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Hyporheic zone hydrology and nitrogen dynamics in relation to the streambed topography of a N-rich stream

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Abstract. The influence of riffle-pool units on hyporheic zone hydrology and nitrogen dynamics was investigated in Brougham Creek, a N-rich agricultural stream in Ontario, Canada. Subsurface hydraulic gradients, differences in background stream and groundwater concentrations of conservative ions, and the movement of a bromide tracer indicated the downwelling of stream water at the head of riffles and upwelling in riffle-pool transitions under base flow conditions. Channel water also flowed laterally into the floodplain at the upstream end of riffles and followed a subsurface concentric flow path for distances of up to 20 m before returning to the stream at the transition from riffles to pools. Differences in observed vs predicted concentrations based on background chloride patterns indicated that the hyporheic zone was a sink for nitrate and a source for ammonium. The removal of nitrate in the streambed was confirmed by the loss of nitrate in relation to co-injected bromide in areas of downwelling stream water in two riffles. Average stream water nitrate-N concentrations of 1.0 mg/L were often depleted to $<$0.005 mg/L near the sediment-water interface. Consequently, an extensive volume of the hyporheic zone in the streambed and floodplain had a large unused potential for nitrate removal. Conceptual models based mainly on studies of streams with low nutrient concentrations have emphasized the extent of surface-subsurface exchanges and water residence times in the hyporheic zone as important controls on stream nutrient retention. In contrast, we suggest that nitrate retention in N-rich streams is influenced more by the size of surface water storage zones which increase the residence time of channel water in contact with the major sites of rapid nitrate depletion adjacent to the sediment-water interface.

Introduction

The effect of streambed topography on stream-subsurface interactions has received increased attention in recent years. Convective flow of stream water into bed sediments can be generated by water flowing over small obstacles such as ripples and dunes in porous bed materials (Thibodeaux & Boyle 1987). Patterns of downwelling water at the upstream face and upwelling water at the downstream face of these roughness elements have been identified by modelling streamflow over small bed forms and by dye tracing experiments in flumes (Thibodeaux & Boyle 1987; Savant et al. 1987). Convective exchanges across the bed also can be produced by larger scale roughness elements associated with pools which alternate with steeper channel units such as riffles, rapids and steps. Temperature and chemistry profiles beneath a riffle-pool unit have been used to indicate vertical convective exchange (White et al. 1987; Hendricks & White 1991). Hydraulic head and tracer experiments have also demonstrated horizontal exchanges in which stream water recharges to streamside sediments above a steeper channel unit (cascade, step) and follows an arc-shaped subsurface flow path that returns to the stream at the downstream end of the unit (Harvey & Bencala 1993).

Localized stream and groundwater exchanges have a significant potential to influence solute transport and nutrient cycling in stream ecosystems. Studies of longitudinal and depth variations of chemistry beneath a riffle indicate that subsurface water is more characteristic of stream water at the upstream end of the riffle and of groundwater at the downstream end (Hendricks & White 1991; Sterba et al. 1992; Hendricks & White 1995). In some streams, elevated nitrate concentrations occur in downwelling zones of the streambed and along subsurface flowpaths through gravel bars (Holmes et al. 1994; Jones et al. 1995; Wondzell & Swanson 1996). The entry of nutrient-rich hyporheic water at upwelling zones may alleviate nutrient limitation in benthic algal communities (Dahm et al. 1987; Grimm et al. 1991; Valett et al. 1994). These studies, however provide limited data on the vertical and lateral variations in hyporheic zone size and detailed patterns of surface-subsurface hydrologic mixing within this three-dimensional environment which are essential for understanding biogeochemical processes. Previous research on the chemistry of convective exchanges across the streambed have focused on pristine streams with very low nutrient concentrations in which nitrification is often the dominant hyporheic nitrogen transformation process (Triska et al. 1989; Jones et al. 1995). Recently, Jones and Holmes (1996) have proposed that the hyporheic zone of N-limited streams is a source of nitrate, whereas the hyporheic zone functions as a nitrate sink in N-rich streams. At present, knowledge of how hyporheic biogeochemistry differs between oligotrophic and eutrophic streams is limited by an absence of detailed studies of N-rich streams.

This paper examines the exchange of water and solutes in stream riffle-pool units during base flows in a N-rich agricultural stream. The specific objectives were to delineate the lateral and vertical extent of the hyporheic zone and to examine patterns of nitrogen chemistry in relation to spatial variations in the amount of stream water and groundwater mixing in localized subsurface flow paths beneath and to the side of stream riffle-pool units. Hydrometric data in combination with differences in background concentrations of conservative ions in stream and groundwater were used to delineate hyporheic zone size. A comparison of subsurface concentration patterns of conservative ions that result only from the exchange of stream and groundwater with the patterns of reactive elements (dissolved oxygen, ammonium and nitrate) was used to examine transformation processes. Streambed injection experiments were also used to delineate the hyporheic zone and to analyze the behaviour of nitrate in alluvium beneath and to the side of the stream.

Study site

The study site was on Brougham Creek, a 3rd order stream within the Duffin Creek catchment, approximately 50 km west of Toronto, Ontario. The drainage area above the study site is 12.1 km^2 and most of the catchment is in agricultural land use for pasture and corn. In the downstream area of the catchment the stream is entrenched in a small valley up to 20 m below a gently undulating till plain. A confined aquifer in a sand unit which underlies the glacial till and outcrops in the valley sides discharges to the stream.

Within the 50-m study reach the stream width is 4–5 m and low flow discharge in summer and early fall is 70–80 L/s. The reach contains two main riffles, each approximately 8 m in length and a third small riffle located over a sand bar at the downstream end of the reach (Figure 1). Small pools with water depths of 30–40 cm alternate with the riffles where water depths are 5–15 cm (Figure 1). Sediments are cobbles and coarse gravel in the two main riffles and sand with fine gravel in the small downstream riffle. Pools are characterized by sand with some accumulation of silt. A narrow floodplain extends up to 15 m laterally on the east side of the stream and is bounded by a low terrace and adjacent hillslope. On the west side a narrow terrace separates the stream from a 20 m high steeply sloping valley side (Figure 1). Alluvial deposits in the floodplain and adjacent terrace consist of medium to coarse sand and gravel containing buried soil horizons and layers of pebbles and cobbles. These alluvial deposits are underlain by thin bedded stratified silts and clays at depths of 1–2.5 m. In the streambed these silts and clays occur at depths of <0.3 m in several locations. The floodplain and terrace is covered with a mixed forest of box elder (*Acer negundo*) and northern white cedar (*Thuja occidentalis*).

Materials and methods

Hydrology and chemistry

A network of piezometer nests was installed on the floodplain and adjacent terrace to measure hydraulic head and interstitial water chemistry (Figure 1).

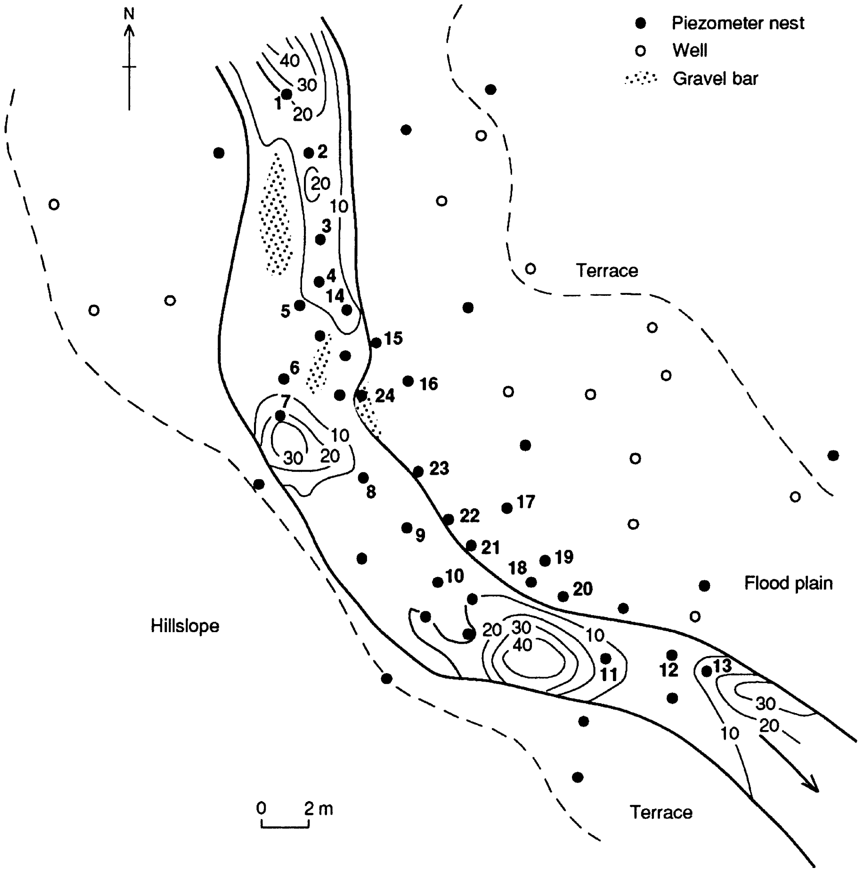

Figure 1. Brougham Creek study site showing landforms, location of piezometers and stream water depths (cm).

Each nest consisted of PVC pipes (1.25 cm ID) with a 20 cm slot zone covered with Nitex mesh installed at a depth of 1.3 m and 1.8 m below the ground surface. Groundwater wells (ABS pipe 3.8 cm ID) perforated throughout their length were installed with each piezometer nest. Additional wells were placed in the floodplain to measure water table elevations.

A longitudinal transect of piezometer nests was installed in the stream bed (sites 1–13) at intervals along the reach (Figure 1). Each nest consisted of 2–5 piezometers located at various depth intervals to the boundary between the stream bed and the underlying stratified silt-clay layer. Piezometers installed at shallow depths of 5–40 cm usually had 5 or 10 cm slot zones, whereas deeper piezometers had 20 cm slot zones.

Horizontal positions and vertical elevations of piezometer nests and wells were mapped using standard surveying techniques. After measurement of water levels, piezometers and wells were pumped out prior to sampling and allowed to refill. Samples of fresh water were collected using a hand operated vacuum pump at 2–4 week intervals during stream base flows in June–October 1993–95. Stream water samples were also collected on each sampling date. Dissolved oxygen (DO) concentrations were measured in water samples in the field using an oxygen meter. Samples were placed on ice in a cooler and transported to the lab where they were stored for a maximum of 12 h at 2–3 °C prior to ammonium analysis and 24–48 h prior to nitrate analysis.

Solute injection experiments

Stream-groundwater exchanges and nitrate transformations in the hyporheic zone were studied by the coinjection of lithium bromide and potassium nitrate into the streambed. Three injection wells consisting of PVC pipes (1.25 cm ID) with a 20 cm slot zone were installed 0.5 m apart perpendicular to stream flow 1 and 1.5 m upstream from sites 3 and 8 respectively in riffle gravels (Figure 1). The injection slot zones were located at 25–35 cm below the streambed surface. Analysis of hydraulic heads and conservative ion chemistry indicated that these injection points were located in areas of downwelling where $>90\%$ stream water was present (see results below). Small amounts of LiBr and KNO_3 were added in a solid state to each injection well at intervals over 3–4 h. These chemicals slowly dissolved in the water flowing through the slot zone and were transported into the hyporheic zone. This procedure avoided the addition of water to the wells which could have produced changes in subsurface flow patterns. Several injection experiments were conducted during the study. On August 8, 1994 LiBr was added to the injection wells upstream from site 3 and the subsequent movement of the Br^- in the stream bed and floodplain was monitored until August 25. An experiment involving the co-injection of LiBr and KNO_3 to the wells upstream from site 8 was conducted on August 21–28, 1995 and a second injection with LiBr and KNO_3 upstream from site 3 was performed between September 25–October 11, 1995. The mass of NO_3^--N injected was 7.5 and 10% of the Br^- mass in the August and September experiments respectively.

Laboratory methods

Ammonium (NH_4^+-N), nitrate + nitrite (NO_3^--N + NO_2^--N), chloride (Cl^-) and silica (SiO_2) were analyzed by automated wet chemistry on a Technicon Autoanalyzer system using standard techniques (Technicon 1977, 1978; Environment Canada 1979). Nitrite was insignificant and is included as nitrate-N.

Water samples were analyzed for bromide (Br^-) with an ion specific electrode.

Delineation of the hyporheic zone

The zone beneath the stream and adjacent floodplain where subsurface water contains $>$10% stream water was considered part of the hyporheic zone (Triska et al. 1989). A two component chemical mixing equation was used to separate water in streambed and floodplain piezometers into stream and groundwater fractions using background Cl^- and Si concentrations in each source water as conservative tracers:

$$\text{stream water \%} = (C_p - C_g)/(C_s - C_g) \times 100 \tag{1}$$

where C_p, C_g and C_s refer to the conservative ion concentration in the piezometer, groundwater and stream respectively. Chloride has been widely used as a conservative tracer because of its conservative and non-adsorptive behaviour (Bencala et al. 1984; Triska et al. 1989, 1990). The status of silica as a conservative tracer is less certain. Several studies to determine the origin of storm runoff in streams demonstrated that silica was conservative when compared to ^{18}O (Hooper & Shoemaker 1986; Durand et al. 1993; Pionke et al. 1993). However, other studies suggest that infiltrating water gains silica due to rapid equilibrium reactions with mineral soils (Maule & Stein 1990; Wels et al. 1991). Dissolved silica is also a biologically active element used by diatoms (Edwards 1974). A conservative tracer (bromide) was also injected into the streambed near the upstream end of riffles. Increases in tracer concentrations at various depths in the streambed and adjacent floodplain after the injections provided qualitative evidence that some portion of subsurface water comes from stream water.

Results

Riparian zone and streambed subsurface hydrology

The water table was always 50–90 cm beneath the riparian zone during summer base flows. Hydraulic heads in piezometers at 1 and 2 m depths in the floodplain alluvial deposits indicated horizontal groundwater flow towards the stream. The phreatic surface contours for stream base flow conditions showed that groundwater flow paths from the eastern valley slope were perpendicular to the stream channel (Figure 2a). Groundwater entering the floodplain to the west of the stream followed an oblique path towards the channel. At

Table 1. Means ± SD of variables for stream water and groundwater during base flows in June-October 1994–95. The *t*-statistic for means is significantly different ($p < 0.05$) for all variables.

Variable (mg L^{-1})	Stream water	Groundwater
Chloride (Cl)	47.3 ± 1.9	14.4 ± 1.5
Silica (SiO_2)	6.2 ± 0.2	11.0 ± 0.8
Nitrate (NO_3-N)	1.02 ± 0.14	0.006 ± 0.008
Ammonium (NH_4-N)	0.03 ± 0.02	0.92 ± 0.22
Dissolved oxygen (DO)	12.6 ± 1.6	2.1 ± 0.8

piezometer sites 15–24 subsurface flow in the stream bank area was parallel to the stream. Hydraulic heads in piezometers located at sites 1–13 along the stream channel varied with reference to the stream surface. Negative heads of -1 to -3 cm suggested downwelling of water into the streambed at the upstream end of riffles, whereas positive heads of +1 to +2 cm at the downstream end of riffles indicated upwelling of water (Figure 3a). Several mid-riffle piezometer nests had heads which were similar to the stream surface elevation.

Riparian zone and stream chemistry

Stream water Cl^- and Si concentrations during June–October base flows varied from 41–50 mg/L and 5.9–6.5 mg/L respectively. These high Cl^- concentrations may be related to the use of deicing salts on roads in the catchment. The chemistry of groundwater discharging from the hillslope to the east and the low terrace and adjacent floodplain to the west of the stream was similar among sampling dates. Concentrations of Cl^- (12–17 mg/L) and Si (10.0–12.1 mg/L) were significantly lower and higher respectively than stream water values (Figure 2, Table 1). However, Cl^- and Si concentrations in subsurface water sampled from sites 15–24 adjacent to the stream bank were either similar to stream concentrations, or were intermediate between stream and groundwater concentrations (Figures 1 and 2). Chloride and Si concentrations did not vary with depth in the riparian zone with the exception of two sites located near the channel where Cl^- and Si concentrations at 1 m depth were similar to stream values, but at 2 m concentrations were similar to groundwater (Figure 2).

Nitrate-N concentrations in floodplain and terrace piezometers ranged from 0.002–0.02 mg/L, whereas stream water concentrations were 0.9–1.4 mg/L. Stream water NH_4^+-N concentrations were 0.02–0.06 mg/L in comparison to riparian groundwater concentrations of 0.65–1.3 mg/L (Table 1). Water from piezometer nests at sites 15–24 had nitrate concentrations similar

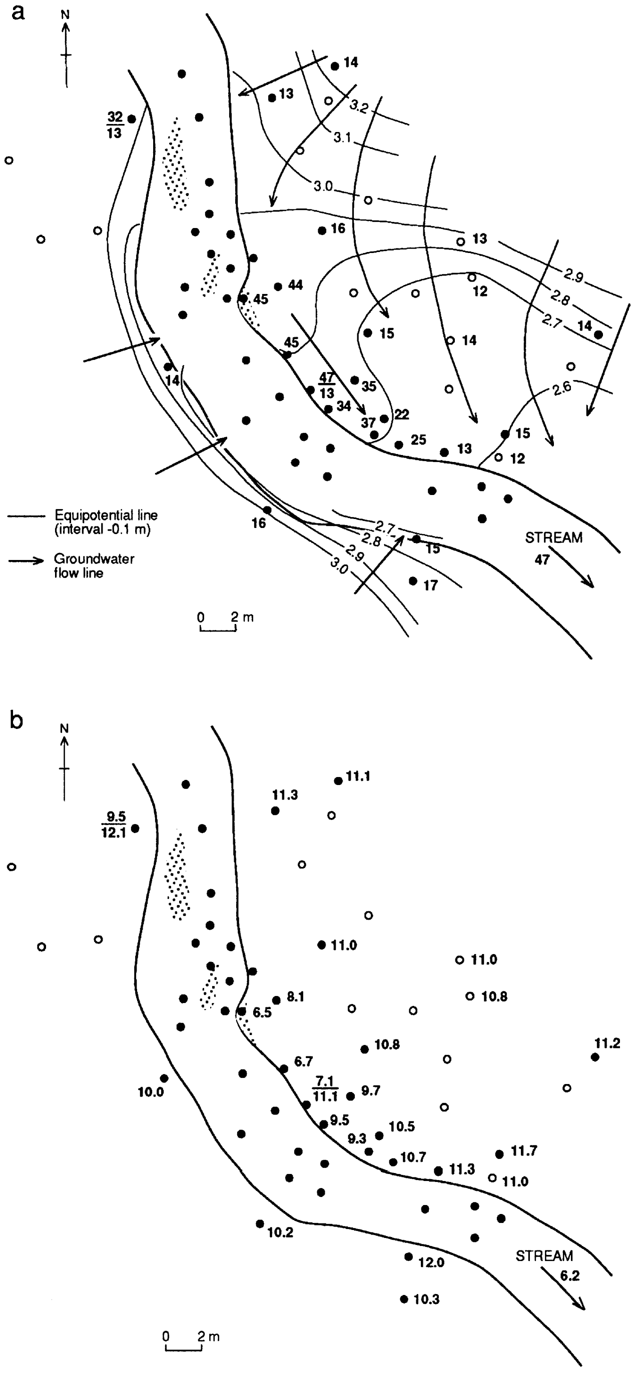

Figure 2. Riparian zone hydrology and chemistry; (a) mean chloride concentrations (mg/L) and groundwater flow lines for June-October base flows, (b) mean silica concentrations (mg/L) for June-October base flows. For piezometer nests where chemistry differed with depth, the upper and lower values indicate groundwater concentrations at depths of 1.2–1.4 and 1.7–1.9 m respectively.

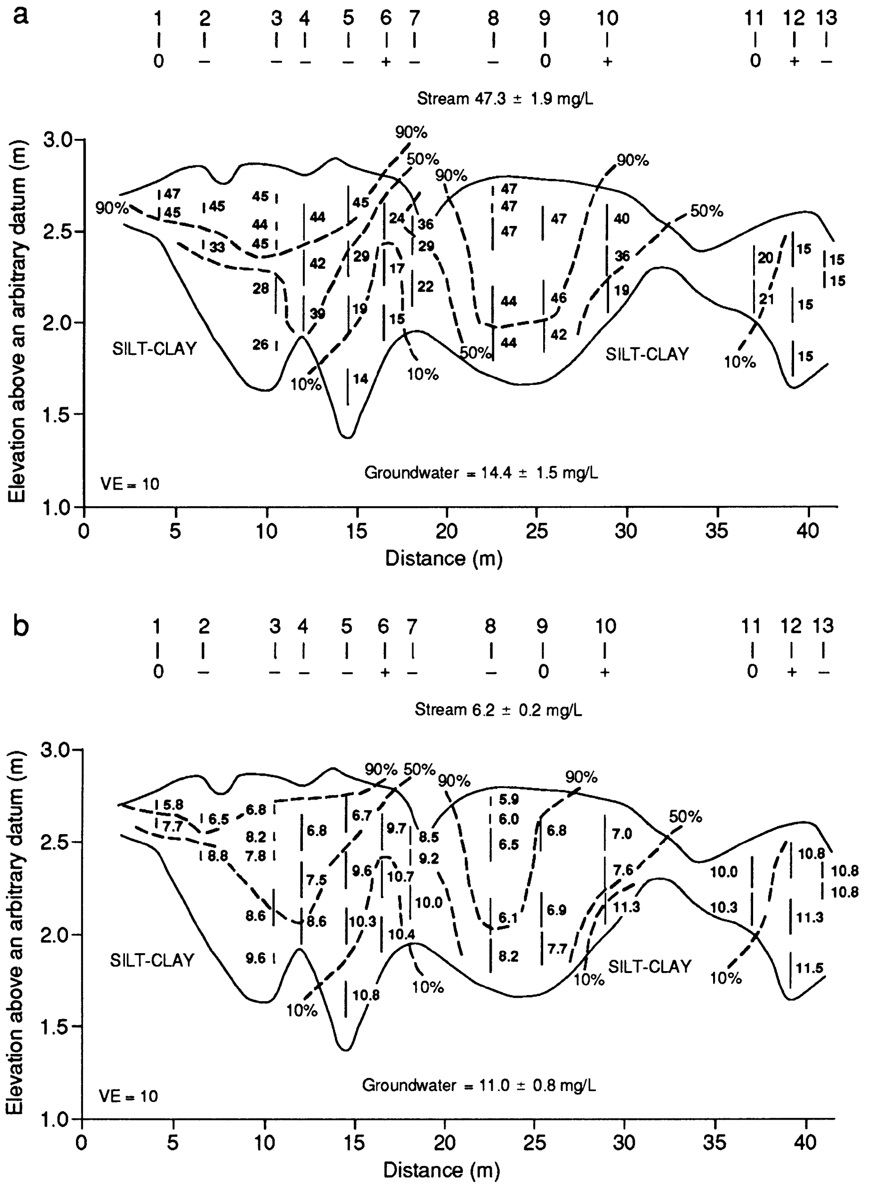

Figure 3. Patterns of conservative ions along the longitudinal transect beneath the streambed during base flows in June-October 1994–95; (a) mean chloride concentrations (mg/L), (b) mean silica concentrations (mg/L). The dashed lines indicate the depth of 10%, 50% and 90% stream water calculated from a two component chemical mixing equation using mean stream and groundwater concentrations. Patterns of hydraulic head in piezometers are indicated by symbols under site numbers; 0 = hydraulic heads similar to stream water surface, — = negative hydraulic heads (downwelling water), + = positive hydraulic heads (upwelling water). Vertical exaggeration of transect is ×10.

to groundwater elsewhere in the floodplain, whereas NH_4^+-N concentrations were generally lower varying from 0.1 to 0.6 mg/L. Groundwater DO concentrations were relatively uniform (range 0.9–3.7 mg/L)and differed significantly from stream DO values of 10.3–14.6 mg/L (Table 1).

Delineation of the hyporheic zone

Patterns of subsurface Cl^- and Si concentrations in the streambed were similar among sampling dates, consequently, mean concentrations for 10 sampling days in June–October 1994–1995 were used to indicate typical conservative ion patterns in the streambed during summer and early fall base flows. Concentrations of Cl^- and Si were similar to stream water values at depths which varied from 15–25 cm at sites 1 and 2 to 60–80 cm at sites 3,4,8 and 9 in riffles (Figure 3). Hydraulic head data indicated that stream water downwelled into sediments at these locations. In contrast, Cl^- and Si concentrations were similar to groundwater concentrations at depths that ranged from the underlying silt-clay layer to within 10–30 cm of the streambed surface at riffle-pool transitions where hydraulic heads indicated upwelling water (Figure 3).

The chemical mixing equation was used to separate streambed pore water into stream water and groundwater fractions using the mean Cl^- and Si signatures of the two source waters (Table 1). Chloride and Si concentrations for piezometers at sites 15–24 located adjacent to the stream were excluded from the calculation of mean groundwater chemistry because both conservative ion chemistry and subsurface flow path direction suggested the possibility of stream and groundwater mixing in this zone (see results below).

The mixing equation based on Cl^- suggested that $>90\%$ stream water penetrated to maximum depths of 35–45 cm in the riffle at sites 3 and 4 and to 80 cm in the riffle at sites 8 and 9 (Figure 3a). Below this zone $>50\%$ stream water was present at depths that extended to the boundary of the silt-clay layer. At the riffle-pool transitions the chemical mixing model indicated that the 10% stream water boundary of the hyporheic zone extended upwards from the silt-clay boundary to shallower depths. Using Si in equation 1 revealed a pattern of stream water movement into the bed which was similar to the pattern based on Cl^-, although the depth of penetration of $>90\%$ stream water in the two upstream riffles was less extensive (Figure 3b). In the stream bank area where hydrologic data indicated subsurface flow parallel to the stream, the mixing equation based on mean Cl and Si suggested that 90% and 63% stream water respectively was present at site 16, whereas 60% and 37% stream water respectively was observed at site 17. At site 21, located 0.5 m from the channel margin, the% stream water derived from Cl^- and Si was 72% and 68% respectively.

The extent of the hyporheic zone was also investigated using Br^- as a tracer. Bromide was injected into the riffle 1 m upstream from site 3 at a depth of 25–35 cm on August 8, 1994 (Figure 1). After 24 h, Br^- concentrations remained constant in the 15–25 cm depth piezometer at site 3, but increased from background levels of 0.5 mg/L to concentrations of 11 mg/L at 34–45 cm, 178 mg/L at 60–80 cm and 427 mg/L at 95–100 cm. Although the main flow of channel water in this riffle followed a path from sites 3 to 7, the Br^- tracer was not detected in the streambed at sites 4–7 throughout the experiment. Instead the Br^- plume moved laterally and entered the streambank at site 15 and extended to site 16 after 3 days (Figure 1). Seventeen days after the tracer addition to the streambed, Br^- had moved 4–5 m laterally into the bank and extended in an arc-shaped flow path within the floodplain parallel to the channel for 20 m before it curved back into the streambed sediments in the pool between sites 10 and 11 (Figure 4a). A cross-section of the streambed and adjacent floodplain along the path of the Br^- plume indicated that the maximum concentration occurred at depth near the boundary between the alluvium and the silt-clay layer (Figure 4c). Bromide was injected at the same location in the streambed on September 25, 1995. This Br^- plume followed a pattern similar to the 1994 injection reaching site 15 between day 1 and 2, site 16 by day 3 and site 17 by day 7 (Figure 4b). In contrast to the 1994 injection, Br^- concentrations increased to 8–12 mg/L in the deepest piezometer (65–85 cm) at site 4 between day 7 and the termination of measurements on day 16, but there was no evidence of increase in the streambed at sites 5–7 (Figures 1 and 4b).

Bromide injected into the riffle upstream from site 8 on August 20, 1995 also flowed laterally into the floodplain to the east of the channel following an concentric subsurface flow path that reached site 20 by day 4 (Figures 1 and 5a). By day 5, the Br^- had re-entered the channel bed at site 11 increasing levels to 8 and 10 mg/L at depths of 10–30 and 30–50 cm respectively. By day 8 the plume was present in the small downstream riffle at depths of 40–60 cm in the bed near the west bank of the stream (Figure 5b). No Br^- increase was observed in piezometers at sites 12 and 13 in this riffle (Figure 1). The chemical mixing model based on Cl^- and Si indicated that these sites were located in groundwater outside the hyporheic zone.

Although the highest Br^- concentration occurred in the stream bank during this experiment, Br^- also increased in riffle sediments downstream from the injection point. At site 8, 1.5 m downstream, Br^- concentrations at depths of 60–80 and 80–100 cm increased to 28.1 and 2.3 mg/L within 24 h. After 4 days the plume had extended downwards from the injection point to the silt-clay boundary at sites 8 and 9 and then followed an upward flow path towards the streambed surface at the riffle-pool transition (Figure 6).

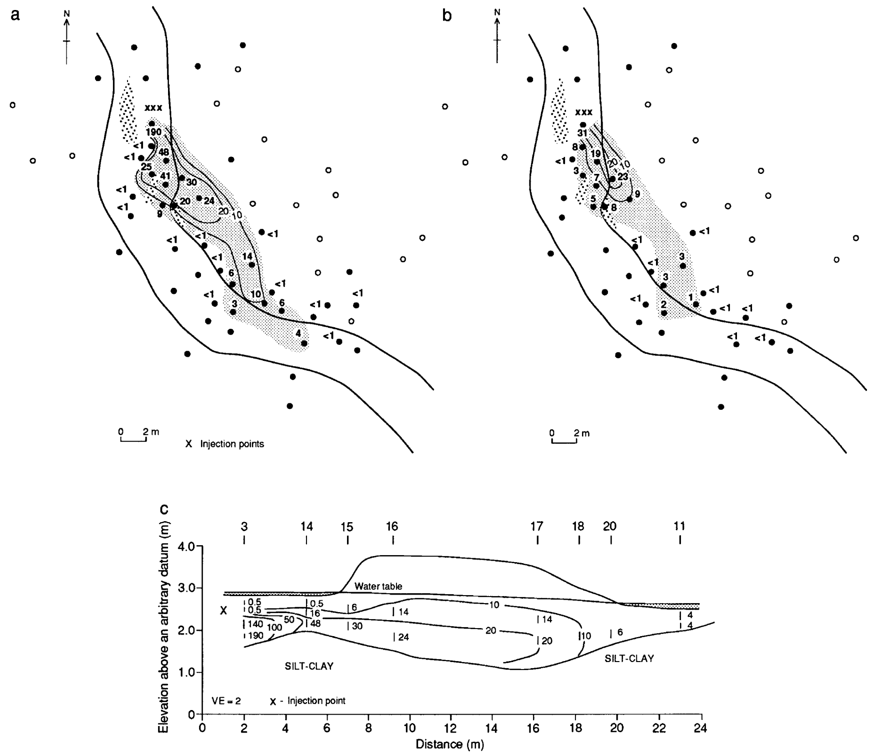

Figure 4. Map of distribution of bromide tracer in the streambed and floodplain. Bromide was injected in a solid state in the streambed at 25–35 cm depth in an area of downwelling water; (a) bromide on day 17 after injection on August 8, 1994, (b) bromide on day 16 after injection on September 25, 1995, (c) vertical cross-section of streambed and floodplain showing bromide on day 17 after the August 8, 1994 injection. Bold numbers indicate the highest bromide concentration (mg/L) at each piezometer nest. Lines are contours of equal bromide concentration. Background bromide concentrations in stream and subsurface were 0.4–0.7 mg/L.

Hyporheic chemistry patterns

Streambed pore water DO, nitrate and ammonium were similar among sampling dates during low stream flows in 1994–95 and mean concentrations were therefore used to examine patterns of chemistry in the streambed. Mean DO concentrations of >6 mg/L occurred to depths of 35–40 cm in the upstream head and middle zones of the two major riffles within the study reach (Figure 7a). In contrast, DO concentrations of <2 mg/L, similar to groundwater values, extended upwards towards the streambed surface in the riffle-pool transition zones. Mean NO_3^--N concentrations declined rapidly with depth except in riffle gravels at sites 8 and 9 where concentrations of

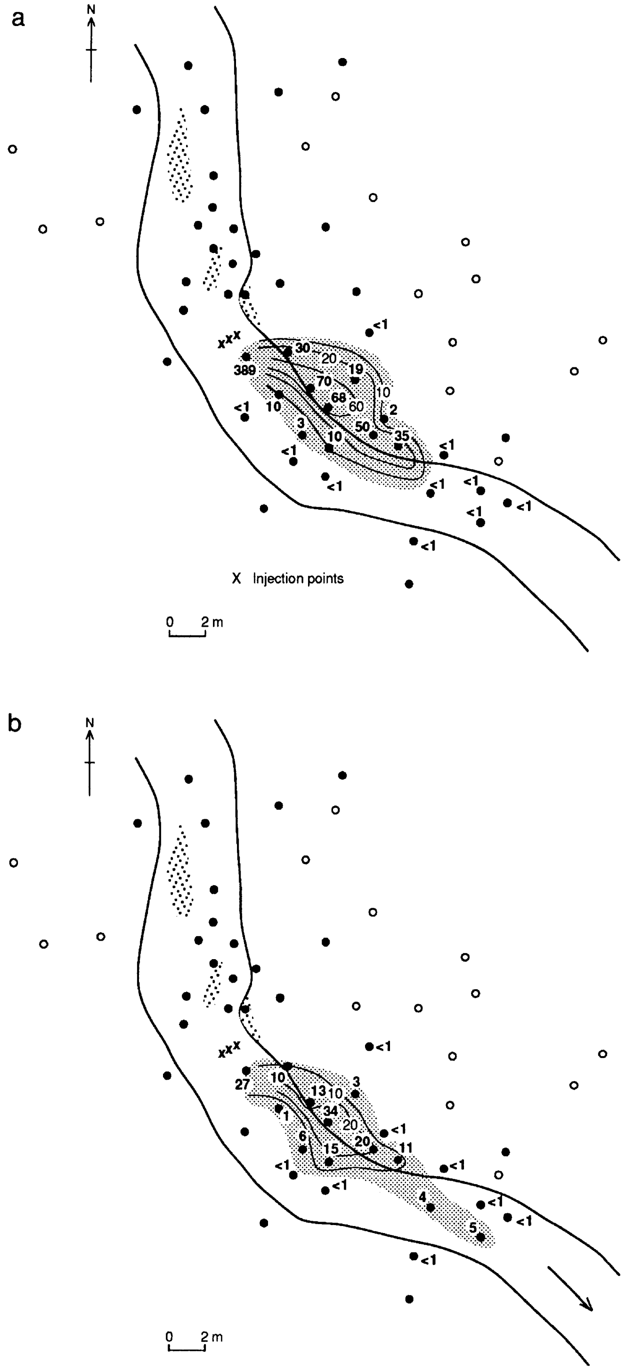

Figure 5. Map of distribution of bromide tracer in the streambed and floodplain. Bromide was injected in a solid state to the streambed at 25–35 cm depth on August 21, 1995 in an area of downwelling water; (a) bromide on day 4, (b) bromide on day 8. Bold numbers indicate the highest bromide concentration (mg/L) at each piezometer nest. Lines are contours of equal bromide concentration. Background bromide concentrations in stream and subsurface were 0.4–0.7 mg/l.

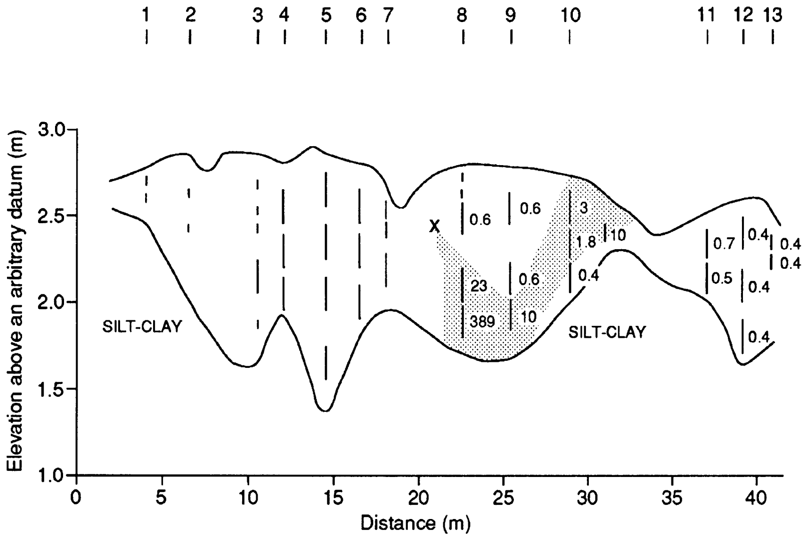

Figure 6. Longitudinal transect beneath the streambed showing the distribution of bromide tracer four days after injection in a solid state to the streambed at 25–35 cm depth on August 21, 1995 in an area of downwelling water.

$>$0.8 mg/L extended to 35–40 cm (Figure 7b). Elsewhere, NO_3^--N concentrations were frequently $<$0.1 mg/L at depths of $>$10–20 cm particularly at the downstream end of the two main riffles. Mean NH_4^+-N concentrations showed an increase with depth and distance downstream (Figure 7c). Concentrations of $<$0.4 mg N/L occurred to depths of 60–80 cm in the upstream and middle sections of the two major riffles, and higher concentrations of 0.6–1.0 mg N/L extended upwards from the silt-clay boundary to depths of 15–20 cm at the base of these riffles. Mean DO, nitrate and ammonium concentrations in the small downstream riffle-pool unit (sites 11–13) were similar to groundwater concentrations and showed little variation vertically or longitudinally.

If it is assumed that reactive elements are transported identically to a conservative ion such as Cl^- in the hyporheic zone, then observed concentrations of the reactive elements should be similar to predicted concentrations computed from the fraction of stream and groundwater at various depths derived from the Cl^- based chemical mixing equation. DO was only measured on 4 sampling dates so that sufficient data were not available for statistical analysis. However, if DO was transported identically to Cl^-, mean observed DO values were only 15–55% of predicted DO at all depths within the hyporheic zone except for sites 3 (15–20 and 35–40 cm) and site 8 (5–10 and 15–20 cm).

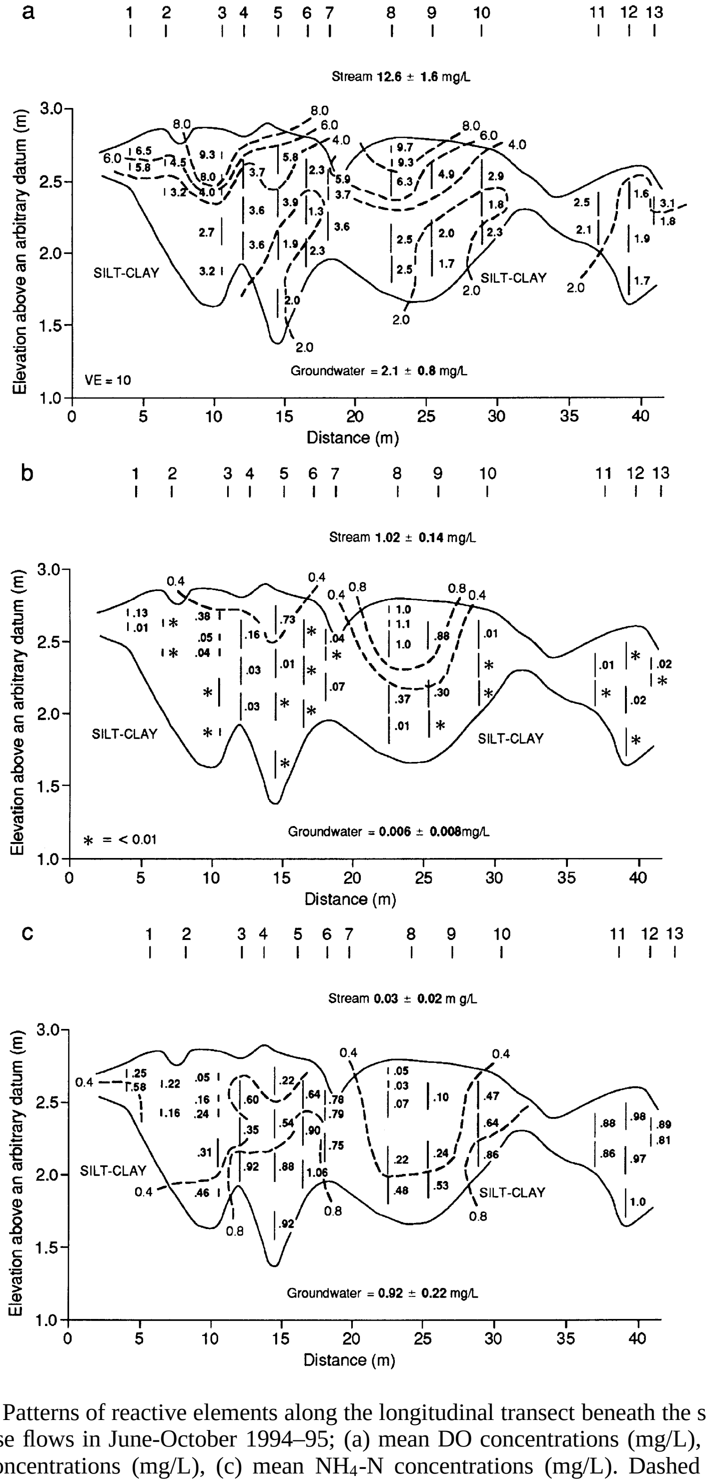

Figure 7. Patterns of reactive elements along the longitudinal transect beneath the streambed during base flows in June-October 1994–95; (a) mean DO concentrations (mg/L), (b) mean NO_3-N concentrations (mg/L), (c) mean NH_4-N concentrations (mg/L). Dashed lines are contours of equal concentration in mg/l. Vertical exaggeration of transect is ×10.

Table 2. Difference between mean measured and calculated nitrate-N in interstitial water in the streambed hyporheic zone at locations where n $\geq$ 7. Statistical significance ($P <$ 0.05) was determined by a *t*-test on signed ranks.

Site (depth cm)	n	Mean diff* (μg/L)	Site (depth cm)	n	Mean diff (μg/L)
1 (5–10)	7	-0.92	7 (40–60)	7	-0.19
(15–20)	8	-0.82	8 (5–10)	10	-0.02 NS
2 (20–25)	8	-0.90	(15–20)	10	$+0.06$ NS
(40–45)	8	-0.66	(20–40)	10	$+0.03$ NS
3 (15–20)	10	-0.69	(60–80)	10	-0.60
(35–40)	10	-0.97	(80–100)	9	-0.80
(95–100)	10	-0.46	10 (10–30)	10	-0.82
5 (10–30)	7	-0.29	(30–50)	10	-0.61
(40–60)	7	-0.41	(50–70)	9	-0.12
(70–90)	7	-0.14	11 (10–30)	10	-0.13
7 (10–20)	8	-0.56	(30–50)	10	-0.15
(20–30)	8	-0.41			

* A negative number represents apparent loss of nitrate from the water
NS indicates the null hypothesis that mean measured = mean calculated nitrate was accepted

Statistical significance (95% confidence level) of differences between observed vs predicted nitrate and ammonium concentrations within the streambed hyporheic zone was determined with a Wilcoxon signed ranks test (Iman & Conover 1993). Shallow piezometers to depths of 40 cm in the riffle at site 8 had no significant difference between observed and calculated nitrate. Elsewhere in the streambed, mean observed nitrate was significantly less than mean predicted nitrate (Table 2). Average observed nitrate concentrations were frequently $<$10% of predicted concentrations indicating considerable depletion during transport. Loss of nitrate represented by average % of predicted concentration for individual piezometers was significantly correlated with interstitial DO (r = 0.60, p = $<$0.05), but was not significantly correlated with% surface water (r = 0.22, p = $>$0.05). Nine of the 23 piezometers with sufficient data for analysis had mean observed ammonium concentrations not significantly different from predicted (Table 3). Of the other 14 piezometers where differences were significant, 13 had mean observed ammonium concentrations which varied from 1.3 to 3.7× higher than predicted values suggesting considerable ammonium production. This ammonium production was significantly correlated with% surface water (r = 0.48, p = $<$0.05), but had no significant correlation with DO (r = 0.09, p = $>$0.05).

Table 3. Difference between mean measured and calculated ammonium-N in interstitial water in the streambed hyporheic zone at locations where n ≥ 7. Statistical significance ($p < 0.05$) was determined by a *t*-test on signed ranks.

Site (depth cm)	n	Mean diff* (mg/L)	Site (depth cm)	n	Mean diff (mg/L)
1 (5–10)	7	+0.14	7 (40–60)	7	+0.05 NS
(15–20)	8	+0.38	8 (5–10)	10	+0.01 NS
2 (20–25)	8	+0.16	(15–20)	10	−0.01 NS
(40–45)	8	−0.14	(20–40)	10	+0.03 NS
3 (15–20)	10	−0.01 NS	(60–80)	10	+0.13
(35–40)	10	+0.12	(80–100)	9	+0.21
(95–100)	10	+0.10	10 (10–30)	10	+0.21
5 (10–30)	7	+0.12	(30–50)	10	+0.15
(40–60)	7	+0.38	(50–70)	9	+0.01 NS
(70–90)	7	+0.09 NS	11 (10–30)	10	+0.06 NS
7 (10–20)	8	+0.18	(30–50)	10	+0.09 NS
(20–30)	8	+0.28			

* A positive number represents apparent gain of ammonium
NS indicates the null hypothesis that mean measured = mean calculated ammonium was accepted

Table 4. Difference between mean measured and calculated nitrate-N and ammonium-N in porewater from floodplain piezometers in the hyporheic zone at locations where n ≥ 7. Statistical significance ($p < 0.05$) was determined by a *t*-test on signed ranks.

Site (depth cm)	n	Mean diff NO_3-N mg/L	Mean diff NH_4-Nmg/L
16 (135–155)	10	−0.81	+0.15
16 (195–210)	10	−0.70	+0.28
17 (125–145)	10	−0.38	+0.30
17 (170–190)	8	−0.69	+0.24
21 (120–140)	7	−0.72	+0.36

The behaviour of nitrate and ammonium in the hyporheic zone that extended laterally into the floodplain was assessed by comparing observed concentrations with concentrations predicted from chloride in piezometer nests at sites 16, 17 and 21 where sufficient data was available for statistical analysis. Results indicated a pattern similar to the streambed with observed nitrate significantly higher and observed ammonium significantly lower respectively than predicted concentrations (Table 4).

Table 5. Concentrations of bromide (mg/L) and nitrate-N (mg/L) in the hyporheic zone after streambed solute injection in riffle gravels upstream from site 8.

Site (depth cm)	Dist. from inject. pt. (m)	Initial		2 days		4 days		8 days	
		Br	NO_3-N	Br	NO_3-N	Br	NO_3-N	Br	NO_3-N
				Streambed					
8 (20–40)	1.5	0.4	0.96	0.7	1.0	0.6	1.07	0.8	1.05
(60–80)		0.4	0.22	52.3	1.7	22.9	0.58	1.1	0.38
(80–100)		0.4	0.01	339.0	11.1	389.0	8.15	27.5	0.03
9 (20–40)	4.5	0.6	0.84	0.7	0.86	0.6	0.94	0.7	0.90
(60–80)		0.6	0.27	0.6	0.44	0.6	0.36	0.7	0.41
(80–100)		0.5	0.002	14.9	0.02	10.1	0.002	1.2	0.002
				Floodplain					
21 (120–140)	8.0	0.5	0.002	0.5	0.002	68.2	0.002	34.0	0.0002

The transport response of the conservative Br provided a basis for analyzing the reactivity of nitrate in the hyporheic zone during injection experiments in August and September 1995. Pore water samples 1.5 m downstream from the injection point at site 8 (60–80) and (80–100 cm) depths showed increases of Br^- and nitrate above ambient levels within 24 h and reached maximum concentrations of 1.7 mg N/L at 60–80 cm and 11.1 mg N/L at 80–100 cm after 2 days before declining slowly towards background values by 8 days (Table 5). Although the NO_3^--N mass comprised 7.5% of the Br mass in this injection, these maximum NO_3^--N concentrations were only 3.3% of the Br^- concentrations in the piezometers. At site 9, 4.5 m downstream Br^- concentrations also increased at 80–100 cm depth to 14.9 mg/L by day 2 and 10.1 mg/L by day 4, whereas NO_3^--N concentrations only increased from initial values of 0.002 to 0.02 mg/L on the second day and returned to initial values by day 4. In the floodplain adjacent to the riffle 8 m from the injection point, Br^- increased after 4 days to 68 mg/L and declined to 34 mg/L by day 8. Assuming nitrate was transported identically to Br^-, predicted NO_3^--N concentrations were 5.1 and 2.5 mg/L on these dates, however observed concentrations remained at background values of 0.002 mg/L during this period.

Within 3 days of the streambed injection in September 1995, large increases in nitrate concentration occurred in the deeper piezometers at site 3, 1 m downstream from the injection point. At this site elevated nitrate concentrations were evident for 10 days after the injection (Table 6). The NO_3^--N mass was 10% of the Br^- mass injected in the stream bed, but NO_3^--N

Table 6. Concentrations of bromide (mg/L) and nitrate-N (mg/L) in the hyporheic zone after streambed solute injection in riffle gravels upstream from site 3.

Site	Dist. from	Initial		3 days		7 days		10 days	
(depth cm)	inject. pt. (m)	Br	NO_3-N	Br	NO_3-N	Br	NO_3-N	Br	NO_3-N
				Streambed					
3 (35–40)	1	0.5	0.005	25.0	0.004	8.1	0.016	13.0	0.002
(60–80)		0.5	0.002	99.0	3.04	52.5	0.27	43.7	0.09
(95–100)		0.5	0.002	170.0	6.84	93.0	1.17	60.3	0.61
14 (30–50)	4	0.6	0.15	0.8	0.11	1.0	0.14	1.9	0.12
(60–80)		0.6	0.02	14.3	0.004	25.6	0.004	32.2	0.004
				Floodplain					
15 (60–80)	6	0.6	0.006	0.9	0.008	3.6	0.002	9.2	0.004
(140–160)		0.6	0.004	13.4	0.002	25.3	0.014	28.8	0.002
16 (130–150)	8	0.5	0.006	1.6	0.002	9.4	0.008	14.5	0.002
(175–195)		0.5	0.010	0.9	0.006	17.3	0.012	26.4	0.0002

concentrations at 60–80 cm were only 3% of Br^- concentrations after 3 days and declined to 0.2% after 10 days. Similarly at 80–100 cm NO_3^--N levels were 4% of Br^- after 3 days and declined to 1% by 10 days. Although Br^- concentrations increased to 25–32 mg/L in the stream bed 4 m downstream at site 14 (60–80 cm), and in floodplain piezometers 6 and 8 m respectively from the injection point, no clear pattern of nitrate increase was observed in these locations.

Discussion

The use of conservative ions in a two-component chemical mixing equation to separate stream and groundwater fractions in the streambed and adjacent floodplain indicated the existence of local zones of stream water recharge. The convective exchange of water between the stream and the subsurface in both a vertical and horizontal direction in the study reach was confirmed by paths of bromide tracer movement. Several types of evidence suggest that surface-subsurface exchange of water was controlled mainly by streambed topography. Areas of positive and negative vertical hydraulic gradient in the streambed were associated with alternating riffles and pools. Tracer injections with Br^- showed the vertical downwelling of water at the head of riffles and upwelling at riffle-pool transitions. Tracer experiments also demonstrated the lateral recharge of stream water into the floodplain at the upstream end of riffles, the movement of this water by a subsurface arc-shaped flow path around the riffle and re-entry to the stream bed in a downstream pool.

Variations in hydraulic properties of subsurface sediments may also influence water exchanges. A decrease in sediment thickness over an impermeable layer can produce discharge towards the surface (Hinton et al. 1993). Hydraulic heterogeneities do not appear to strongly influence the location of spatially distinct areas of exchange between stream water and the hyporheic zone in Brougham Creek. Vertical upwelling and downwelling zones were consistently related to riffle-pool locations but not to the depth of the relatively impermeable silt-clay surface. Although upwelling water occurred in a riffle-pool transition at site 10 where the depth of the silt-clay boundary decreased from 1 to 0.3 m beneath the stream bed, upwelling was also observed in the riffle-pool transition at site 6 where the silt-clay zone was at a depth of $>$1.5 m.

Our study is the first to examine both vertical and horizontal exchanges of water to assess the three-dimensional nature of the hyporheic zone associated with large scale streambed topographic features. Previous studies have focused on either vertical exchanges beneath the streambed (Hendricks & White 1991; Valett et al. 1994), or horizontal subsurface exchanges between the stream and floodplain alluvium (Harvey & Bencala 1993). In Brougham Creek streambed, the hyporheic zone extended in a vertical direction to the silt-clay boundary at depths of 0.9–1.1 m beneath the two main riffles, but was located at only 0.1–0.3 m in the riffle-pool transitions. In a horizontal direction the stream-filled arc-shaped flow paths in the floodplain penetrated laterally up to 4–5 m from the channel margin and extended downstream for 10–20 m. Along these subsurface flow paths in the floodplain, the hyporheic zone extended downwards from the water table to the silt-clay surface at depths of 1–1.7 m. The lower boundary of the hyporheic zone in the streambed and the adjacent floodplain appears to be restricted in some locations by the configuration of the silt-clay layer. For example, the chemical mixing equation based on Cl^- indicated $>$80% stream water in riffle gravels adjacent to the silt-clay surface at sites 8 and 9. If the alluvium was deeper at these locations it is possible that the 10% stream water boundary of the hyporheic zone would have extended to greater depth.

The vertical and lateral dimensions of the hyporheic zone in Brougham Creek appear to be quite similar to those of other hyporheic zones influenced by streambed topography. White et al. (1987) found that surface water downwelled to depths of at least 50 cm at the upstream head of a riffle in a Michigan sand-bed stream. Stream water recharge around channel steps followed a flow path that penetrated 2–3 m laterally and extended 1–10 m downstream in the streamside alluvium of St Kevin's Gulch, Colorado (Harvey & Bencala 1993).

In this mountain stream, horizontal exchange between the stream and adjacent alluvium was controlled by channel steps with water surface slopes of 20% or greater. Our data suggest that such horizontal exchanges can occur with smaller changes in channel slope. In Brougham Creek riffles with slopes of 2–3% alternate with pools which have surface water slopes of $<1\%$.

Well defined patterns of DO, nitrate and ammonium were associated with areas of downwelling and upwelling water beneath the streambed in Brougham Creek. In downwelling areas at the head and mid sections of riffles, DO and nitrate declined and ammonium increased with depth. The mixing of ammonium-rich relatively anoxic groundwater with channel water in areas of upwelling at riffle-pool transitions produced an overall increase in ammonium and a decrease in DO with distance downstream beneath the riffles. Reactive elements did not show any clear trends along the concentric stream-filled flow paths within the floodplain. Despite the presence of $>80\%$ stream water in the initial portion of this lateral flow path, DO and nitrate concentrations were similar to groundwater values. Similar patterns of reactive solute concentrations in areas of vertical downwelling and upwelling have been reported in other stream hyporheic zones (Hendricks & White 1991, 1995; Valett et al. 1994; Holmes et al. 1994).

Differences in observed vs predicted concentrations based on background Cl^- patterns revealed nitrate depletion within the Brougham Creek hyporheic zone. The removal of nitrate in the streambed was confirmed by the loss of nitrate in relation to coinjected bromide in sites of downwelling water in two riffles. Nitrate loss from interstitial water in hyporheic zone sediments may result from uptake by benthic algae and microbes for growth or denitrification, the reduction of nitrate to gaseous N forms by bacteria under anaerobic conditions. At most hyporheic sites where nitrate was depleted, concentrations of NH_4^+-N varied from 0.2–0.8 mg/L suggesting that nitrate is unlikely to be required for growth. Although nitrate loss was related to DO content, hyporheic DO concentrations were >2 mg/L. Denitrification activity in the oxic zones of surface sediments has been attributed to the occurrence of anoxic microsites (Holmes et al. 1996). We did not directly measure denitrification in Brougham Creek, however previous research showed high rates of denitrification in lab incubations of 0–5 cm depth riffle and pool sediments from several adjacent streams in the Duffin Creek watershed (Hill 1983; Hill & Sanmugadas 1985).

With the exception of a few riffle sites, nitrate concentrations in Brougham Creek bed sediments were <0.01 mg N/L at depths of >20–30 cm, although mean channel water concentrations were approximately 1.0 mg/L. Laterally in the floodplain portion of the hyporheic zone, trace levels of nitrate occurred even at sites adjacent to the channel margin. This pattern suggests that nitrate in advected channel water was rapidly depleted near the sediment-water interface at most sites. The significant difference between observed and predicted nitrate values found at vertical depths of $>$30 cm in the streambed and laterally in the floodplain therefore indicate a potential for nitrate depletion rather than actual loss at these sites. The rapid removal of high concentrations of injected nitrate at depths of 0.6–1.0 m in the streambed confirms that these areas of the hyporheic where background nitrate is at trace concentrations, have a large potential nitrate removal capacity.

In N-rich agricultural streams, nitrate is frequently depleted by denitrification in the upper few cm of the streambed and the principal limiting factor controlled denitrification is the rate at which nitrate is supplied from channel water (Christensen & Sorensen 1988; Christensen et al. 1989). In N-limited streams, the location of denitrification activity may differ among streams. Triska et al. (1993) found that denitrification activity in Little Lost Man Creek occurred at sites with minimal channel exchange which were distant from the stream. In contrast, denitrification was confined mainly to locations where channel water entered the subsurface zone in gravel bars of Sycamore Creek, Arizona (Holmes et al. 1996). Here denitrification was linked to greater availability of organic carbon and higher rates of nitrification which provided a nitrate source.

Recent conceptual models suggest that stream element retention is determined by the proportion of channel water which passes through the hyporheic zone, subsurface water residence times and rates of sediment biogeochemical processes (Findlay 1995; Valett et al. 1996). In a comparative study of three mountain streams, Valett et al. (1996) found that increased nitrate retention was correlated with longer water residence times in extensive hyporheic zones. In contrast, our data suggest that nitrate retention in Brougham Creek was not influenced by the overall extent of channel water-groundwater mixing and water residence times in the hyporheic zone. We suggest that in N-rich agricultural streams, where nitrate is rapidly removed near the streambed sediment-water interface, nitrate retention may be influenced more by the size of surface water storage zones rather than by the dimensions of the hyporheic zone. Storage in areas of slowly moving surface water in pools and eddies increases the residence time of channel water in contact with streambed sediment surfaces.

Although ammonium concentrations in the hyporheic zone were lower than groundwater concentrations, differences between observed and predicted concentrations indicated considerable ammonium production at many locations beneath the stream channel and adjacent floodplain. These data suggest that mineralization of organic N to ammonium is important and exceeds rates of microbial uptake in the hyporheic zone. Dissimilatory reduction of nitrate to ammonium is probably not a major source of increased ammonium concentration in interstitial water because this process occurs mainly in highly anaerobic organic-rich sediments (Sorensen 1978; Koike & Hattori 1978; Gordon et al. 1986). Furthermore, concentration patterns indicate that nitrate was depleted near the streambed surface, whereas ammonium production occurred at depths of 0.5–1.0 m below riffles and in the floodplain at considerable distances from the channel margin. Evidence of ammonium production in combination with trace levels of nitrate at many locations suggest that nitrification is a minor process in the hyporheic zone.

Concentration patterns in the Brougham Creek hyporheic zone indicate that upwelling water at the base of riffles is a source of ammonium to the stream. In Sycamore Creek, an N-limited desert stream, inputs of nitrogen-rich hyporheic water increased nitrate concentrations in channel water adjacent to upwelling zones (Valett et al. 1994). This supply of nitrate-rich water promoted algal growth and produced higher standing crops of benthic algae at upwelling sites. We did not detect any elevation of ammonium concentrations in channel water adjacent to upwelling sites in our study. The relatively high inorganic N concentrations in channel water during summer base flows may also limit the effects of upwelling hyporheic water on algal production in Brougham Creek.

The pattern of hyporheic zone nitrate depletion and ammonium production observed in this study differs considerably from nitrogen dynamics observed in stream hyporheic zones where nitrification is the dominant nitrogen transformation process. Increased nitrate concentrations along subsurface flow paths of advected channel water have been attributed to a coupling of organic N mineralization and nitrification (Jones et al. 1995; Wondzell & Swanson 1996). Ammonium in groundwater can also support nitrification in hyporheic zones. In a northern California stream, high ammonium concentrations in groundwater entering the aerobic hyporheic zone were depleted by nitrification during transport towards the channel (Triska et al. 1990; Triska et al. 1993). Denitrification has also been measured in these stream hyporheic zones, but generally occurs at a lower rate than nitrification (Duff & Triska 1990; Holmes et al. 1996).

Recently, Jones and Holmes (1996) proposed that nitrification is dominant and the hyporheic zone is a nitrate source in streams where interstitial water is well oxygenated and the concentration of nitrate in channel water is low. Conversely, the hyporheic zones of N-rich streams with low interstitial oxygen concentrations function as nitrate sinks. They hypothesize that this relationship occurs because low nitrate systems often have limited amounts of labile organic matter, whereas streams high in nitrate are also frequently enriched in organic matter which stimulates subsurface respiration and the development of anoxic conditions. Most previous research has focused on streams with low surface water nitrate concentrations where the hyporheic is a nitrate source. Data for N-rich streams are limited. Pinay et al. (1994) showed that denitrification produced rapid nitrate depletion from channel water concentrations of 4–5 mg N/L to <1.0 mg N/L as water flowed through a gravel bar in the Garonne River, France. The dominance of hyporheic nitrate removal in Brougham Creek, where mean channel water nitrate-N concentrations are 1.0 mg/L, adds additional support for the relationship proposed by Jones and Holmes (1996).

Conclusions

In Brougham Creek, hydrometric, background conservative ion and injected tracer data reveal a complex three-dimensional hyporheic zone in which vertical and horizontal stream-subsurface water exchanges with the streambed and floodplain were controlled by stream channel riffle-pool units. The hyporheic zone in this nitrate enriched agricultural stream functioned as a nitrate sink and an ammonium source. These nitrogen dynamics differ considerably from patterns observed in N-limited streams where nitrification is frequently the dominant nitrogen transformation process.

Recent conceptual models of hyporheic zone influence on stream ecosystems have emphasized the extent of surface-subsurface hydrologic exchange and water residence times in sediments as important controls on stream nutrient retention. These models have been based mainly on studies of streams with very low nutrient concentrations in mountain and desert landscapes. Our study suggests that these models may be less applicable to high N streams where nitrate removal occurs at the sediment-channel water interface and extensive areas of the hyporheic at depth in the streambed and laterally in the floodplain have an unused potential for nitrate depletion. A greater focus on the description of hyporheic processses in N-rich streams would provide a broader perspective on how hyporheic zone biogeochemistry differs among streams and how these differences may influence stream ecosystems.

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References

Bencala KE, Kennedy VC, Zellweger GW, Jackman AP & Avanzino RJ (1984) Interactions of solutes and streambed sediments, 1, an experimental analysis of cation and anion transport in a mountain stream. Water Resour. Res. 20: 1791–1803

Christensen PB & Sorensen J (1988) Denitrification in sediment of lowland streams: Regional and seasonal variation in Gelbaek and Rabis Baek, Denmark. FEMS Microbiol. Ecol. 53: 335–344

Christensen PB, Nielsen LP, Revsbech NP & Sorensen J (1989) Microzonation of denitrification activity in stream sediments as studied with a combined oxygen and nitrous oxide microsensor. Appl. Environ. Microbiol. 55: 1234–1241

Dahm CN, Trotter EH & Sedell JR (1987) Role of anaerobic zones and processes in stream ecosystem productivity. In: Averett RA & McKnight DM (Eds) Chemical Quality of Water and the Hydrological Cycle (pp 157–178). Lewis, Chelsea, Michigan USA

Duff JH & Triska FJ (1990) Denitrification in sediments from the hyporheic zone adjacent to a small forested stream. Can. J. Fish. Aquat. Sci. 47: 1140–1147

Durand P, Neal M & Neal C (1993) Variations in stable oxygen isotope and solute concentrations in small submediterranean montane streams. J. Hydrol. 144: 283–290

Edwards AMC (1974) Silicon depletion in some Norfolk rivers. Freshw. Biol. 4: 267–274

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

Findlay S (1995) Importance of surface-subsurface exchange in stream ecosystems: The hyporheic zone. Limnol. Oceanogr. 40: 159–164

Gordon AS, Cooper WJ & Scheidt DJ (1986) Denitrification in marl and peat sediments in the Florida Everglades. Appl. Environ. Microbiol. 52: 987–991

Grimm NB, Valett HM, Stanley EH & Fisher SG (1991) Contribution of the hyporheic zone to stability of an arid-land stream. Verh. Internat. Verein. Limnol. 24: 1595–1599

Harvey JW & Bencala KE (1993) The effect of streambed topography on surface-subsurface water exchanges in mountain catchments. Water Resour. Res. 29: 89–98

Hendricks SP & White DS (1991) Physicochemical patterns within a hyporheic zone of a northern Michigan River, with comments on surface water patterns. Can. J. Fish. Aquat. Sci. 48: 1645–1654

Hendricks SP & White DS (1995) Seasonal biogeochemical patterns in surface water, subsurface hyporheic, and riparian groundwater in a temperate stream ecosystem. Arch. Hydrobiol. 134: 459–490

Hill AR (1983) Nitrate-nitrogen mass balances for two Ontario rivers. In: Fontaine TD & Bartell SM (Eds) Dynamics of Lotic Ecosystems (pp 457–477). Ann Arbor Science, Ann Arbor, Michigan

Hill AR & Sanmugadas K (1985) Denitrification rates in relation to stream sediment characteristics. Wat. Res. 19: 1579–1586

Hinton MS, Schiff SL & English MC (1993) Physical properties governing groundwater flow in a glacial till catchment. J. Hydrol. 142: 229–249

Holmes RM, Fisher SG & Grimm NB (1994) Parafluvial nitrogen dynamics in a desert stream ecosystem. J. N. Am. Benthol. Soc. 13: 468–478

Holmes RM, Jones JB, Fisher SG & Grimm NB (1996) Denitrification in a nitrogen-limited stream ecosystem. Biogeochem. 33: 125–146

Hooper RP & Shoemaker CA (1986) A comparison of chemical and isotopic hydrograph separation. Water Resour. Res. 22: 1444–1454

Iman RL & Conover WJ (1983) A Modern Approach to Statistics. John Wiley and Sons, New York

Jones JB, Fisher SG & Grimm NB (1995) Nitrification in the hyporheic zone of a desert stream ecosystem J. N. Am. Benthol. Soc. 14: 249–258

Jones JB & Holmes RM (1996) Surface-subsurface interactions in stream ecosystems. Trends Ecol. Evol. 11: 239–242

Koike I & Hattori A (1978) Denitrification and ammonia formation in anaerobic coastal sediments. Appl. Environ. Microbiol. 35: 278–282

Maule CP & Stein J (1990) Hydrologic flow path definition and partitioning of spring meltwater. Water Resour. Res. 26: 2959–2970

Pinay G, Haycock NE, Ruffinoni C & Holmes RM (1994) The role of denitrification in nitrogen retention in river corridors. In: Mitsch WJ (Ed) Global Wetlands: Old World and New (pp 107–116). Elsevier, Amsterdam

Pionke HB, Gburek WJ & Folmar GJ (1993) Quantifying stormflow components in a Pennsylvania watershed when ^{18}O and storm conditions vary. J. Hydrol. 148: 169–187

Savant SA, Reible DD & Thibodeaux LJ (1987) Convective transport within stable river sediments. Water Resour. Res. 23: 1763–1768

Sorensen J (1978) Capacity for denitrification and reduction of nitrate to ammonia in a coastal marine sediment. Appl. Environ. Microbiol. 35: 301–305

Sterba O, Uvira V, Mathur P & Rulik M (1992) Variations of the hyporheic zone through a riffle in the R. Morava, Czechoslovakia. Reg. Rivers: Res. Manag. 7: 31–43

Technicon (1977) Nitrate and nitrite in water and seawater. Industrial Method 158-71 W1A. Technicon Industrial System, Tarrytown, NY

Technicon (1978) Ammonia in water and seawater. Industrial Method 154-71 W/B. Technicon Industrial System, Tarrytown, NY

Thibodeaux LJ & Boyle JO (1987) Bed-form generated convective transport in bottom sediment. Nature 325: 341–343

Triska FJ, Kennedy VC, Avanzino RJ, Zellweger GW & Bencala KE (1989) Retention and transport of nutrients in a third order stream in northwestern California: Hyporheic processes. Ecology 70: 1893–1905

Triska FJ, Duff JH & Avazino RJ (1990) Influence of exchange flow between the channel and hyporheic zone on nitrate production in a small mountain stream. Can. J. Fish. Aquat. Sci. 47: 2099–2111

Triska FJ, Duff JH & Avanzino RJ 1993) The role of water exchange between a stream channel and its hyporheic zone in nitrogen cycling at the terrestrial-aquatic interface. Hydrobiol. 251: 167–184

Valett HM, Fisher SG, Grimm NB & Camill P (1994) Vertical hydrologic exchange and ecological stability of a desert stream ecosystem. Ecology 75: 548–560

Valett HM, Morrice JA, Dahm CN & Campana ME (1996) Parent lithology, surface-groundwater exchange and nitrate retention in headwater streams. Limnol. Oceanogr. 41: 333–345

Wels C, Cornett RJ & Lazerte BD (1991) Hydrograph separation: A comparison of geochemical and isotopic tracers. J. Hydrol. 122: 253–274

White DS, Elzinga CH & Hendricks SP (1987) Temperature patterns within the hyporheic zone of a northern Michigan river. J. N. Am. Bentol. Soc. 6: 85–91

Wondzell SM & Swanson FJ (1996) Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream. II: Nitrogen cycling. J. N. Am. Benthol. Soc. 15: 20–34