream-bank interface have a disproportionately high rate of nitrate transport and processing. In contrast, adjacent points show an absence of inflow of nitrate-rich stream water.

Our analysis indicates the rapid loss of nitrate in relation to co-injected bromide in many of the plot-scale piezometers. The pore water in the near stream sediments often contained very little dissolved oxygen; therefore redox conditions were such that denitrification could occur. Laboratory incubations of sediments from the gravel layer and overlying organic-rich horizon adjacent to the stream margin at Vivian Creek and other riparian sites in southern Ontario clearly revealed considerable denitrification potential in these near channel sediments (Hill et al. 2004). Several piezometers showed a lag response with rates of removal only increasing to >70% several days after the bromide- nitrate co-injection reached these locations. A lag in potential denitrification measured as N_2O production also occurred in some lab incubations of riparian sediments from Vivian Creek (Hill et al. 2004). Similar time lags have been previously reported for sites where ambient nitrate levels were low and denitrifiers must build up in numbers (Aelion and Shaw 2000). The low rate of nitrate depletion observed in some piezometers was probably the result of temporary saturation of the removal process due to the large concentration of nitrate transported to these sites.

Previous research on stream hyporheic zones has identified hot spots of denitrification in stream channels at locations where stream water downwells into the streambed (Hill et al. 1998; Duff and Triska 2000; Storey et al. 2004). The results of this study indicate that nitrate removal hotspots are not necessarily confined to downwelling zones at the head of riffles in lowland headwater streams, but may extend along the margin of large stretches of losing stream reaches. In stream reaches where organic-rich bank sediments have low hydraulic conductivities, the oxic–anoxic interface may occur over very short distances at the channel margin. In contrast, stream inflow in areas of highly conductive coarse sediments may maintain elevated levels of DO and NO_3^- for considerable distances into the riparian zone.

Conclusion

The majority of riparian zone studies have focussed on the transformation of chemistry as water is transported along hydrologic pathways from uplands to the stream. Our data indicate that sustained bank seepage inland during stream base flows can also exert a dominant influence on riparian zone biogeochemistry in some landscapes. Reversed hydraulic gradients can induce flow from the stream channel particularly in summer and autumn that maintain saturated riparian sediments for considerable distances from the channel. In these near-stream zones the stream-bank interface along entire stream reaches is frequently a zone of enhanced biogeochemical activity where oxic stream water with elevated nitrate levels that are typical of agricultural streams are depleted rapidly and accumulation of NH_4^+ occurs in more anaerobic inland environments. The occurrence of high levels of chemical transformation along this stream inflow pathway is influenced by riparian sediment characteristics. In many lowland agricultural landscapes, riparian sediments contain conductive coarse sand and gravel layers as well as widespread organic-rich horizons and woody debris at various depths (Hill et al. 2004). These heterogeneous sediments provide preferential zones of increased hydrological flux as well as large supplies of organic carbon that promote nitrate depletion by denitrification.

McClain et al. (2003) have emphasized the importance of increasing our ability to predict the spatial distribution of hot spots of biogeochemical activity in relation to landscape hydrogeologic settings. We suggest that a zone of enhanced biogeochemical activity induced by prolonged stream bank seepage inland is likely to occur at the interface between the riparian zone and the stream channel in landscapes drained by perennial streams where relatively wide flat riparian areas receive little or no discharge from adjacent hillslopes.

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