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Comparison of nitrogen solute concentrations within alder (*Alnus incana* ssp. *rugosa*) and non-alder dominated wetlands

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Abstract:

This study examined differences in nitrogen solutes and groundwater flow patterns between a riparian wetland dominated by the N_2-fixing shrub, *Alnus incana* ssp. *rugosa*, and an upstream coniferous forested riparian wetland along a stream of the Adirondack Mountains, where some surface waters are susceptible to nitrogen excess. Channel water NO_3^- was up to 16 μmol l^{-1} greater in the alder reach, with peaks following maxima in groundwater dissolved inorganic nitrogen (DIN). NO_3^- at 25 cm depth was 30 μmol greater in the alder than in the conifer reach in April, and 24 μmol l^{-1} greater than channel water and 30 μmol l^{-1} greater than that of 125 cm groundwater in June. Dissolved organic nitrogen and NH_4^+ concentrations increased between 25 and 75 cm depths in both wetlands during the growing season. Inorganic nitrogen increased between the hillslope and stream in both wetlands, with the greatest increases in the alder reach during the dormant season. Greatest subsurface DIN (120 μmol l^{-1}) occurred at 75 cm in the alder reach, within 1 m of the stream, between November (120 μmol l^{-1} NH_4^+) and a January thaw (60 μmol l^{-1} each of NH_4^+ and NO_3^-). Concentrations of deeper groundwater at 125 cm during this period were lower (10–30 μmol l^{-1}). Lateral flow from the stream channel occurred in the alder reach during the dormant season, and channel water contribution to groundwater was correlated strongly to NO_3^- at 25 cm. These results indicate that nitrification is stimulated in the presence of alders and oxidized exchange flow, producing NO_3^- that may contribute to elevated channel water NO_3^- during periods of peak flow. Copyright © 2004 John Wiley & Sons, Ltd.

KEY WORDS riparian; wetlands; nitrogen; *Alnus*; Adirondack Mountains

INTRODUCTION

Surface waters in the Adirondack Mountains in New York State, such as seepage and drainage lakes with thin glacial till in surrounding watersheds, are sensitive to atmospheric deposition of acid anions due to low acid neutralizing capacity (ANC; Driscoll *et al*., 1991, 1998). Although significant declines in SO_4^{2-}, NO_3^- and Cl^- concentration in deposition have occurred in the region with correlated declines in lake water SO_4^{2-}, the ANC of many surface waters has not increased (Driscoll *et al*., 1998). While there has been increased examination of NO_3^- as an acid anion (Likens *et al*., 1998) and of wetland influence on nitrogen transport between hillslopes and streams (Cirmo and McDonnell, 1997), the influence of nitrogen-fixing alder shrubs on spatial and temporal patterns of nitrogen chemistry in wetlands of the region has not been quantified.

The actinorhizal N_2-fixing shrub, speckled alder, *Alnus incana* ssp. *rugosa* (DuRoi) Clausen, often occurs along stream sides and in wetlands in the northeastern USA and Canada (Furlow, 1979). Speckled alder dominates the Scrub-Shrub 1 (SS1) wetland cover type (Cowardin *et al*., 1979), the second largest wetland cover type after coniferous forest (FO4) in the Adirondack Mountains (Roy *et al*., 1996). Nitrogen fixation

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in a riparian SS1 alder wetland in the central Adirondacks was estimated to be 37–43 kg ha^{-1} $year^{-1}$ (Hurd *et al*., 2001). In other parts of eastern North America, nitrogen accretion in speckled alder wetlands may be 85–167 kg ha^{-1} $year^{-1}$ (Daly, 1966; Voigt and Steucek, 1969). Speckled alders in the region derive 85–100% of foliar nitrogen from fixation (Hurd *et al*., 2001) and do not resorb foliar nitrogen prior to litter fall (Bischoff *et al*., 2001).

Elevated nitrification and nitrogen leaching occur in alder (*A. rubra* (Bongard) and *A. incana* ssp. *tenuifolia* (Nuttall) Breitung) stands of western North America (Coats *et al*., 1976; Van Miegroet and Cole, 1984, 1985; Binkley *et al*., 1992; Hart *et al*., 1997), flood plain soils with *A. incana* ssp. *tenuifolia* (Van Cleve *et al*., 1993), and drained peatlands dominated by *A. glutinosa* (L.) Gaertner (Kazda, 1995). In an Adirondack forested watershed, the presence of speckled alder increased NO_3^- content and net nitrification rate of wetland soil (Ohrui *et al*., 1999). Stottlemyer *et al*. (1995) measured average soil NO_3^- of 56·5 mg m^{-2} in speckled alder stands, which is three times that of sugar maple stands, seven times that of spruce stands, and 10 times that of birch stands at Isle Royale in northern Michigan, USA. Stottlemyer *et al*. (1995) also measured greatest nitrification under alders between July and the following May, and noted that alder stands occurred on previously flooded low-elevation sites, where soils were saturated to within 5 cm of the surface into June.

Recent studies have focused on hydrological interactions with nitrogen transformations in riparian and hyporheic zones (Dahm *et al*., 1994; Cirmo and McDonnell, 1997; Hedin *et al*., 1998; Hill and Lymburner, 1998). Goldman (1961), Dugdale and Dugdale (1961), Coats *et al*. (1976) and Wondzell and Swanson (1996) have considered the contribution of western *A. tenuifolia* or *A. rubra* to surface water inorganic nitrogen or primary productivity, but the effects of alders on riparian ground and surface water nitrogen in eastern North America remain unquantified.

This study compares seasonal and spatial patterns of nitrogen solutes between a riparian wetland dominated by N_2-fixing alders (classified as SS1) and an upstream wetland dominated by conifers (FO4), in a region where many surface waters are sensitive to anthropogenic sources of nitrogen and acidity. Because dense alders in these ecosystems fix nitrogen of approximately 40 kg ha^{-1} $year^{-1}$ (85–100% of annual foliar nitrogen (Hurd *et al*., 2001)), and may stimulate nitrification (Ohrui *et al*., 1999), we expected elevated concentrations of nitrate and other nitrogen solutes in the alder wetland, particularly during periods of low biological nitrogen demand (autumn and winter). Moreover, we expected that nitrogen solute concentrations in shallow groundwater would increase between hillslope and stream in the alder wetland, due to low biological demand by nitrogen-fixing vegetation (Hurd *et al*., 2001), stimulated riparian nitrogen mineralization (Van Cleve *et al*. 1993) and potential oxygenation of near-stream soils by exchange flow (contribution of oxygenated channel water) that may stimulate nitrification but decrease denitrification (Triska *et al*., 1989, 1993).

SITE DESCRIPTION

Research was conducted on the upper Adjidaumo stream at the Huntington Wildlife Forest (HWF) located in the central Adirondack Mountain region of New York (Figure 1). The HWF is a National Atmospheric Deposition Program (NADP) and National Trends Network (NTN) monitoring site, and has been the locus of many biogeochemical studies (Raynal *et al*., 1985; Johnson and Lindberg, 1992; Mitchell *et al*., 1994, 1996; Ohrui *et al*., 1999).

Soils, surficial geology, and bedrock geology at HWF are typical of the Adirondack region and are described in Somers (1986) and Ohrui *et al*. (1999). Mean annual temperature is 4·4 °C, with a dormant mean of −2·8 °C and a growing-season mean of 14·3 °C. Mean annual precipitation is 101 cm (Shepard *et al*., 1989). Upland vegetation is mixed northern hardwood forest. The lower elevations are characterized by red spruce (*Picea rubens* Sarg.), balsam fir (*Abies balsamea* (L.) Miller), eastern hemlock (*Tsuga canadensis* (L.) Carr.), and yellow birch (*Betula alleghaniensis* Britton). Speckled alder dominates a 5 ha SS1 wetland along the Adjidaumo stream, and other riparian wetlands at HWF (Bischoff *et al*., 2001; Hurd *et al*., 2001).

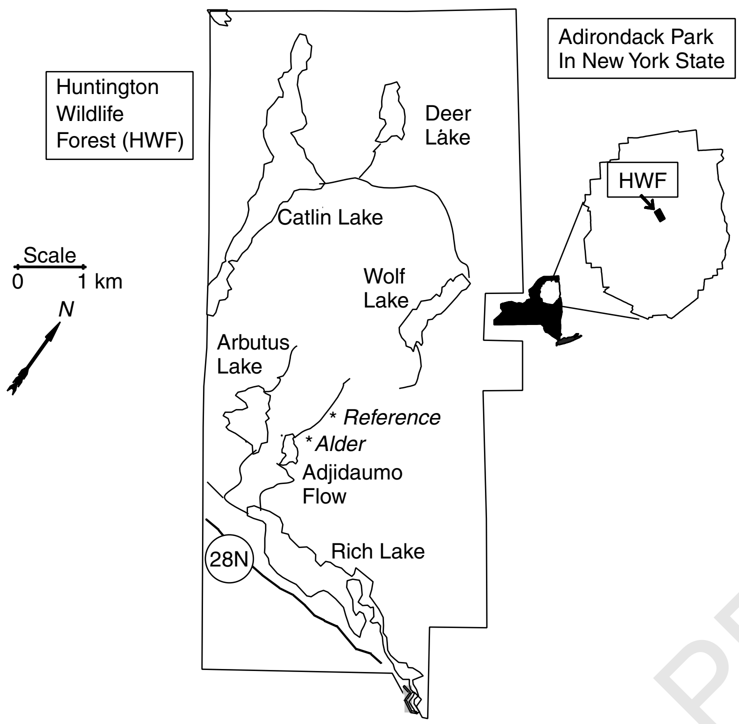

Figure 1. Study site locations at HWF in the Adirondack Park of New York State

METHODS

Nitrogen concentrations and groundwater flow patterns were compared in two wetland reaches of Adjidaumo stream. Vegetation cover was estimated by line intercept, with three transects in each reach running perpendicular to the stream. The first reach, classified as SS1, was dominated by speckled alder (59% cover) and *A. balsamea* (41%), with *Calamagrostis canadensis* (Michx.) P. Beauv. (36%) and *Clematis virginiana* L. (35%) dominating the ground layer. The distance between hillslope and stream is approximately 30 m. Beaver activity at the downstream end of this reach resulted in visible, year-round loss of channel water to the wetland. The reference reach, classified as FO4, was approximately 500 m upstream (Figure 1), with a distance between hillslope and stream of approximately 30 m. Canopy vegetation in this reach was dominated by *P. rubens* (33%), *A. balsamea* (16%), *T. canadensis* (17%) and *B. alleghaniensis* (15%), with *C. canadensis* (25%) and *Rubus* spp. (23%) dominating the ground layer.

Water sampling and analysis

Both wetland reaches were instrumented in May 1996 with three transects of nested piezometers to sample the hydrologic head and the concentrations of NO_3^-, NH_4^+, total nitrogen, and Cl^- as a hydrologic tracer, at 20–25, 70–75, and 120–125 cm depths. The 20–25 cm depth corresponded to maximum depth to water table, immediately below the rooting zone. Organic substrate was generally present at 70–75 cm, and the 125 cm piezometers penetrated till or alluvium in both wetlands. Piezometers were constructed of 2·54 cm ID PVC capped at the bottom, and slotted and screened for the bottom 5 cm to facilitate water collection. Transects ran perpendicular to the stream between the channel and hillslope, and were spaced 10 m apart. The first three piezometer nests were spaced at 5 m intervals within transects starting $\leq$1 m from the stream (evenly throughout alder or coniferous wetland cover), with the fourth nest placed at the wetland–hillslope margin approximately 30 m from the stream. Piezometers were installed at 125 cm at 1 and 6 m from the stream in the alder site, but could only be installed in two nests in the reference site. One shallow well (1·5 m depth, 7·6 cm ID PVC) was installed in May 1997 in a hollow of each wetland to monitor water table elevation.

Groundwater samples for chemical characterization were collected monthly between April 1997 and April 1998, except for some mid-winter months. Water levels were measured monthly between April 1997 and April 1998 to determine horizontal (75 cm depth) direction of groundwater flow. Piezometers were evacuated following water level measurement, allowed to recharge and then sampled the following day using a hand-operated vacuum pump. Channel water was sampled in duplicate in each reach. Samples were transported from the field in ice chests and stored at 2 °C prior to analysis. Concentrations of NO_3^- and Cl^- were analysed by ion chromatography (Dionex QIC-2), NH_4^+ by Wescan analyser, and total dissolved nitrogen (TDN; 25 and 125 cm depths) by Technicon II autoanalyser following persulphate digestion (Solorzano and Sharp, 1980; Ameel *et al*., 1993). Dissolved organic nitrogen (DON) was calculated by subtracting the sum of NO_3^- and NH_4^+ (dissolved inorganic nitrogen, DIN) from TDN.

Statistical analysis

Whole-site comparisons used means of all piezometers of a given depth between 1 and 11 m from the stream ($n = 9$). Piezometers at the hillslope margin, where alder did not occur, were not included in whole-site comparisons. Water chemistry data were log-transformed because of variance heterogeneity, and subjected to analysis of variance and t tests to detect site or depth differences by sample date ($\alpha = 0{\cdot}05$) for all months.

Site differences in inorganic nitrogen gradients from the hillslope boundary to the stream were compared in April 1997 (snowmelt), June 1997 (beginning of growing season), November 1997 (pre-snowpack dormant season), and January 1998 (winter thaw), using an analysis of response curves approach for repeated measures (Meredith and Stehman, 1991) in space. Dates were selected to correspond to periods of peak nitrogen export in channel water (McHale• *et al*., 2002), to periods of high nitrogen demand within wetlands, and to dormant periods prior to nitrogen inputs from snowpack. The response curves repeated analysis is appropriate due to the non-randomized piezometer locations within transects, and because nitrogen gradients could be represented by linear (B) or quadratic (Q) polynomials. Two coefficients for polynomials of unequally spaced samples were constructed following Robson (1959): $B_{ij} = -11y_{ij1} - 6y_{ij6} - y_{ij11} + 18y_{ij30}$, and $Q_{ij} = 98{\cdot}3y_{ij1} - 31{\cdot}2y_{ij6} - 110{\cdot}6y_{ij11} + 43{\cdot}5y_{ij30}$, where i indicates site, j indicates replication (experimental unit within site) and 1, 6, 11 and 30 represent the distance in metres from the stream. Analysis of B examines the site by linear distance interaction and the linear distance main effect, and analysis of Q examines the site by quadratic distance interaction and the quadratic distance main effect. Mean and cubic polynomials could be constructed for orthogonality. However, only linear and quadratic polynomials were used in the analysis, because cubic patterns were not observed, and differences in site means were tested previously. In January, only distances 1, 11, and 30 could be sampled, and coefficients for Q and B were calculated accordingly (Robson, 1959). All statistical analyses were conducted with SAS version 6·12 (SAS Institute, 1996).

AQ1

Estimation of channel water and deep groundwater contributions to shallow groundwater

The influence of channel water on riparian DIN in the beaver-flooded alder wetland was estimated from the fractions of channel water and deep groundwater in shallow groundwater, then correlating the channel water fraction with NO_3^- and NH_4^+ concentrations. A two-component mixing model (Sklash and Farvolden, 1979) utilizing Cl^- as a hydrologic tracer was used to estimate the percentage channel water in groundwater (Hill and Lymburner, 1998) at 25 and 75 cm depths, where

$$\text{Channel Water Fraction}\,\frac{Q_c}{Q_{sg}} = \frac{C_{sg} - C_g}{C_c - C_g}$$

and C_{sg} is the Cl^- concentration of shallow groundwater, C_g is the Cl^- concentration of groundwater at 125 cm, and C_c is the Cl^- concentration of channel water. Cl^- has been used as a conservative tracer to estimate ground and soil water fractions of streamflow in a similar Adirondack wetland, but such use was limited by changing concentration in near-stream soils during storms (McHale *et al.*,• 2002). This model assumes only two sources to shallow groundwater (channel water and deep groundwater) and, therefore, is limited under conditions of snowmelt or substantial precipitation. Nevertheless, typical groundwater discharge patterns in riparian wetlands, visible flow of channel water through the alder wetland, and shallow groundwater Cl^- concentrations that exceeded 1–3 μmol l^{-1} typical of rain or snow (NADP/NTN, 1999) suggest that this assumption was generally met. Shallow groundwater at the base of the hillslope was very similar in Cl^- concentration to 125 cm groundwater, and so was considered to be the same water source. If shallow groundwater Cl^- concentrations were slightly outside the range of end-member concentrations, estimates were rounded to 0 or 100%. Estimates of percentage channel water were then used with piezometric data to interpret potential hydrologic effects on nitrogen solutes.

AQ2

RESULTS

Channel water seasonal patterns in nitrogen concentration

NO_3^- was consistently greater in the alder reach, with the greatest difference during spring snowmelt in 1997 (Figure 2). Peak NO_3^- concentrations in 1998 occurred in a January thaw (Figure 2c), with greater NO_3^- in the alder reach (Figure 2a). Ammonium concentrations were $\leq$5 μmol l^{-1} throughout the year in both reaches. Concentrations of DON increased through the growing season in both reaches (Figure 2b). Hence, when DIN concentrations decreased in summer, as much as 60% of TDN was DON.

Groundwater levels and flow

Groundwater levels in the wetland hollows varied between −10 and +7 cm of the surface in the alder wetland and between −15 and +10 cm of the wetland surface in the upstream coniferous wetland between May 1997 and May 1998. The hollows of the alder wetland remained more saturated during the dormant season, following increased flooding by beaver in summer 1997 (Figure 3a).

Ground elevation in both wetlands decreased approximately 15 cm between hillslope and stream. Although we did not characterize the underlying substrate, approximate horizontal flow patterns were inferred from piezometric surfaces at 75 cm (Figure 4). A beaver dam at the downstream end of the alder reach resulted in visible loss of channel water to this wetland across seasons, and an elevated water table (Figure 3a).

Seasonal trends in riparian groundwater nitrogen

25 cm depth. NO_3^- concentrations at 25 cm were 30 μmol l^{-1} greater in the alder reach during spring snowmelt in 1997 (Figure 3b). NO_3^- concentrations remained greatest at this shallow depth in the alder reach until a melt event in January 1998, and were statistically greater in the alder wetland in May, August, September, and November 1997 (Figure 3b), despite a higher water table (Figure 3a). Ammonium concentrations increased in both wetlands at 25 cm following snowmelt of 1997, until falling to low levels during the January thaw (Figure 2a). Ammonium concentrations were significantly greater in the reference wetland than in the alder reach in September 1997.

DON in shallow groundwater increased to nearly 100 μmol l^{-1} from 10 μmol l^{-1} in the alder stand during the growing season, then decreased gradually until after the January melt of 1998 (Figures 3c and 2c). DON comprised 27% of TDN in May 1997, and 71% in July. This fraction gradually decreased in the alder wetland until the January• thaw, when DON was only 14% of TDN, then it began to increase again until spring (Figure 3c). DON in the reference wetland remained lower, but followed similar seasonal trends (Figure 3c). During the entire sampling period, Cl^- concentrations at this depth did not differ (Figure 3c) in the two wetlands.

AQ4

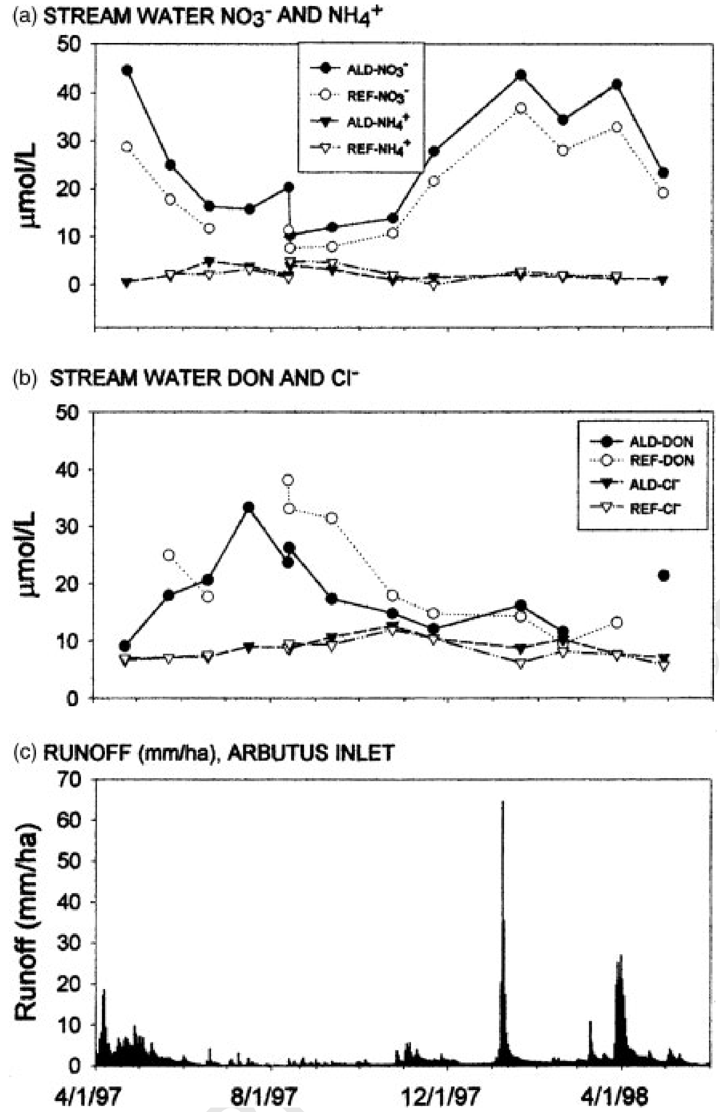

Figure 2. Nitrogen and chloride concentrations in channel water of alder and reference reaches. Values are means of duplicate samples: (a) NO_3^- and NH_4^+; (b) DON and chloride; (c) runoff, measured at the adjacent Arbutus Inlet catchment (Mitchell *et al.*, 2001•) AQ3

75 cm depth. Significantly greater NO_3^- concentrations occurred in the alder reach at 75 cm in September 1997, with the highest concentrations observed in both wetlands during the January 1998 snowmelt (Figure 5a). Ammonium was the dominant form of DIN at this depth; it peaked in autumn at both sites, then was depleted from or diluted in groundwater through the remainder of the dormant season (Figure 5a).

125 cm depth. NO_3^- concentrations in shallow till or alluvium of the alder reach were low ($\leq$10 µmol l^{-1}) in April 1997, the period of greatest NO_3^- concentrations in shallow horizons. Peaks at this depth did occur in September 1997 and in January• during the early melt (Figure 5b). AQ5

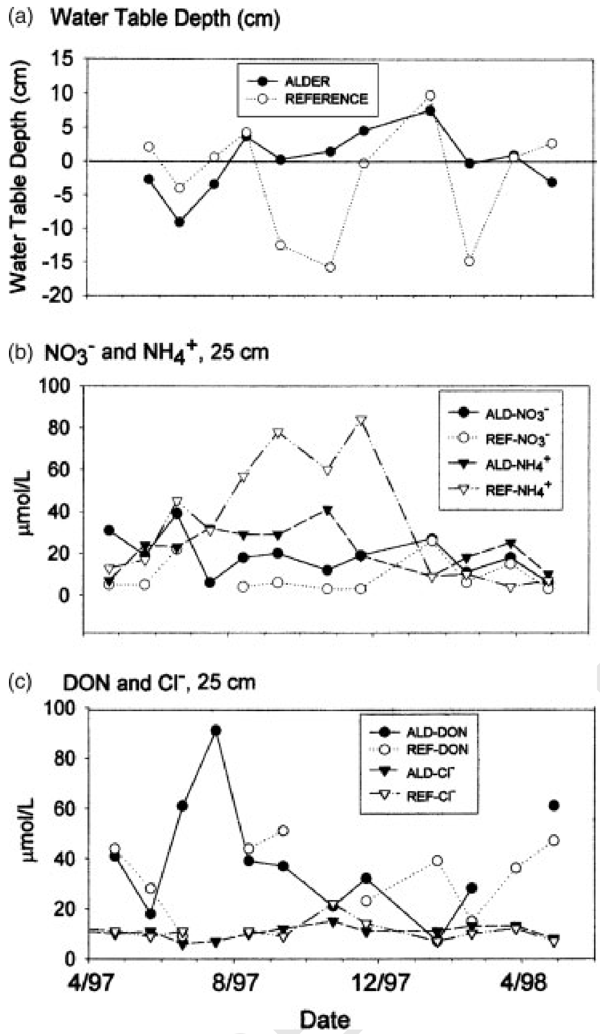

Figure 3. Water table depth above ground surface and solute concentrations in groundwater of alder and reference reaches, 25 cm depth. Solute values are concentration means between 1 and 11 m from the stream ($n = 9$): (a) Water table depth; (b) NH_4^+ and NO_3^-; (c) DON and chloride

Ammonium concentration at this depth increased through the growing season in the alder wetland, peaked in August, then steadily declined through the dormant season (Figure 5b). This did not occur in the reference wetland, where NH_4^+ remained $\leq$10 µmol l^{-1}.

DON at the alder site was significantly less at 125 cm than at 25 cm between June 1997 and April 1998, except for November and January, and increased from 14 µmol l^{-1} in April 1997 (38% of TDN) to 38 µmol l^{-1} (57% of TDN) in July 1997. Concentrations of DON then rapidly decreased as DIN concentrations increased in late summer. DON also increased in the reference site, from 11 µmol l^{-1} (41% of TDN) in April 1997 to 27 µmol l^{-1} (69% of TDN) in August 1997.

Spatial gradients in riparian groundwater nitrogen

April: late snow melt. In April 1997, the greatest DIN concentrations, dominated by NH_4^+, occurred close to the stream at 75 cm in the alder site (Figure 6a). DIN at 25 cm did not vary widely across the alder reach, and was dominated by NO_3^- (Figure 6a and b).

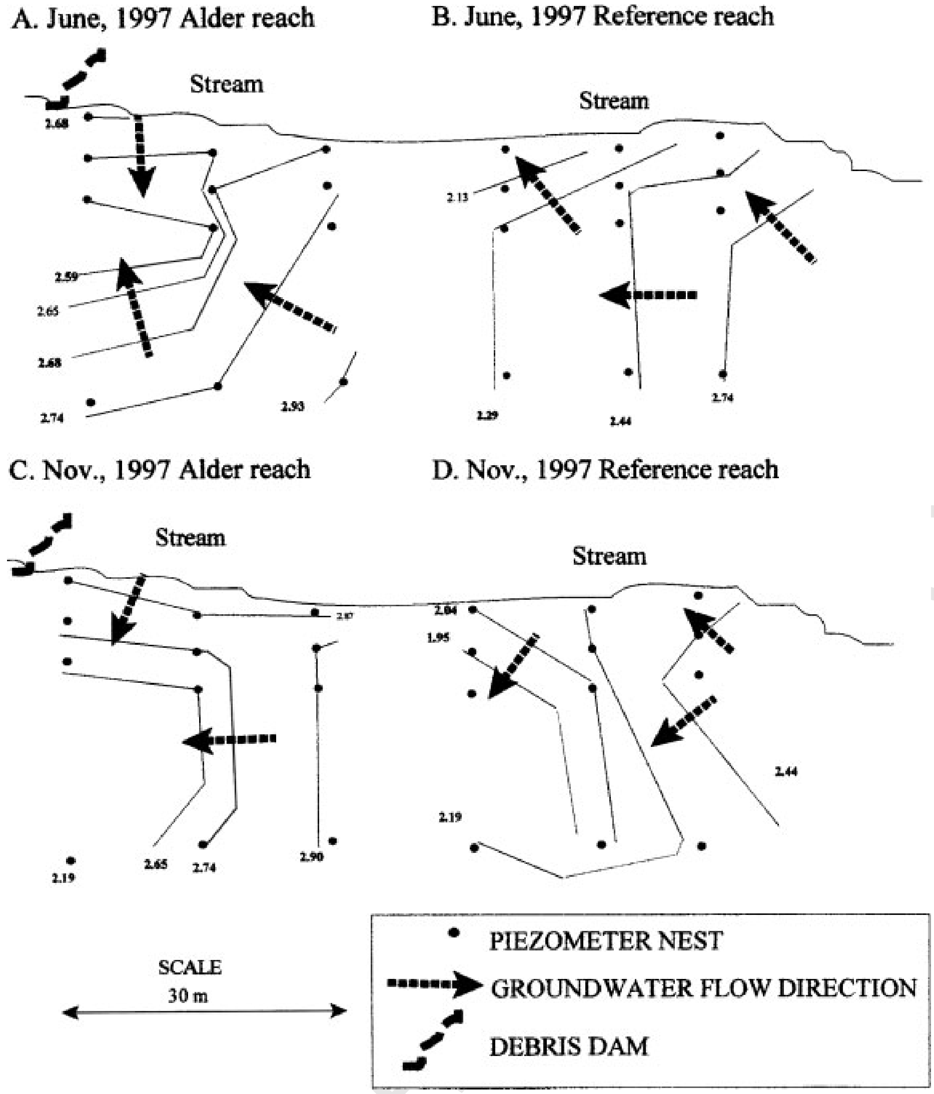

Figure 4. Groundwater flow in alder and reference reaches. Elevations of piezometric surfaces are for 75 cm depth piezometers, relative to an arbitrary datum of 3·05 m: (a) June 1997, alder; (b) June, 1997, reference; (c) November 1997, alder; (d) November 1997, reference

Estimated channel water contribution to groundwater at 75 cm in the alder site was 21% at 1 m, 40% at 6 m, 16% at 11 m, and 0% at the hillslope margin. Groundwater Cl^- concentrations did not vary widely by site or distance from stream at 25 cm (Figure 6c), and suggest source water fractions of 50–76% channel water in the alder wetland at this shallow depth. Loss of channel water behind the debris dam occurred in the alder reach during this month of high flow.

June 1997: early growing season. In June 1997, no significant differences in nitrogen gradients were detected between sites (B or Q), with DIN showing a general increase between the hillslope and stream. At 25 cm, near-stream DIN at the alder site was dominated by NO_3^-, and a significant increase between hillslope and stream occurred for NO_3^- at the alder site ($p = 0{\cdot}03$) and DIN at both sites (alder $p = 0{\cdot}02$; reference $p = 0{\cdot}04$) (Figure 7a and b).

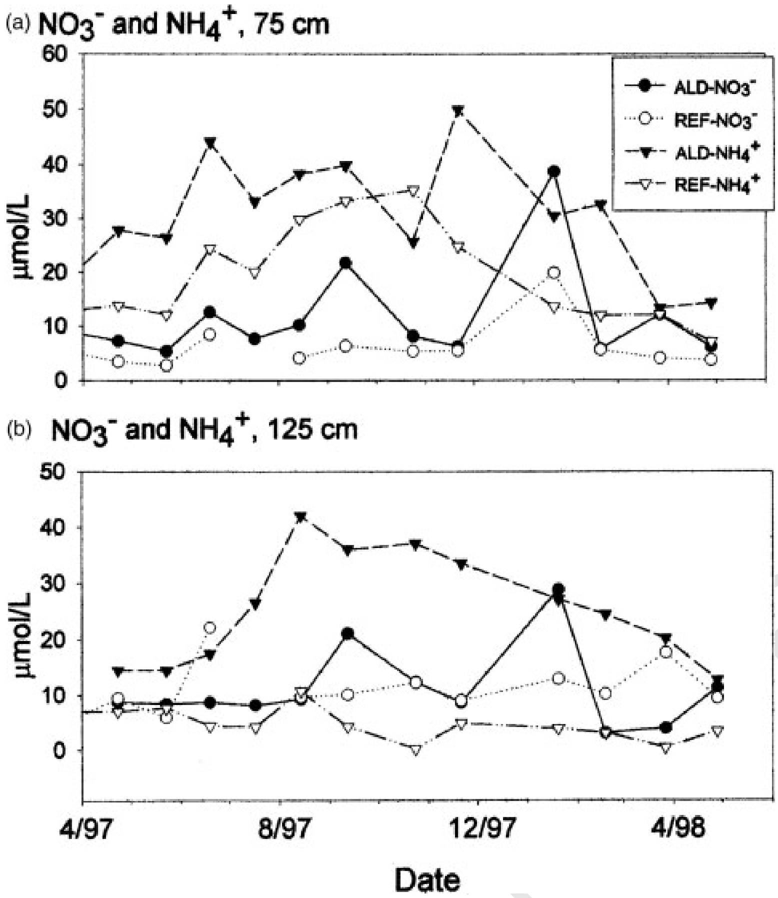

Figure 5. Solute concentrations in groundwater of alder and reference reaches. Values are concentration means between 1 and 11 m from the stream ($n = 9$): (a) NO_3^- and NH_4^+ at 75 cm depth; (b) NO_2^- and NH_4^+ at 125 cm depth

Figure 7c shows the Cl^- concentrations of shallow groundwater. Water at 25 cm depth at the alder site in June was an estimated 100% groundwater at the hillslope boundary, but 87–100% surface water between 1 and 12 m from the stream. In contrast, near-stream groundwater at 75 cm was estimated to be 0–30% channel water. Horizontal groundwater flow at 75 cm in June 1997 was dominated by flow toward the stream, except near the debris dam in the alder reach (Figure 4a and b).

November: dormant season prior to snow cover. In November 1997, DIN at 75 cm was greatest (129 µmol l^{-1}) at the alder site next to the stream, dominated by NH_4^+ (Figure 8a). A significant gradient in NH_4^+ occurred between hillslope and stream (B, $p = 0{\cdot}01$; Q, $p \leq 0{\cdot}01\bullet$) at the alder site only, causing a significant linear (B, $p = 0{\cdot}04$) and quadratic (Q, $p = 0{\cdot}01$) distance by site interaction. AQ6

Concentrations of DIN at 25 cm between hillslope and stream varied between 30 and 50 µmol l^{-1} for the alder reach and between 30 and 144 µmol l^{-1} at the reference reach due to the high NH_4^+ concentrations. The greatest NO_3^- concentrations, 22 µmol l^{-1} (Figure 8b) occurred at the alder site close to the stream.

Groundwater Cl^- concentrations were similar between sites and depths, except at 25 cm in the alder reach where channel water diluted Cl^- (Figure 8c). Estimated channel water contribution to groundwater at 25 cm was 100% at 1 m, 55% at 6 m, 86% at 11 m, and 0% at the hillslope margin. NO_3^- was correlated positively, and NH_4^+ negatively, with percentage channel water at 25 cm (Figure 9). Estimated channel water

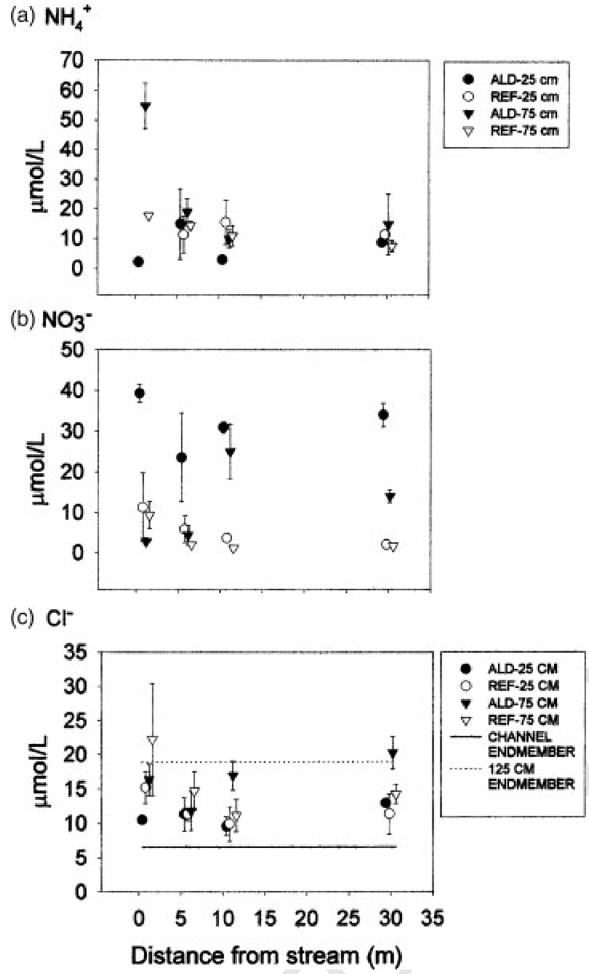

Figure 6. Spatial patterns of groundwater solutes across alder and reference reaches at 25 and 75 cm depths, April 1997: (a) DON ($NO_3^- + NH_4^+$); (b) NO_3^-; (c) chloride. Values are mean plus/minus standard error

contribution to groundwater at 75 cm was 33% at 1 m, 55% at 6 m, 80% at 11 m and 29% at the base of the hillslope. Groundwater flow patterns in the alder reach in November 1997 showed channel water loss to shallow groundwater just upstream of the debris dam, and mixing with discharging and hillslope groundwater 10–15 m from the stream (Figure 4c).

January 1998: mid-winter thaw. The greatest concentrations of NO_3^- in groundwater (60 μmol l^{-1}) occurred immediately next to the stream in January 1998 at 75 cm, where NO_3^- and NH_4^+ were elevated similarly (Figure 10a). A significant quadratic distance by site interaction occurred at 75 cm for NH_4^+ (Q, $p = 0{\cdot}04$), and a significant linear distance by site interaction occurred at this depth for DIN (B, $p = 0{\cdot}05$). Slopes of these gradients differed from zero for NH_4^+ (Q, $p = 0{\cdot}02$), DIN (B, $p = 0{\cdot}03$), and NO_3^- (B, $p = 0{\cdot}06$) at the alder site only.

NO_3^- and NH_4^+ did not differ between sites at 25 cm (Figure 10b). At the alder site, NO_3^- at 25 cm was positively correlated with percentage channel water ($r^2 = 0{\cdot}95$), whereas greatest NO_3^- and NH_4^+ at 75 cm occurred close to the stream with 0% channel water.

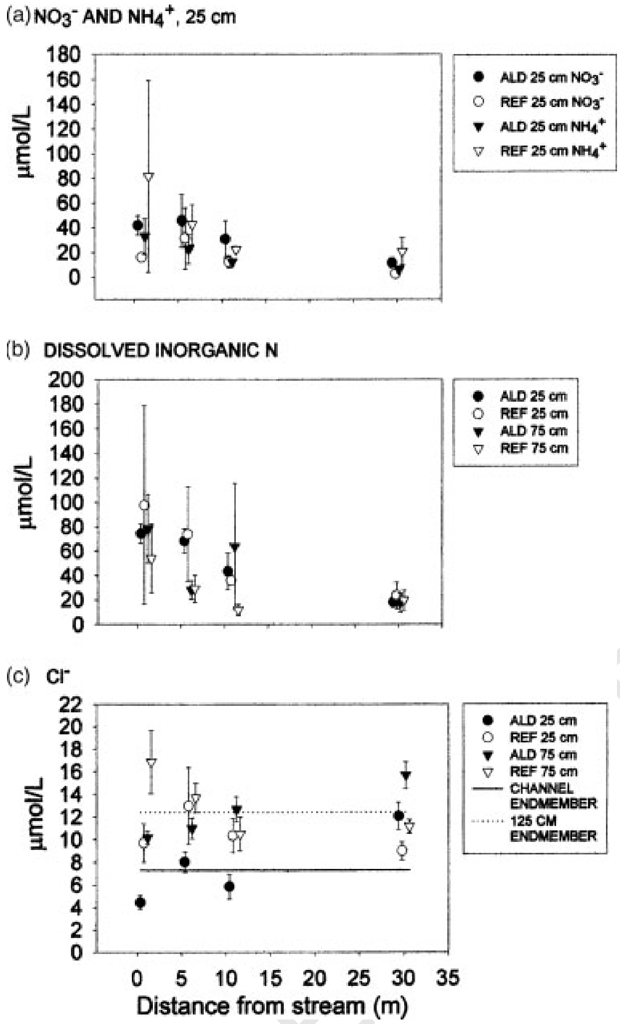

Figure 7. Spatial patterns of groundwater solutes across alder and reference reaches, June 1997: (a) NO_3^- and NH_4^+ at 25 cm depth; (b) DON ($NO_3^- + NH_4^+$) at 25 and 75 cm depths; (c) chloride at 25 and 75 cm depths. Values are mean plus/minus standard error

Groundwater Cl^- concentrations at 25 cm within the alder reach decreased strongly between the hillslope and stream (Figure 10c). Estimated channel water contribution to groundwater at 75 cm was 0% at 1 m from the stream, 14% at 11 m, and 2% at the hillslope margin. Estimated channel water contribution to groundwater at 25 cm was 100% at 1 m, 37% at 11 m, and 0% at the hillslope margin.

DISCUSSION

Channel water seasonal patterns in nitrogen concentration

NO_3^- concentration of channel water was consistently elevated in the alder reach (Figure 2a). Site differences in channel water NO_3^- were greatest during April 1997, and peak NO_3^- concentrations in 1998 occurred in a January thaw. Both peaks corresponded with melt-induced discharge (Figure 2), and thus with peak NO_3^- exports. Peak NO_3^- in summer (Figure 2a) occurred at the alder site during the

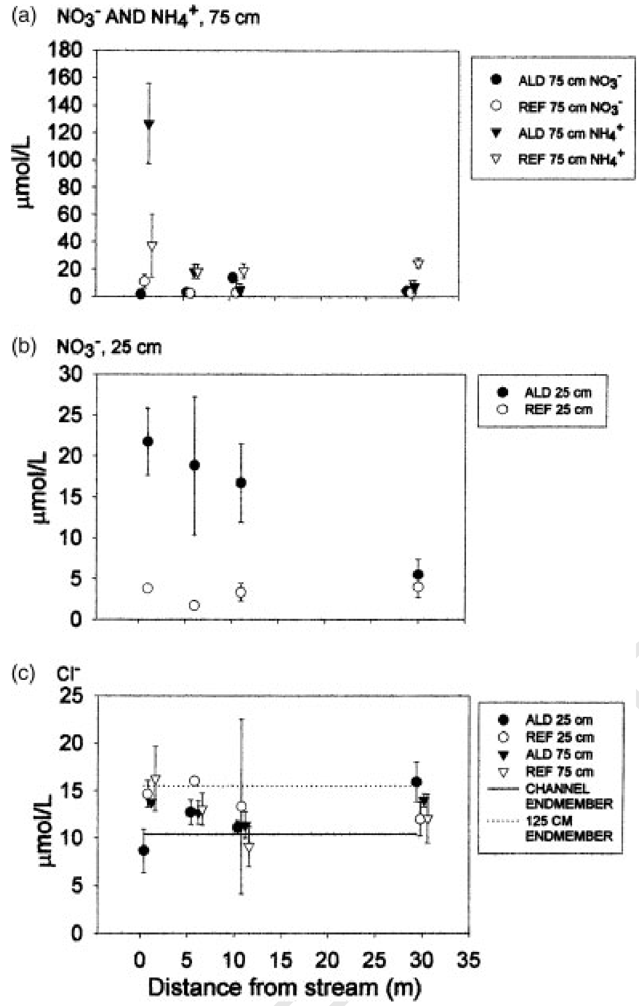

Figure 8. Spatial patterns of groundwater solutes across alder and reference reaches, November 1997: (a) NO_3^- and NH_4^+ at 75 cm depth; (b) NO_3^- at 25 cm depth; (c) chloride at 25 and 75 cm depths. Values are mean plus/minus standard error

onset of an August rain event (33 mm), following peaks in 25 cm groundwater NO_3^- in June (Figure 3b). Elevated NO_3^- in shallow peat of the alder wetland prior to an event-induced increase in channel water NO_3^- suggests that nitrification during periods of low water table (Figure 3a) may have contributed to an NO_3^- flush in the ensuing event (Creed *et al.*, 1996). Voigt and Steucek (1969) concluded that speckled alder contributes NO_3^- to surface water based on a small sample of channel water above (5 µmol l^{-1}) and below (8 µmol l^{-1}) alders in Connecticut, USA. Goldman (1961) measured greater NO_3^- in spring water with *A. incana* ssp. *tenuifolia* (5 µmol l^{-1}) than without (0·5 µmol l^{-1}), between June and October, at Castle Lake California, USA. Photosynthetic activity within the lake was also greater on the side of the lake with alder springs, indicating that alder-fixed nitrogen alleviated nitrogen limitation of aquatic organisms (Goldman, 1961). It is possible that till-derived NO_3^- contributed to the differences in NO_3^- in channel water in the present study, flowing via steep drainage patterns in the watershed and entering the stream between the two study reaches. However, we found relatively low NO_3^- concentrations in shallow (125 cm) near-stream substrate.

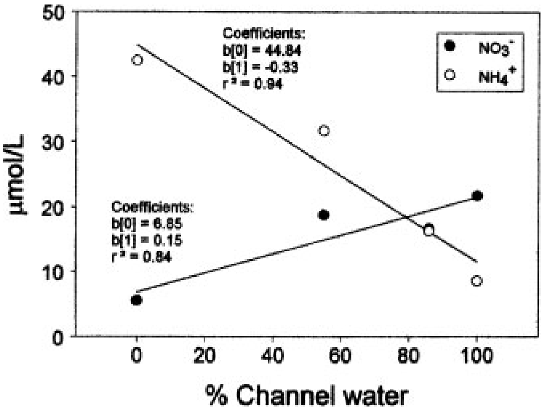

Figure 9. Linear relationships between channel water fraction in groundwater and NO_3^- and NH_4^+ concentration in groundwater at 25 cm depth, November 1997

As much as 60% of TDN in channel water during summer was DON; this shows the importance of seasonal nitrogen loss as DON in watersheds that are influenced by nitrogen deposition, as well as in undisturbed watersheds (Hedin *et al*., 1995). However, DON concentration did not differ in the two reaches throughout the sampling period.

Seasonal trends in groundwater nitrogen

25 cm depth. Elevated NO_3^- in the alder wetland and similar Cl^- concentrations in the two wetlands indicate that a common source of water was enriched in NO_3^- in the alder reach. Estimated channel water fractions of 50–76% and the loss of water from the stream in April 1997 suggest that channel water contributed to elevated NO_3^- in shallow peat of the alder wetland. Oxidized channel water could have been a direct NO_3^- source, or an O_2 source to nitrifying organisms, as soil-derived NO_3^- may dominate NO_3^- leaching in melt events in the region (Rascher *et al*., 1987; Kendall, 1998). Nitrate in the alder reach at 25 cm remained elevated relative to the reference after channel water concentrations had decreased and biotic uptake had commenced, suggesting net NO_3^- production, concurrent with increasing DON concentrations (Figure 3).

Inorganic nitrogen accumulated as NH_4^+ in the rooting zone of both wetlands during the growing season (Figure 3b). Summer peaks in DON in shallow groundwater were approximately two times greater at 25 cm than at 125 cm, and preceded or coincided with peak DIN concentrations. These patterns suggest that this DON was wetland derived and was later transformed to NH_4^+ or NO_3^-.

75 cm depth. High NH_4^+ concentrations at 75 cm in both wetlands may have resulted from ammonification of organic nitrogen through the summer and early autumn, or non-assimilatory reduction of NO_3^- (Hill, 1996) advected from the channel. The latter mechanism seems less likely, because NH_4^+ accumulated in the reference wetland, where hydrologic gradients were directed toward the channel. Minimum NH_4^+ concentrations at depth occurred in March or April in both years, corresponding to peaks in channel water NO_3^-. Nitrate at 25 and 75 cm increased during the winter declines in NH_4^+, suggesting that NH_4^+ was nitrified and then flushed from the peat. NO_3^- flushing is hypothesized to occur after nitrification is facilitated by a lowered water table, and NO_3^- is flushed into the stream as the water table rises through the unsaturated zone in ensuing rain or melt events (Creed *et al*., 1996; Cirmo and McDonnell, 1997). This mechanism seems likely for these systems, because more NO_3^- is present during autumn in dense alder stands than in other wetlands AQ7 (Kiernan• *et al*., 2002), and because the riparian zone floods substantially during winter (Figure 3a).

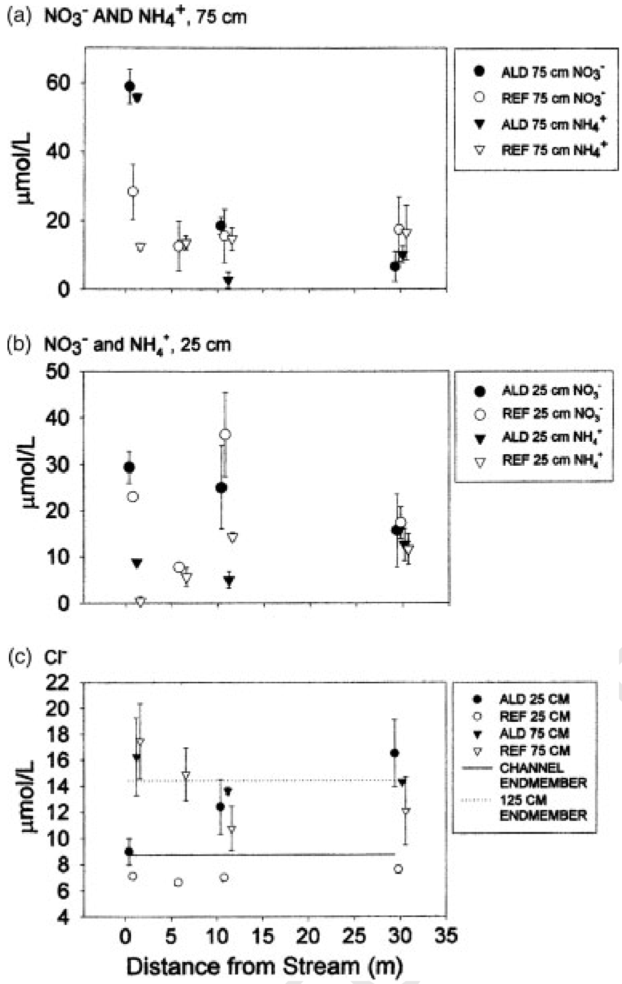

Figure 10. Spatial patterns of groundwater solutes across alder and reference reaches, January 1998: (a) NO_3^- and NH_4^+ at 75 cm depth; (b) NO_3^- and NH_4^+ at 25 cm depth; (c) chloride at 25 and 75 cm depths. Values are mean plus/minus standard error

125 cm depth. NO_3^- concentrations at 125 cm in the alder stand were ≤ 10 μmol l^{-1} in April 1997, the period of greatest NO_3^- concentrations in shallow horizons. These data indicate that groundwater in shallow mineral substrate was not a source of NO_3^- during peak NO_3^- discharge in April 1997.

Spatial gradients in riparian groundwater nitrogen

In April 1997, DIN dominated by NH_4^+ was elevated close to the stream at 75 cm in the alder reach (Figure 6a). Both piezometric and Cl^- data showed channel water influx to the alder wetland. Whether near-stream nitrogen at 75 cm was derived from channel water or ammonification is uncertain. NO_3^- dominating the DIN at 25 cm in the alder reach (Figure 6b) may have been derived from the stream, or from nitrification within or above the reach, as channel water contributed strongly to shallow groundwater. It is not likely that this NO_3^- was directly from meltwater, as low NO_3^- concentrations occurred in the reference wetland where melt was still occurring, and Cl^- concentrations suggested strong channel water source to shallow soils.

In June 1997, water at 25 cm depth at the alder site was an estimated 100% groundwater at the hillslope boundary, but was 87–100% channel water between 1 and 11 m from the stream. NO_3^- concentrations at 25 cm depth 1–11 m from the stream were two or more times that of 125 cm groundwater or channel water (Figures 2a, 5a, and 7a), suggesting that near-stream nitrification rates were elevated during a period of low water table (Figure 3a), and that denitrification and biotic uptake were low. Triska *et al*. (1993) found a low denitrification potential and a high nitrification potential of near-channel sediment slurries, each attributable to high O_2 supply from advected channel water. Denitrification potential further from the channel, where exchange flow was unimportant, was limited by NO_3^- (Triska *et al*., 1993). NO_3^- limitation of denitrification also occurred in a permanently saturated *A. glutinosa* swamp (Westermann and •Kiær Ahring 1987). Hedin *et al*. (1998) found denitrification limited by dissolved organic carbon (DOC) in riparian sediments in Michigan, USA. Supply of DOC and associated organic acids in some Adirondack surface waters is positively correlated with percentage of watershed as wetland (Driscoll *et al*., 1998), and so DOC may not limit wetland denitrification in these systems. Modeled DIN output from the same watersheds is negatively correlated with % wetland area, implicating broad classes of wetlands as DIN sinks (Driscoll *et al*., 1998). In a broad survey of temperate fens and bogs, alder-dominated fens demonstrated the highest rates of denitrification (Aerts *et al*., 1999), but denitrification rates and limits are expected to vary in wetlands of different flooding regimes (Gold *et al*., 1998).

In November, NO_3^- at 25 cm increased to 22 μmol l^{-1} close to the stream at the alder site (Figure 8b). The positive correlation between NO_3^- and the percentage channel water (Figure 9), and the hydrologic flow lines (Figure 4c) suggest that NO_3^- at this shallow depth was stream derived. However, NH_4^+ reached 129 μmol l^{-1} at 75 cm next to the stream in the alder reach, and may have been substrate for nitrification at the redoxcline between these two depths (Triska *et al*., 1989; Cirmo and McDonnell, 1997). Lack of correlation of NH_4^+ at 75 cm with percentage channel water ($r^2 = 0{\cdot}23$) shows little channel water influence on the elevated NH_4^+ concentrations.

The greatest NO_3^- concentrations at 75 cm (60 μmol l^{-1}) occurred in the alder reach within 1 m from the stream in January 1998 (Figure 10a). NO_3^- concentrations of channel water (Figure 2a) and 125 cm groundwater (Figure 5b) were less, indicating that the hyporheic zone is a source for NO_3^-. This pattern fits the conceptual model of Triska *et al*. (1989), where the interactive hyporheic zone hosts nitrification stimulated by groundwater-derived NH_4^+ and stream-derived O_2, and demonstrates higher NO_3^- concentration than either channel water or groundwater. Moreover, NO_3^- was not derived from horizontally flowing groundwater at this depth, because of low DIN further from the stream (Figure 10a). Slopes of NH_4^+ and DIN increased between hillslope and stream at the alder site only, and percentage channel water at 75 cm was low across the wetland (0–14%), indicating that the alder wetland was a source of DIN to ground and stream water. Mean NO_3^- concentrations at 25 cm varied little between sites or with distance from the stream (Figure 10b), indicating a similar meltwater influence on shallow NO_3^- in both wetlands.

CONCLUSIONS

Subsurface DIN concentrations were consistently greatest in the alder wetland, close to the stream, and NO_3^- concentrations in channel water were greater in the alder reach than in the upstream reference reach, particularly during peaks in stream water discharge and NO_3^- concentration. These patterns suggest that alder shrub wetlands do not decrease nitrogen in groundwater flowing between hillslopes and streams, but may even increase nitrogen solutes in riparian ground and surface waters. Groundwater in shallow till or alluvium (125 cm) had low NO_3^- concentrations relative to shallower groundwater in the alder reach. These results suggest that nitrification is stimulated in shallow peat in the presence of alders and oxidized exchange flow, and that the NO_3^- produced is transported to the channel. Ammonium and DON concentrations increased through the growing season in both wetlands, then decreased through the dormant season, suggesting that riparian groundwater is an important transient nitrogen pool regardless of cover type. The wetlands in this study were classified by dominant wetland cover labels in the region, forested conifer (FO4) and alder-dominated SS1 (Roy *et al*., 1996), and differed in pattern, and likely in source and processing of nitrogen solutes. To understand better the role of riparian wetlands in mediating nitrogen concentrations in streams, future studies should examine the specific fate of nitrogen fixed within alder shrub wetlands, as well as of hillslope-derived nitrogen that is discharged into these naturally nitrogen-rich wetlands, prior to entering surface waters.

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