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Wetland nitrogen dynamics in an Adirondack forested watershed

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Abstract:

Wetlands often form the transition zone between upland soils and watershed streams, however, stream–wetland interactions and hydrobiogeochemical processes are poorly understood. We measured changes in stream nitrogen (N) through one riparian wetland and one beaver meadow in the Archer Creek watershed in the Adirondack Mountains of New York State, USA from 1 March to 31 July 1996. In the riparian wetland we also measured changes in groundwater N. Groundwater N changed significantly from tension lysimeters at the edge of the peatland to piezometer nests within the peatland. Mean N concentrations at the peatland perimeter were 1·5, 0·5 and 18·6 μmol L^{-1} for NH_4^+, NO_3^- and DON (dissolved organic nitrogen), respectively, whereas peatland groundwater N concentration was 56·9, 1·5 and 31·6 μmol L^{-1} for NH_4^+, NO_3^- and DON, respectively. The mean concentrations of stream water N species at the inlet to the wetlands were 1·5, 10·1 and 16·9 μmol L^{-1} for NH_4^+, NO_3^- and DON, respectively and 1·6, 28·1 and 8·4 μmol L^{-1} at the wetland outlet. Although groundwater total dissolved N (TDN) concentrations changed more than stream water TDN through the wetlands, hydrological cross-sections for the peatland showed that wetland groundwater contributed minimally to stream flow during the study period. Therefore, surface water N chemistry was affected more by in-stream N transformations than by groundwater N transformations because the in-stream changes, although small, affected a much greater volume of water.

Stream water N input–output budgets indicated that the riparian peatland retained 0·16 mol N ha^{-1} day^{-1} of total dissolved N and the beaver meadow retained 0·26 mol N ha^{-1} day^{-1} during the study period. Nitrate dominated surface water TDN flux from the wetlands during the spring whereas DON dominated during the summer. This study demonstrates that although groundwater N changed significantly in the riparian peatland, those changes were not reflected in the stream. Consequently, although in-stream changes of N concentrations were less marked than those in groundwater, they had a greater effect on stream water chemistry—because wetland groundwater contributed minimally to stream flow. Copyright © 2004 John Wiley & Sons, Ltd.

KEY WORDS Adirondack Mountains; hyporheic zone; nitrogen; riparian; wetland; dissolved organic nitrogen

INTRODUCTION

During the past two decades many researchers have studied the effect of near-stream wetlands on stream water N chemistry. Wetlands often form the transition between upland soils and the watershed outlet, and consequently, the transformation, retention or mobilization of N at these ecotonal boundaries can regulate N concentration at the watershed outlet.

Hill (1996) suggested that a better understanding of NO_3^- regulation in riparian zones requires that patterns of NO_3^- removal in the near-stream zone be related to groundwater flowpaths. The effect of riparian zones

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on groundwater NO_3^- transport depends on the interaction of NO_3^- with vegetation and sediments, flow pathways and residence time. The vegetation and sediments of some riparian wetlands may be hydrologically isolated so that upland water may bypass the biologically active components of the wetland by flowing under or through riparian wetlands with little chemical transformation (Bowden, 1987). The N cycling characteristics of these active biological and hydrogeological systems change rapidly (i.e. on the time-scale of hours to days) especially during rainfall and snowmelt–runoff events (Cirmo and McDonnell, 1997), therefore the frequency of chemical and hydrological measurements can be important. Wetland N retention can vary seasonally with net export during dormant season high flows and net retention confined to biologically active seasons (Devito *et al*., 1989). Additional research is needed that integrates hillslope- and plot-scale wetland research with watershed-scale hydrological processes to better understand how wetland processes affect watershed scale N fluxes (Price and Waddington, 2000).

Varied results from N cycling studies during the past two decades show the effect that differences in the biological and hydrogeological setting can have on wetland N cycling. High rates of NO_3^- removal have been measured in wetlands bordering agricultural lands in Maryland (USA), North Carolina (USA), Scotsman Valley (New Zealand) and Rabis Bæk (Denmark) (Brinson *et al*., 1984; Peterjohn and Correll, 1984; Cooper, 1990; Brüsch and Nilsson, 1993). Burns and Nguyen (2002) measured removal of injected NO_3^- in groundwater within a wetland bordering pastoral land in Hamilton, New Zealand, but found little or no retention of storm water NO_3^- transported over the surface of the wetland. In a study of N removal efficiency in wetlands in Sweden, denitrification and hydraulic residence time were concluded to be the most important factors for N removal (Jansson *et al*., 1994).

Studies of forested riparian wetlands have not produced consistent results with respect to N retention or loss. In a study of five wetlands on the Canadian Shield, Devito *et al*. (1989) found that there was no significant net retention of N within the wetlands, but there was transformation of inorganic N to organic N. Retention occurred only during summer low flows, with net export during winter and spring. Warwick and Hill (1988) observed conservative transport of added NO_3^- in two rivulets within a small forested wetland in southeastern Ontario, Canada. Limited N loss was attributed to low initial NO_3^- concentrations in surface and groundwater and short hydraulic residence time within the riparian zone. In ponded systems, where hydraulic residence times are long, headwater wetlands may act as sinks for NO_3^- (Cirmo and Driscoll, 1993). Within-stream NO_3^- loss or transformation also can be an important N sink (Grimm and Fisher, 1984; Duff and Triska, 1990; Triska *et al*., 1993; Peterson *et al*., 2001).

We examined the effect of two wetlands, one riparian peatland and one beaver meadow, on stream water N concentrations and flux in the Archer Creek watershed in the central Adirondack Mountains of New York State. Groundwater N dynamics were examined in the riparian peatland. Sediment was the largest N pool in the riparian peatland, which was a site of active N cycling (Bischoff *et al*., 2001). These wetlands formed a zone of transition between upland soils and the watershed outlet and therefore could play an important role in regulating N concentrations at the watershed outlet. Watershed outlet NO_3^- concentrations can be in excess of 70 μmol L^{-1} during snowmelt and are about 5 μmol L^{-1} during summer low flows. High NO_3^- concentrations in surface waters can contribute to surface water acidification and the subsequent mobilization of monomeric aluminum as well as downstream eutrophication (Schofield and Trojnar, 1980; Gubala *et al*., 1991). We have focused this study on N dynamics during spring snowmelt and into the growing season because this is the period of maximum N export in the Adirondack Mountains (Schaefer *et al*., 1990; McHale *et al*., 2000).

SITE DESCRIPTION

The study was conducted in the Archer Creek watershed within the Huntington Wildlife Forest in the central Adirondack Mountains of New York State, USA (43° 59′N, 74° 14′W). The 135 ha watershed contains the main inlet stream to Arbutus Lake (Figure 1). The watershed ranges in elevation from 516 to 741 m and is

characterized by steep slopes draining to a flat valley bottom with an average slope of 11%. The watershed is drained by a third-order perennial stream that ranged in flow at the outlet from 0·0001 to 4·5 mm h^{-1} from 1 January 1995 to 31 December 1998. Flow at the watershed outlet was measured every 15 min at an HL-Flume installed in January 1995. The climate is cool, moist and continental. Precipitation averaged 1010 mm and the mean annual temperature was 4·4 °C from 1951 to 1980 (Shepard *et al*., 1989). We have chosen to define the water year the same as that used for Hubbard Brook Experimental Watershed, 1 June to 31 May (Likens and Bormann, 1995). Hubbard Brook has a similar climate and hydrological properties as the uplands at the Archer Creek watershed, but a much longer record of stream flow (Scott, 1987; Likens and Bormann, 1995). During the 1995–1996 hydrological year at Archer Creek (1 June to 31 May) precipitation totalled 1298 mm and 47% of outflow occurred from March through to May. Ninety-three per cent of total dissolved N export during the 1995–1996 hydrological year occurred during the dormant season (October–May) (McHale *et al*., 2000).

Overstory vegetation on the upland watershed slopes is a mixed northern hardwood forest composed of *Fagus grandifolia* Ehrh. (American beech), *Acer saccharum* Marsh. (sugar maple), *Betula alleghaniensis* Britt. (yellow birch); conifers including *Picea rubens* Sarg. (red spruce), and *Abies balsamea* (L.) Miller (balsam fir) are present at higher elevations and at the valley bottom. *Pinus strobus* (white pine) is found at the uppermost elevations in the watershed. Mineral soils on watershed slopes are coarse, loamy, mixed frigid, Typic Haplorthods in the Becket–Mundal association, and are typically <1 m in thickness (Somers, 1986). Soils are underlain by a thin bouldery glacial till derived from local bedrock. Bedrock in the watershed is mainly granitic gneiss with some gabbro–amphibolite.

Two wetlands were studied, one, a riparian peatland (Figure 1), was dominated by *Picea rubens, Betula alleghaniensis, Alnus incana* (L.) Moench. (N fixing speckled alder) and *Acer rubrum* (red maple). The herbaceous undergrowth in the peatland was dominated by *Sphagnum* spp., *Osmunda cinnamomea* and a variety of sedges (Bischoff *et al*., 2001). The second wetland was an abandoned beaver meadow (Figure 1)

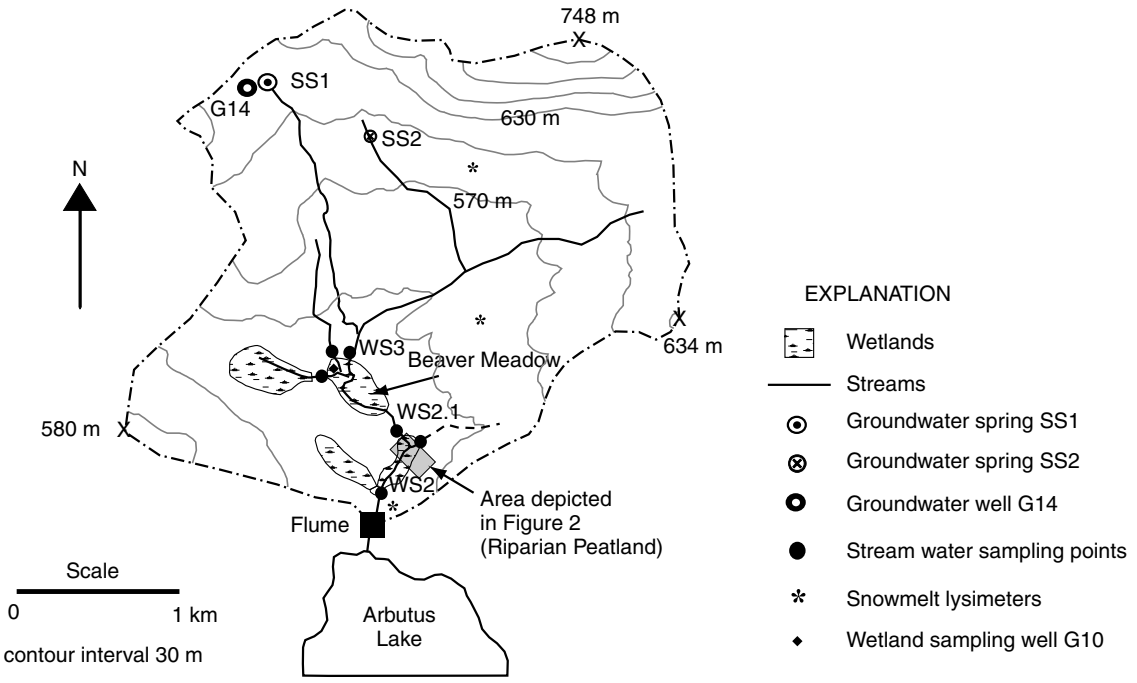

Figure 1. The Archer Creek watershed Huntington Wildlife Forest, New York State

upstream from the peatland, which had been free of beaver activity for 10–15 years, as evidenced by an abandoned dam and the initial stages of overstory regrowth. The overstory in the beaver meadow consisted of standing dead timber with *P. rubens* present along the margins. Herbaceous vegetation in the wetland was dominated by a variety of graminoids (grasses and sedges) with some *Sphagnum* spp. These two wetlands are typical of near-stream wetlands throughout the Adirondack Mountains that are often affected by beaver activity. Wetlands comprise 4% of the Archer Creek watershed as estimated from a watershed map.

Soils in the riparian peatland are Greenwood Mucky peats (Somers, 1986) that range from 1 to 5 m in thickness. Several coarse sand layers are present from 0·5 to 1·5 m depths in the peatland. The thickness of peat and the presence of sand layers were detected using ground penetrating radar (GPR), and by taking cores using a Russian peat borer (Bricker-Urso *et al*., 1989). The GPR estimates of peat depth were confirmed by inserting a stainless steel rod into the peat until the peat–till interface was reached. The peat–till interface was identified when the rod met with substantial resistance and sandy clay was observed on the rod tip. Soils in the beaver meadow were a mixture of Greenwood Mucky peats and hydric soils with a high sand content. The streams within the beaver meadow did not pass through the largest peat deposit which was located along the north-eastern edge of the beaver meadow.

Both of the wetlands are depressional wetlands that form the transition between the upland areas of the watershed and the outlet where the stream drains into Arbutus Lake. Essentially all of the water leaving the watershed passed through these wetlands either as surface or groundwater flow. The beaver meadow has three surface water inlets and one surface water outlet. Archer Creek is the main channel within the beaver meadow and is fed by two smaller tributaries within the wetland (Figure 1). The peatland has one surface water inlet and one surface water outlet. There is a small rivulet that forms at the base of a watershed hollow at the peatland perimeter. Surface flow in the hollow was intermittent and occurred only during the high flows associated with snowmelt. At the peatland perimeter, water from the hollow created a zone of permanent saturation that formed the rivulet. The water table was always within 0·05 m of the peatland surface during the study in monitoring well M2 located adjacent to the permanently saturated zone at the base of the hollow (Figure 2); the water table in well M2 showed little fluctuation compared with monitoring well M1 located adjacent to Archer Creek (Figure 2).

METHODS

Hydrology

Precipitation and air temperature were recorded at a meteorological station operated by the Huntington Wildlife Forest 1·5 km from the Archer Creek watershed. Stream discharge was monitored at 15-min intervals at an HL-Flume at the watershed outlet throughout the study period. Discharge at other stream sampling sites was estimated by prorating discharge at the flume by drainage area (Devito and Dillon, 1993). The elevation of the water table in the riparian peatland was monitored at two locations, at the break in the hillslope at the wetland boundary (monitoring well M2) and 5 m from the stream (monitoring well M1) (Figure 2). Water table elevation was recorded hourly using pressure transducers inserted into 50·8 mm diameter wells installed to a depth of 1·5 m and screened the entire interval. A total of 11 piezometer nests (containing two or three piezometers each) were installed in three transects parallel to the stream channel in the peatland (Figure 2). The piezometers were constructed from 12·7 mm diameter PVC pipe slotted for 0·1 m at the bottom, screened with nylon mesh to prevent siltation and installed to depths of 0·5, 1·5 and 2·5 m. Hydraulic head readings were taken manually biweekly using a water level indicator and a network of boardwalks across the wetland. Water samples were collected from piezometers biweekly throughout the study period. Owing to low recharge rates, head readings were taken, piezometers were pumped dry, capped and water samples were taken 1 or 2 days later. Groundwater samples were pumped slowly into the collection vessel to prevent oxidation of the samples. Individual piezometers yielded a small volume of water, which made it necessary to composite water samples at each piezometer depth within each transect parallel to the stream. For example, all 0·5 m

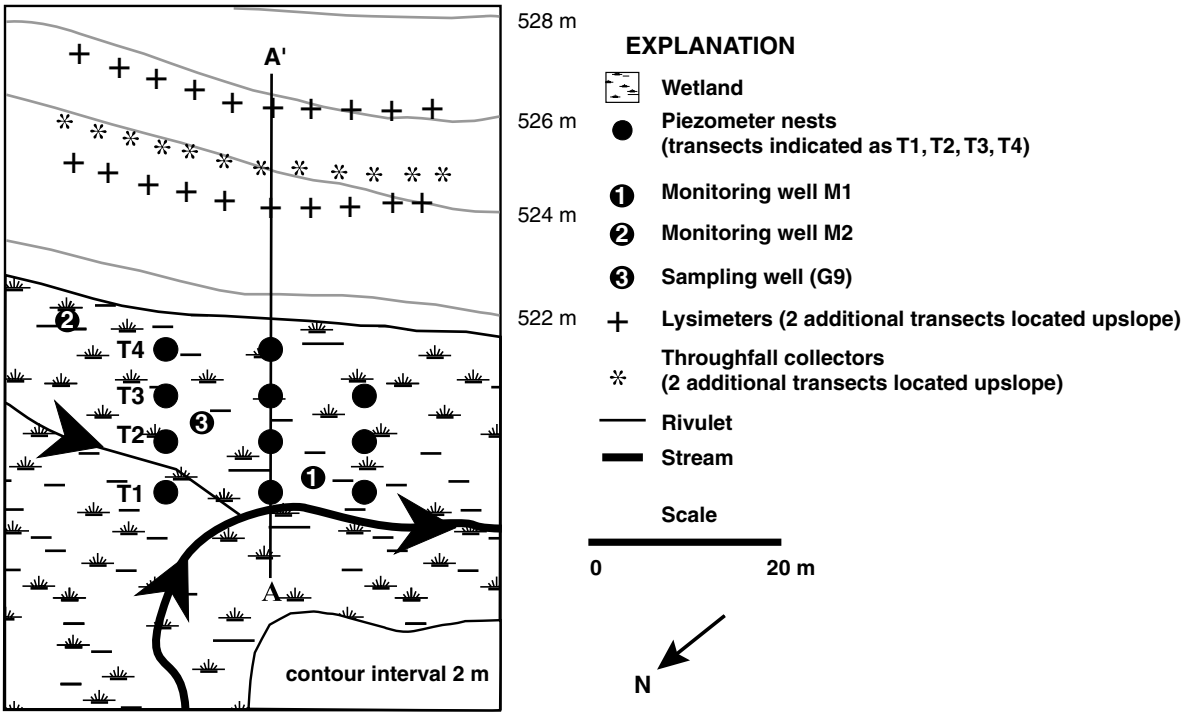

Figure 2. Riparian peatland instrumentation (Location is shown in Figure 1)

depth piezometers in transect T1 were combined into one sample. Compositing groundwater samples within transects limited our ability to describe the spatial variability of groundwater chemistry in the wetland to the variability across transects. Therefore the chemistry reported for the piezometers is an average condition across the area of the wetland encompassed by the piezometers in each transect. This sampling strategy did allow us to describe the variability of wetland groundwater at each depth at 5-m intervals from the hillslope to the stream. Five piezometer nests were selected randomly for hydraulic conductivity measurements using the Hvorslev water level recovery test (Freeze and Cherry, 1979). All wetland instrumentation and grid points were surveyed and the survey grid was georeferenced using a Trimble Pathfinder® Global Positioning System unit.

Water chemistry

Stream samples were collected at the watershed outlet (the HL-Flume), at all surface water inlets to the wetlands, at the wetland outlets and at two sites in the headwaters of the watershed (SS1 and SS2) (Figure 1). Samples were collected approximately daily from 1 March 1996 to 30 April 1996 and weekly from 1 May 1996 to 31 July 1996. Stream sampling sites were selected to quantify stream water chemistry at the watershed outlet, at the inlets and outlets of the wetlands, and at sites in the headwaters to provide stream water chemistry in the upland area of the watershed. Mineral soil water was collected using 1 bar porous cup tension lysimeters (38 mm diameter) at depths of 0·15 and 0·5 m. Lysimeters were evacuated to 276 kPa one day prior to sampling. Three transects of ten pairs of lysimeters each were co-located with throughfall collectors with one additional transect located at the break in the hillslope at the valley bottom (Figure 2).

All water chemistry samples were collected in clean, opaque, 500 mL polyethylene bottles and stored at 4 °C until analysed using suppressed ion chromatography (NO_3^- and Cl^-), ion coupled plasma injection (Ca^{2+} and Mg^{2+}), atomic adsorption spectroscopy (Na^+ and K^+) and a Wescan Ammonia Analyzer (NH_4^+) (Shepard

et al., 1989). Total dissolved N (TDN) was determined by persulfate digestion (Ameel *et al*., 1993). Dissolved organic N (DON) concentration was calculated by subtracting dissolved inorganic nitrogen ($NO_3^- + NH_4^+$) from TDN. If $NO_3^- + NH_4^+$ equalled or exceeded TDN (<3% of all samples), DON was recorded as zero.

Solute budgets

Solute flux was estimated at the three inflows to the beaver meadow, at the two inflows to the peatland and at the outlet of the peatland (Figure 1). Fluxes were estimated by multiplying total daily flow by daily stream water concentration at each site. Daily concentrations were linearly interpolated between sampling points for days that samples were not collected (McHale *et al*., 2000). Solute fluxes for multiple inflows to each wetland were summed to obtain the total surface water solute input to the wetlands. Percent retention (%RS) was calculated as $\%RS = ((\text{surface water input} - \text{surface water output})/\text{surface water input}) \times 100$ (Devito and Dillon, 1993). A negative net retention value indicated a net loss.

Error estimates

Fisher and Likens (1973) found that estimates of annual discharge based on watershed area were ±10% of empirical measurements in Bear Brook watershed, New Hampshire, an area with a similar climate, soils and vegetation to Archer Creek watershed. Assuming an error of ±10% for annual ungauged stream flow in Archer Creek watershed, the average error for monthly ungauged stream flow was estimated as ±37% ($SD/\sqrt{n}$; $n = 5$ months). The standard deviation for N flux calculations was estimated by summing flux calculations for 2-week intervals to remove within-data-set correlation related to seasonal effects on N flux and then calculating the standard deviation of those values.

RESULTS

Hydrology and water chemistry

The peak runoff during the study period was 1·4 mm h^{-1} on 23 April 1996 (Figure 3a). Thirty-four per cent of the total runoff for the study period occurred during April. The watershed was approximately 90% snow free by 1 May, however, 51 mm of snow fell on 6 May 1996. During peak runoff a considerable amount of overland flow was observed in the wetlands. Well hydrographs (Figure 3b) indicated that the water table was above the ground surface in both the near-stream zone and at the hillslope–wetland interface for most of the period from 16 to 24 April 1996. The water table at well M2 remained within 0·05 m of the wetland surface throughout the study (Figure 3b).

Mean spring throughfall NO_3^- concentrations were higher and base cation concentrations were lower than other watershed waters sampled during the study period (Figure 4). The concentration of NO_3^- and NH_4^+ decreased vertically through the hillslope mineral soil profile. The concentration of DON was higher in O-horizon soil water than in throughfall; B-horizon soil water had lower DON concentrations than the O-horizon (Figure 4). Groundwater springs SS1 and SS2 had high NO_3^- and base cation concentrations relative to other water sampled. High concentrations of NH_4^+ and DON were found in the peatland groundwater, but little NO_3^- was detected (Figure 4), suggesting a mineralization of organic N to NH_4^+, but little nitrification. The high NH_4^+ concentrations suggest that precautions to avoid oxidizing groundwater after pumping piezometers and during sampling were successful and that little or no oxidation occurred. Low rates of nitrification are common in saturated substrates owing to low levels of dissolved oxygen (Howard-Williams and Downes, 1993). Nitrate concentrations in the stream were higher than in near-stream wetlands. Dissolved organic N and NH_4^+ concentrations were considerably greater in the peatland than in stream water at the watershed outlet. The sum of base cations was 622–707 μmol L^{-1} in the groundwater springs and in the peatland but relatively low (106–265 μmol L^{-1}) elsewhere in the watershed (Figure 4).

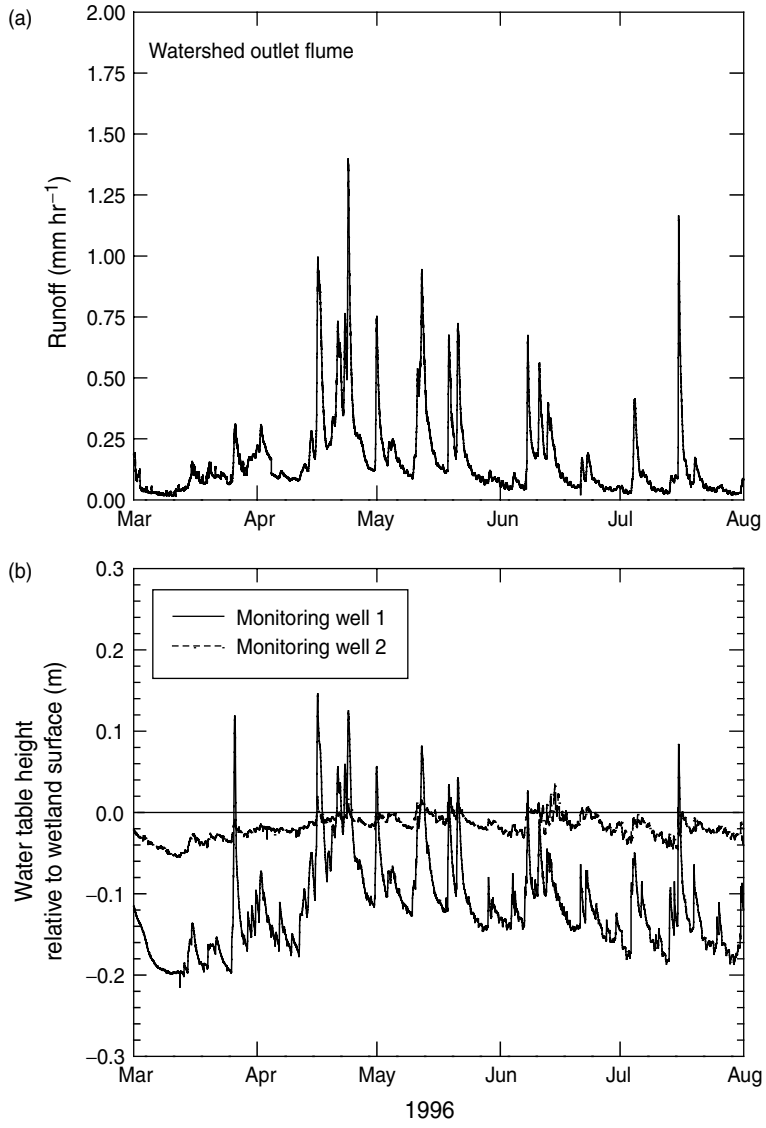

Figure 3. (a) The Archer Creek watershed outlet hydrograph at HL-flume (location is shown in Figure 1). (b) Well hydrographs for peatland monitoring wells M1 and M2 (locations are shown in Figure 2)

Spring (March–May 1996) and summer (June and July 1996) NO_3^- concentrations were significantly different (Student's *t*-test assuming unequal variance: $\alpha = 0{\cdot}05$) for throughfall, wetland groundwater, rivulet water and stream water at the flume (Figure 4). Spring and summer NH_4^+ concentrations were significantly different only at the watershed outlet. Differences between seasonal DON concentrations were significant for throughfall, stream water and shallow soil water (Figure 4). Hillslope soil water and peatland groundwater N concentrations were substantially different throughout the study. Archer Creek N water chemistry changed little as the stream passed through the wetlands during both seasons (Figure 5). Nitrate concentration decreased through the wetlands during both seasons, DON increased from W3 to the flume during the spring and summer, although the increase was greater during the summer (Figure 5).

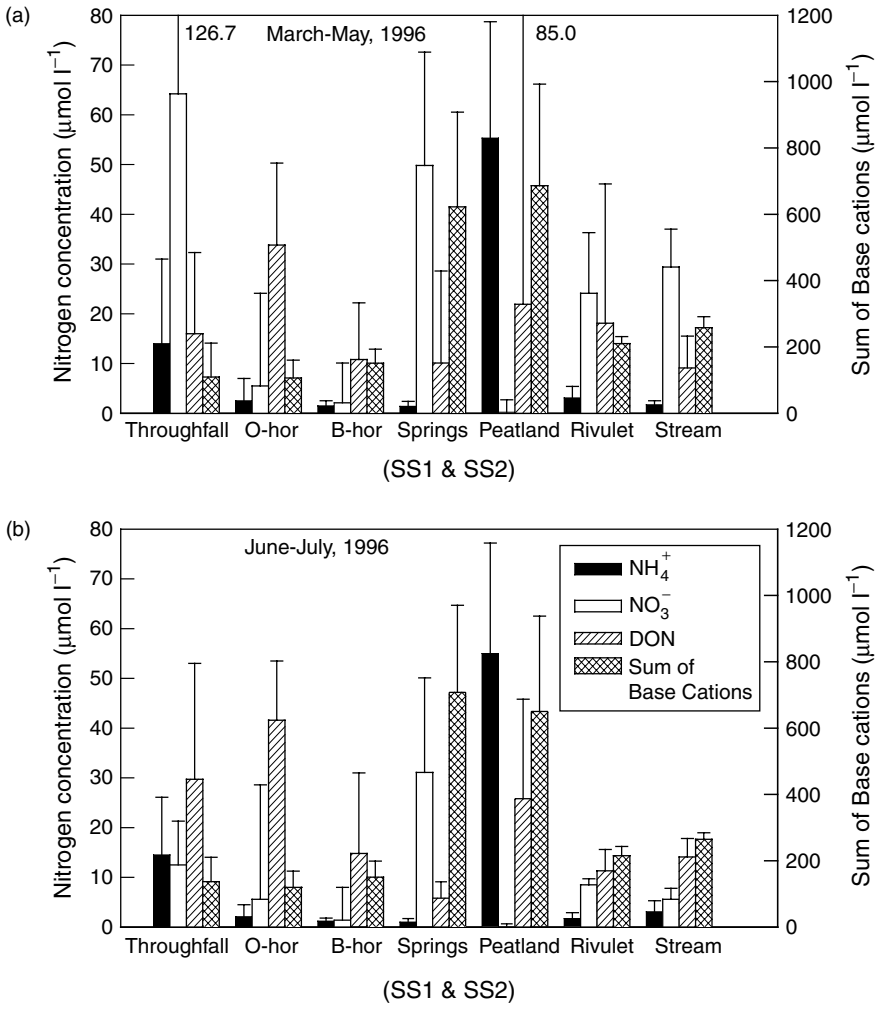

Figure 4. Spatial patterns in Archer Creek watershed chemistry including nitrogen species and sum of base cations for (a) spring (1 March to 31 May 1996) and (b) summer (1 June to 31 July 1996). Values are means for the time period indicated. Error bars denote ±1 standard deviation of the mean

Chemical flux calculations

The beaver meadow retained more NO_3^- than the peatland during the spring and summer (Table I). The beaver meadow was a source of DON during the spring and the peatland was a DON sink during the same period. There was little change in DON flux through the wetlands during the summer. Both of the wetlands were a source of NH_4^+ during the spring and a sink for NH_4^+ during the summer. Chloride behaved conservatively through the wetlands during the study period similar to previous studies (Bazemore *et al.*, 1994; Jenkins *et al.*, 1994). Differences in Cl : N ratios (Table II) show that the changes in NO_3^-, NH_4^+ and DON fluxes were caused mainly by transformation with little or no dilution from surface water, groundwater or unchannelized soil water inputs.

The greatest percent retention of NH_4^+ and NO_3^- occurred during the summer in both of the wetlands (Table III). The beaver meadow was a small source of DON to stream water throughout the study, however, the peatland retained DON during the spring and was a slight source of DON during the summer (the increase in DON flux was within the flux error estimate).

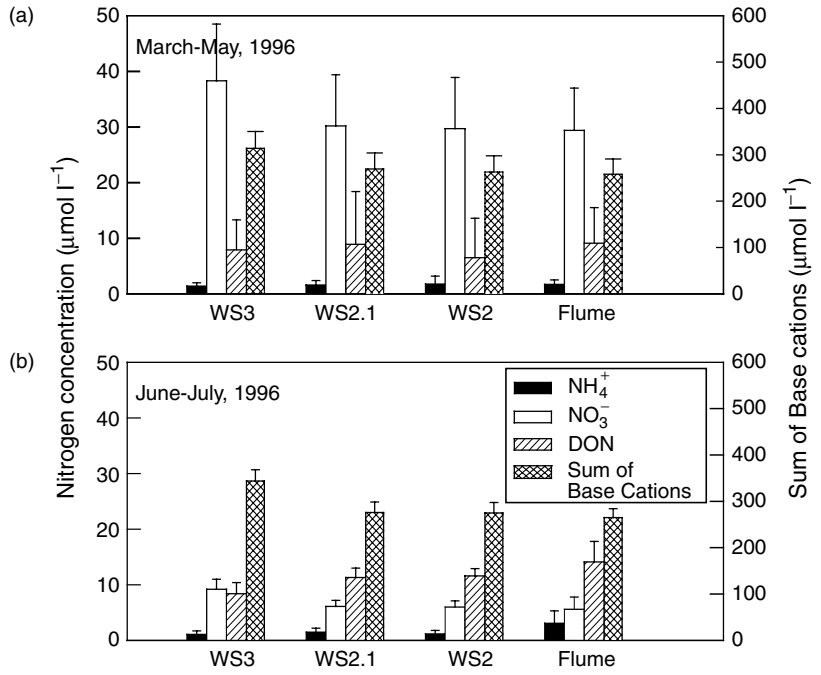

Figure 5. Longitudinal stream water nitrogen and base cation chemistry of Archer Creek for (a) spring (1 March to 31 May 1996) and (b) summer (1 June to 31 July 1996) (Locations are shown in Figure 1)

Hydrological cross-sections of the riparian peatland

Hydrological cross-sections were constructed from piezometer readings taken biweekly throughout the study period. Seasonal averages show that the area occupied by the piezometers was a recharge zone throughout the study period (Figure 6a and b). During spring, the movement of water in the wetland was directed toward the centre of the wetland (Figure 6a). The stream was a source of water to the wetland during spring high flows. During summer, shallow groundwater flow was directed from the hillslope to the stream (Figure 6b). These results suggest that groundwater did not contribute substantially to stream flow because head gradients were only directed toward the stream in the summer and during that time the head gradients were small (0·1–0·2 m) (Figure 6). The hydraulic conductivity of the peat was also low (calculated in a piezometer nest 3 m from the stream channel $4{\cdot}2 \times 10^{-5}$, $2{\cdot}6 \times 10^{-5}$ and $4{\cdot}8 \times 10^{-4}$ m s^{-1} at 0·5, 1·5 and 2·5 m depths respectively). There were sand layers within the peat that ranged from 2 to 10 mm in thickness at depths of 0·5–1·5 m that probably had higher hydraulic conductivity than the surrounding peat. A GPR survey of the wetland indicated that although the layers were not contiguous from the hillslope to the stream, they were extensive and could probably have allowed for more rapid transmittal of water through the peatland than flow through the peat matrix. The piezometer head data do not provide evidence for rapid transmittal of groundwater through these layers, but that could be an indication of the scale at which the measurements were taken (0·5 m intervals of depth). If head readings were taken at a finer scale or if the sand layers were targeted with piezometers their effect on groundwater flow in the wetland could have been better described. The sand layers were not targeted for this study because their presence and extent was not identified until well into the study.

Groundwater profiles

Ammonium and NO_3^- groundwater and stream water concentrations were highest during the spring (Figure 7). Mid-depth piezometers provided the highest NH_4^+ concentrations throughout the study (Figure 7).

Table I. Stream solute flux from the beaver meadow and the peatland in Archer Creek Watershed. The input to the beaver meadow is the sum of the three surface water inlets. The inlet to the peatland is treated as the outlet of the beaver meadow. The input to the peatland is the sum of the peatland inlet and the rivulet. All fluxes are given in mol ha^{-1} day^{-1} ± 1 standard deviation (locations shown in Figure 1)

Location	Spring (1 March to 31 May 1996)				Summer (1 June to 31 July 1996)			
	NH_4^+	NO_3^-	DON	Cl^-	NH_4^+	NO_3^-	DON	Cl^-
Beaver meadow input	$0{\cdot}07 \pm 0{\cdot}01$	$1{\cdot}4 \pm 0{\cdot}16$	$0{\cdot}48 \pm 0{\cdot}10$	$0{\cdot}46 \pm 0{\cdot}04$	$0{\cdot}09 \pm 0{\cdot}004$	$0{\cdot}23 \pm 0{\cdot}03$	$0{\cdot}30 \pm 0{\cdot}05$	$0{\cdot}26 \pm 0{\cdot}02$
Beaver meadow outlet	$0{\cdot}09 \pm 0{\cdot}1$	$1{\cdot}2 \pm 0{\cdot}1$	$0{\cdot}52 \pm 0{\cdot}08$	$0{\cdot}45 \pm 0{\cdot}04$	$0{\cdot}04 \pm 0{\cdot}004$	$0{\cdot}17 \pm 0{\cdot}01$	$0{\cdot}30 \pm 0{\cdot}02$	$0{\cdot}26 \pm 0{\cdot}02$
Peatland input	$0{\cdot}09 \pm 0{\cdot}01$	$1{\cdot}2 \pm 0{\cdot}12$	$0{\cdot}53 \pm 0{\cdot}14$	$0{\cdot}45 \pm 0{\cdot}04$	$0{\cdot}04 \pm 0{\cdot}004$	$0{\cdot}17 \pm 0{\cdot}02$	$0{\cdot}30 \pm 0{\cdot}02$	$0{\cdot}26 \pm 0{\cdot}03$
Peatland outlet	$0{\cdot}10 \pm 0{\cdot}01$	$1{\cdot}1 \pm 0{\cdot}13$	$0{\cdot}44 \pm 0{\cdot}04$	$0{\cdot}46 \pm 0{\cdot}04$	$0{\cdot}03 \pm 0{\cdot}002$	$0{\cdot}16 \pm 0{\cdot}01$	$0{\cdot}31 \pm 0{\cdot}03$	$0{\cdot}25 \pm 0{\cdot}02$

Table II. Chloride to N species ratios for wetland inputs and outputs, 1 March to 31 July 1996. The inlet to the peatland is treated as the outlet of the Beaver meadow (locations shown in Figure 1)

Location	Cl^- : NH_4^+	Cl^- : NO_3^-	Cl^-:DON
Beaver meadow inlet	6·8	0·42	0·93
Peatland inlet	5·5	0·50	0·86
Peatland outlet	5·3	0·51	0·97

Table III. Percentage retention of nitrogen species and chloride for the beaver meadow and the peatland (locations are shown in Figure 1) during the spring (March–May 1996) and summer (June and July 1996). Retention is calculated based on flux in mol ha^{-1} day^{-1} as ((input − output)/input) × 100. Total retention indicates the retention from the sedge wetland inputs and the peatland output

Location	Spring (1 March to 31 May 1996)				Summer (1 June to 31 July 1996)			
	NH_4^+	NO_3^-	DON	Cl^-	NH_4^+	NO_3^-	DON	Cl^-
Beaver meadow	−15·9	14·6	−7·5	1·6	54·5	26·8	−0·3	−2·6
Peatland	−12·1	2·0	16·5	−2·1	66·2	27·5	−6·6	1·2
Total retention	−33·3	16·3	8·0	−0·85	66·2	27·5	−6·6	1·2

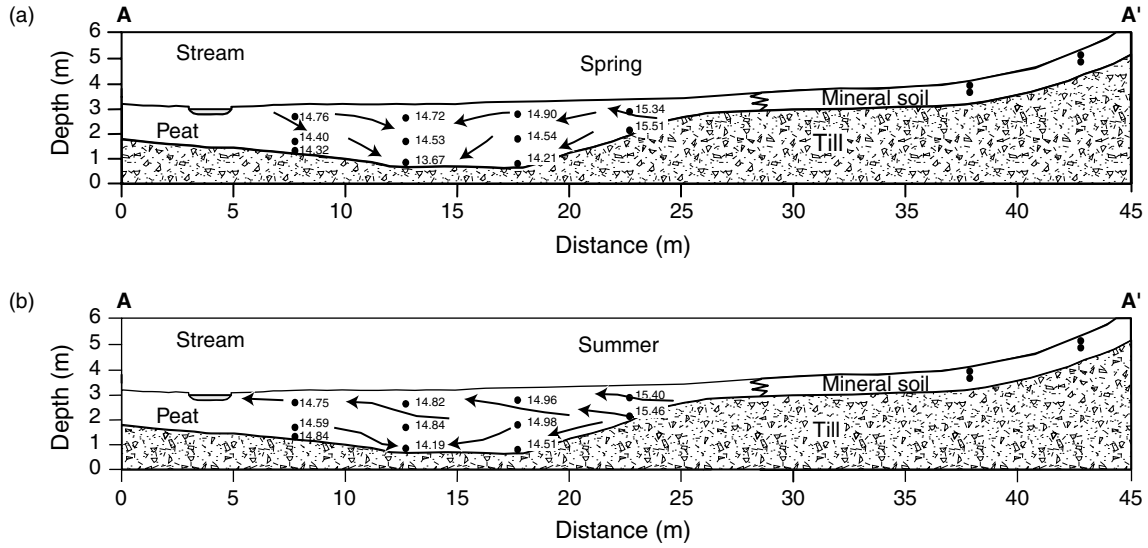

Figure 6. Hydrological cross-section A–A' within the peatland during (a) spring (1 March to 31 May 1996) and (b) summer (1 June to 31 July 1996). Head measurements are given in metres with the elevation of the outlet flume as an arbitrary datum (locations are shown in Figure 2)

There was no consistent pattern in NO_3^- groundwater concentration with depth within the peatland; NO_3^- concentrations were low throughout the study period. Dissolved organic N concentrations generally increased with depth in the peatland during the spring and decreased with depth during the summer (Figure 8). Peatland groundwater chloride concentrations were substantially higher than those measured in soil water or stream water throughout the study (Figure 8) which may be indicative of an older, deeper groundwater source to the peatland. Ammonium, DON and Cl^- concentrations in peatland groundwater were higher than those

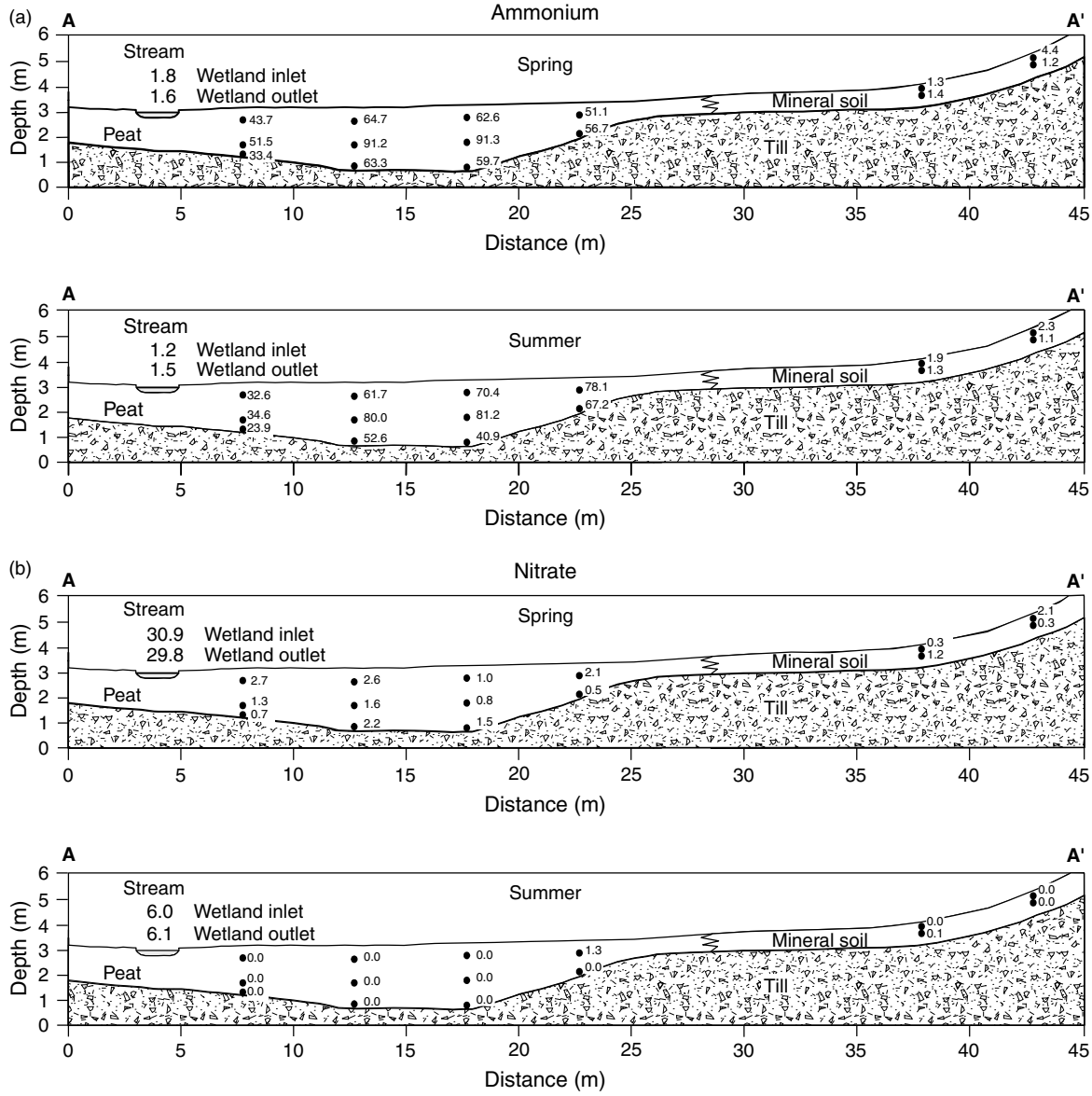

Figure 7. Hillslope soil water and peatland groundwater chemistry profiles along cross-section A–A' for (a) NH_4^+, (b) NO_3^- during spring (1 March to 31 May 1996) and summer (1 June to 31 July 1996). Values are composite samples from three piezometer transects in the wetland and are given in μmol L^{-1}. Inlet and outlet values refer to the peatland inlet and outlet stream water chemistry

measured in stream water throughout the study, whereas stream water NO_3^- concentrations were higher than those measured in peatland groundwater.

DISCUSSION

Hillslope soil water and peatland groundwater chemistry were considerably different (Figure 4). The N chemistry of soil water and groundwater changed substantially as it moved down slope from the hillslope to

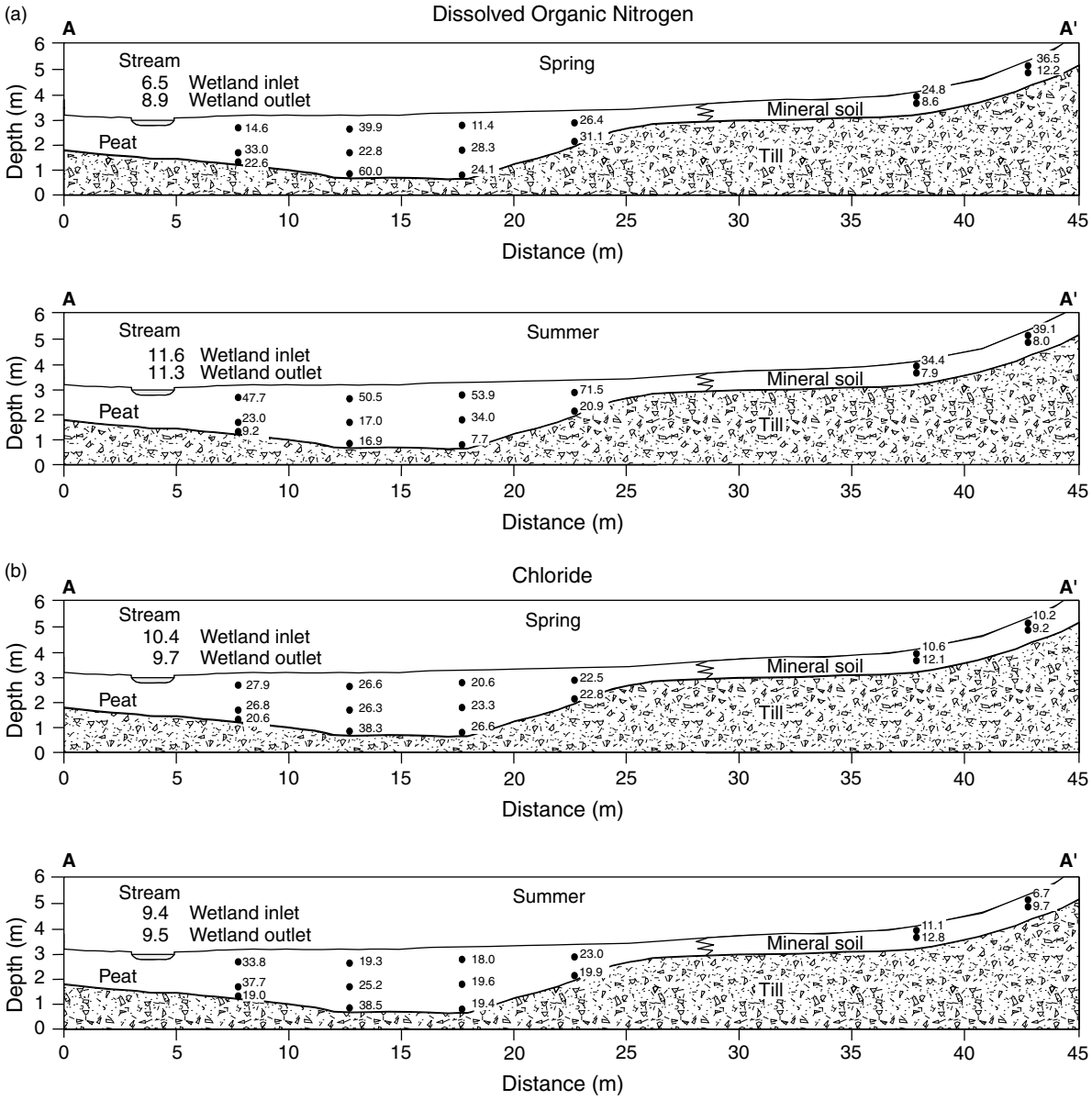

Figure 8. Hillslope soil water and peatland groundwater chemistry profiles along cross-section A–A′ for (a) DON, (b) Cl^- during spring (1 March to 31 May 1996) and summer (1 June to 31 July 1996). Values are composite samples from three piezometer transects in the wetland and are given in μmol L^{-1}. Inlet and outlet values refer to the peatland inlet and outlet stream water chemistry

the peatland (Figure 7a). Ammonium concentration illustrates the change most clearly. Nitrate concentration was low in both soil water and peatland groundwater (Figure 7b). Dissolved organic N concentrations were variable within the peatland and the hillslope soil water was within the range of concentrations measured in the peatland (Figure 8a). The high peatland chloride and sum of base cation concentrations, relative to the hillslope soil water, may be indicative of a deeper groundwater source to the peatland (Figure 4 and Figure 8b). Piezometers developed into the till layer would be required to characterize this water source. Despite the large

changes in upland soil water as it moved into the peatland, neither the peatland nor the beaver meadow had a marked effect on stream water chemistry (Figure 5). Chloride flux did not change through the wetlands, which suggests stream CL^{-1} was transported conservatively through the wetlands. Therefore, the change in Cl : N ratios through the wetlands probably was caused by in-stream transformation rather than dilution from surface-, soil- or groundwater. The probable source of in-stream transformation of N is uptake by vegetation and microbial immobilization (Burns, 1998). Nonetheless, the changes in N flux are small, in some cases within one standard deviation, and the error associated with estimating the subwatershed flows by prorating flow at the outlet based on area are large. The strongest conclusion that can be drawn from the N stream water flux calculations is that the wetlands did not affect stream water N flux greatly.

The wetlands have the potential to influence the chemistry of water leaving the watershed because they are located in the valley bottom forming a transition between the uplands and the watershed outlet. The reducing conditions within the peatland, as evidenced by the high NH_4^+ concentration of peatland groundwater, could have served as an N sink through assimilatory reduction of NO_3^- to NH_4^+ and subsequent denitrification or through transformation N by assimilatory reduction of NO_3^- to NH_4^+ or to organic N through uptake by vegetation and microbial immobilization. Although TDN flux decreased through the wetlands during both seasons, that decrease was small (Table I). These results suggest that wetland processes had a small effect on stream water N flux.

The wetlands might have retained a disproportionately large amount of N (15%) relative to their percentage of the total watershed area (4% of 135 ha) according to a concurrent study of N storage and cycling within the riparian peatland (Bischoff *et al*., 2001). Upland terrestrial soils at Huntingdon Forest have been identified as an N source (Mitchell *et al*., 1992). Bischoff *et al*. (2001) identified the wetlands as an area of N storage owing to vegetative uptake and storage in wetland soils. Bischoff *et al*. (2001) speculated that the wetlands were responsible for essentially all of the N retention within the Archer Creek watershed. Although the influence of the wetlands on stream water chemistry appears small, it is significant because there could be a net annual loss of N from the watershed in their absence (McHale *et al*., 2000; Bischoff *et al*., 2001).

According to Brinson (1993) three basic properties control wetland function: (i) geomorphic setting, (ii) water source and (iii) hydrodynamics. Hydrodynamics appear to control the effect of the riparian peatland on watershed N chemistry. There was a marked change in water chemistry from the hillslope lysimeters to the peatland piezometers, but that change was not reflected in the stream. The riparian peatland did not affect stream water chemistry because it only contributed a small amount of groundwater to the stream (Figure 6). During the period of greatest annual flow (the spring) peatland groundwater was directed away from the stream toward the centre of the wetland. The stream supplied water to the wetland according to the hydrological cross-sections, indeed water was above the surface of the wetland for more than a week at the height of spring melt (Figure 3b). Although surface water across the wetland might have provided an opportunity for surface water nutrient exchange with wetland sediment, water chemistry measurements do not indicate any large exchange of wetland nutrients. Surface water and wetland sediments did not interact significantly because of the short residence time of surface water in the wetland. At the height of spring melt, when the wetland was inundated, water flowed quickly across the top of the wetland from the inlet to the outlet. Wetland groundwater flow was directed toward the centre of the peatland throughout the study period.

During the summer shallow peatland groundwater flow was directed toward the stream, however, head gradients were small (0·65 m across a distance of *c*.20 m). As a result, there was little interaction between wetland groundwater and stream water as the stream passed through the wetland. Thus the majority of upland water bypassed the biologically active components of the wetlands in a manner similar to that described by Bowden (1987). Bowden (1987) described two cases where bypassing might occur, floating mats where upland water passes under and riparian systems where upland water passes by the biologically active areas of the wetland. The peatland rivulet also delivered water across the peatland from a hillslope hollow at the peatland perimeter to Archer Creek with little chemical change. These findings are similar to results from a sheep-grazed pastoral watershed in New Zealand where high NO_3^- surface water passed through a riparian wetland with little reduction of NO_3^-, despite a significant capacity for removal of NO_3^- in the shallow

subsurface (Burns and Nguyen, 2002). The hydrological isolation of the wetland in their case resulted from the presence of well-defined surface water channels that allowed stream water to pass through the wetland with a short residence time. Jansson *et al*. (1994) identified water retention time as the most critical factor for removing N in Swedish wetlands. The results from Archer Creek also suggest that the hyporheic zone (the zone of sediment immediately surrounding the stream channel that is influenced by stream processes) is small allowing little interaction of stream water with the surrounding wetland. This observation is supported by the low hydraulic conductivity of the peat.

The direction and magnitude of groundwater flow can change with season; uplands and wetlands can become hydrologically disconnected during low flows (Devito *et al*., 1996). Different methods for estimating groundwater flow (i.e. head gradient/hydraulic conductivity measurements, tracer studies and water balance estimates) can give substantially different results (Nuttle and Harvey, 1995; Tobias *et al*., 2001). During spring high-flows the magnitude of groundwater flow may be underestimated by the head gradient/hydraulic conductivity method used in this study as compared with results from tracer experiments (Tobias *et al*., 2001). Hydraulic conductivity measurements may not account for preferential flow paths that can be important during high flows. Although the direction of flow is typically well-characterized by head gradient/hydraulic conductivity measurements the magnitude of that flow can be underestimated by as much as four times during the spring (Tobias *et al*., 2001). An underestimate of groundwater flow through the riparian peatland could result in an underestimate of the effect of the near-stream wetlands on stream water chemistry in the watershed; however, the small change in N flux through the wetlands strongly supports our conclusion that the stream by-passed the biologically active components of the wetlands and that the wetlands contributed a small amount of groundwater to the stream relative to that contributed by upland tributaries.

Stream water NO_3^- concentrations were the most seasonally variable of all N species (Figure 5). All water sources, except soil water, had statistically significantly different mean seasonal NO_3^- concentrations. A decrease in watershed NO_3^- concentrations is typical during the growing season when biotic demand increases. There was an 11·2% increase in NO_3^- retention through the wetlands during the summer as compared with the spring (Table III). The wetlands were neither a source nor a sink for DON during the summer; during the spring the beaver meadow was a small source of DON, but the peatland retained 16·5% of stream water DON inputs (Table III). The DON flux was less at all sampling sites during the summer than during the spring (Table I), however, DON concentrations were higher (Figures 2 and 3). Flow had a greater effect on DON flux than concentration at these sites. Although stream water DON concentrations increased at each site (except the riparian peatland rivulet) during the summer, stream flow decreased enough to cause a decrease in DON flux. Probable sources for the higher stream water DON concentrations during the summer include throughfall and soil water.

Nitrate and DON flux accounted for the majority of TDN flux from the wetlands (NO_3^-, 65%; DON, 29%) during the study period. The wetlands retained NO_3^- throughout the study period, although more strongly during the summer; in contrast, DON was retained during the spring (although only in the peatland), but lost during the summer. The different behaviour of NO_3^- as compared with DON resulted in a net retention of TDN of about 16% during both seasons. Devito *et al*. (1989) measured an even greater seasonal trend in N retention in five Precambrian watersheds in southeastern Canada where N was lost during the dormant season and retained during the growing season. Unlike Devito *et al*. (1989), we did not consider the role of particulate N in total N retention because of the large number of spring samples collected and the labour intensive demands of the persulfate digestion used in the laboratory. Particulate N can be a considerable source of N loss through wetlands, especially during low-flow periods (Howard-Williams and Downes, 1993).

Nitrate accounted for the majority of TDN flux during the spring whereas DON accounted for the highest percentage of TDN flux during the summer. This seasonal shift is significant because NO_3^- may contribute more directly to downstream eutrophication and acidification causing leaching of monomeric aluminum (Gubala *et al*., 1991). Previous studies have identified wetlands as a source of organic acids such as DOC and DON (Cirmo and Driscoll, 1993; Devito *et al*., 1989); the beaver meadow was a small source of DON during the spring whereas the riparian peatland was a sink. The wetlands were neither a source nor a sink for

DON during the summer. These results support the conclusion that the wetlands were hydrologically isolated and that stream water bypassed the biologically active components of the wetlands.

CONCLUSIONS

The importance of one riparian wetland and one beaver meadow to N water chemistry and flux was evaluated in an Adirondack headwater watershed that is 'leaking' excess N. Total dissolved N flux during the summer was about one-third that estimated for the spring and the dominant form of dissolved N loss shifted from NO_3^- during the spring to DON during the summer.

Although these wetlands were located at the interface between the upland portion of the watershed and the watershed outlet, they had little affect the N chemistry of stream water exiting the watershed despite large differences between the biogeochemical environments in the upland and the wetlands. Nearly all of the water leaving the watershed passed through one or both of the wetlands yet there was no marked change in stream water chemistry through the wetlands. The wetlands exhibited a hydrological 'isolation' effect. Explanations for this effect may include (i) the wetlands did not typically contain standing water, rather stream water passed through the wetlands in well-defined channels, (ii) the wetland substrate had a low hydraulic conductivity allowing for little interaction between stream water and wetland groundwater. Ponded systems in the Adirondacks have been shown to be much larger sinks for NO_3^- than the wetlands in this study (Cirmo and Driscoll, 1993). Nonetheless, the wetlands influence on stream water chemistry is ecologically significant because there could be a net annual loss of N from the watershed if the wetlands were not present (McHale *et al*., 2000; Bischoff *et al*., 2001).

Research conducted in the riparian peatland identified a large difference between hillslope soil water and peatland groundwater. Taken alone, these results suggest that the peatland controlled the N chemistry of water passing through it. However, our data indicate that this subsurface flow path did not account for a substantial amount of the water passing through the peatland and therefore did not greatly influence the N chemistry of water leaving the watershed. A recent review of Canadian wetland research concluded that ecosystem management requires integration of plot-scale results with all hydrological processes of the system (Price and Waddington, 2000). The results of this study emphasize the danger in relating results of plot-scale wetland research or wetland research done within first-order watersheds in wetlands that do not have well-defined stream inlets to larger watersheds with more complex hydrology. Water residence time and hydrological setting affect the rates of wetland N cycling processes such as assimilatory reduction, denitrification, vegetative uptake and microbial immobilization. The magnitude of those changes must be placed in the context of other N transformations and fluxes within the watershed to evaluate their effect on watershed scale N cycling.

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