Freshwater Biology (2006) **51,** 854–864 doi:10.1111/j.1365-2427.2006.01535.x

Nitrogen retention in the riparian zone of catchments underlain by discontinuous permafrost

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SUMMARY

1. Riparian zones function as important ecotones that reduce nitrate concentration in groundwater and inputs into streams. In the boreal forest of interior Alaska, permafrost confines subsurface flow through the riparian zone to shallow organic horizons, where plant uptake of nitrate and denitrification are typically high.
2. In this study, riparian zone nitrogen retention was examined in a high permafrost catchment (approximately 53% of land area underlain by permafrost) and a low permafrost catchment (approximately 3%). To estimate the contribution of the riparian zone to catchment nitrogen retention, we analysed groundwater chemistry using an end-member mixing model.
3. Stream nitrate concentration was over twofold greater in the low permafrost catchment than the high permafrost catchment. Riparian groundwater was not significantly different between catchments, averaging 13 μM overall. Nitrogen retention, measured using the end-member mixing model, averaged 0.75 and 0.22 mmol N m^{-2} day^{-1} in low and high permafrost catchments, respectively, over the summer. The retention rate of nitrogen in the riparian zone was 10–15% of the export in stream flow.
4. Our results indicate that the riparian zone functions as an important sink for groundwater nitrate and dissolved organic carbon (DOC). However, differences in stream nitrate and DOC concentrations between catchments cannot be explained by solute inputs from riparian groundwater to the stream and differences between streams are probably attributable to deeper groundwater inputs or flows from springs that bypass the riparian zone.

Keywords: denitrification, discontinuous permafrost, groundwater, mixing model, nitrate

Introduction

Riparian zones can be important sites for reducing nitrogen concentration in groundwaters and the input of nitrogen into streams (Lowrance, Todd & Asmussen, 1984; Peterjohn & Correll, 1984; Cooper, 1990). Assimilation by plants and microbes, and consumption via denitrification are the primary mechanisms accounting for the loss of nitrate as ground water flows through riparian zones. In the boreal forest of interior Alaska, terrestrial primary production is commonly nitrogen limited (Van Cleve *et al.*, 1983) and thus plant assimilation in the riparian zone is probably an important sink. Further, nitrate loss via denitrification is generally enhanced in riparian zones where anoxic conditions and soil rich in organic matter provide optimal conditions (Hedin *et al.*, 1998; Devito *et al.*, 2000; Hill *et al.*, 2000; Sobczak, Findlay & Dye, 2002).

In the boreal forest of interior Alaska, catchments are underlain by discontinuous permafrost, which is an important feature controlling catchment hydrology and the flow of water through the riparian zone (Slaughter & Kane, 1979). Permafrost affects catchment hydrology by confining the majority of groundwater flow to shallow organic soil horizons (Woo,

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1986). Where permafrost is absent, soil water may infiltrate into deeper mineral soil horizons. Over the summer, change in thaw depth within the active layer (soil above permafrost that seasonally thaws and freezes) allows groundwater flow to shift from organic to mineral horizons (Carey, 2003). This shift in flow from organic to mineral horizons is likely to impact rates and the major transformations of nitrogen in the riparian zone (Hill, 1996).

The following question was addressed in two boreal forest catchments with varying extents of permafrost: how does riparian zone nitrogen retention vary in catchments with a differing extent of permafrost? To address this question, we analysed groundwater chemistry in two boreal forest catchments and used an end-member mixing model to calculate loss and production of solutes as water flowed through the riparian zone. This method provided an estimate of the contribution of the riparian zone to N retention within the two catchments.

Methods

Study site

The research was conducted in the Caribou Poker Creeks Research Watershed (CPCRW), which is located approximately 50 km northeast of Fairbanks, Alaska, U.S.A. and is associated with the Bonanza Creek Long Term Ecological Research Program. The catchments are characterised by rolling forested hills with saturated soils in valley bottoms. Vegetation patterns in the CPCRW vary with aspect and location across the landscape. North-facing slopes are dominated by black spruce [*Picea mariana* (Mill.) B.S.P] and white spruce [*P. glauca* (Moench) Voss]. South facing-slopes are dominated by deciduous forests of paper birch (*Betula papyrifera* Marsh.) and quaking aspen (*Populus tremuloides* Michx). Vegetation in the valley bottom is distinct from upland forests. Valley bottom widths typically range from 50–75 m and vegetation is dominated by dwarf birch (*B. nana* L.), bog blueberry (*Vaccinium uliginosum* L.), willow (*Salix* spp.) and to a lesser extent thin-leaf alder (*Alnus tenuifolia* Nutt.).

In this study, a low and a high permafrost catchment were studied. The distribution of permafrost in interior Alaska is largely a function of aspect and winter temperature, with north-facing slopes and valley bottoms generally underlain by permafrost (Viereck *et al*., 1983). Approximately 3% of the low permafrost catchment (previously reported as C2) was underlain by permafrost, whereas approximately 53% of the high permafrost catchment (C3) was underlain by permafrost (Yoshikawa, Hinzman & Gogineni, 2002). Thaw depth reaches a maximum in August or September (Van Cleve, Barney & Schlentner, 1981). We were not able to provide data for replicate watersheds, which is a common limitation of many watershed studies (Likens *et al*., 1977; Swank & Waide, 1988).

Stream discharge was measured over the study period using permanently installed flumes near the mouth of each catchment. Stream stage height was recorded with a datalogger (Campbell Scientific, Inc., Logan, UT, U.S.A.) and then converted to discharge using rating equations (L.D. Hinzman and W.R. Bolton, University of Alaska Fairbanks, unpublished data).

Groundwater chemistry and hydrologic fluxes

Groundwater chemistry and hydrology were analysed by: (i) measuring groundwater chemistry using riparian zone wells, (ii) identifying hydrologic sources contributing to riparian zone ground water and (iii) using the results from an end-member mixing model in conjunction with nitrate and dissolved organic carbon (DOC) concentrations to calculate solute retention in the riparian zone. The end-member mixing model provided a prediction of nitrate and DOC concentrations in the absence of catchment biological processes.

Groundwater chemistry Groundwater wells were installed in each catchment in April 2003 in transects ($n = 6$) that extended laterally from the stream-riparian interface to the riparian-upland boundary. Transects consisted of four wells each. The first three wells were installed at distances from the steam channel of 1, 5 and 10 m. The last well was installed at the edge of the valley bottom adjacent to the hill slope at distances from 15 to 30 m depending on the valley bottom width. Transects spanned a 300 m reach of stream in both catchments. Wells were constructed of polyvinyl chloride (PVC) pipe (1.25 cm i.d.) that were installed to a depth of 1 m; wells were perforated with 3 mm holes spaced every 5 cm from 10 to 95 cm below the soil surface. Stream and groundwater samples were collected every 2 weeks in 2003 from

May 22 to August 11. Groundwater samples were stored at 4 °C until analysis (within 48 h of sampling). Additionally, thaw depth was measured in conjunction with collection of groundwater samples at each well location by inserting a graduated stainless-steel depth probe into the soil until permafrost was contacted (thaw depth was also measured in 2004).

Groundwater nitrate production/loss

End member mixing model The spatial variation in conservative solutes such as calcium and sodium in well water indicated that the direction of groundwater flow was not simply from upslope through the riparian zone to the stream but that riparian zone groundwater was a mixture of hill slope and stream water. Accordingly, mixing of stream and groundwater in the riparian zone was characterised using calcium in a two end-member mixing model (Genereux, Hemmond & Mulholland, 1993), with an additional term for concentration effects because of evapotranspiration and partitioning of solutes between frozen and unfrozen phases of groundwater (i.e. exclusion; Zukowski & Tumeo, 1991). Thus, for the end-member mixing model, the following equations were solved simultaneously:

$$1 = f_{\mathrm{sw}} + f_{\mathrm{gw}} \tag{1}$$

$$\mathrm{Ca}_{(\%)\mathrm{well}} = f_{\mathrm{sw}}\mathrm{Ca}_{(\%)\mathrm{sw}} + f_{\mathrm{gw}}\mathrm{Ca}_{(\%)\mathrm{gw}} \tag{2}$$

$$[\mathrm{Ca}]_{\mathrm{well}} = (f_{\mathrm{sw}}[\mathrm{Ca}]_{\mathrm{sw}} + f_{\mathrm{gw}}[\mathrm{Ca}]_{\mathrm{gw}})E \tag{3}$$

where f is the fraction of well water derived from stream (sw) and ground water (gw), $\mathrm{Ca}_{(\%)}$ is the proportion of base cations accounted for by calcium (i.e. [Ca]/[Ca] + [Mg] + [Na]) in each source and well, [Ca] is the concentration of calcium and E is the concentrating effect of evapotranspiration and exclusion. We used calcium in the mixing model as opposed to other solutes such as sodium or chloride because calcium had the greatest difference in concentration between end members and thus provided the greatest resolution of source water contribution. The stream water end-member was determined from a stream sample collected on each sampling date. In CPCRW, calcium concentration in both subcatchments was usually high in stream water relative to groundwater. The groundwater end-member was assumed to be the average of the well samples with the five lowest calcium concentrations. On all dates these ground water end-member wells were located at the upland-riparian boundary.

To verify that calcium was conservative, as assumed for the mixing model, the model was run using the stream and ground water concentrations of sodium (Bailey, Buso & Likens, 2003). Using the f_{sw} and f_{gw} values obtained with calcium, we solved eqn (3) by substituting the $[\mathrm{Ca}]_{\mathrm{sw}}$ and $[\mathrm{Ca}]_{\mathrm{gw}}$ terms with the sodium concentration in the source waters and calculated a predicted concentration for sodium in each well.

Solute retention and production The retention or production of nitrate and DOC in the riparian zone was determined from the difference in observed concentration in wells versus concentration predicted by the end-member mixing model. Predicted nitrate and DOC concentration in wells were solved by substituting nitrate or DOC concentration for calcium concentration in eqn 3. Nitrate and DOC retention/production rates (R) were translated to an area specific rate as:

$$R = \frac{C_{\mathrm{obs}} - C_{\mathrm{pred}}}{T_{\mathrm{res}}} Z_{\mathrm{gw}} \tag{4}$$

where C_{obs} is the solute concentration measured in groundwater samples, C_{pred} is the concentration predicted from the end-member mixing model (eqn 3), T_{res} is residence time of the soil water in the valley bottom and Z_{gw} is the mean depth of groundwater in the riparian zone above permafrost. Z_{gw} was assumed to be equal to the active layer depth. T_{res} was estimated by:

$$T_{\mathrm{res}} = \frac{V_{\mathrm{gw}}}{Q_{\mathrm{gw}}} \tag{5}$$

where V_{gw} is the volume of soil water in the valley bottom and Q_{gw} is the discharge rate of groundwater into the stream per unit length of stream (L s^{-1} m^{-1}). V_{gw} was estimated by:

$$V_{\mathrm{gw}} = A_{\mathrm{vb}} Z_{\mathrm{al}} \phi \tag{6}$$

where A_{vb} is the valley bottom area, Z_{al} is the active layer depth (assuming complete saturation) and ϕ is porosity. A whole valley bottom rate of nitrate/DOC retention or production was calculated as the product of R and A_{vb}.

To calculate Q_{gw}, conservative solute slug injections were conducted at four fixed points along the stream length on four dates between June and August 2002 to measure gain in stream discharge. A sodium chloride tracer was injected upstream of a well-mixed riffle and electrical conductivity was measured continuously every second at a downstream distance of 30 m from the injection point using a Campbell datalogger. The generation of a concentration-time curve allowed for the calculation of stream discharge at each point along the reach (Rantz, 1982). Lateral inflow of groundwater from the riparian zone was calculated as the difference in stream discharge between the upstream and downstream ends of the reach. Lateral inflow expressed as L m^{-1} s^{-1} was regressed against stream discharge at the flume to develop standard curves of groundwater flow. Solute retention was calculated for all dates except the late July point when the stream was flooding and discharge was much greater than was sampled by slug injection in 2002.

Laboratory analyses

Gravimetric soil moisture was measured on replicate soil cores taken adjacent to the groundwater wells (Jarrell *et al.*, 1999). Soil organic matter content was determined from ash free dry mass (AFDM) from the difference in dry and AFDM of incubation soil (Sollins *et al.*, 1999). Soil porosity was measured on soil cores collected on one date by adding a known volume of water to a known volume of dried soil (Elliott *et al.*, 1999).

Soil extractions were conducted for water extractable DOC and nitrate on replicate cores taken adjacent to the cores used to determine soil moisture content (Robertson *et al.*, 1999). Soil samples were dried at 95 °C, transferred to 200 mL plastic beakers, amended with 50 mL of nanopure water and mixed thoroughly with a glass stirring rod. After 3 h, water from the extraction was filtered using a 0.7 μm glass fibre filter.

For groundwater samples, cations (Ca^{2+}, K^+, Mg^{2+}, Na^+ and NH_4^+) and anions (Cl^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) were analysed on a Dionex DX-320 Ion Chromatograph (Dionex Corporation, Sunnvale, CA, U.S.A.). Soil extractions were only analysed for anions. For both groundwater samples and soil extractions, DOC and total dissolved nitrogen (TDN) were determined using a Shimadzu TOC-5000 analyser (Shimadzu Scientific Instruments, Columbia, MD, U.S.A.) plumbed to an Antek 7050 nitric oxide chemoluminescent detector (Antek Electronic Ltd. Co., Houston, TX, U.S.A.). Conductivity was measured on groundwater samples using a conductivity meter.

Statistical analyses

One-way analysis of variance (ANOVA) was used to detect differences between mean nitrate and DOC concentrations in stream water across dates. Two-way ANOVA was used to detect differences in groundwater nitrate and DOC between catchments and among sampling dates. One-way ANOVA was used to detect differences in active layer depth between catchments. Linear regression was used to examine the relationship between groundwater solute concentration and thaw depth. To validate the end-member mixing model, predicted sodium concentration was plotted against observed sodium concentration. Ninety-five per cent confidence intervals were generated to determine if the slope varied significantly from one. A two-way ANOVA was used to detect differences between observed and predicted nitrate and DOC concentrations in ground water between catchments. Significant results from ANOVAS were further analysed with Tukey's multiple comparison.

Results

Stream and ground water chemistry

Stream nitrate concentration was always greater in the low permafrost catchment, averaging 34 μM compared with 22 μM in the high permafrost catchment ($P = 0.008$; Fig. 1a; Table 1). The concentration of nitrate in stream water was two- to threefold greater than the concentration in riparian zone groundwater in both catchments. Riparian zone groundwater was not significantly different between catchments ($P = 0.10$) averaging 13 μM overall (Table 1).

Stream DOC concentration averaged 1494 and 1019 μM in the high and low permafrost catchments, respectively ($P = 0.20$; Fig. 1b). In contrast to nitrate, the concentration of DOC in riparian groundwater was two- to threefold greater than in stream water in both catchments, except during a flood in July, when stream DOC concentration increased considerably in both catchments. Comparing ground water concentration between catchments, mean groundwater DOC concentration was significantly higher in the high

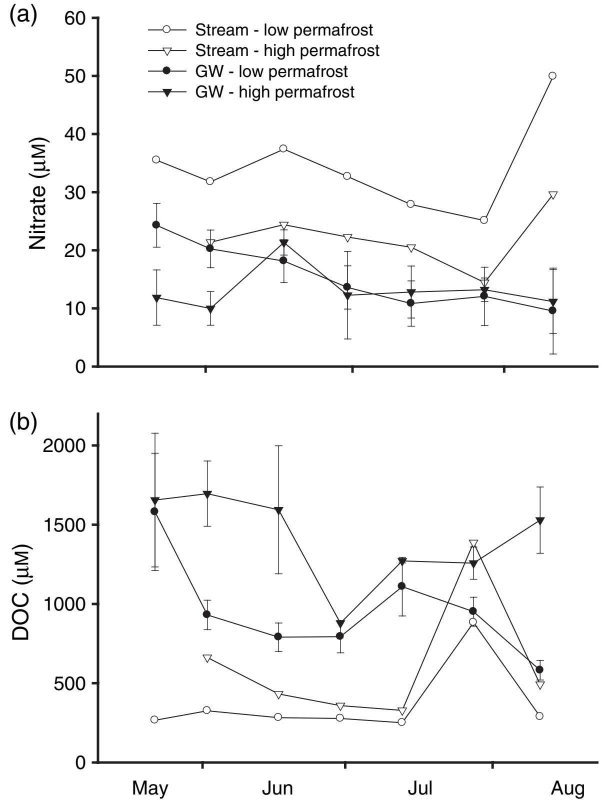

Fig. 1 Temporal variation in stream and ground water (GW) nitrate (a) and dissolved organic carbon (DOC) (b) from 2003. Groundwater data points are averages (±SE) from all well samples.

Table 1 Summary of riparian ground and soil water solute concentrations and standard error (SE) in Caribou Poker Creek Research Catchments in interior Alaska

Variable	Low permafrost [mean (SE)]	High permafrost [mean (SE)]
Ca (μM)	309 (28)	228 (82)
Cl (μM)	158 (36)	80 (13)
DOC (μM)	1019 (57)	1494 (103)
DON (μM)	54 (3)	84 (11)
K (μM)	19 (4)	19 (6)
Mg (μM)	106 (6)	49 (9)
Na (μM)	322 (22)	498 (82)
NH_4^+ (μM)	30 (12)	8 (5)
NO_2^- (μM)	2.1 (0.2)	1.9 (0.4)
NO_3^- (μM)	12.2 (0.9)	13.7 (2.2)
PO_4^{3-} (μM)	1.3 (0.9)	0.2 (0.1)
SO_4^{2-} (μM)	128 (11)	158 (31)
Conductivity (μS cm^{-1})	91 (5)	92 (14)
Organic matter (%)	28 (2)	32 (3)
Soil moisture (%)	2.3 (0.3)	1.2 (0.1)
Water extractable DOC (μmol C g^{-1})	216 (55)	250 (64)
Water extractable nitrate (μmol N g^{-1})	3.1 (1.8)	2.1 (0.5)

DOC, dissolved organic carbon; DON, dissolved organic nitrogen.

permafrost catchment than the low permafrost catchment ($P = 0.002$; Fig. 1b; Table 1).

Thaw depth increased significantly over the growing season in both 2003 and 2004 ($P < 0.0001$). In 2003, thaw depth increased from 15 to 45 cm in the high permafrost catchment and from 18 to 32 cm in the low permafrost catchment (Fig. 2) and was not significantly different between catchments. A similar seasonal pattern in thaw depth was observed during most of 2004. In September of 2004, however, thaw depth declined with the greatest change in the low permafrost catchment ($P < 0.05$; Fig. 2b).

To determine if change in thaw depth affected solute concentrations, we regressed mean groundwater nitrate and DOC concentrations against depth of thaw. Groundwater nitrate concentration was negatively correlated with thaw depth in the low permafrost catchment ($r = -0.91$, $P = 0.004$). In the high permafrost catchment, however, groundwater nitrate was not significantly correlated with thaw depth and DOC concentration was not significantly correlated with thaw depth in either catchment ($P > 0.05$).

Groundwater nitrate retention/production

The relative composition of base cations in stream and ground water samples were linearly aligned between two source waters (Fig. 3a) which, as previously described in the methods, was interpreted as two source waters contributing to riparian groundwater. For the majority of groundwater samples, the concentration of calcium reflected simple hydrologic mixing of the two source waters (i.e. data points are aligned in a linear fashion between the stream and groundwater end-members). In several instances, however, the concentration of calcium was enriched (Fig. 3b), which in our model we attributed to evapotranspiration and/or exclusion. In further support of evaporation affecting calcium concentration, the model results using calcium and sodium produced similar results. Ninety-five per cent confidence intervals bounding the regression line relating predicted and observed sodium concentrations encompassed a slope of 1 (Fig. 4),

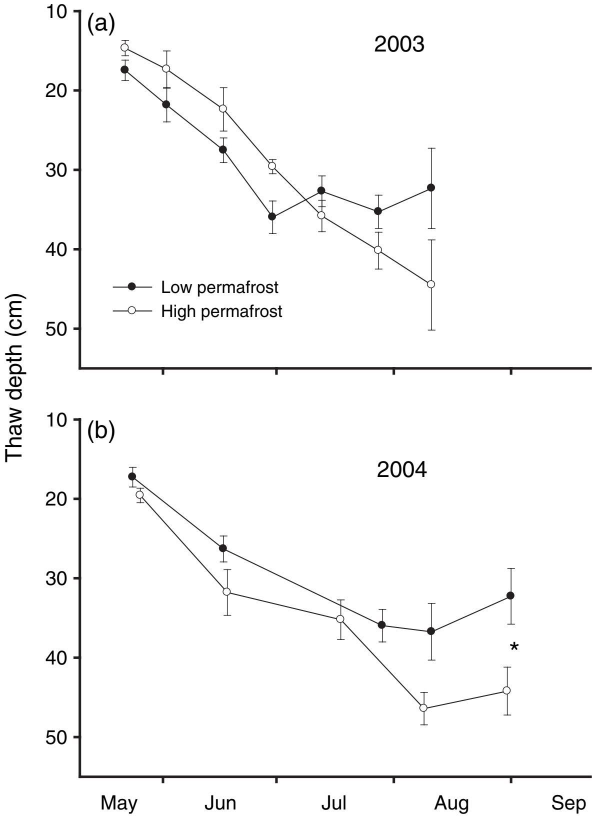

Fig. 2 Seasonal variation in thaw depth in the valley bottom of the low and high permafrost catchments in (a) 2003 and (b) 2004. Data points are averages (±SE) from all sampling points. Asterisk (*) indicates thaw depths that are significantly different between catchment ($P < 0.05$).

indicating that the calcium behaved conservatively and the enrichment term was warranted (Fig. 4).

In contrast to the frequent enrichment in calcium concentration in well water (Fig. 3b), nitrate concentration was typically below the mixing line and DOC concentration was highly variable (Fig. 5). For nitrate in the low permafrost catchment, the mean observed concentration of 15 μM was only 38% of the mean predicted value of 37 μM in ($P < 0.05$; Fig. 6a). In contrast, in the high permafrost catchment, the mean observed nitrate concentration of 15 μM was not significantly different than the predicted value ($P > 0.05$). In both catchments, observed DOC concentration were significantly lower than predicted concentration ($P < 0.05$; Fig. 6b).

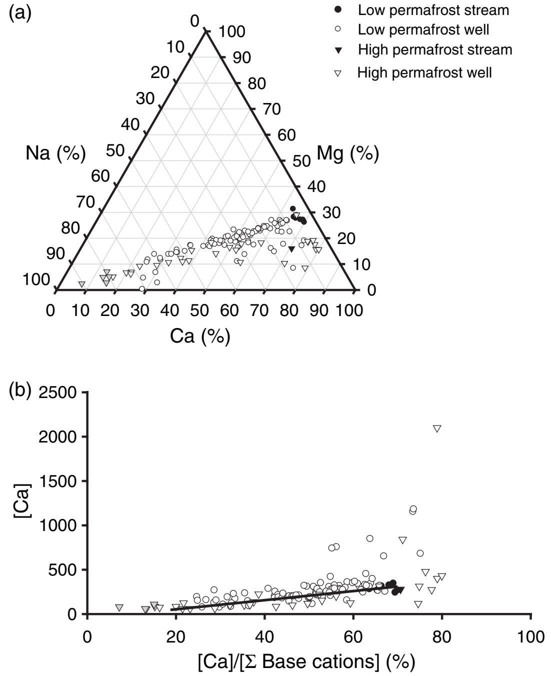

Fig. 3 (a) Ternary plot of groundwater base cation chemistry. Each axis represents the percent base cation concentrations relative to the sum of all of three concentrations. (b) Scatter plot of stream and ground water Ca concentration versus percent Ca. The black line connects mean values for groundwater end-members (shaded grey) and stream water end-members.

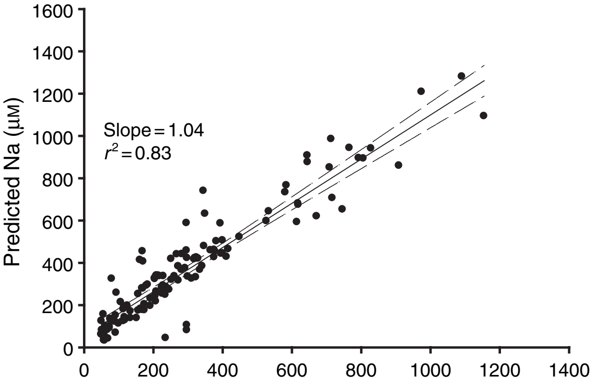

Fig. 4 Relationship between observed and predicted sodium concentrations generated from the end-member mixing model. The regression line (solid) is bounded by 95% confidence intervals (dashed). The slope of the regression line is not significantly different from one, demonstrating the validity of the model.

Nitrate retention rate in the riparian zone calculated from groundwater chemistry and the end-member mixing model averaged 0.75 and 0.22 mmol N m^{-2} day^{-1} in the low and high permafrost catchments, respectively and was not significantly different ($P = 0.52$; Fig. 7a). DOC retention rate was not significantly different between catchments either,

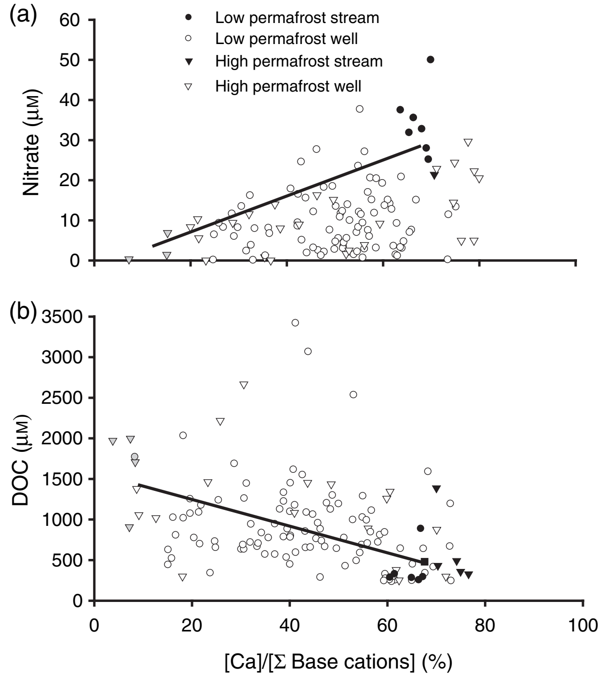

Fig. 5 Scatter plot of (a) nitrate and (b) DOC versus percent Ca. The line connects the average values for the groundwater (shaded grey) and stream water end-members and represents the predicted concentration if solutes are solely regulated by mixing of source waters.

averaging 31 and 19 mmol C m^{-2} day^{-1} in the low and high permafrost catchments, respectively (Fig. 7b).

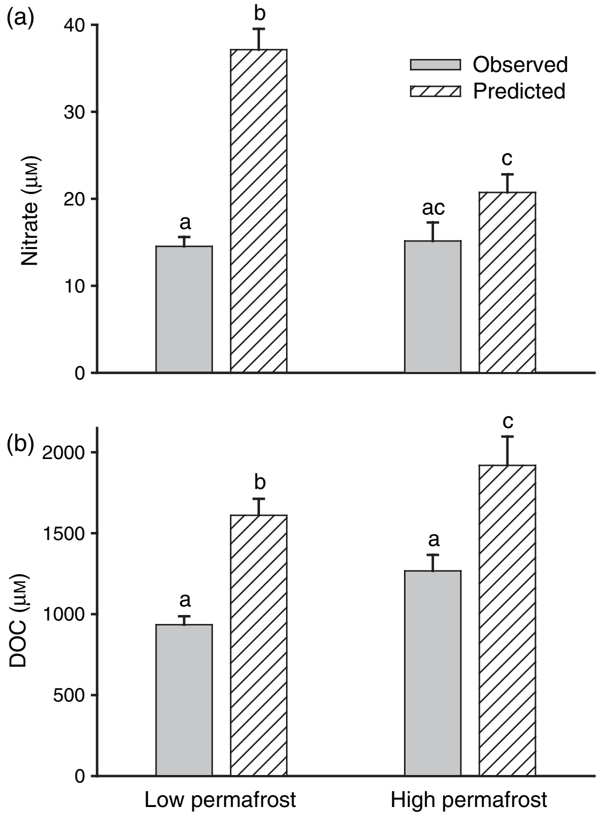

Fig. 6 Predicted and observed (±SE) groundwater nitrate (a) and DOC (b) concentrations for the high and low permafrost catchments. Predicted values generated from an end-member mixing model. Letters denote significantly different means by Tukey's multiple comparison (ANOVA; $P = 0.05$).

Discussion

Permafrost, hydrology and stream water chemistry

The effect of permafrost on catchment hydrology has important consequences for stream water chemistry (MacLean *et al.*, 1999). Permafrost prevents deep infiltration of water and confines groundwater flow to shallow organic horizons. Streams draining permafrost-dominated catchments typically have a high dissolved organic matter (DOM) concentration and low dissolved mineral and nitrogen concentrations (MacLean *et al.*, 1999; Jones *et al.*, 2005). The absence of permafrost allows for infiltration of surface water through mineral soil, where absorption can reduce DOM in soil water (McDowell & Wood, 1984).

In the present study, stream water nitrate concentration was greater in the low permafrost stream, as has been previously reported (MacLean *et al.*, 1999; Jones *et al.*, 2005). However, nitrate concentration in riparian groundwater did not differ between catchments. This lack of difference in riparian zone nitrate concentration suggests that stream water nitrate concentration is probably primarily controlled by deeper groundwater or flows from springs that by pass the riparian zone. DOC concentration in stream water did not vary significantly between catchments, but in riparian groundwater, DOC concentration was significantly greater in the high permafrost catchment than in the low permafrost catchment. This difference in riparian DOC concentration is potentially because of several factors, including a greater DOC concentration in water flowing from the permafrost-dominated uplands of the high permafrost catchment to the riparian zone, differences in riparian soil carbon stocks between catchments and varying DOC inputs from riparian vegetation to groundwater. The observed difference in stream chemistry between catchments is consistent with an effect of permafrost.

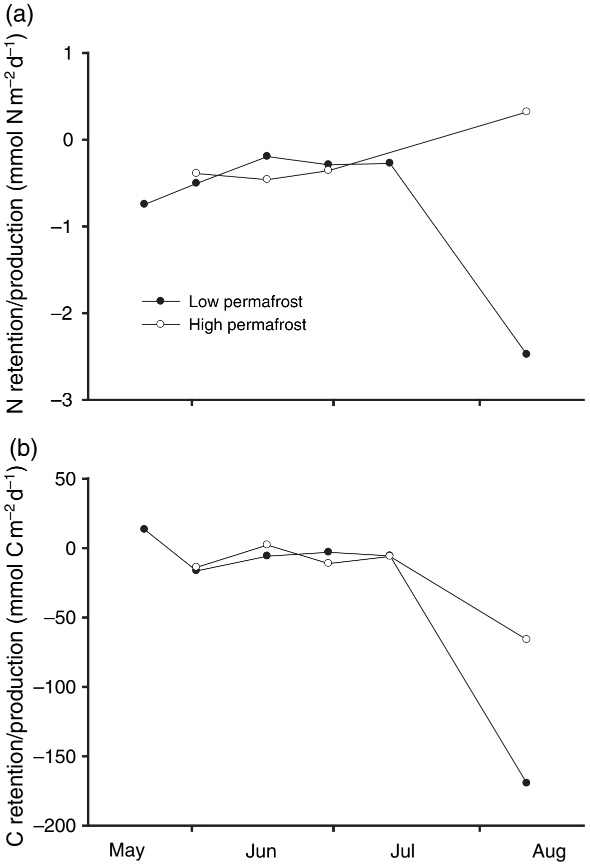

Fig. 7 Seasonal variation in (a) nitrogen and (b) carbon retention/production in the riparian zone of the high and low permafrost catchments. Positive value reflects the production of groundwater nitrogen or carbon. A negative value reflects the removal of nitrogen or carbon from groundwater flow.

However, as the catchments were not replicated in this study, we cannot conclusively attribute this effect to permafrost.

In regions underlain by discontinuous permafrost, a seasonal increase in thaw depth potentially allows groundwater to flow from organic to mineral soil horizons, which in turn may affect nitrate and DOC production and retention (Carey, 2003; Kawahigashi *et al.*, 2004). For example, during periods when flow is primarily through organic horizons, soil may serve as a source of DOC. As thaw depth increases from organic to mineral horizons, sorption of DOC to mineral particles can occur, reducing input to streams (McDowell & Wood, 1984). Interestingly, however, in the present study, thaw depth explained little of the variance in groundwater chemistry, indicating that changes in thaw depth do not appear to be a primary control on seasonal changes in groundwater nitrate or DOC concentration.

Storms can also influence DOC concentration in stream water by leaching of DOC in soil (Bechtold, Edwards & Naiman, 2003). In the present study, stream DOC concentration spiked in both catchments following a flood in July, although no response was detected in riparian groundwater. This observed increase in stream water DOC concentration was presumably because of the direct transfer of soil DOC to surface water (Hornberger, Bencala & McKnight, 1994).

Retention of nitrogen in the riparian zone

The use of an end-member mixing model in this study provided a powerful tool for evaluating hydrologic mixing of stream and groundwater and for detecting sources and sinks of nitrate and DOC in the riparian zone. In both catchments, the riparian zone functioned largely as a nitrate sink (Fig. 5a, reflected by the majority of data points beneath the black hydrologic mixing line), with nitrate presumably removed from groundwater either by plant uptake or denitrification. For DOC, riparian zones functioned as sinks overall, although a number of wells showed DOC production (Fig. 5b). DOC production in riparian groundwater is probably attributable to decomposition of particulate organic carbon and rhizodeposition from riparian vegetation. DOC loss from groundwater flow paths can result from either biotic (heterotrophic respiration) or abiotic mechanisms (adsorption to mineral soil particles).

Subsurface hydrology is an important control for nitrogen transformations in the riparian zone (Hedin *et al.*, 1998; Devito *et al.*, 2000; Hill *et al.*, 2000). In riparian zones, the intersection of flow paths of nitrate-rich water with soil rich in organic carbon typically promotes substantial nitrate loss via denitrification (Hedin *et al.*, 1998; Hill, 2000). Based on data from Caribou Poker Creeks Research Watershed, MacLean *et al.* (1999) hypothesised that denitrification in the riparian zone is an important mechanism regulating stream nitrogen concentration and that in low permafrost catchments the slow movement of subsurface water through mineral horizons allows greater denitrification. The riparian zone functions as important control point for the flux of nutrients between terrestrial and aquatic ecosystems, in part because of denitrification (Lowrance *et al.*, 1984;

Peterjohn & Correll, 1984; Cooper, 1990; Naiman & Décamps, 1990; Hill *et al.*, 2000).

In addition to loss by denitrification, retention of groundwater nitrogen is strongly influenced by riparian vegetation (Peterjohn & Correll, 1984; Groffman, Gold & Simmons, 1992), which can retain nitrogen either directly through uptake or indirectly by stimulating microbial activity in the rhizosphere (Schade *et al.*, 2001). Nitrogen retention is often increased in riparian zones where groundwater flow is restricted to shallow subsurface flow paths that enhance the interaction with shallow organic soil and riparian plants (Peterjohn & Correll, 1984; Cooper, 1990; Hill, 1996). In the boreal forest, the influence of plants on groundwater nitrate concentration is likely to occur when the active layer confines groundwater flow to the rooting zone of plants.

Characterising catchment hydrology is particularly difficult in regions with discontinuous permafrost, where zones of preferential flow (macropores, interhummock regions, water tracks) complicate hydrologic processes (Carey & Woo, 2000). Compared with the high permafrost catchment, the riparian zone of the low permafrost catchment had a shallower maximum active layer depth, higher soil moisture content and longer residence time of water. The observation that maximum active layer depth was greater in the high permafrost catchment is somewhat surprising (Fig. 2). This difference may have been driven by differences in soil moisture in the active layer soil, which influences soil heat capacity (Hinzman, Goering & Kane, 1998). High soil moisture content and the greater heat capacity in the active layer of the low permafrost catchment may have reduced thawing and, thus, restricted thaw depth to relatively shallow soil horizons.

Nitrogen loss from boreal forest catchments

Nitrogen export in streams draining boreal forest catchments with discontinuous permafrost is greater than inputs from atmospheric deposition (Stottlemyer, 1992, 1997; Jones *et al.*, 2005) and counter to patterns observed in temperate forests where catchments tend to retain nitrogen (Vitousek *et al.*, 1982). This loss is surprising because nitrogen limits terrestrial primary production in interior Alaska (Van Cleve *et al.*, 1983; Bonan, 1990). Moreover, the loss of nitrogen may be substantially greater given that loss via dentrification was not included in budget calculations (Jones *et al.*, 2005).

To assess the importance of the riparian zone for catchment nitrogen retention in, nitrate retention rate (estimated from the end-member mixing model) was compared with annual rates of nitrogen export in streams (export data from Jones *et al.*, 2005). To scale retention rates to the catchment, riparian zone nitrogen retention rates were multiplied by the fraction of the catchment accounted for by the valley bottom (<1% in each catchment). Relative to the nitrogen flux in stream flow, riparian nitrogen retention averaged 6 and 3 mmol N m^{-2} $year^{-1}$ in the low and high permafrost catchments, respectively. In terms of whole catchment budgets, in the low permafrost catchment, 15% of the nitrogen moving toward the stream was retained by processes in the riparian zone and in the high permafrost catchment, 10% of the nitrogen was retained (calculated as riparian zone retention divided by riparian zone retention plus stream export).

Riparian zone functioning with permafrost

In the boreal forest, the riparian zone functions to reduce nitrate concentration in ground water. As is the case in many agricultural and temperate systems (Peterjohn & Correll, 1984; Groffman *et al.*, 1992), the riparian zone in this study functioned both as nutrient filter and a source of organic matter to the stream. The rate of nitrogen retention in riparian zones underlain with permafrost, however, results from a complex interaction among not only the rate of nitrate and DOC supply and the extent of anoxia, but also the rate of subsurface flow. Subsurface flow through these riparian zones appears to be complex and may be governed largely by zones of preferential flow, which allow for rapid transport of water and solutes through the riparian zone to the stream. These regions of high flow reduce residence time of water in the valley bottom and contact time of subsurface flow with roots and organic soil, which probably reduces the influence of plants and microbes on groundwater nitrate concentration compared with many temperate ecosystems.

Acknowledgments

We thank E. Betts, J. Eichmiller, N. Lisuzzo and J. Rohrs for help in the field and laboratory. We thank L. Hinzman, K. Kielland and two anonymous reviewers who provided valuable comments on the manuscript. This research was part of the Bonanza Creek LTER (Long-Term Ecological Research) programme (funded jointly by NSF grant DEB-0423442 and USDA Forest Service, Pacific Northwest Research Station grant PNW01-JV11261952-231).

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(Manuscript accepted 20 January 2006)