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# Buried organic-rich horizons: their role as nitrogen sources in stream riparian zones

**Alan R. Hill**

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**Abstract** The effect of water table fluctuations on the interaction between nitrogen mineralization in buried organic-rich soil horizons and nitrate mobilization into groundwater was examined in the riparian zone of a small headwater agricultural catchment in southern Ontario, Canada. Riparian soils contained buried organic layers and lenses overlying a poorly sorted gravel layer at a depth of 0.8–1.0 m. The riparian water table in summer 2006 generally remained within 0.4 m of the surface, whereas during a major drought in 2007 the water table declined to >1.9 m in August and riparian soils above the gravel layer inland from the stream remained unsaturated from mid-June to early November. Mean daily net N mineralization and nitrification rates during 2–4 week in situ soil incubations were 0.2–1.35 mg N $kg^{-1}$ $day^{-1}$ in 0–10 cm surface soils in May–September 2006, whereas N mineralization and nitrification were negligible at 30–45 and 60–75 cm soil depths. In summer and fall 2007, high daily rates of N mineralization and nitrification of 0.3–0.8 mg N $kg^{-1}$ $day^{-1}$ occurred at 30–45 and 60–75 cm depths that were similar to surface soil rates. The soil nitrate pool at 60–75 cm depth was 16× larger in autumn 2007 in comparison to 2006. During high water tables in November 2006 groundwater in the gravel layer had low $NO_3^-$–N concentrations of <0.1 mg $l^{-1}$. In contrast, after the drought in 2007 nitrate was flushed into groundwater as the water table rose to within 30–50 cm of the surface in December. An extensive area of high $NO_3$–N concentrations (3–18 mg $l^{-1}$) occurred inland from the stream bank. This zone of high nitrates declined gradually by April 2008 probably as a result of denitrification. These results indicate that buried organic deposits at depth within riparian areas can be important nitrogen sources during major water table drawdowns. The influence of these episodes of mineralization at depth during droughts on riparian groundwater chemistry and the emissions of greenhouse gases to the atmosphere merit further research.

**Keywords** Riparian zone · Net N mineralization · Nitrification · Water table · Soil organic matter · Groundwater

A. R. Hill (✉)
Department of Geography, York University, Toronto, ON, Canada
e-mail: hill@yorku.ca

## Introduction

Researchers interested in the biogeochemistry of stream riparian zones have recently begun to focus on the extent and distribution of buried organic horizons in these landscapes and their role as hot spots of microbial activity. Hill et al. (2004) found buried organic-rich layers ranging from 0.4 to 3 m depths in

4 of 5 headwater riparian zones in agricultural landscapes in Ontario, Canada. A survey of 22 riparian zones in first to fourth order streams in Rhode Island USA revealed widespread buried organic horizons varying in organic carbon content from <1 to 44% (Gurwick et al. 2008a). These recent results reinforce an extensive earlier literature that documents the occurrence of buried soils in riparian zones after episodes of accelerated soil erosion and valley bottom sedimentation resulting from European settlement in eastern North America (Happ et al. 1940; Costa 1975; Trimble 1981; Fitzpatrick and Knox 2000). Other studies have documented buried organic layers in relic channels and channel bar deposits that result from natural fluvial processes of overbank deposition and stream migration (Brakenridge 1988; Fustec et al. 1991; Brown 1996). The organic matter content of fine sediments deposited by overbank sedimentation may also represent an important carbon store in the subsurface riparian environment (Walling et al. 2006).

Laboratory incubations of subsurface organic-rich sediments amended with nitrate and acetylene have indicated the potential for considerable denitrification at riparian sites in Europe and North America (Hill et al. 2004; Well et al. 2005). High rates of in situ denitrification have been reported at depths of several meters in buried channel sediments (Fustec et al. 1991; Devito et al. 2000; Hill et al. 2000). Recent evidence suggests that carbon mineralization can occur in buried horizons that are several thousand years old as well as in more recent sediments (Gurwick et al. 2008b). These data suggest that buried organic layers at considerable depths, which are generally older than shallow sediments, may also play an important role in depleting nitrate along deeper groundwater flow paths in riparian zones. Currently, this research on riparian biogeochemistry has been concerned with the role of organic matter at depth in the removal of nitrates. The potential for buried organic layers to function as nitrogen sources has not been studied. Baldwin and Mitchell (2000) have noted that limited research has been conducted on the effects of wetting and drying on nutrient cycling in floodplain soils. The few data available on nitrogen dynamics in relation to water table fluctuations are based on studies of surface riparian soils (Hefting et al. 2004; Koschorreck 2005; Cavanaugh et al. 2006).

The flushing of nitrate and other solutes from near-surface soils on hillslopes to streams as a result of a rising water table during storm events has received increased attention in recent years (Creed et al. 1996; McHale et al. 2002; Weiler and McDonnell 2006). The flushing of soil nitrate accumulated in unsaturated soils into riparian groundwater during recharge events has also been reported (Butturini et al. 2003; Lamontagne et al. 2005, 2006; Schilling et al. 2006). Episodes of nitrate flushing can increase exports to downstream ecosystems and contribute to freshwater acidification and the eutrophication of coastal waters (Vitousek et al. 1997). Currently, the interactions between biogeochemical and hydrological processes that regulate the accumulation and flushing behavior of nitrates and other solutes are not well understood (Burns 2005).

The present study examines interactions between nitrogen mineralization and nitrification in buried organic-rich soil horizons and groundwater chemistry in the riparian zone of a small headwater agricultural catchment. Two major questions are asked. (1) How does soil N mineralization and nitrification at depth respond to water table variations? (2) What is the effect of subsurface soil nitrogen dynamics on groundwater nitrogen chemistry?

## Study sites

The study was conducted in a riparian site located in an agricultural watershed northeast 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 riparian site 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 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. The vegetation of the 30–40 m wide riparian site was characterized by a dense herbaceous plant community of grasses sedges and forbs (*Aster simplex*, *Epilobium hirsutum*, *Eupatorium maculatum* and *Mentha* spp.) inland and *Impatiens capensis* along the stream bank.

The riparian soil was an entisol with a 0.8–1.0 m deep mix of loamy sand and sandy loam overlying a poorly sorted 15–30 cm thick coarse grained layer containing 20–35% coarse sand and gravel and 6–15% silt + clay (Hill et al. 2004). Dark brown or black organic-rich patches and layers up to 6–10 cm thick containing small twigs and charred wood fragments frequently occurred at depths of 50–75 cm in an area that extended 20–25 m inland from the stream channel. Some small organic-rich patches and wood fragments were also observed in the underlying gravel in several locations. These buried organic deposits appear to post-date European settlement in the early to mid nineteenth century. Saturated hydraulic conductivities in the gravel layer were variable with values ranging from 3 to >160 cm day$^{-1}$ (Duval and Hill 2006). The coarse grained layer was underlain by outwash silt at depths of 0.8–0.9 m near the field-riparian margin and at 1.1–1.2 m near the stream. The silt formed an aquitard with low hydraulic conductivities of <0.02 cm day$^{-1}$ beneath the riparian zone.

## Methods

### Soil sampling

Riparian soils were sampled at 10 sites located along piezometer transects within 25 m of the stream bank (Fig. 1). Samples were taken with a 15 × 3.2 cm diameter split core sampler at depth intervals of 15 cm to a depth of 75 cm. Bulk density of the samples was determined as oven-dry mass per unit of volume based on core volume. Soil samples were also collected by auger at 75–90 cm depths without determination of bulk density. Soil samples were analyzed for total organic carbon (TOC) and total N (TN) by dry combustion (LECO CHN Element Analyzer). The procedure for carbon used two sample splits. One subsample was subjected to high temperature combustion (1350°C) to determine total carbon. The second subsample was oxidized initially at low temperature (500°C) to remove organic carbon and then the remaining inorganic carbon in the pretreatment sample was determined by high temperature (1350°C) and carbon dioxide analysis (Girard and Klassen 2001).

### Nitrogen mineralization and nitrification

Net N mineralization and nitrification rates were estimated by the buried polyethylene bag technique (Eno 1960; Binkley and Hart 1989). Cores from 0–10, 30–45 and 60–75 cm depths were collected adjacent to the 10 soil sampling sites and placed relatively undisturbed in polyethylene bags and buried at the same depth interval. The selection of these depth intervals provided a comparison of nitrogen dynamics in the surface riparian soil, in overbank sediment

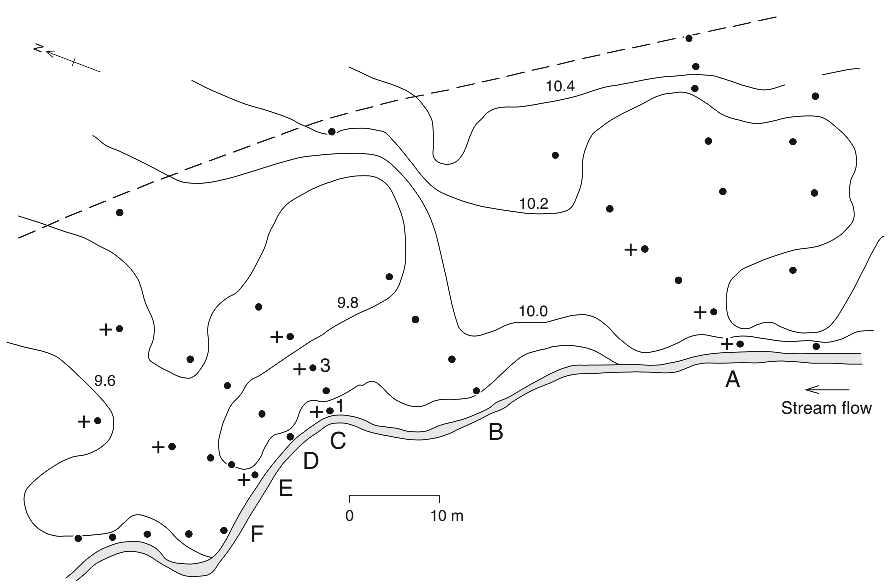



**Fig. 1** Topographic map of the Vivian Creek riparian zone showing piezometer transects and sites of soil incubation. Topographic contours at 0.2 m intervals above an arbitrary datum. Letters indicate piezometer transects; piezometers are indicated by *dots*. *Dashed line* represents riparian-agricultural boundary. + Indicates sites of buried bag soil incubations and measurements of soil organic carbon and nitrogen content

deposits with relatively uniform organic matter content at 30–45 cm depth and in the horizon at 60–75 cm depth which contained carbon-rich layers and lens. Cores were also incubated at 45–60 cm at two of the 10 sites where buried organic layers were observed at this depth. A second core was collected adjacent to the initial cores for determination of initial $NO_3^-$ and $NH_4^+$ levels. Samples were incubated for 14–28 days between May and October 2006.

In 2007 incubations began in late July after it was evident that an extended summer drought was occurring. Incubations continued at 2–3 week intervals until early November. Soil samples were returned to the lab where they were refrigerated until processed within 18 h of sampling. Ten gram field-moist samples of each initial and incubated soil core were extracted with 50 ml of 2 M KCL and the filtrates were analyzed for $NH_4$ and $NO_3^-$ using a Technicon autoanalyzer (Technicon 1977, 1978). Additional subsamples were dried at 105°C for 24 h to estimate dry mass of extracted soil and field moisture content. Net N mineralization estimates were calculated by subtracting initial values of $NH_4^+$–N + $NO_3^-$–N from the final incubation values. Net nitrification was determined by the difference in $NO_3^-$–N concentration. Incubated soils collected at 30–45 and 60–75 cm during August 2007 sampling periods were also analyzed for TOC and TN by dry combustion. The Pearson product-moment correlation was used to examine relationships between these soil characteristics and both net N mineralization and nitrification rates in the August incubations.

### Groundwater hydrology and chemistry

Piezometer installation is described in detail by Duval and Hill (2006). Briefly, single piezometers with 20 cm slot zones were installed at depths of 0.8–1.2 m in the coarse-grained layer along transects that extended from the stream across the riparian zone (Fig. 1). In addition fully screened wells and nests of piezometers at depths of 0.5–2.0 m were installed at several locations along the field-riparian perimeter and at one location on each transect in the riparian zone.

Hydraulic heads were measured at least monthly in May–November 2006–2008. Water chemistry data was collected in June and November 2006 and on several dates in spring and autumn 2007 and 2008. All piezometers were emptied and allowed to refill before water was sampled. Testing for ammonium and nitrate was done through colorimetric determination using an 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.

## Results

### Soil organic carbon and nitrogen contents

Soil inorganic carbon levels were generally <0.6% in the 0–60 cm depth, but were more variable ranging up to 4% at 60–75 and 75–90 cm. The mean TOC content of the riparian soil from the ten sites was relatively uniform to a depth of 75 cm (Table 1). Variability increased considerably in the 45–60 and 60–75 cm layers where TOC values in individual soil samples ranged from <1 to 14% as a result of differences in the depth of organic-rich layers and lenses across the riparian area. Considerable variability was also present at some of the soil sampling

**Table 1** Total organic carbon and total nitrogen content of Vivian Creek riparian soils

| Soil depth (cm) | TOC% | TOC (kg $m^{-2}$) | N% | N (kg $m^{-2}$) | C:N ratio |
|---|---|---|---|---|---|
| 0–15 | 6.6 ± 0.35 | 8.0 | 0.63 ± 0.02 | 0.76 | 10.5 |
| 15–30 | 4.2 ± 0.35 | 6.0 | 0.40 ± 0.03 | 0.58 | 10.5 |
| 30–45 | 4.0 ± 0.44 | 7.1 | 0.37 ± 0.08 | 0.65 | 10.8 |
| 45–60 | 4.1 ± 0.98 | 8.7 | 0.35 ± 0.08 | 0.74 | 11.7 |
| 60–75 | 3.4 ± 1.20 | 8.4 | 0.26 ± 0.09 | 0.64 | 13.0 |
| 75–90 | 1.6 ± 0.51 | | 0.11 ± 0.03 | | 15.0 |

Values are means ± 1 SE of soil samples from 10 sites

sites where cores within a radius of 1 m differed by 2–3× in TOC content at 45–60 and 60–75 cm depths. Total mean N content was higher in the 0–15 cm layer than in the deeper soil layers where N% declined to 0.26% at depths of 60–75 cm and to 0.11% at 75–90 cm depth. Higher TN variability in the 45–60 and 60–75 cm depth layers was linked to differences in the depth of the organic-rich horizons. Soil C:N ratios increased gradually from 10.5:1 at 0–15 cm to 11.7:1 at 45–60 cm and then rose to 13:1 in the 60–75 cm and 15:1 in the 75–90 cm layer. Soil bulk density increased progressively with depth from 0.8 g $cm^{-3}$ at 0–15 cm to 1.6 g $cm^{-3}$ at 60–75 cm depth. Consequently, despite a decline in TOC% and N% with depth the mean mass of TOC and N remained relatively constant (Table 1).

## Water table fluctuations and groundwater flow patterns

Figure 2 shows seasonal water table variations for 2006–2008 in piezometer nest 1 and 3 on the C transect that is representative of sites at the stream margin and areas of the riparian zone >5 m from the channel respectively. In 2006, July and September–October months were 30–50% wetter than the long-term average. During the summer the water table often remained within 40 cm of the ground surface throughout the riparian zone and only declined briefly to depths of >80 cm in late August. Consequently, only the surface soil incubations remained above the water table in 2006. Summer and autumn 2007 were the driest recorded in the past 40 years. Stream seepage inland still maintained the water table above the gravel layer at the bank margin but a few meters inland the water table declined to >1 m below the surface by late June and reached a depth of >1.9 m in August (Fig. 2). Water table levels rose gradually in September and October but were still at a depth of >0.9 m over a large area of the riparian zone in early November. Soil incubations at all three depth intervals were unsaturated for approximately 5 months in 2007. Rainfall amounts in summer 2008 were similar to the long-term average. The water table inland from the stream bank declined to the base of the gravel layer in July before rising gradually to within 0.5 m of the surface in September (Fig. 2).

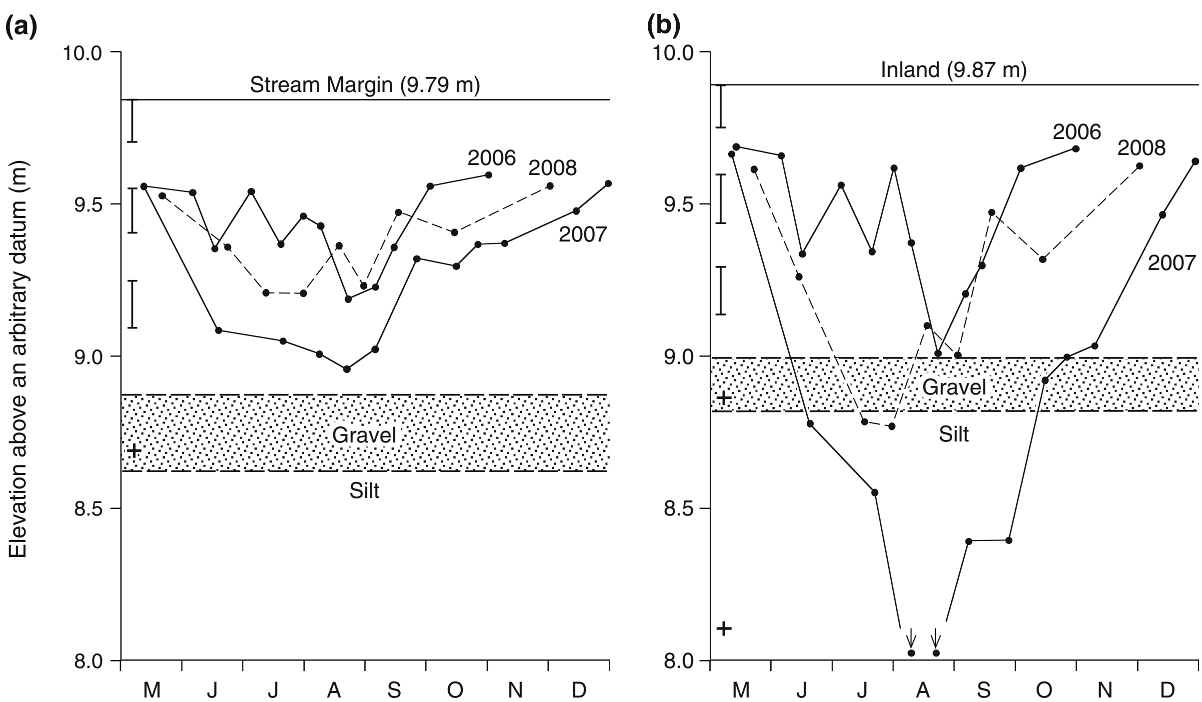



**Fig. 2** Riparian zone water table fluctuations in 2006–2008. **a** Stream margin at transect C1, **b** inland at transect C3. *Vertical bars* indicate depths of soil N mineralization incubations, + indicates base of piezometer

The piezometer and well network in May–October 2006 indicated that subsurface flow mainly occurred from the field in an oblique down-valley direction across the riparian zone to the stream. Periods in which stream inflow induced a reversed water table gradient inland were restricted to mid-July and late August to early September. During these intervals of flow reversal riparian sediments remained saturated above the confining layer except briefly in late August when the saturated zone only extended 10–18 m inland. In 2007, during the drought period, subsurface flow from the field into the riparian area was absent from June to mid-December and the dominant flow direction was from the stream into the riparian zone. The area of saturated riparian sediments above the silt layer was frequently only 5–10 m wide and declined to a width of only 2–3 m during July and August before gradually increasing to 20–30 m by mid-December.

During the high water table period in spring 2008 subsurface flow occurred across the riparian zone from the field to the stream. By late June hillslope inflow had ceased and stream seepage sustained a reversed water table gradient inland across the riparian area. The zone of saturated sediments above the silt contracted to a width of approximately 10 m in July before expanding progressively across the riparian zone by mid-September. During the late autumn subsurface flow shifted to a field to stream direction across the riparian zone.

## Net nitrogen mineralization and nitrification

In 2006 mean daily rates of net N mineralization in the 0–10 cm depth were variable among sampling dates, ranging between 0.2 and 0.75 mg $kg^{-1}$ $day^{-1}$ with a high peak of 1.35 mg $kg^{-1}$ $day^{-1}$ in mid to late June (Fig. 3). Net nitrification rates accounted for >90% of net mineralization rates. There was little evidence of N mineralization or nitrification in 30–45 and 60–75 cm depths. Small negative values occurred in most sampling periods suggesting N immobilization or denitrification. Incubations conducted in the 45–60 cm depth at 2 sites also showed patterns similar to the 30–45 and 60–75 cm depths. Daily net mineralization and nitrification rates in 2007 for the late July to October period in the 0–10 cm depth were similar to the same months in 2006 (Fig. 4). Total net N mineralization and nitrification on an area basis during this period in 2006 and 2007 was 23.1 vs. 31.7 kg $ha^{-1}$ and 27.8 vs. 30.4 kg $ha^{-1}$ respectively.

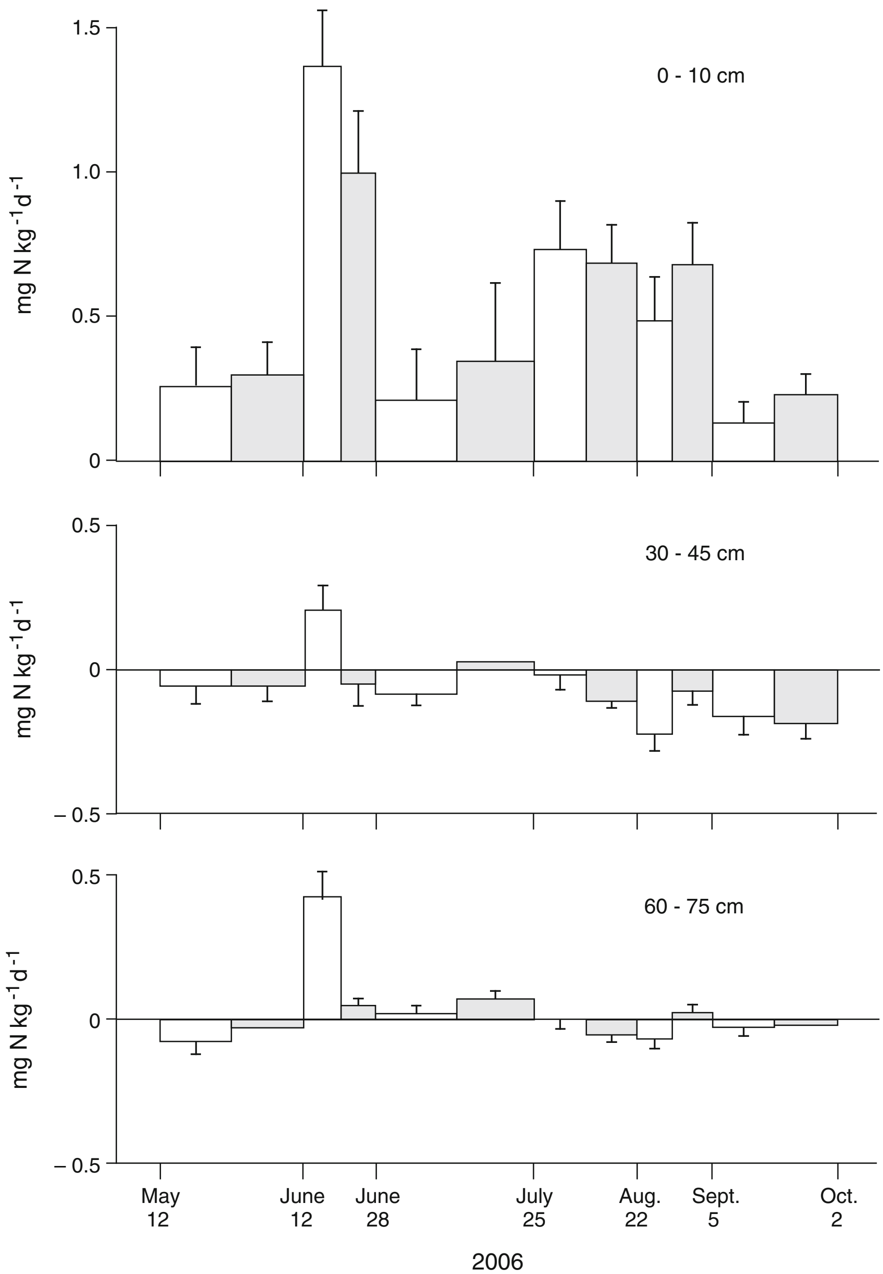
In contrast to 2006, high daily rates of net N mineralization and nitrification were observed in 30–45 and 60–75 cm depths for all sampling dates in 2007 (Fig. 4). Similar rates also occurred for the incubations at two sites at the 45–60 cm depth. The proportion of mineralized N that was nitrified at 30–45 and 60–75 cm depths increased from approximately 60% in early August to 70–75% in late August and then to >90% for later sampling periods. Daily net mineralization at 30–45 and 60–75 cm depths in August showed a significant positive correlation with soil TOC ($r = 0.65$, $p < 0.01$), TN ($r = 0.63$, $p < 0.01$) and moisture content ($r = 0.69$, $p < 0.01$). Net mineralization rates were <0.1 mg $kg^{-1}$ $day^{-1}$ in incubated soil samples with <1% TOC, whereas rates were 0.8–2.2 mg $kg^{-1}$ $day^{-1}$ in samples from organic-rich patches with 8–14% TOC. Nitrification was positively correlated with soil TOC ($r = 0.77$, $p < 0.01$), TN ($r = 0.76$, $p < 0.01$) and soil moisture ($r = 0.67$, $p < 0.05$). Soil TOC had a significant positive correlation with soil moisture levels in August 2007 ($r = 0.81$, $p < 0.01$).

Daily rates of net mineralization and nitrification were similar among the 0–10, 30–45 and 60–75 cm depths for most sampling intervals in 2007. However, on an area basis total net mineralization and nitrification for the late July to early November period were considerably larger at depth because of an increase in soil bulk density. Net mineralization for this period increased from 41.6 kg $ha^{-1}$ at 0–10 cm to 79.4 kg $ha^{-1}$ at 30–45 cm and 91.9 kg $ha^{-1}$ at 60–75 cm. Similarly net nitrification was 40.5, 69.4 and 93.6 kg $ha^{-1}$ at the three depth intervals respectively. The proportion of total soil N mineralized at 30–45 and 60–75 cm depths during the 2007 drought was 1.2–1.4%.

## Ammonium and nitrate pools

Pools of extractable $NH_4^+$–N in 2006 and 2007 were considerably larger in the deeper soil layers than at 0–10 cm depth (Fig. 5). This larger pool at depth was a result of the greater bulk density in the subsurface as extractable ammonium concentrations per kg were similar at the two depths. Ammonium content at 0–10 and 30–45 cm were generally lower in late summer

**Fig. 3** Net N mineralization and nitrification (*shaded bars*) at three riparian soil depths in 2006. Values are means ± 1 SE of soil samples from 10 sites for each incubation period




and fall of 2007 than in 2006. Soil $NO_3^-$–N content in 2006 was much larger at 30–45 cm in comparison to 0–10 cm because of the increase in bulk density with depth (Fig. 5). Although bulk density at 60–75 cm was 40% greater than at 30–45 cm the nitrate pool in the deeper layer was very low in late summer and near zero in September 2006. Soil nitrate content in 2007 at all three depth intervals increased gradually to maximum values in November. The soil nitrate pool at 60–75 cm depth in 2007 was considerably larger than in 2006 ranging from 3× larger in mid-summer to 16× larger in November.

## Groundwater nitrogen

Major contrasts were evident in patterns of nitrate concentration in the riparian gravel pore water beneath buried organic-rich sediments in 2006 vs.

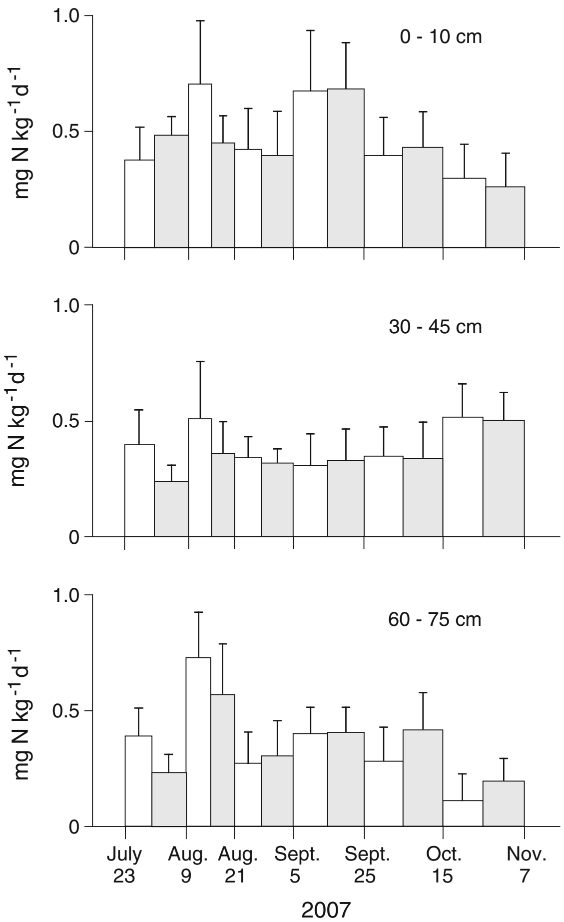



**Fig. 4** Net mineralization and nitrification (*shaded bars*) at three riparian soil depths in 2007. Values are means ± 1 SE of soil samples from 10 sites for each incubation period

2007. During high water table conditions in mid-June and early November 2006, $NO_3^-$–N concentrations were generally <0.05 mg $l^{-1}$ except for a few isolated patches that were >0.10 mg $l^{-1}$(Fig. 6a, b). This pattern of low nitrate concentrations was also present in spring 2007 prior to the summer drought (Fig. 7a). In early November 2007 a few localized areas of high $NO_3^-$–N concentration ranging from 1 to 3.0 mg $l^{-1}$ occurred as the area of saturated sediments above the silt confining layer began to expand inland (Fig. 7b). By mid-December a stream to field water table gradient was still present and the riparian area near the riparian field boundary remained unsaturated above the silt layer although closer to the stream the water table was within 30–50 cm of the ground surface. A large area of elevated $NO_3^-$–N values of >3.0 mg $l^{-1}$ in the gravel layer extended from the middle to the upstream portion of the riparian zone where values in two piezometers were 15–18 mg $l^{-1}$ (Fig. 7c). Low $NO_3^-$–N levels of <0.5 mg $l^{-1}$ occurred in the downstream portion of the riparian zone and in a narrow area along the channel. In late December a field to riparian zone hydraulic gradient occurred across a considerable area of the riparian zone although stream inflow was still present near the channel. The area of high $NO_3^-$–N concentrations was less extensive with levels showing a decline along transect B. Values of 1–7 mg N $l^{-1}$ persisted along transect C and in the upstream portion of the riparian zone where the localized area of 15–18 mg N $l^{-1}$ adjacent to the cedar stand was still observed (Fig. 7d).

Ground water during the high water table period in early April 2008 showed a large decline in nitrate concentrations from December 2007 levels. However, a few piezometers on transect C and in the upstream riparian area had $NO_3^-$–N concentrations of 0.5–1.9 mg $l^{-1}$ (Fig. 8a). By mid-June gravel pore water $NO_3^-$–N concentrations were generally <0.1 mg $l^{-1}$ throughout the riparian zone (Fig. 8b). Following a summer season in which riparian sediments >6–10 m inland from the channel were unsaturated above the silt in July, localized patches of higher $NO_3^-$–N concentration ranging from 1 to 2.6 mg $l^{-1}$ occurred in the gravel layer in mid-September. These patches were still present in approximately the same locations in early December 2008 (Fig. 8d).

Spatial variations in ammonium concentrations differed considerably from nitrate patterns in the riparian gravel layer pore water. Elevated $NH_4^+$–N concentrations of 1–3 mg $l^{-1}$ occurred in many of the stream bank piezometers on all sampling dates in 2006–2008 (Figs. 6, 9). Under high water table conditions in June and November 2006, $NH_4$–N concentrations inland from the channel generally ranged from 0.12 to 0.45 mg $l^{-1}$ (Fig. 6c, d). Similar concentrations persisted inland in May 2007 (data not shown). After the summer 2007 drought, the narrow zone of high $NH_4^+$–N concentrations at the stream margin declined rapidly to <0.1 mg $l^{-1}$ throughout the riparian area in December 2007 (Fig. 9). The same pattern of very low ammonium concentrations was present in April 2008 (Fig. 9d). However, in

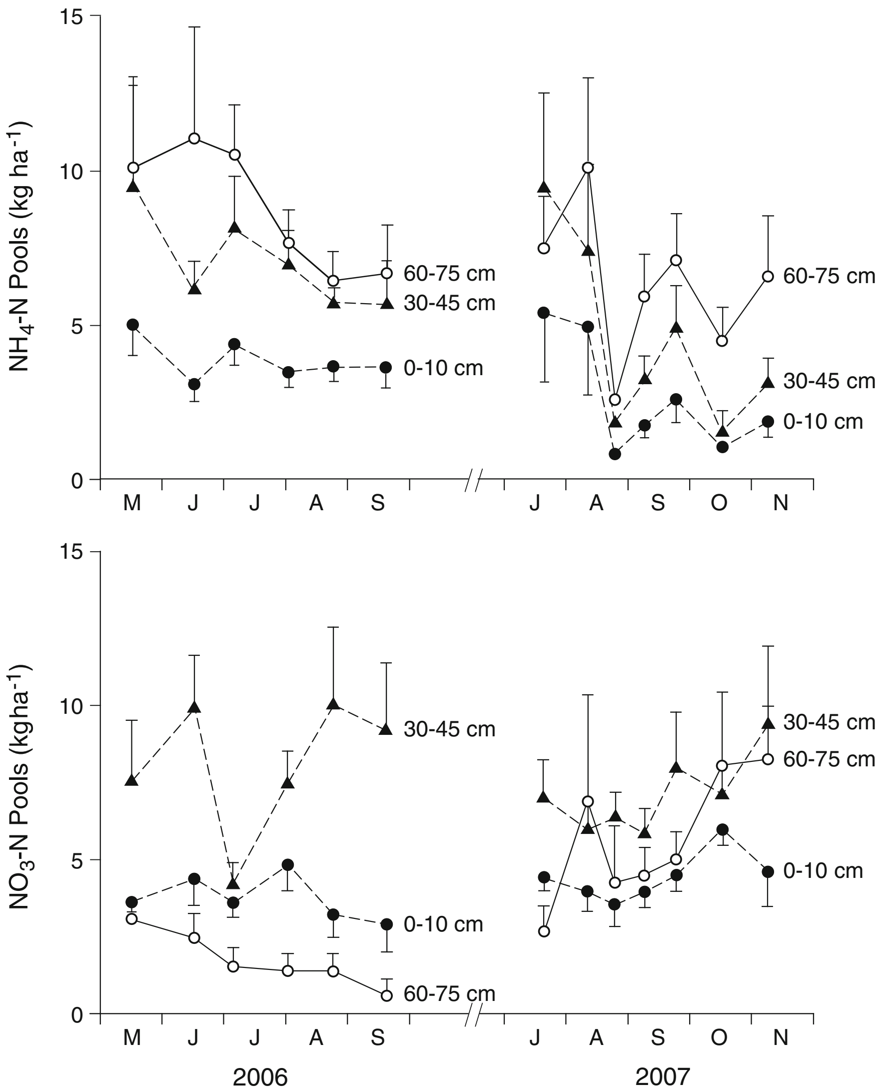



**Fig. 5** Seasonal variations in ammonium and nitrate–N pools at three riparian soil depths in 2006 and 2007. Values are means ± 1 SE of soil samples from 10 sites

autumn 2008 the zone of high $NH_4^+$–N concentration at the stream margin declined more slowly inland where levels were similar to June and November 2006 ranging between 0.1 and 0.5 mg $l^{-1}$(data not shown).

## Discussion

### Buried stores of organic matter

Few studies have measured the amount of organic carbon and nitrogen stored in riparian alluvial sediments. The mean mass of TOC and TN in the 0–75 cm depth profile of 38.2 and 3.4 kg $m^{-2}$ respectively at Vivian Creek was similar or higher than those recorded in other studies. Riparian soils to 75 cm depth in two Japanese forest watersheds had 17.6–19.8 kg $m^{-2}$ of TOC and 1.1–1.3 kg $m^{-2}$ of N (Ohrui and Mitchell 1998). Adair et al. (2004) reported 1.1–1.3 kg $m^{-2}$ of soil N to a depth of >1 m in mature Populus forested floodplains along the Green and Yampi rivers in a semi-arid region of Colorado USA. Brunet et al. (2008) estimated that 4.5–5.5 kg $m^{-2}$ of organic N was stored in the upper 1.5 m of floodplain sediments of the river Adour in an agricultural catchment in southwest France.

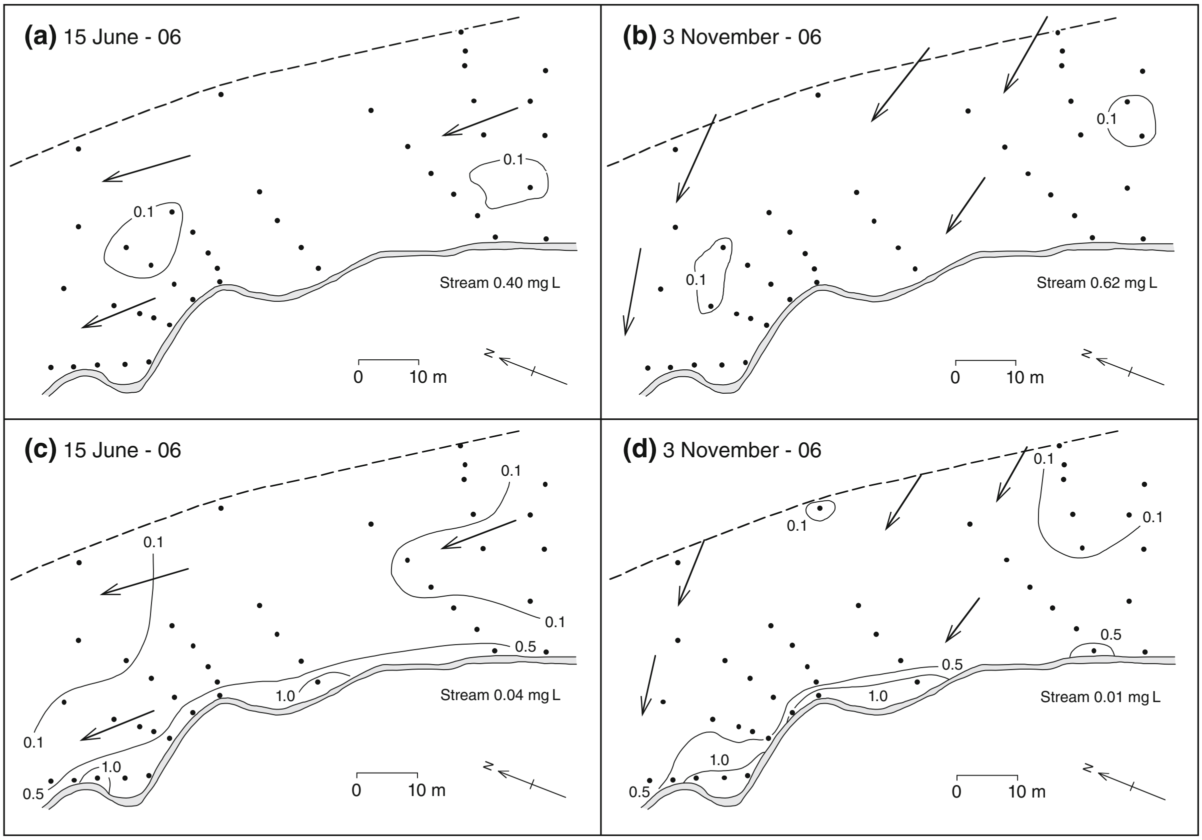



**Fig. 6** Seasonal patterns of pore water $NO_3$–N (**a** and **b**) and $NH_4$–N (**c** and **d**) concentrations (mg $l^{-1}$) in the riparian gravel layer in June and November 2006. *Arrows* indicate the direction of subsurface flow. Piezometer locations shown by *filled circle*

## Impact of water table fluctuations on soil N dynamics

The low net mineralization and nitrification rates recorded in the deeper soil layers at the Vivian site in 2006 are similar to rates reported previously in wet surface riparian soils with high water tables (Hill and Shackleton 1989; Ohrui et al. 1999). These low rates may result from immobilization of ammonium that often occurs in moist organic-rich soils (Patrick 1982; Janssen 1996). High rates of N mineralization and nitrification in deeper soil layers in July–October 2007 indicate that significant N mineralization can extend to considerable depths below the ground surface in alluvial soils with buried organic horizons during large water table drawdowns. The increase in the proportion of mineralized N that was nitrified in 30–45 and 60–75 cm depth soils during the drought suggests that the size of the nitrifying bacteria population could have been low initially at these depths. These relationships in deeper soil layers between water table elevation and nitrogen cycling are similar to those identified in 0–20 cm soil depths in a range of European riparian zones (Hefting et al. 2004). These researchers noted that nitrification was absent when the water table was within 10 cm of the surface, whereas high nitrification in 0–20 cm soil horizons was present at sites were the water table was below 30 cm depths.

Most previous studies have only examined N mineralization in surface riparian soils. However, Groffman et al. (2002) recorded higher potential nitrification rates ranging from 0.1 to 0.4 mg N $kg^{-1}$ $day^{-1}$ in laboratory incubations of soils extending to depths of 70–100 cm in urban and suburban riparian zones with lower water tables in comparison to low nitrification rates throughout the soil profile in a forested reference site with a high water table. Mean net N mineralization rates of 0.03 mg N $kg^{-1}$ $day^{-1}$ have also been measured during the growing season

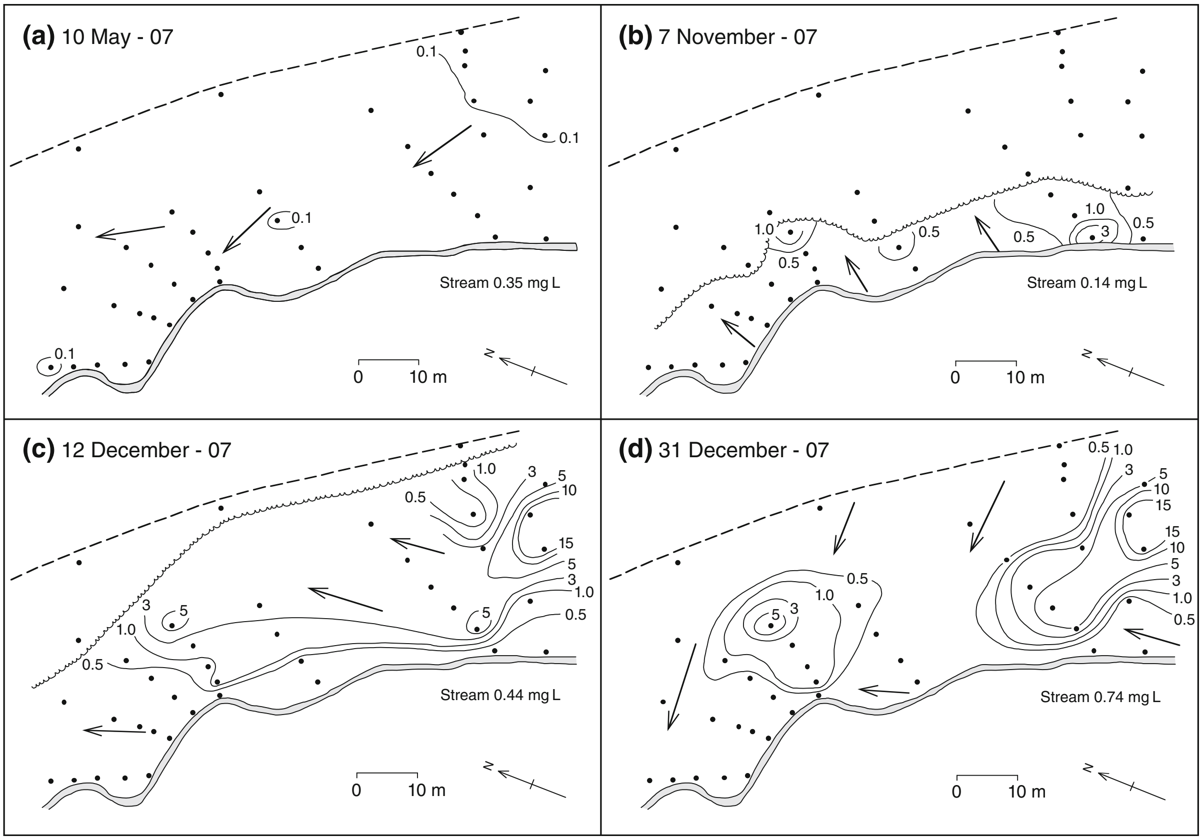



**Fig. 7** Seasonal patterns of pore water $NO_3$–N concentrations in the riparian gravel layer in May–December 2007. *Arrows* indicate the direction of subsurface flow. The wavy line indicates the area of permeable unsaturated sediments overlying the silt. Piezometer locations shown by *filled circle*

in field incubations of soils at 50 cm depth in the tree rooting zone of a desert riparian site in Arizona (Schade et al. 2002).

The significant positive relationships between N mineralization and soil TOC and TN content at depths of 30–45 and 60–75 cm suggest that thin layers and lenses of buried organic matter provide hot spots for N mineralization and nitrification during water table drawdowns. Net N mineralization and nitrification in the deeper soil layers also had a positive correlation with soil moisture. Sediment moisture can decline substantially as a result of water table drawdowns during extended dry periods. Soil moisture values of <20% have been reported to inhibit N mineralization and nitrification (Stanford and Epstein 1974; Foster et al. 1992). Despite a water table decline of >2 m in the summer of 2007 soil moisture content in incubated cores from 30–45 and 60–75 cm at Vivian Creek generally ranged between 30 and 50% and values of <20% only occurred in a few cores from sandy patches with <2% TOC. The strong positive relationship between soil moisture content and soil TOC in August at these depths suggests that the frequent occurrence of buried organic-rich horizons is an important factor in reducing the extent of desiccation at this riparian site.

Despite high rates of net nitrification in soil incubations in the deeper soil layers in summer and autumn 2007 the soil nitrate pool at 30–45 cm was similar to 2006 when limited net nitrification was recorded. The nitrate pool at 60–75 cm in 2007 was considerably larger than in 2006, although the greatest increase only occurred in October and early November at the end of the growing season. It is possible that the soil incubations provide an overestimate of actual nitrification rates at depth within these riparian sediments. Plant uptake of $NH_4^+$ which is prevented in buried bag incubations may reduce the

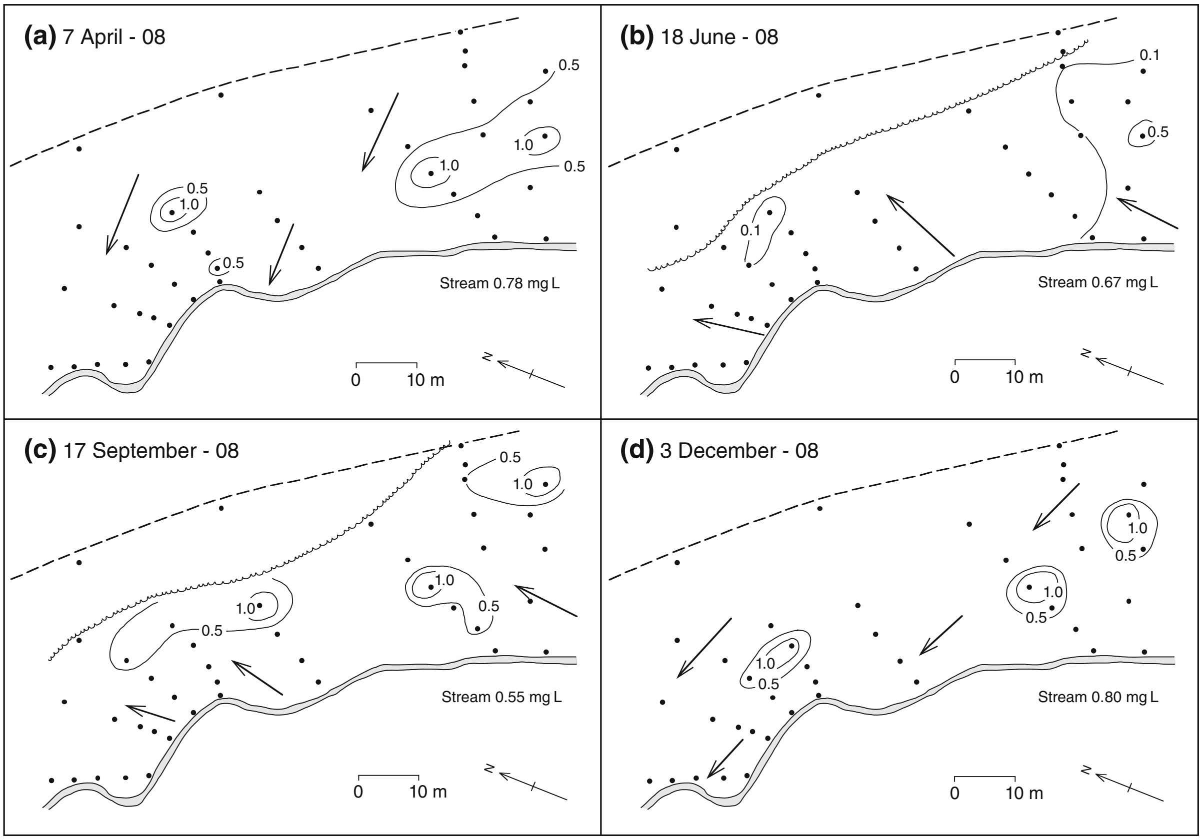



**Fig. 8** Seasonal patterns of pore water $NO_3$–N concentrations (mg $l^{-1}$) in the riparian gravel layer in April–December 2008. *Arrows* indicate the direction of subsurface flow. The wavy line indicates the area of permeable unsaturated sediments overlying the silt. Piezometer locations shown by *filled circle*

ability of nitrifying bacteria to compete for $NH_4^+$ (Zak et al. 1990). Herbaceous plant roots were observed extending to 60–75 cm depth in summer 2007, especially in patches of buried organic matter. Even if nitrification was overestimated, this process clearly resulted in a considerable increase in the soil nitrate content at 60–75 cm depth during the extended summer and early autumn drought in 2007 in comparison to 2006.

A comparison of 2006 and 2007 data indicates that considerable water table drawdowns are required to produce high rates of N mineralization and nitrification in buried organic deposits. Water table data for the Vivian Creek site based on previous research (Vidon and Hill 2004; Duval and Hill 2006) and the present study are available for 7 years (2000–2003) and 2006–2008). These data indicate that a water table decline of >1 m to the base of the riparian gravel layer occurred for 2–5 weeks in 2002, 2003 and 2008 which had June–September rainfall that was similar to the 30 year mean of 320 mm. The riparian water table remained above the gravel layer in 2000 and 2006 in which June–September rainfall was 15–30% above the long-term average. In contrast, the water table declined to >1.5 m and remained below the gravel layer for 9 weeks in 2001 and 16 weeks in 2007 when June–September rainfall was only 67 and 45% respectively of the 30 year mean. The data indicate that high subsurface N mineralization occurs in very dry summer years such as 2007, but is absent in wet summer years similar to 2006. Although N mineralization at depth was not measured in a year with normal summer rainfall, the presence of a few localized patches of elevated nitrate concentration in gravel pore water recorded in autumn 2008 and in a previous study in autumn 2003 (Duval and Hill 2007) suggests that some N mineralization may occur at depth in years with normal summer rainfall.

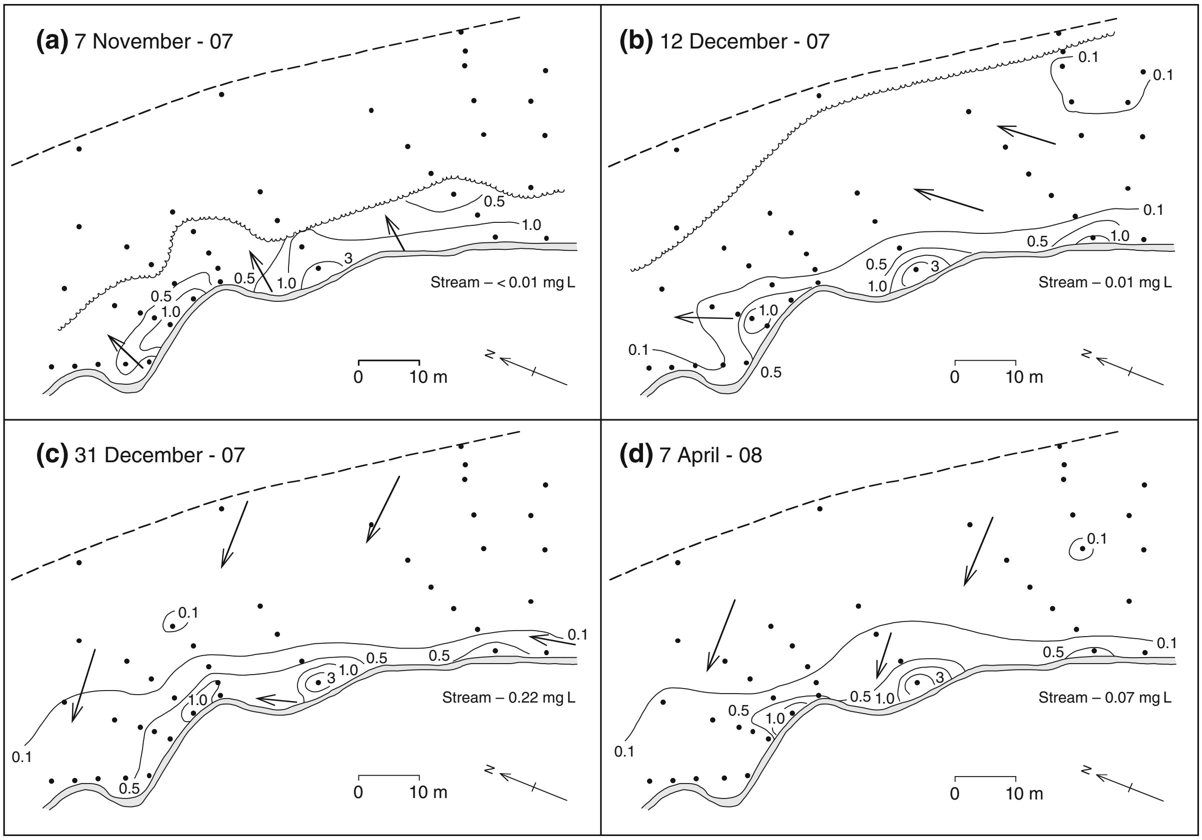



**Fig. 9** Seasonal patterns of pore water $NH_4$–N concentrations (mg $l^{-1}$) in the riparian gravel layer 2007–2008. *Arrows* indicate the direction of subsurface flow. The *wavy line* indicates the area of permeable unsaturated sediments overlying the silt. Piezometer locations shown by *filled circle*

Episodes of deep N mineralization are unlikely to rapidly exhaust the total N content of buried deposits at the Vivian Creek riparian zone. Nitrogen mineralization at 30–45 and 60–75 cm depths in 2007 during the driest summer recorded in the past 40 years was 1.2–1.4% of the total soil N at these depths. If similar deep episodes of N mineralization occurred in 2–4 years each century the nitrogen content in buried horizons would persist for >1500 years. During this long time interval subsurface organic deposits would be renewed by major episodes of overbank sedimentation and the burial of relic channels and channel bar deposits during lateral migration of the stream.

## Nitrate mobilization into riparian groundwater

The elevated nitrate concentrations in gravel pore water in December 2007 indicate that nitrate stored in unsaturated sediments during the earlier major water table drawdown was mobilized as the water table began to rise. Several other researchers have recorded episodes of elevated nitrate concentrations in riparian groundwater during periods of rising water table. Schilling et al. (2006) recorded peak $NO_3^-$–N concentrations of 14–20 mg $l^{-1}$ in groundwater adjacent to an agricultural stream in Iowa during the spring recharge period. Increases in groundwater $NO_3^-$–N concentration in the range of 1–6 mg $l^{-1}$ following floods have also been recorded in riparian zone groundwater inland from semi-arid and subtropical rivers (Butturini et al. 2003; Lamontagne et al. 2005, 2006).

The spatial variations of pore water nitrate concentrations in the gravel layer in December 2007 during the period of rising water table suggests that N dynamics in sediment adjacent to the piezometer depth influence this pattern. Groundwater

$NO_3^-$–N concentrations remained low (<0.2 mg $l^{-1}$) in piezometers located at the channel margin, whereas the highest concentrations occurred inland in the middle and upstream areas of the riparian zone. The overall amount of N mineralization and nitrification at 30–45 and 60–75 cm depth for late July to November 2007 was similar at bankside and inland incubation sites. However, the slot zones of the bank margin piezometers remained below the water table throughout the 2007 drought period, whereas further inland piezometers were unsaturated for several months. The high ammonium values recorded in the majority of these bank margin piezometers in 2006–2008 suggest anaerobic conditions which inhibited nitrification in sediments at this depth in the riparian zone. Similar ammonium values were observed in these bank side piezometers in 2003 when DO concentrations were generally <2.0 mg $l^{-1}$ (Duval and Hill 2007). The lower ammonium concentrations recorded further inland after the 2007 drought in comparison to higher values inland in autumn 2006 and 2008 suggest more aerated sediments in the zone of high nitrate concentrations.

A considerable decline in gravel layer nitrate concentrations occurred at Vivian Creek between December 2007 and April 2008 although patches of elevated nitrate still persisted in the same locations observed in December. This pattern suggests a process of removal by denitrification within the riparian zone. Re-wetting of dry sediments often strongly stimulates denitrification (Groffman and Tiedje 1988; Venterink et al. 2002). Laboratory incubations showed potential denitrification rates in soil layers at 45–85 cm depths at Vivian Creek that were similar to rates in the 0–15 cm soil layer (Hill et al. 2004).

## Export of mobilized groundwater nitrate to streams

Nitrification in unsaturated riparian sediments has been linked to episodes of nitrate export to streams. Schilling et al. (2006) has suggested that nitrates in groundwater leached from unsaturated soils in an Iowa riparian zone may be flushed into the adjacent incised stream during spring recharge events. Nitrate flushing to streams has also been reported in two Japanese forested mountain watersheds where high soil nitrification potentials resulted in the accumulation of nitrates in the near-stream zone (Ohrui and Mitchell 1998). In both of these studies the occurrence of steep hydraulic gradients towards the stream would have increased the potential for nitrate flushing. The hydraulic conductivity of riparian sediments can also influence nitrate export to stream channels. The high hydraulic conductivity of gravel sediments (12–19 m $day^{-1}$) near a Spanish stream resulted in the infiltration of stream water 8–10 m inland within a few hours during an autumn storm (Butturini et al. 2003). The re-establishment of the water table slope towards the stream could result in nitrate flushing during the recession limb of storms at sites with such high hydraulic conductivities.

Several lines of evidence suggest that the nitrate mobilized into riparian groundwater in December 2007 at the Vivian Creek site was not exported to the stream. Stream nitrate concentrations in December 2007 after the drought were similar to concentrations observed in November 2006 after a wet summer and in December 2008 after normal summer rainfalls. A pattern of high ammonium values and low nitrate concentrations persisted in stream bank piezometers throughout the study period. The gradual transition of the reversed water table gradient inland to a hillslope to stream direction and the variable hydraulic conductivity of the poorly sorted gravel layer also inhibited the movement of groundwater nitrate to the stream.

## Riparian zone characteristics in relation to subsurface N mineralization and nitrate mobilization

The results of the present study and the previous literature can be used to provide a summary of important features of riparian zones in humid temperate landscapes that influence the occurrence of N mineralization at depth in riparian sediments and the potential for mobilization of nitrate into riparian groundwater and export to streams (Table 2). Riparian areas linked to thick upland aquifers have continuous and often large groundwater inputs that result in small water table fluctuations and an absence of N mineralization in deeper sediments even during extended dry periods. In contrast, many riparian zones occur in hydrogeologic settings where hillslope discharge to riparian areas is seasonably variable and

**Table 2** Riparian zone characteristics that influence N mineralization at depth during water table drawdowns and the potential for nitrate mobilization into riparian groundwater and export to streams after recharge events

| Riparian zone properties | | | Riparian zone N dynamics | | | |
|---|---|---|---|---|---|---|
| Upland–riparian linkage | Riparian zone water table | Slope angle | Sediment hydraulic conductivity | Subsurface N mineralization and nitrification | Nitrate mobilization into groundwater | Nitrate export to stream |
| Large continuous GW input | Small fluctuations during droughts | Varied slope gradients | Low to high | Low rates | No | No export |
| No GW input in most summers | Moderate/large drawdowns in droughts | Flat to gentle | Low | Moderate to high rates | Yes | No export denitrification in riparian GW |
| No GW input in most summers | Moderate/large drawdowns in droughts | Moderate to steep Incised channel | High | Moderate to high rates | Yes | Export |

*GW* groundwater

often absent in summer (Vidon and Hill 2004). Seasonal water table fluctuations of at least 1–2 m in response to rainfall variations have been recorded in these riparian zones in the USA, Canada and Europe (Bosch et al. 1996; Burt et al. 2002, Vidon and Hill 2004). Water table drawdowns of this magnitude during droughts result in N mineralization and nitrification in buried organic deposits and mobilization of nitrate into groundwater during recharge events.

Riparian topography and soil properties strongly affect the transport and transformation of mobilized nitrate in riparian groundwater. Level or gentle sloping riparian sites have a small hydraulic gradient which in combination with low sediment hydraulic conductivity increase water residence times and favour denitrification within the riparian area (Table 2). In contrast, a higher riparian to stream hydraulic gradient at sites with moderate to steep slopes in association with highly conductive sediments can increase export of groundwater nitrate to the stream. Highly incised stream channels which often occur in urban and agricultural areas increases the depth of unsaturated riparian sediments during dry periods and the hydraulic gradient towards the stream (Groffman et al. 2002; Schilling et al. 2004) enhancing the export of mobilized nitrate in groundwater to the stream.

## Conclusion

This study expands our understanding of the role of buried organic-rich soil horizons in stream riparian zones. In addition to functioning as hot spots for nitrate removal by denitrification along deeper groundwater flow paths, these deposits can also be an important nitrogen source during major water table drawdowns. Nitrogen mineralization and nitrification at depth can occur at rates similar to those measured in surface riparian soils. The nitrate accumulated during these episodes can produce a large increase in nitrate concentrations in riparian groundwater during recharge events.

Climate change caused by global warming is expected to result in increased frequency of both drought and heavy rainfall events. Consequently, there is a need for increased research on the impact of water table fluctuations on the biogeochemistry of buried organic deposits in headwater riparian zones. Large water table drawdowns not only aerate buried carbon but also affect other redox sensitive species. The oxidation of reduced sulphate and the episodic release of $SO_4$ from wetlands after droughts have been linked to stream acidification in some landscapes (Devito et al. 1999). Carbon and nitrogen mineralization at depth in riparian environments may also influence gas exchanges with the atmosphere. Nitrous oxide is a byproduct of nitrification and denitrification (Firestone and Davidson 1989). Increased production of $CO_2$ and $N_2O$ may occur at depth during periods of carbon and nitrogen mineralization in aerated sediments. Subsequent denitrification of nitrate flushed into riparian groundwater as the water table rises my also produce $N_2O$. The extent to which increased production of these greenhouse gases at depth from buried organic deposits would affect emissions to the atmosphere is unclear at present but clearly merits further research.

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