Two adjacent forested catchments: Dramatically different NO_3^- export

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[1] Two adjacent catchments with similar temperate forest cover and podzolic soils have annual nitrate (NO_3^-) export that differs by a factor of 10. Monthly rates of mineralization and nitrification measured by the buried bag technique, soil C/N ratios, and the contribution of microbial NO_3^- to total NO_3^- in the groundwater as determined by analysis of $\delta^{18}O$ in NO_3^- are also similar. In both catchments, maximum NO_3^- export occurs during spring melt, but in the catchment with higher export, NO_3^- concentrations in the stream begin to increase in the fall period. Groundwater NO_3^- concentrations measured in wells are very different in the two catchments with high groundwater NO_3^- in the catchment exhibiting high NO_3^- export. Following spring melt, steeper slopes in the high NO_3^- catchment promote faster drainage, and the water table declines rapidly while high NO_3^- concentrations are maintained in groundwaters. Deeper water tables will preserve high NO_3^- in water infiltrating below the rooting zone and organic-rich upper soil horizons. In the low NO_3^- catchment, slower drainage on shallower slopes lead to an increase in soil saturation, and the NO_3^- disappears from the water before the water table declines. Analyses of $\delta^{15}N$ in NO_3^- during NO_3^- loss do not show evidence of denitrification, although denitrification proceeding to completion in isolated pockets followed by mixing with higher NO_3^- groundwaters would yield the same result. Alternatively, active uptake of NO_3^- by vegetation following spring melt will also deplete the groundwater NO_3^- in the shallow soil depths without isotopic fractionation. The low NO_3^- catchment also has lower NO_3^- in shallow soil waters during spring melt. Shallower slopes promote near-surface flow paths in organic-rich soil horizons which may facilitate denitrification during spring melt. Although the catchment with low NO_3^- export has a large wetland near the catchment outlet, the NO_3^- attenuating capacity of this wetland is largely unused except in the late fall because growing season groundwater concentrations of NO_3^- are undetectable and the wetland is frozen during snowmelt. In the high NO_3^- catchment, organic-rich soils and vegetation in the riparian zone cannot completely attenuate high NO_3^- in discharging groundwaters. In our study, factors controlling NO_3^- in groundwater such as slope, stratigraphy, and hydraulic conductivity can play a larger role than riparian zones in controlling differences in annual NO_3^- export observed between catchments. *INDEX TERMS:* 1615 Global Change: Biogeochemical processes (4805); 1871 Hydrology: Surface water quality; 1831 Hydrology: Groundwater quality; 1890 Hydrology: Wetlands; 1040 Geochemistry: Isotopic composition/chemistry; *KEYWORDS:* nitrate export, forested catchments, stable isotopes, hydrology, wetlands, nitrogen cycling

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1. Introduction

[2] Atmospheric nitrogen (N) deposition to northern temperate forests has increased over the last several decades [e.g., *Nadelhoffer et al.*, 1999]. The net effect of this increase on N cycling in forested catchments is controversial. Undisturbed northern forests are generally expected to be N limited [e.g., *Aber et al.*, 1989]. A subsequent increase in growth due to N fertilization may sequester atmospheric N and carbon (C) in the short term, playing a role in the missing C sink [*Schindler and Bailey*, 1993]. However, N in excess of growth requirements may lead to N saturation [*Aber et al.*, 1989], increased NO_3^- export [*Foster et al.*, 1989], acidification of surface waters [*Dillon and Molot*, 1990; *Murdoch and Stoddard*, 1992; *Stoddard*, 1994] and eutrophication of coastal waters [*Howarth et al.*, 1996]. Recent evidence indicates that NO_3^- export has increased in some streams [*Murdoch and Stoddard*, 1992; *Peterjohn et al.*, 1996] and

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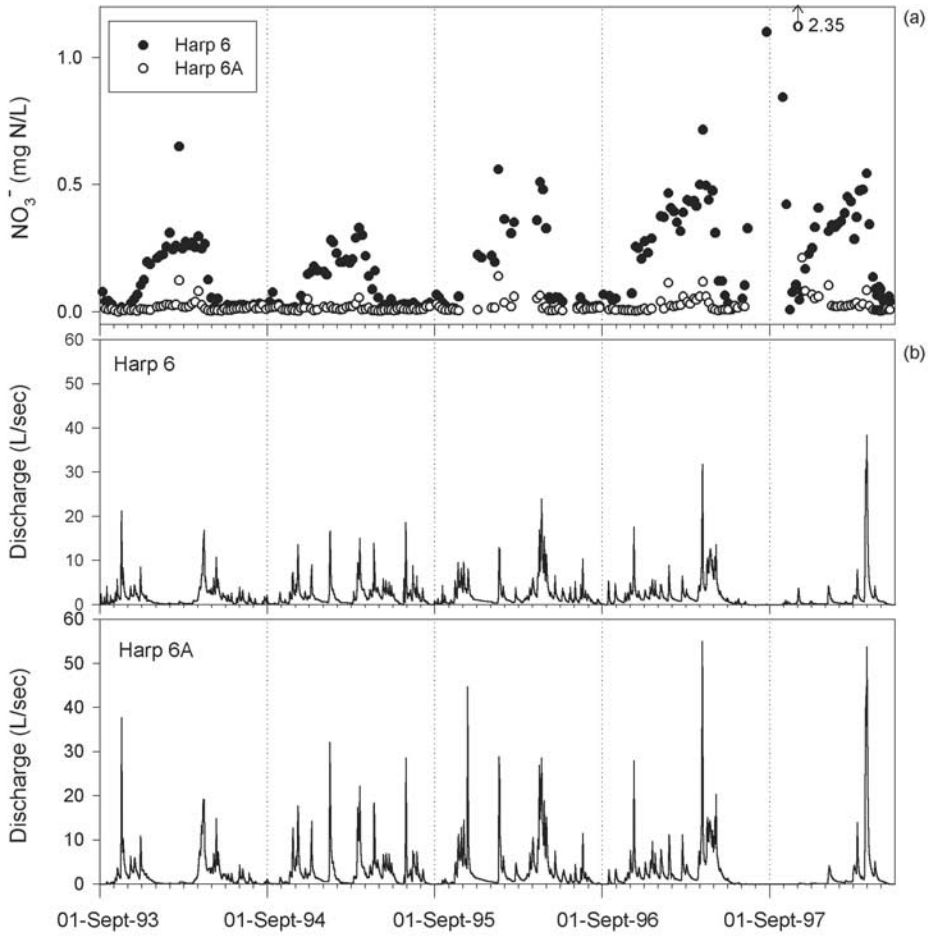

Figure 1. (a) NO_3^- concentration and (b) discharge in Harp 6 and Harp 6a streams, 1993–1998.

that the decline in S deposition has not been matched by equivalent changes in pH and alkalinity [*Jeffries et al.*, 1995].

[3] The relative importance of the processes governing N export from undisturbed forested watersheds is also controversial. Riparian zones have been lauded as the key to understanding catchment N export from forested catchments [*Cirmo and McDonnell*, 1997] and agricultural areas [*Hill*, 1996]. Nitrate attenuation can occur through vegetative uptake and denitrification in the organic-rich sediments bordering streams and along shallow flow paths. Alternatively, nitrate export from forested catchments has been modeled using a combination of flushing of high nitrate source zones (including riparian zones) and draining of high NO_3^- base flow groundwaters [*Creed et al.*, 1998]. In the Catskill region of the eastern USA, it has been suggested that high NO_3^- concentrations are recharged to deep groundwaters during the spring, bypassing vegetation uptake [*Burns et al.*, 1998]. Discharge of this deeper groundwater at base flow conditions governs NO_3^- export in the post-snowmelt period, although riparian processes may partially attenuate some of the NO_3^-.

[4] In this study, processes governing nitrate export are examined in two adjacent catchments in a northern temperate forest. These small catchments receive relatively high N deposition for Eastern Canada (11–15 kgN/ha/yr [*Molot and Dillon*, 1993]) and have the similar vegetation and soils. However, they differ dramatically in NO_3^- export (Figure 1). The catchment with the lowest NO_3^- export has a large treed peatland near the basin outlet. Earlier studies have shown that both catchment physiology and wetland area may have an influence on NO_3^- and other elemental cycling in these headwater catchments [*Dillon et al.*, 1991; *Devito et al.*, 1999a]. The study was initiated to quantify the importance of the wetland relative to hillslope areas in controlling the observed differences in NO_3^- export in order to generalize their role in NO_3^- dynamics of forested headwater catchments.

2. Methods

2.1. Study Site

[5] Harp 6 (10.0 ha) and Harp 6a (15.3 ha) are headwater catchments in the Harp Lake Watershed, located approximately 200 km north of Toronto, Ontario (Figure 2). Mean annual January and July air temperatures are −11.0 and 17.7°C respectively. Annual precipitation averages 900–1100 mm with 240–300 mm as snow. Mean annual runoff is 400–600 mm/yr and 50–75% of annual runoff occurs during snowmelt. Total atmospheric N deposition measured in bulk collectors averaged 11.3 kgN/ha/yr in 1977–1989, with NO_3^- contributing 5.6 kgN/ha/yr [*Molot and Dillon*, 1993].

[6] The forest vegetation of both catchments has been described by *Devito et al.* [1999b]. Upland forests are

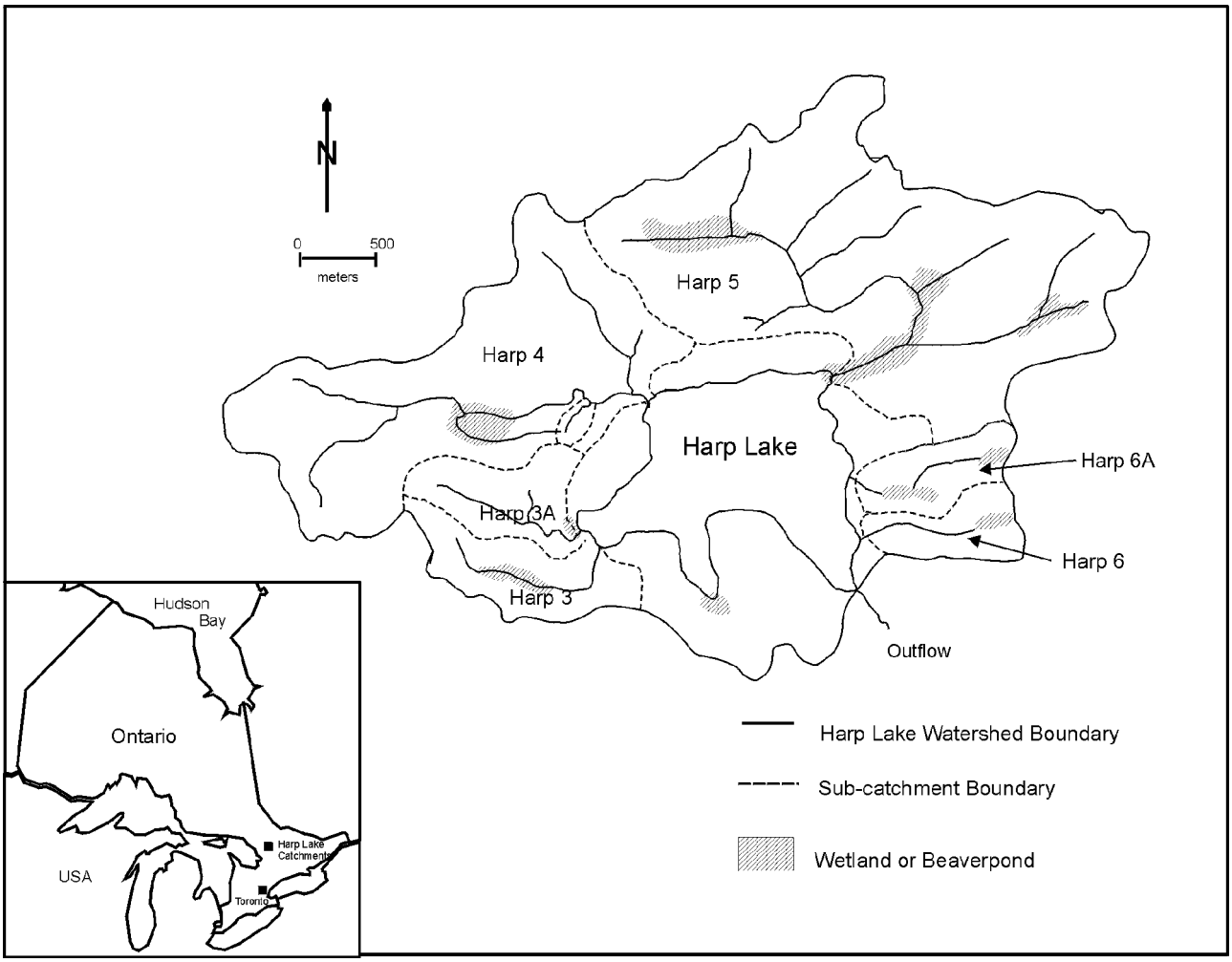

Figure 2. Location of Harp Lake watershed (45°22′50″'N, 79°07′30″'W). Stippled areas indicate wetlands.

dominated by a deciduous forest of maple (*Acer saccharum*, *Acer pennsylvanicum*, *Acer spicatum*) and beech (*Fagus grandiflora*) with some conifer-mixed stands of hemlock-fir (*Tsuga canadensis-Abies balsamea*) and maple. Treed peatlands with fir, hemlock, green ash *(Fraxinus pennsylvanica)*, and eastern white cedar *(Thuja occidentalis)* occur at the head of the Harp 6 stream and within Harp 6a. The largest treed peatland is found proximal to the catchment outlet of 6a. Selective logging for white and red pine (*Pinus strobus* and *P. resinosa*) occurred in the early 1900s.

[7] Upland soils are silt loam texture with developed Podzolic profiles. Soil pH, C/N ratios and %N are similar in the two catchments [*Devito et al.*, 1999b]. Carbonate deficient tills of generally less than 1 m in thickness overly bedrock of biotite hornblende gneiss in Harp 6a and gneiss and diorite in Harp 6. Deeper surficial deposits are found at the base of slopes and in isolated bedrock depressions. In the peatlands, mesic Humisols overly thicker valley bottom basal till deposits. Occasional bedrock outcrops can be observed in both catchments and are more pronounced toward the ridge crests.

2.2. Instrumentation

[8] Groundwater wells and piezometer nests were installed in the two basins (Figure 3). Most wells were

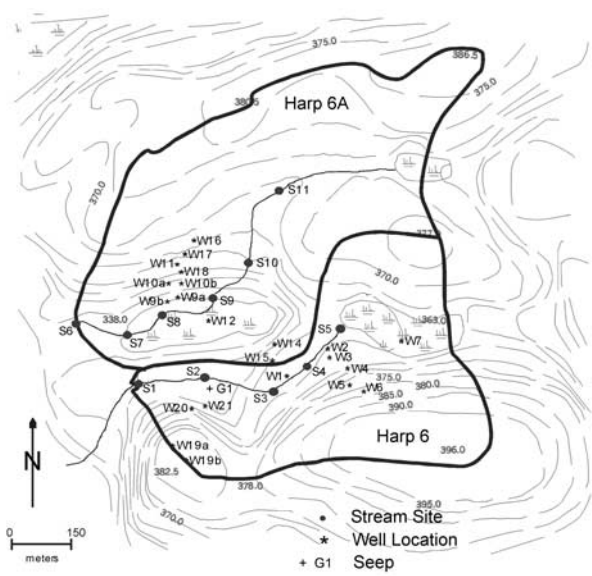

Figure 3. Location of stream sampling sites, wells (W1–W15), piezometers (W16–W21) and the seep (G) in Harp 6 and 6a.

concentrated on the two main hillslopes, one in each catchment, in a transect extending from the riparian zone up the hillslope. Other wells, scattered throughout the basin, provide samples on different hillslope aspects and locations. Wells 1 to 15 are screened over the entire length of the well. Piezometers 16 to 21 are screened over an interval of 20 cm at the bottom of the piezometer. Additional drive point piezometers with a bottom screen of 20 cm were installed at the toe of the slope in 6 and 6A to a depth of 2 m in Harp 6 and to 1.5 m in Harp 6a. One nest of small diameter piezometers with screen intervals of only 5 cm was installed near the base of each of the two main transects.

[9] Soil pits were dug at many locations in the two catchments including the valley bottom and in transects up the hillslope perpendicular to the stream. Horizon thickness and soil texture were noted. Soil texture and stratigraphy are similar to nearby catchment Harp 4–21 where soil hydraulic conductivities and flow paths have been studied extensively [*Hinton*, 1998; *Hinton et al.*, 1998]. Soil cores were collected at 50–100 sampling sites in the lower section of the catchments at depth intervals of 0–10 cm and 10–20 cm to determine the NO_3^- inventories prior to spring melt and in the fall of 1998. C/N ratios were determined on a set of cores from all sampling sites and in a soil pit in Harp 6 where soils were collected by soil horizon. During spring melt, waters running over the surface or in shallow soil horizons (under LFH or at A/B contact) were sampled for chemical analysis.

[10] Bulk precipitation samples were collected at the Dorset Research Centre located approximately 20 km southeast of Harp Lake Watershed and in the Harp Watershed at the meteorological site located in Harp 5 (Figure 2). Three throughfall collectors constructed of plastic eavestroughs were deployed under the deciduous and mixed forest canopies in the Harp 6 and 6a subwatersheds. All precipitation and throughfall samples were collected on an event basis.

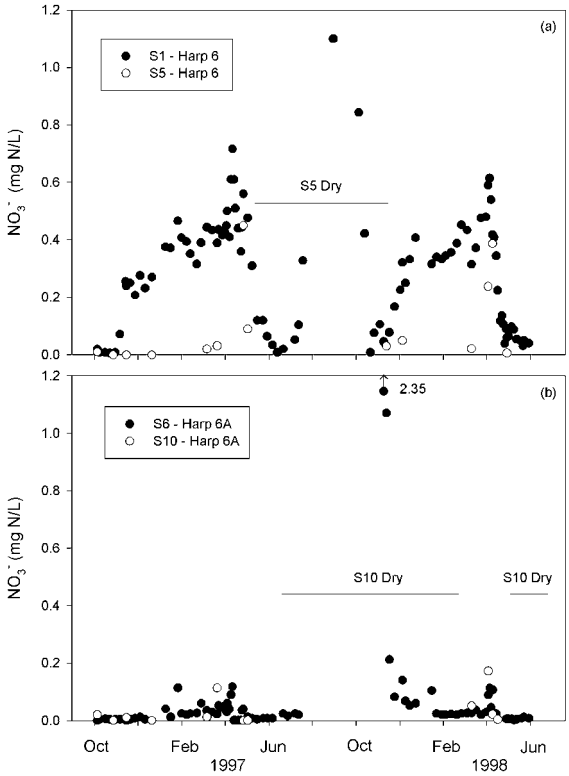

Figure 4. NO_3^- concentration in stream sampling points (see Figure 3) from November 1997 to July 1998: (a) sites S1 and S5 in Harp 6 and (b) sites S6 and S10 in Harp 6a. Periods without weekly samples from June to November for S6 and S1 indicate periods of no streamflow. High NO_3^- concentrations were observed for 14 days following the start of continuous streamflow in Harp 6 and for 7 days following the start of continuous streamflow in Harp 6a.

3. Chemical and Isotopic Analysis

[11] Samples were collected from the streams, piezometers, wells and in snow cores and filtered to 0.45 μm. Samples were transported in coolers to University of Toronto or Wilfrid Laurier University for analysis of NO_3^- by standard methods [*Stainton et al.*, 1977]. To determine NO_3^- inventory, soil samples were extracted by shaking 5 g subsamples for 1 hour with 50 mL of 2M KCl. Extracts were filtered to 0.45 μm and analyzed for NO_3^-. Quantification of rates of mineralization and nitrification followed *Devito et al.* [1999b].

[12] Samples for analysis of $\delta^{18}O$ and $\delta^{15}N$ in NO_3^- were filtered to 0.45 μm and frozen until the samples could be processed rapidly. Subsequent handling of samples and analysis procedures follow *Spoelstra et al.* [2001] with the exception that all stream and piezometers were ultrafiltered using a 1000 Dalton membrane prior to loading on the ion exchange column. Ultrafiltration removes DOM which can interfere with $\delta^{18}O-NO_3^-$ analysis. Samples are reported in δ ‰ notation relative to Vienna-SMOW for $\delta^{18}O$ and Standard Air for $\delta^{15}N$. Replicate analysis of samples typically yields a precision of ±1‰ in $\delta^{18}O$ and ±0.5‰ in $\delta^{15}N$.

[13] Sample collection for chemical and isotopic analysis began in 1996 and continued through the spring melt of 1999. For simplicity in presentation, this paper will focus on samples collected in the fall of 1997 and spring melt of 1998. Precipitation samples collected in 1996 are used in the calculation of the weighted average $\delta^{18}O$ of NO_3^- in precipitation as the sample analysis for 1996 is most complete.

4. Results and Discussion

[14] Both Harp 6 and 6a receive similar atmospheric deposition but the NO_3^- export from Harp 6 exceeds that from Harp 6a catchment by an order of magnitude. Throughfall NO_3^- concentrations and $\delta^{18}O$-NO_3^- measured at Harp in the same storm are similar between vegetation types and the two catchments, although coniferous trees potentially trap more dry deposition. Harp 6a has a slightly higher percentage of conifer trees [*Devito et al.*, 1999b] and, if anything, should have a higher deposition. It is unlikely that deposition in Harp 6 significantly exceeds that in Harp 6a.

4.1. Stream Concentrations and Export of NO_3^-

[15] Stream NO_3^- concentrations and export are significantly elevated in Harp 6 compared to Harp 6a (Figures 1 and 4). Sustained high NO_3^- concentrations correspond to

peak discharge during snowmelt events in both catchments. Peak NO_3^- concentrations in Harp 6 are 2–3 fold higher than in Harp 6a. Although both catchments have very low to nondetectable NO_3^- by June, the decline in NO_3^- concentrations following spring melt is more rapid in Harp 6a than in Harp 6 (Figures 1 and 4). In late fall, nitrate concentrations in Harp 6 begin to increase progressing to the peak in spring whereas in Harp 6a, NO_3^- concentrations above 0.050 mg/L are only observed during the spring melt period and immediately following drought. The correspondence between high NO_3^- concentrations and high discharge in Harp 6 leads to an average yearly NO_3^- retention of only 0.73 in Harp 6 compared to 0.97 in Harp 6a in the period 1977–1989 [*Molot and Dillon*, 1993].

[16] More intensive sampling beginning in 1996 reveals very high NO_3^- concentrations, up to 2.4 mgN/L, in both catchments immediately following the onset of streamflow in the fall after a prolonged drought period. These high concentrations persisted for only a few days in Harp 6a but up to a few weeks in Harp 6 (Figure 4). High NO_3^- values (up to 7.5 mgN/L in Harp 6) also appear associated with drought in the 23 year data record at this research site (P. Dillon, unpublished data, 2000). Routine stream sampling on a weekly or biweekly schedule may miss these high values.

[17] To determine the source of the higher stream NO_3^- concentrations, samples were collected at various positions along the stream length (Figure 3). In Harp 6a, the stream has similar but low NO_3^- along the length even during spring melt, although the upper reaches above the wetland (S10) are often dry (Figure 4b). In Harp 6, stream NO_3^- concentrations are much higher at S1 than S5, especially during the fall and winter, suggesting that there is an input of NO_3^- from the hillslopes in the lower reaches of the stream.

4.2. Mineralization, Nitrification, and Soil NO_3^- Inventories

[18] Annual rates of mineralization and nitrification are similar in Harp 6 and 6a (Figure 5a) [*Devito et al.*, 1999b]. Rates were determined monthly in 1995 and 1996 by the buried bag technique [e.g., *Westermann and Crothers*, 1980] in transects up the hillslopes dominated by deciduous vegetation. One transect with mixed conifer (predominantly hemlock, *Tsuga canadensis*) and deciduous vegetation (maples) had lower rates of nitrification. Both mineralization and nitrification rates in the peatland were very low (Figure 5a). Applying these vegetation community specific rates to the areal vegetation coverage observed in the two catchments results in a net nitrification of 59 kgN/ha/yr in Harp 6 compared to 42 kgN/ha/yr in Harp 6a [*Devito et al.*, 1999b]. This difference, a factor of 1.4, is largely a function of the difference in area covered by wetlands and mixed-conifer uplands and cannot explain the ten-fold difference in NO_3^- export between the two catchments. In addition, annual NO_3^- export is 50-fold less than annual areal nitrification rates in Harp 6a indicating the importance of NO_3^- retention processes within these forested catchments.

[19] Inventories of NO_3^- (Figure 5b) and NH_4^+ [*Devito et al.*, 1999b] in the soil were similar between catchments. Spatial variability was often large even within the same vegetation community [*Devito et al.*, 1999b]. Because of the high NO_3^- concentrations observed at peak snowmelt, and the importance of mineralization and nitrification under the snowpack [*Devito et al.*, 1999b], soil inventories of NO_3^- were determined prior to the snowmelt and in the late fall of 1998. There is a consistent trend of the highest NO_3^- inventories observed at the highest elevation in each transect of the deciduous stands for both the monthly data in 1995–96 and the 1998 spring and fall inventories. However, there is no difference in the NO_3^- inventories at a given hillslope position, the maximum observed NO_3^- inventory or the average inventory between the two catchments on any of the sampling dates.

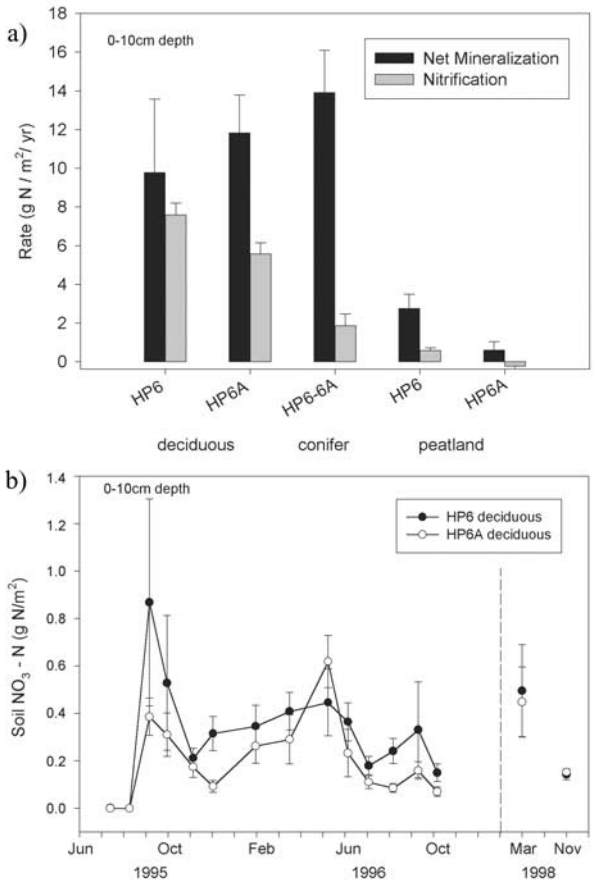

Figure 5. (a) Mean monthly nitrification and mineralization rates at 0–10 cm. Error bars are ±1 standard error. (b) Mean monthly NO_3^- inventories in Harp 6 and 6a at 0–10 cm. Error bars are ±1 standard error. The nitrification, mineralization, and NO_3^- inventory in the 10–20 cm core depth are significantly less than in the 0–10 cm depth [*Devito et al.*, 1999b]. The stands marked "conifer" are mixed deciduous-conifer stands.

[20] Ratios of C:N in the forest floor and mineral soil of the deciduous stands in Harp 6 and 6a are 18 to 20, well below the critical range (25–27), and indicate the potential for high nitrification rates and nitrate leaching [*Gunderson et al.*, 1998]. The C/N ratios in the wetlands are much higher (27–34) and favor high immobilization by soil microbes [*Janssen*, 1996].

4.3. Nitrate Concentrations in Groundwaters

[21] Striking differences are observed between the NO_3^- concentrations of groundwaters in 6 and 6a. In both catch-

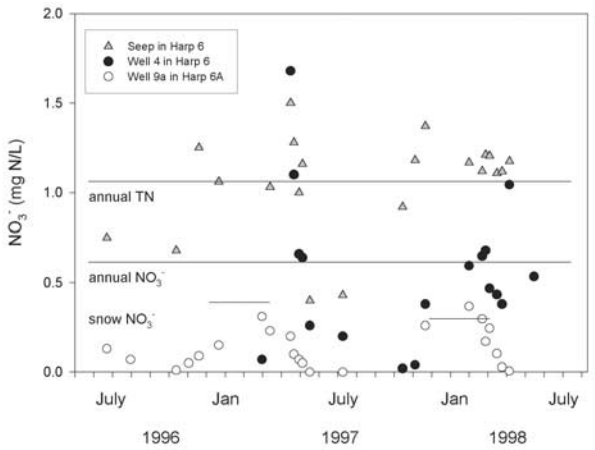

Figure 6. Groundwater NO_3^- concentrations in well 4 and the groundwater seep in Harp 6 and well 9a in Harp 6a. The mean annual TN deposition and the mean annual NO_3^- deposition (dates are from *Molot and Dillon* [1993]) and the NO_3^- concentration in the snowpack measured prior to spring melt in 1997 and 1998 are also shown as horizontal lines. Peak stream discharge during snowmelt occurred on 6 April 1997 and 1 April 1998. Other groundwater wells in Harp 6 and Harp 6a show the same pattern as illustrated here.

ments, NO_3^- concentrations in groundwaters rise throughout the fall recharge period to maximum concentrations during the snowmelt period (Figure 6). In Harp 6a, the groundwater NO_3^- concentrations at peak melt approach concentrations measured in the snowpack. However, NO_3^- concentrations in Harp 6 are always greatly elevated above 6a and can exceed snowpack concentrations. In addition, groundwater NO_3^- concentrations in Harp 6a rapidly reach nondetectable levels after snowmelt whereas high NO_3^- concentrations are maintained in the groundwaters of Harp 6.

[22] Toward the lower reaches of the catchment, one groundwater seep discharges from the base of the steepest section of the hillslope in Harp 6 (G1 in Figure 3). This seep flows all summer except during years with prolonged drought periods in contrast to the hillslope wells and streams which are frequently dry in the summer months. Hillslope water tables are transient in the summer throughout much of the two basins because of the shallow soil depth (less than 1 m) and the high water demand of the vegetation. Thus, the seep drainage is likely typical of water in the lower soil horizons at the toe of the slope and possibly the upper fractured bedrock on the hillslope. In the seep, NO_3^- concentrations are always elevated (Figure 6). A dilution following snowmelt was observed at the end of spring melt in 1997 but not in 1998.

[23] Because groundwaters were largely sampled using wells and not piezometers, high NO_3^- concentrations year-round in the seep but not in shallow wells could imply that only deeper groundwaters contain nitrate. Examination of all wells and piezometers immediately following peak melt throughout both catchments shows that NO_3^- concentrations in all short screen interval piezometers, shallow wells and deeper groundwater wells (except two narrow piezometers with 5 or 10 cm screens) in Harp 6 are elevated compared to 6a (Figure 7). In addition, the stratigraphy observed in the soil pits reveals that the highest hydraulic conductivities are in the upper soil horizons, not at depth. This often results in perched water tables in the B horizon at near stream positions during the fall. Thus the contribution of waters from shallower soil horizons to samples drawn from wells likely exceeds deeper contributions. Groundwater nitrate concentrations at spring melt and also in the fall (not shown) are thus higher at all depths in Harp 6 compared to Harp 6a.

[24] Nitrate concentrations in Harp 6 wells and the seep throughout the spring melt period in 1997 and 1998 are higher than NO_3^- concentrations measured in the snowpack (0.37 ± 0.03 mgN/L in 1998, n = 4). High initial spring melt NO_3^- concentrations could reflect preferential early elution of NO_3^- from the snowpack [e.g., *Johannssen and Henriksen*, 1978; *Maclean et al.*, 1995] but would be diluted in the wells sampled over the well screen interval by contributions from the remaining snowpack. Nitrate concentrations in groundwaters also exceed the volume weighted average annual NO_3^- in precipitation at the Harp catchment (0.5 mgN/L [*Molot and Dillon*, 1993]; Figure 6). However, only concentrations at peak melt and in the seep exceed the volume weighted average annual precipitation total N (TN of 1.0 mgN/L [*Molot and Dillon*, 1993]). The groundwater NO_3^- concentrations do not exceed the volume weighted average annual NO_3^- concentration in precipitation corrected for evapotranspiration in the basin (yield 0.5 to 0.6 [*Dillon et al.*, 1991]). Thus, NO_3^- concentrations alone do not discount atmospheric deposition as the sole source of the high groundwater NO_3^- in Harp 6 even though the hillslopes retain both NO_3^- and TN.

[25] High N uptake rates are generally observed for maple-beech forests (e.g., 70–80 kg/ha/yr [*Mitchell et al.*, 1992]). The input of atmospheric N is small compared to the annual N requirements of the forests (on the order of 10%). The bulk of the N requirement is supplied by soil N cycling processes. Groundwater nitrate can be derived from both

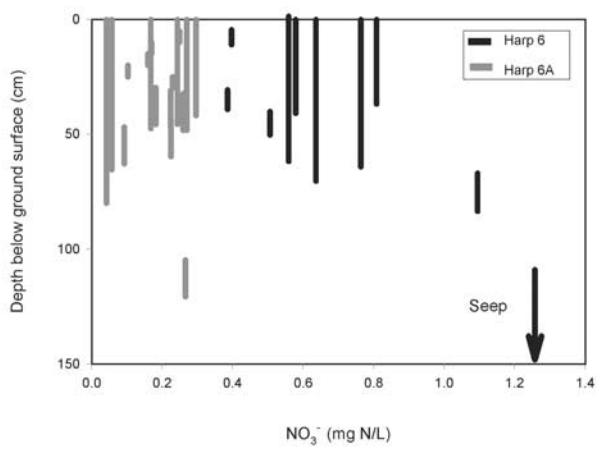

Figure 7. Groundwater NO_3^- concentrations in all wells and piezometers in Harp 6 and 6a on 8 April 1998. Length of bar corresponds to the screened interval. The depth of the groundwaters contributing to the one groundwater seep in Harp 6 is unknown. However, the seep flows when nearby water tables wells at 65 cm below ground surface are dry.

atmospheric deposition of NO_3^- and from nitrification in the soil. However, if soil N mineralization is balanced by uptake in the growing season, little soil-derived nitrate may be available for export. Mineralization and nitrification also occur at significant rates in the nongrowing season in the Harp watershed with 23% of the annual net nitrification occurring under the snowpack [*Devito et al.*, 1999b]. Although microbial production of NO_3^- can be substantial compared to atmospheric inputs, it is the balance between production and uptake that will govern the availability of NO_3^- to be flushed below the rooting zone to the groundwater table on the hillslopes during periods of groundwater recharge.

4.4. Isotopic Ratios in NO_3^-

[26] The $\delta^{15}N$ of NO_3^- in the two catchments is remarkably similar. Precipitation and throughfall values of $\delta^{15}N$ in NO_3^- range between −5‰ and −2‰ (Figure 8). Nitrate in the groundwaters and streams of the two catchments are generally more enriched in $\delta^{15}N$ than precipitation, ranging from 1‰ to 4‰ in nonsnowmelt periods and are similar to values of $\delta^{15}N$ in Dissolved Organic Nitrogen (S. L. Schiff, unpublished data, 2000). Groundwater $\delta^{15}N$ values lighter than 0‰ in wells all correspond to the main snowmelt period or to recharge to wells in late fall 1997 during an early winter melt event. Nitrate sampled in the snowpack is slightly more enriched in $\delta^{15}N$ than precipitation $\delta^{15}N$. Although care was taken to ensure that the snow near the soil-snow interface was not included in the samples, the enriched $\delta^{15}N$ could possibly be due to translocation of soil nitrate into the snowpack.

[27] None of the samples showed significant isotopic enrichment due to denitrification. Field studies in shallow aquifers [*Bottcher et al.*, 1990; *Aravena and Robertson*, 1998; *Mengis et al.*, 1999] have shown that the residual NO_3^- pool becomes increasingly enriched during microbial denitrification with a fractionation factor for $^{15}N/^{14}N$ of 1.014 to 1.030. A loss of 50% of the NO_3^- in groundwater with an initial $\delta^{15}N$ of −2‰ to +4‰ should enrich the $\delta^{15}N$ above 12‰ if a low fractionation factor of 1.014 is used. Either denitrification is unimportant, or it proceeds to completion in localized areas and therefore does not affect the $\delta^{15}N$ isotopic signature of the NO_3^- pool. The $\delta^{15}N$ is more sensitive to fractionation than $\delta^{18}O$ during denitrification. Typically, the ratio of the enrichment of $\delta^{15}N$ to $\delta^{18}O$ is observed to lie between 1.4 and 2.1 [*Mengis et al.*, 1999]. The lack of significant enrichment in the $\delta^{15}N$ of NO_3^- allows us to use the $\delta^{18}O$ in NO_3^- to examine the source of nitrate in the streams and groundwaters in these catchments.

[28] Analysis of $\delta^{18}O$ in NO_3^- demonstrates the importance of NO_3^- from nitrification to groundwater NO_3^- in the two catchments. Atmospheric NO_3^-, measured in both throughfall and bulk rain collectors, exhibits a wide range in $\delta^{18}O$ from 30‰ to 54‰ with an average weighted value in 1996 of 42‰. Values of $\delta^{18}O$ measured in snow cores prior to snowmelt averaged 47‰ in 1996, 53‰ in 1998 and 50‰ in 1999. Nitrification of soil or atmospheric NH_4^+, on the other hand, results in $\delta^{18}O$ values in NO_3^- that are substantially lighter than the atmospheric source. Laboratory [*Andersson and Hooper*, 1983; *Hollocher*, 1984] and field [*Bottcher et al.*, 1990; *Aravena and Robertson*, 1998; *Mengis et al.*, 1999; *Wassenaar*, 1995] studies indicate that

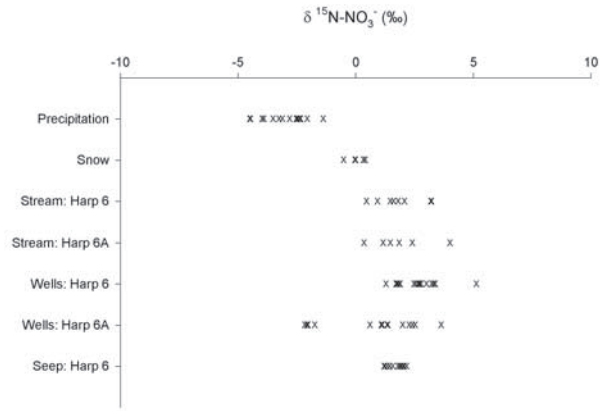

Figure 8. $\delta^{15}N$ in NO_3^- in precipitation, streams, and wells at Harp 6 and 6a and the seep in Harp 6.

the isotopic signature of microbial nitrate is derived from both the $\delta^{18}O$ of the soil water and the $\delta^{18}O$ of soil O_2 in a ratio of 2 to 1 respectively. For a mean groundwater $\delta^{18}O$ of −11‰ to −12‰ measured at Harp Watershed and using atmospheric O_2 as a surrogate for the soil O_2 (23.5‰), the microbial end−member for $\delta^{18}O$ in NO_3^- should be approximately 0‰. Thus the $\delta^{18}O$ of atmospheric NO_3^- and microbial NO_3^- from nitrification are widely separated at Harp Lake and can be used to examine the origin of the NO_3^- in the streams and groundwaters [e.g., *Spoelstra et al.*, 2001].

[29] In the groundwater wells, the $\delta^{18}O$ in NO_3^- varies seasonally. In fall and winter, $\delta^{18}O$ ranges between 5‰ and 9‰. Highest values (15‰ to 24‰) occur at peak snowmelt when water tables are at or near ground surface. Samples obtained from groundwater wells are a mixture of the shallow groundwaters above the compacted basal till layer. Thus, as water tables rise to the near surface during spring melt, the isotopic signature of the deeper waters is mixed with lighter $\delta^{18}O$ in NO_3^- from the snowpack. As the water table declines following spring melt, the $\delta^{18}O$ in NO_3^- returns to fall and winter values in both Harp 6 and Harp 6a.

[30] Analysis of $\delta^{18}O$ in NO_3^- from the groundwater wells shows that the NO_3^- recharged to the groundwater system is largely microbial in origin. Although there remains the possibility that NO_3^- produced in the summer could be isotopically enriched in $\delta^{18}O$ [*Kendall*, 1998; *Kendall and Aravena*, 1999], the fate of this nitrate is likely consumption by vegetation within the catchment. Nitrate pools in the soils are lower in the summer (Figure 5). Groundwater recharge in the summer/early fall growing season is insignificant. Isotopic signatures of NO_3^- in groundwaters reflect the NO_3^- available to be leached at the time of recharge from the late fall and winter through snowmelt. During early fall, values of $\delta^{18}O$ in NO_3^- similar to the predicted microbial end-member (e.g., 1.0‰ on 7 November 1997) can be observed in the Harp streams in the first pulse of nitrate that follows summer drought. These observed low $\delta^{18}O$ values support the use of the predicted microbial end-member to roughly estimate the contribution of microbial nitrate to the total nitrate. Using the average $\delta^{18}O-NO_3^-$ of precipitation (42‰) as the atmospheric end-member, the microbial N contribution in the groundwater well samples varies from approximately 80−90% during

fall/winter recharge to a minimum of 50% during peak spring melt. If the in situ microbial end-member is enriched compared to the predicted value, the contribution of microbially derived nitrate will be higher than estimated here. Microbial-derived NO_3^- is the major source of NO_3^- in groundwaters in both catchments even though the groundwater NO_3^- concentrations are quite different. This is consistent with the soil core results which did not show a difference in NO_3^- inventories between the two catchments.

4.5. Importance of Slope in Determining Groundwater NO_3^- Concentrations

[31] The most obvious difference between Harp 6 and 6a is in the groundwater NO_3^- concentrations. Rates of mineralization, nitrification and NO_3^- inventories in soils are similar in the two catchments. Isotopic analysis of nitrate in wells show no difference in the relative contribution of microbial nitrate to the total nitrate reaching the water table.

[32] Groundwater NO_3^- concentrations are affected by both the groundwater flow regime and the supply of NO_3^- available to infiltrating waters at the time of water table recharge. In Harp 6 and 6a, differences in groundwater flow are related to slope and the location of compact layers in the discharge zone at the bottom of the hillslopes. Soil pits dug in transects up both hillslopes show that till depths are similar, generally about 70–80 cm with a few isolated pockets of deeper till deposits likely in bedrock hollows. Hydraulic conductivities (K) are similar in the B horizons of the two catchments with the upper soil K largely controlled by macropore soil development processes. However, near the base of the slope, the water table is deeper in Harp 6 than 6a even though the hydraulic conductivity is similar (Figure 9a). Slopes at the lower end of the well transect in Harp 6 are 10° compared to 6° in Harp 6a. In Harp 6, slopes increase to 23° in the hillslope above the groundwater seep whereas the maximum slopes in Harp 6a are 16°. The increase in hydraulic gradient in Harp 6 due to the steeper slope, leads to deeper water tables, increased drainage and shorter groundwater residence times.

[33] Vegetation can only access soil nitrate in the rooting zone. In Harp 6, the increased drainage and deeper groundwater tables limit the potential for nitrate uptake by vegetation on the hillslope until the water table rises close to the stream. High NO_3^- concentrations in the groundwater seep year-round indicate that high NO_3^- water recharged to deeper groundwaters remains there. Similarly, deep wells installed in Harp 6 at the base of slope in fall 1998 also have high NO_3^- (>1 mgN/L at 1.0, 1.5 and 2.0 m) throughout the year. High NO_3^- waters must reside on the hillslope in either the very lowest soil horizons or in fractures of the surficial bedrock in order to sustain the groundwater seep. This high NO_3^- water is transmitted more readily downslope following groundwater recharge in the fall.

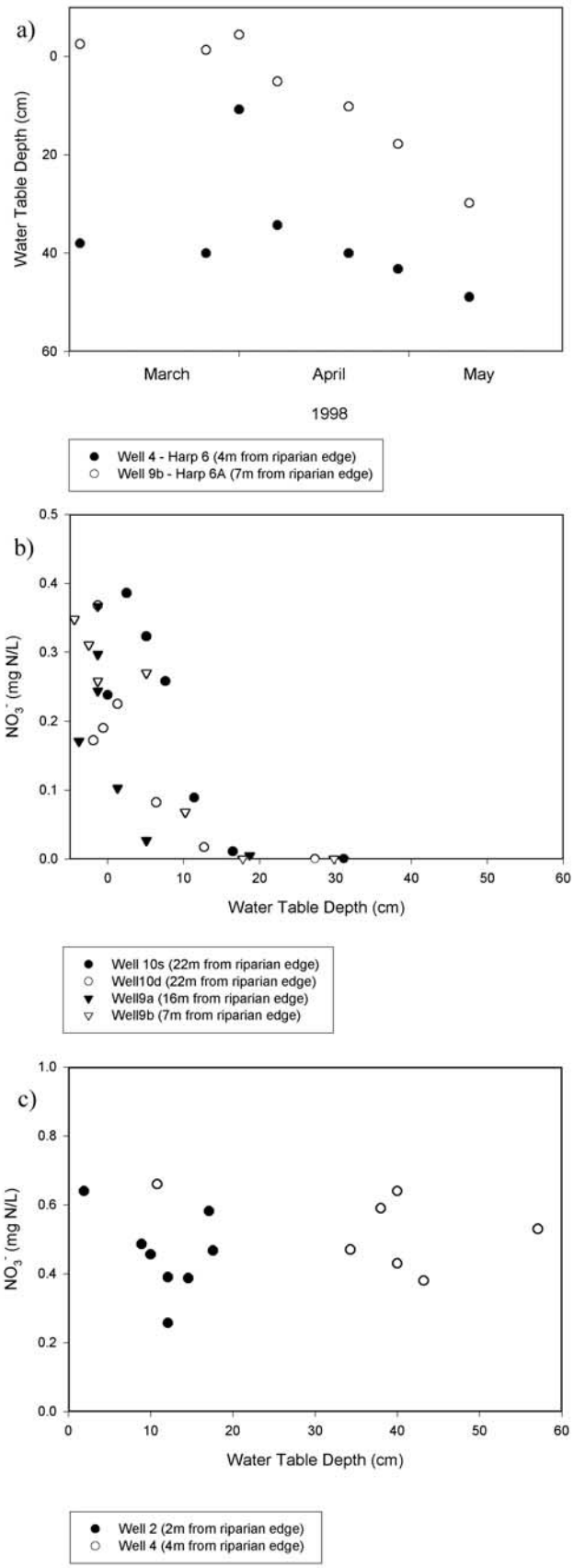

Figure 9. (oppposite) (a) Depth to water table below ground surface with time in two wells; well 4 in Harp 6 (4 m from the riparian edge) and well 9b in Harp 6A (7 m from the riparian edge) in 1998. (b) Nitrate concentrations in groundwater wells versus depth to water table below ground surface in Harp 6a in 1998. (c) Nitrate concentrations in groundwater wells versus depth to water table below ground surface in Harp 6 in 1998.

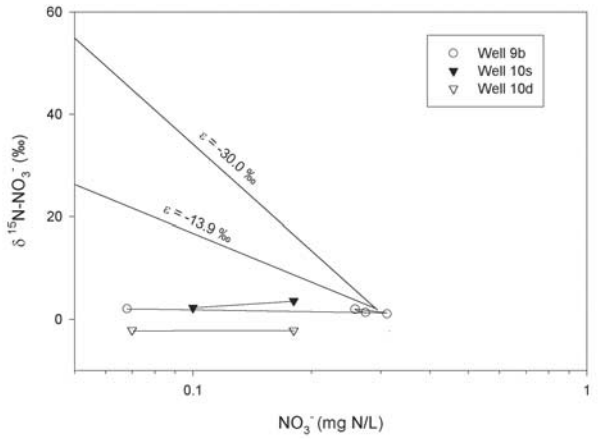

Figure 10. $\delta^{15}N$ in NO_3^- and NO_3^- concentrations in groundwater wells before and after snowmelt. Lines connect data in temporal sequence.

[34] Groundwater flow in both catchments is focused into shallower soil horizons close to the stream due to the presence of deeper compacted layers of lower hydraulic conductivity in the soil profiles adjacent to and within the valley bottoms. Perched water tables have been observed in soil pits in both catchments during drier periods with water flow continuing in the mid-B horizon at 20–40 cm. In Harp 6a, the compact layer occurs at a shallower depth than in Harp 6 and, combined with the lower hydraulic gradient for the hillslope, leads to discharge at the surface near the wetland during snowmelt periods. Within these shallow soil depths, NO_3^- concentrations decline quickly after peak snowmelt (Figures 9a and 9b) and NO_3^- disappears from the groundwater before a substantial decline in water table. In contrast, NO_3^- concentrations in groundwaters in Harp 6 remain high but the water table drops rapidly below 50 cm due to the more rapid drainage of the steeper slope (Figures 9a and 9c).

[35] Rapid removal of NO_3^- in shallow groundwaters immediately following snowmelt could be a result of vegetative uptake or denitrification in Harp 6a. To assess whether denitrification could be important, isotope ratios of NO_3^- were measured in groundwater wells during the period of NO_3^- decline. There is no enrichment of $\delta^{15}N$ (Figure 10) or $\delta^{18}O$ (Schiff, unpublished data) in these samples as NO_3^- decreases indicating that denitrification is not enriching the NO_3^- that is measured. Denitrification could be progressing to completion in small pockets of the flow system. Mixing of this zero nitrate water with higher NO_3^- water would fortuitously yield the observed trend of no isotopic enrichment with declining NO_3^- concentrations. However, the decline in NO_3^- occurs simultaneously in all wells along the hillslope transect in Harp 6a instead of progressively along the flow path. Ground vegetation is observed to become active immediately following snowmelt with small herbacious plants such as trout lilies visible above the forest floor within a week of spring melt in 1998. Trees also actively assimilate NO_3^- prior to bud break [*Jonassan and Shave*, 1999]. With groundwaters at shallow depths and at a slower rate of groundwater flow, the vegetation could consume the NO_3^- immediately following the spring melt period in Harp 6a. In contrast, in Harp 6, groundwater levels decline rapidly to below the rooting depth (well 4, Figures 9a and 9c) and high NO_3^- concentrations are preserved. High NO_3^- concentrations are observed in the discharge area of the riparian zone (well 2) because of the continued drainage of high NO_3^- water from the hillslope above which overwhelms the capacity of the riparian zone to attenuate NO_3^-. Steeper slopes preserve NO_3^- in groundwater by storing infiltrated NO_3^- below the rooting zone following spring melt.

4.6. Differences in NO_3^- Supply to Infiltrating Waters During Snowmelt

[36] After leaf fall, during the period of fall recharge, NO_3^- concentrations in groundwater rise in both catchments (Figure 6). However, groundwater NO_3^- concentrations at maximum saturation during peak melt are substantially higher in Harp 6 compared to Harp 6a. This large difference in NO_3^- concentrations in groundwaters at high water tables in the two catchments must reflect either a contribution from deeper groundwaters with high NO_3^- (because of storage below the rooting zone) in Harp 6 or a difference in the supply of NO_3^- to infiltrating groundwaters between the catchments. Soil NO_3^- inventories conducted monthly in 1995, 1996 (Figure 5b) and the inventories conducted prior to spring melt in 1998 do not indicate any notable difference between the two catchments.

[37] Shallow waters flowing on the surface, in the A soil horizon or most often at the A/B horizon interface (10–12 cm) in both catchments were sampled in 1997 and 1998 at peak snowmelt. The results are startling. Nitrate concentrations were much higher on the slope of Harp 6 (>0.7 mgN/L) than in Harp 6a (<0.4 mgN/L; Figure 11). Similar results were obtained in the spring melt of 1997. Shallow flow in these uppermost soil horizons is observed during

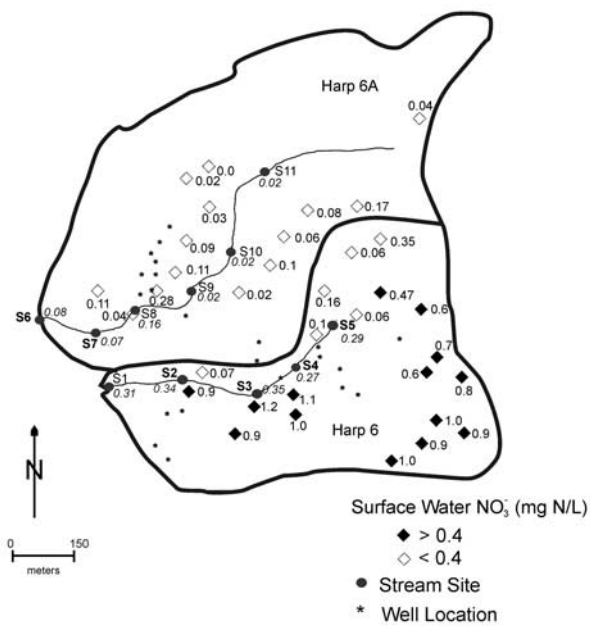

Figure 11. NO_3^- concentrations (mg N/L) in spring overland flow and shallow subsurface flow (0–10 cm) on 1 April 1998. NO_3^- concentrations (mg N/L) at stream sampling sites are shown in italics.

snowmelt but only rarely (not even yearly) in fall storms of exceptionally high rainfall intensity. The large difference in NO_3^- concentrations in shallow soil waters between the two catchments is distinctive. Furthermore in Harp 6a, these shallow soil waters have lower NO_3^- concentrations than the groundwaters sampled in the wells at the same time. Infiltration of these shallow waters is limited under these very saturated conditions by the underlying low hydraulic conductivity tills and is unlikely to be responsible for the decline in NO_3^- concentrations in groundwater following spring melt. Shallow flow only occurs for a short time when the ground is saturated. However, the contrast between the two catchments indicates that there are differences in the nitrate inventories or cycling in shallow soil zones in these catchments.

[38] One possibility is that N inventories and N cycling rates are an artifact of the collection method. Severing roots during sample collection, incubation, or storage prior to analysis may affect the observed rates and inventories [*Lamontagne*, 1998]. However, artifacts would be expected to affect soil sampled in both catchments equally. Another possibility is that the current soil sample design missed highly localized spatial differences in NO_3^- inventories. The highest inventories were often observed at the highest topographic elevations in each catchment but the soil inventories were not designed to preferentially sample these locations.

[39] A third possibility is that there is a difference in the timing of NO_3^- release because of differences in the predominant aspects of the two catchments. The main hillslope in Harp 6A faces south whereas the main hillslope in Harp 6 faces north. During spring melt, nitrate can be preferentially eluted early from the snowpack. In one study [*Johannssen and Henriksen*, 1978] the first 20–30% of the melt contained 70–80% of the NO_3^-. To ascertain that we did not miss an earlier pulse of high nitrate that had infiltrated prior to peak melt, we had installed small piezometers with a screened interval of only 5 cm. Concentrations of NO_3^- above snowmelt values were not found at any depth in Harp 6a. In addition, shallow soil waters were collected one week past peak melt to see if the NO_3^- concentrations changed with the progression of the melt. Nitrate concentrations remained high in Harp 6 and low in Harp 6a.

[40] Dilution of the nitrate in the infiltrating water with water of zero nitrate in Harp 6a is consistent with both the distributions of NO_3^- concentrations and the isotopic ($\delta^{18}O$ and $\delta^{15}N$) analyses of NO_3^-. Because the $\delta^{18}O$–NO_3^- in the groundwaters is similar in both catchments, the relative contribution of microbial and precipitation nitrate must be similar. Dilution with water containing zero nitrate will not alter the isotopic composition (either $\delta^{18}O$ or $\delta^{15}N$) of the infiltrating water but will affect the nitrate concentrations. Although there is no isotopic evidence for denitrification in shallow groundwater samples that were run during the spring melt period, denitrification could be occurring in shallow soil horizons prior to infiltration. *Hill et al.* [1999] have observed rapid removal of NO_3^- following storm events in the surface soils of nearby Plastic catchment. In Harp 6a, groundwater in all shallow wells and groundwater discharging at the wetland (site S8) had higher NO_3^- concentrations than the shallow soil water samples. Persistent higher water tables in Harp 6a during spring melt force meltwater at peak melt to run through shallow organic-rich soil horizons either in the litter or within the A horizon. Steeper slopes in Harp 6, typically meant that shallow waters were often sampled at the soil A/B interface or after discharge to surface from underlying soil. It is possible that this difference in the flow path for shallow waters at peak snowmelt facilitated denitrification only in Harp 6a. Only fortuitous sampling would allow this scenario to be checked using isotopes. Shallow waters in 6a would have to be sampled partway through the denitrification process when sufficient NO_3^- remains for isotopic analysis but without any mixing with other waters. Other methods of assessing denitrification potential such as N_2O evolution [e.g., *Groffman and Tiedje*, 1989; *Hill et al.*, 1999] may prove more successful.

[41] Although the reason for the difference in NO_3^- concentrations of shallow soil waters during spring melt is unknown, a clear difference exists between the two catchments. Discharge of deeper groundwaters of higher NO_3^- in Harp 6 into the surface soils would only occur in areas where the till depth decreases abruptly (i.e., bedrock lip) forcing deeper water held in lower hydraulic conductivity layers into more conductive shallow soil layers. This stratigraphic constraint would have to occur throughout the lower catchment and was not observed at the surface or in any of the soil pits or well installations. Discharge of deeper groundwaters is unlikely to explain the widespread pattern of higher NO_3^- concentrations across the catchment. Isotopic analysis of nitrate combined with nitrate concentrations are consistent with the possibility of denitrification (proceeding to completion) in shallow soil horizons on lesser slopes.

4.7. Importance of Riparian Zones

[42] Although infiltrating waters reaching the water table have differing NO_3^- concentrations in the two catchments, groundwater NO_3^- concentrations may be subsequently modified as the water discharges through the riparian zones. Organic-rich sediments in riparian zones have been shown to facilitate denitrification [i.e., *Cirmo and McDonnell*, 1997].

[43] During the spring melt, the streams at Harp 6 and 6a are primarily affected by the thawing of the wetlands. Wetland surface soil temperatures hover around 0°C in the winter and ice forms in the hollows [*Devito et al.*, 1999b]. Concentrations of NO_3^- in the pore waters of the wetland throughout the year are always nondetectable and nitrification rates are negligible [*Devito et al.*, 1999b]. During the snowmelt period, the accumulated ice on the wetland surface remains frozen. The frozen surface and high water tables force the hillslope water to discharge over the surface of the wetland [i.e., *Devito and Dillon*, 1993]. In Harp 6a outflow, NO_3^- concentrations (0.11 mgN/L on 1 April 1998) are elevated in comparison to the wetland input at S10 (0.02 mgN/L) by groundwaters discharging from the hillslope measured in the wetland at S8 (0.39 mgN/L). This is also evident in Harp 6 where high stream NO_3^- concentrations similar to groundwaters are observed at S5 (Figure 4a) just below the wetland. Attenuation of NO_3^- at peak melt is thwarted by frozen conditions.

[44] Following peak melt, stream NO_3^- concentrations decline more rapidly than groundwater NO_3^- (Figures 4 and

6). Thawing of the wetlands between 1 and 8 April 1998 (observed in the wetland groundwater wells) leads to a sharp decline in NO_3^- to nondetectable levels (<0.003 mgN/L) in the water leaving the wetlands by April 8 in both Harp 6 and 6a (Figures 4a and 4b). Water tables remain above the wetland surface, limiting interaction of the hillslope groundwaters discharging at the wetland edge with the organic-rich sediments. Groundwater nitrate (average 0.26 mgN/L in Harp 6a and 0.55 mgN/L in Harp 6 on 8 April) is diluted by the large pool of melting wetland surface water. Disappearance of nitrate from the groundwaters on the hillslope in Harp 6a is coincident with the subsequent draining of the wetland. Thus the primary role of the wetland during late spring melt is dilution of hillslope runoff.

[45] During the late spring, summer and early fall, water tables are nonexistent in the hillslope tills and wetland NO_3^- concentrations are nondetectable. In Harp 6a, the stream entering the lower wetland seldom flows (Figure 4b). When it flows, the stream has no NO_3^-. Thus, although the organic-rich sediments in the large wetland at the base of Harp 6a have the potential to function as an important N sink, the wetland receives no nitrate from upslope in the catchment during the growing season. Only nitrate received directly from atmospheric deposition enters the wetland where vegetation and the microbial community compete vigorously for N due to the high C/N ratios (34 [*Devito et al.*, 1999b]. In the late fall and winter, groundwater NO_3^- concentrations on the hillslopes rise above concentrations in the 6a stream outflow. At this time of the year, the riparian wetland attenuates the NO_3^- in the discharging groundwaters.

[46] In Harp 6, although there is no large wetland at the base of the catchment, the small streamflows over and through organic-rich sediments in the valley bottom where nitrate attenuation could occur. In the spring, groundwater NO_3^- concentrations are high (Figure 9c), discharge is high, and the natural attenuating capacity of this small riparian zone is overwhelmed (Figure 4a). In the summer, water tables are deep. Although NO_3^- concentrations in the deeper groundwaters are high, discharge from these deeper high nitrate groundwaters is low. Attenuation of the discharging nitrate through either denitrification in organic sediments or vegetation uptake is not complete in 1997 or 1998. During the fall, stream concentrations increase coincidentally with increases in groundwater discharge and NO_3^- concentrations, suggesting that the ability of the riparian zone to attenuate the increased load of groundwater nitrate is low in the fall. Thus, in Harp 6, although the wetland at the head of the catchment attenuates nitrate from the surrounding hillslope, the riparian zone along the length of the stream is unable to completely attenuate high NO_3^- in the discharging groundwaters except during summer low flow conditions.

4.8. Nitrate Export and Slope

[47] A positive relationship between topographic slope and nitrate has been noted by other researchers [e.g., *Dillon et al.*, 1991; *D'Arcy and Carignan*, 1997]. *D'Arcy and Carignan* [1997] attributed the relationship to the capacity of organic-rich sediments in riparian zones to attenuate nitrate by denitrification. In this study, groundwater concentrations of NO_3^- in the two catchments are different before the NO_3^- reaches the riparian zone. During periods of high water tables and low biological activity at low temperatures, the attenuating capacity of riparian zones is overwhelmed. Organic-rich sediments in valley bottom deposits may not be able to completely attenuate high nitrate concentrations observed in some hillslope groundwaters.

[48] In this study, higher nitrate concentrations are evident in the groundwaters on the hillslope with a higher topographic slope. Although the factors leading to the differences in NO_3^- supply to the water table are unknown, the topography and stratigraphy govern the ability of the hillslope vegetation to access the NO_3^- by governing the depth of the water table below the surface. On the steeper hillslopes, faster drainage and deeper water tables work to preserve NO_3^- in deeper groundwaters below the rooting zone. Shallow water tables may also facilitate denitrification by maintaining near saturated conditions in organic-rich soil horizons. Further work is needed on the factors affecting concentrations of NO_3^- delivered to hillslope water tables. Because the relationship between slope and nitrate export has been observed in other studies, the observation that steeper slopes preserve higher NO_3^- concentrations may be widespread. Thus, the observed relationship of NO_3^- concentrations with slope may be a result of hillslope hydrology rather than processes in the riparian zone.

5. Summary and Implications

[49] Two adjacent catchments with similar soils, vegetation and N deposition differ in nitrate export by a factor of ten. Seasonal patterns in stream nitrate concentrations are similar but the values differ in magnitude. Soil mineralization, nitrification and nitrate inventories appear similar in the two catchments based on common techniques. The main difference is the groundwater NO_3^- concentrations. In one catchment, values only approach snowpack concentrations during spring melt and rapidly decline following melt to nondetectable levels. Thus, although a large wetland is located at the base of the catchment, the attenuating ability of this wetland is not needed during the growing season and is limited in the spring melt period when it is frozen and water tables are high. Isotope ratios of nitrate ($\delta^{15}N$ and $\delta^{18}O$) do not indicate the presence of denitrification. Shallow soil waters have NO_3^- concentrations below groundwater concentrations during peak melt suggesting that denitrification could occur in shallow organic-rich soil horizons. Vegetative uptake or denitrification proceeding to completion within the groundwater zone are responsible for the rapid decline in groundwater NO_3^- following peak snowmelt.

[50] In the other catchment, nitrate concentrations in deeper groundwaters below the rooting zone exceed snowpack values. Stratigraphy and topography facilitate the rapid decline of the water table following spring melt and thus limit the ability of the vegetation to access groundwater NO_3^-. High concentrations of NO_3^- infiltrating below the rooting zone during spring melt are preserved. During the summer growing season, water flux is low and the organic-rich riparian sediments partially attenuate the nitrate. During the fall, winter and spring, the attenuating capacity of the small stream-side riparian zone is overwhelmed, leading to

increased stream NO_3^- concentrations and export. In this study riparian zones play only a limited role in nitrate attenuation. Thus the ten-fold difference in export between these two catchments results from a difference in slope which controls water table dynamics.

[51] Are these two adjacent catchments reflective of different positions in the time trajectory of nitrogen saturation [e.g., *Aber et al.*, 1989]? Although one catchment has higher surface soil water nitrate concentrations available for groundwater recharge in the spring, it is not clear why this occurs or whether there has been any change with time. A decrease in nitrate retention is another hallmark of nitrogen saturation [*Dillon and Molot*, 1990]. However, there is no evidence that the nitrate retention in Harp 6 has decreased in the past 25 years [*Dillon et al.*, 1991]. Until the origin of the higher nitrate supply to the water table in the one catchment is known, little can be concluded about the proximity of these adjacent catchments to nitrogen saturation. However, in this study, riparian zones do not play a major role. More attention should be focused on the recharge of nitrate to groundwaters and water table dynamics in relation to nitrogen cycling of forested headwater catchments. It is the combination of the hydrogeologic setting (slope and stratigraphy) combined with the factors controlling nitrate concentrations in recharging waters that govern the contrast in nitrate export in these two adjacent catchments.

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