

A field-based study of soil water and groundwater nitrate release in an Adirondack forested watershed

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[1] Nitrate (NO_3^-) movement was studied using a combination of isotopic, chemical, and hydrometric data within the 135 ha Archer Creek watershed in the Adirondack Mountains of New York from January 1995 to December 1996. This research was conducted to identify sources of stream water NO_3^- and the mechanisms that deliver NO_3^- to the stream to test two hypotheses: (1) Soil water NO_3^- concentrations are highest after dry periods and subsequently lower with each storm. (2) Stream water NO_3^- concentrations are controlled by groundwater during growing season low flows and by soil water during the dormant season and during storms. Antecedent moisture conditions and season had little effect on mean soil water NO_3^- concentrations before storms (range of $1.1\text{--}5.1\ \mu\text{mol L}^{-1}$ throughout the study). High soil water NO_3^- concentrations (up to $136\ \mu\text{mol L}^{-1}$) were found only at the watershed ridge top during the 1996 snowmelt and early summer. Results from isotopic hydrograph separations and chemical end-member mixing analysis showed that soil water and till groundwater dominated stream base flow and storm flow during six monitored storms. Near-stream wetland groundwater and event water contributed little to streamflow during most conditions. Near-stream groundwater contributions to streamflow were significant only during very low base flow ($<0.05\ \text{mm h}^{-1}$) during the summer and fall. Highest stream water NO_3^- concentrations coincided with peaks in the till groundwater contribution according to isotopic hydrograph separations using $\delta^{18}\text{O}$ and chloride as conservative tracers. A conceptualization of streamflow generation and watershed NO_3^- release is described in which hillslope hollows are the principal zones of soil water and till groundwater mixing in the watershed and till groundwater is the main source of stream water NO_3^- during both base flow and storms. **INDEX TERMS:** 1615 Global Change: Biogeochemical processes (4805); 1860 Hydrology: Runoff and streamflow; 1871 Hydrology: Surface water quality; 1806 Hydrology: Chemistry of fresh water; **KEYWORDS:** Adirondack Mountains, biogeochemistry, hydrology, nitrate flushing, nitrogen saturation, watershed

1. Introduction

[2] Evaluation of factors that affect NO_3^- loss from watersheds has been the focus of much recent research [Creed *et al.*, 1996; Hill, 1996; Cirino and McDonnell, 1997]. Nitrate has been identified as a source of episodic acidification [Wigington *et al.*, 1996a, 1996b] and the coincident release of monomeric aluminum to surface waters [Gubala *et al.*, 1991]. Because NO_3^- is highly mobile, it can contribute to the depletion of soil base cations causing changes in elemental balances and possible forest decline [Johnson *et al.*, 1985; Federer *et al.*, 1989; Zöttl and Hüttl, 1989; Cronan and Grigal, 1995]. Some studies have used the presence of NO_3^- in stream water during the growing season as an indication of N saturation [Stoddard, 1994; Lovett *et al.*, 2000]. Although high NO_3^- concentrations have been measured during summer base flow

in several watersheds [i.e., Burns *et al.*, 1998; Creed and Band, 1998a], a decoupling of deep and shallow groundwater systems has been hypothesized as the cause of the high concentrations rather than a direct contribution of atmospheric N in excess of biotic demand.

[3] Creed *et al.* [1996] have hypothesized two possible mechanisms for NO_3^- release in midlatitude humid watersheds based on stream water chemistry: (1) a flushing mechanism, where NO_3^- that accumulates in upper soil layers is flushed to the stream by a rising water table during storms, and (2) a draining mechanism, where NO_3^- rich snowmelt water recharges deep groundwater via preferential flow paths and is subsequently released slowly over the year. These hypotheses were developed using stream water data from the Turkey Lakes watershed (TLW), a sugar maple dominated watershed with a stand age of 150–300 years. These mechanisms suggest that the release of NO_3^- is controlled mainly by watershed hydrology. More recently, Hill *et al.* [1999] reported a high biological utilization of a limited soil N supply in the white pine dominated Plastic Lake watershed in southeastern Ontario, Canada, with a stand age of ~ 70 years. Although a considerable amount of moderate to high NO_3^- event water moved through the soil via preferential flow paths, the NO_3^- was immobilized in the surface soil layers, and there was little soil NO_3^- available to be flushed [Hill *et al.*, 1999]. These results emphasize the role that the biota can play in regulating NO_3^- loss in subsurface runoff. The Creed *et al.* [1996] and Hill *et al.* [1999] studies are not necessarily contradictory. The different controls of NO_3^- release described by the two studies show that general watershed characteristics such as

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stand age and soil depth as well as the scale at which studies are conducted (hillslope versus watershed outlet) are important considerations, especially regarding a nutrient cycle as complex as that of nitrogen.

[4] An important step to better understanding the sources of stream NO_3^- and the hypothesized pathways that deliver NO_3^- to the stream is to identify geographic sources of stream water both during and between storms. Sources of stream water have been identified in previous studies using conservative isotopic tracers [Hooper and Shoemaker, 1986; Pearce et al., 1986; Dewalle et al., 1988; McDonnell, 1990; Waddington et al., 1993; Hinton et al., 1994] and chemical tracing approaches [Hooper et al., 1990; Christopherson and Hooper, 1992]. Conservative isotopic tracers are limited in that they infer water source without providing information about flow paths. Several studies have used a combined approach of isotopic, chemical, and hydrometric data to identify both sources of stream water and flow paths [Kendall et al., 1999; McGlynn et al., 1999; Bazemore et al., 1994; Wels et al., 1990]. Other studies have shown that evolution of water chemistry along flow paths can play an important role in determining the chemistry of water that reaches the stream [Burns et al., 1998; Evans and Davies, 1998; Anderson et al., 1997].

[5] This paper reports the results of a field-based study of watershed NO_3^- release that examines the link between soil water and stream water NO_3^- concentrations. The study was conducted in the Archer Creek watershed that has a stand age of ~ 100 years, between that of Plastic Lake [Hill et al., 1999] and Turkey Lakes [Creed et al., 1996] watersheds. By sampling soil water, stream water, and groundwater for 2 years across storms, seasons, and antecedent moisture conditions, we examined the mechanisms for NO_3^- release and tested the following hypotheses: (1) Soil water NO_3^- concentrations are highest after dry periods and subsequently lower with each storm. (2) Stream water NO_3^- concentrations are controlled by groundwater during growing season low flows and by soil water during the dormant season and during storms. A combination of isotopic, chemical, and hydrometric data was used to provide multiple constraints on our conceptualization of NO_3^- loss during base flow and storm runoff.

2. Site Description

[6] The 135 ha Archer Creek watershed is the main inlet watershed to Arbutus Lake, located in the Huntington Wildlife Forest (HF) ($43^\circ 59'N$, $74^\circ 14'W$) within the central Adirondack Mountains of New York State (Figure 1). Bedrock in the watershed is mainly granitic gneiss with some gabbro-amphibolite. Mineral soils are coarse, loamy, mixed frigid, Typic Haplorthods in the Becket-Mundal association and are typically <1 m in thickness [Somers, 1986]. Mineral soils are characterized by high organic concentrations ($2.10\text{--}20.8 \text{ mol C kg}^{-1}$) and considerable coarse fragments ($5\text{--}32\%$) [Mitchell et al., 1992a]. There is a distinct Oi horizon ~ 5 cm in thickness; the A horizon is $0\text{--}5$ cm thick containing fine and medium roots. A strongly leached E horizon, $0\text{--}2$ cm thick, is present in most areas. The B horizon is $25\text{--}50$ cm thick and contains some clay and many coarse fragments. The C horizon is $20\text{--}40$ cm in thickness and is underlain by bedrock or glacial till. Greenwood mucky peats are present in valley bottom wetlands and range from 1 to 5 m in thickness [Somers, 1986; J. Doolittle, unpublished ground penetrating radar data, personal communication, 1998]. Soils are underlain by a thin bouldery glacial till derived from local bedrock. The watershed is characterized by a low drainage density (1.68 km km^{-2}), mean slope is 11% , and total relief is 225 m.

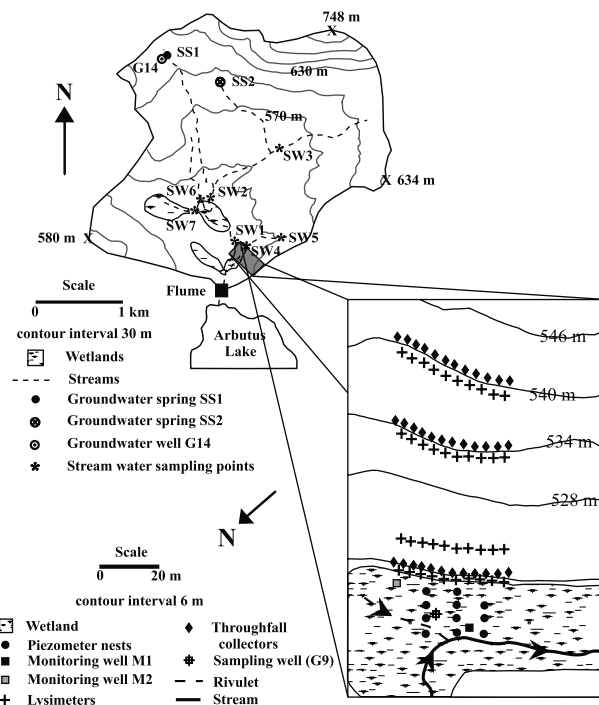


Figure 1. Archer Creek watershed at Huntington Wildlife Forest in the Adirondack Mountains of New York State.

[7] Overstory vegetation is mainly composed of northern hardwoods. Major species include *Fagus grandifolia* Ehrh. (American Beech), *Acer saccharum* Marsh. (sugar maple), *Betula alleghaniensis* Britt. (yellow birch), and *Abies balsamea* (L.) Mill. (balsam fir). *Alnus incana* (L.) Moench. (speckled alder) that fixes N is present along Archer Creek within one forested wetland. Conifers, including *Picea rubens* Sarg. (red spruce) and *Tsuga canadensis* (L.) Carr. (eastern hemlock), dominate in riparian zones and at higher elevations. The stand age is ~ 100 years. About 50% of the watershed is northern hardwoods, 31% is mixed northern hardwood/coniferous, and 19% is dominated by conifers.

[8] 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]. During the period of study (1 January 1995 to 31 December 1996), annual precipitation averaged 1181 mm, and the mean annual temperature was 5.4°C . Precipitation and air temperature were measured hourly at a meteorological station 1.5 km from the watershed. The HF is also a National Atmospheric Deposition Program (NADP) and National Trends Network (NTN) site. NADP wet-only weekly precipitation chemistry was used for this study. Dry deposition of NO_3^- and NH_4^+ was estimated from 1 May 1986 to 30 April 1988 at this site and accounted for 55% of NO_3^- and 12% of NH_4^+ deposition; organic N deposition was not measured [Shepard et al., 1989]. The Arbutus Lake watershed has been the site of several recent N studies focused on the importance of dissolved organic nitrogen in watershed N flux [McHale et al., 2000], the impact of near-stream wetlands on stream water N and DOC chemistry [McHale, 1999; Inamdar et al., 2000], the effect of landscape position on N mineralization and nitrification [Ohrui et al., 1999], and nitrogen storage in wetland and terrestrial vegetation [Bischoff et al., 2001]. Ohrui et al. [1999] compared N mineralization and nitrification at three landscape positions within the Archer Creek watershed. Mineralization and nitrification rates were estimated for ridge topsoils beneath a northern hardwood stand (ridge zone), at a

midslope position beneath a mostly coniferous stand (hillslope zone), and at the valley bottom in wetland soils beneath a coniferous stand (wetland zone). Higher N mineralization rates were recorded for hillslope soils ($107 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in the ridge zone and $82 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in the hillslope zone) compared to the wetland zone ($39 \text{ kg N ha}^{-1} \text{ yr}^{-1}$). The highest nitrification rates were in the ridge zone ($29 \text{ kg N ha}^{-1} \text{ yr}^{-1}$), and lowest were in the hillslope zone ($2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) [Ohrui *et al.*, 1999]. In the wetland, nitrification rates were $13 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. Ohrui *et al.* [1999] concluded that vegetation type and soil moisture had the greatest impacts on N mineralization and nitrification.

[9] Mitchell *et al.* [1992a] compared soil N cycling between Huntington Forest and Turkey Lakes watershed [Creed *et al.*, 1996]. Mineral soils were identified as the largest pool of N at both of the sites. There was a much lower NO_3^- leaching rate from HF soils than from those in TLW ($18 \text{ mol ion charge ha}^{-1} \text{ yr}^{-1}$ versus $1300 \text{ mol ion charge ha}^{-1} \text{ yr}^{-1}$ respectively). The difference in NO_3^- leaching rates was attributed mainly to differences in vegetative uptake (HF stand age is 100 years; TLW is 300 years); however, differences in soil C:N ratios and the absence of slowly decomposing *Fagus grandifolia* Ehrh. (American Beech) leaf litter were also suggested as possible reasons for differences in NO_3^- leaching rates [Mitchell *et al.*, 1992a].

3. Methods

3.1. Data Collection

[10] Discharge was recorded every 15 min at an HL flume at the watershed outlet (Figure 1). Groundwater level was recorded hourly in two wetland wells (Figure 1) using pressure transducers. One well was located 1.5 m from Archer Creek, and the second was located at the hillslope-riparian zone interface. Daily solar radiation was measured with a solar pyranometer at a meteorological station operated by HF staff at a clearing 1.5 km from the watershed. Leaf area index (LAI) was measured for a northern hardwood site adjacent to the Arbutus watershed during the Integrated Forest Study [Mitchell *et al.*, 1992b]. Daily solar radiation and LAI were used to estimate evapotranspiration.

[11] Stream samples were collected biweekly from 1 January 1995 to 31 December 1996, daily during spring snowmelt, and approximately hourly during six storms. Storm sampling was conducted using an automated sampler. Longitudinal and spatial surveys of surface water chemistry were conducted biweekly throughout the watershed during the study period. All first-order perennial streams were sampled and used to investigate possible geographic sources of water to the mainstream (Figure 1). Two of the perennial streams were identified as groundwater springs (SS1 and SS2, Figure 1) owing to high solute concentrations and because they emerged from the ground surface close to the sampling point. Sampling locations for these springs were chosen as far upstream as possible while still being able to consistently obtain a sufficient amount of water for chemical analyses.

[12] Throughfall, soil water, and wetland groundwater collectors were located in transects within an intensive research hillslope (Figure 1). Throughfall was collected biweekly using three transects of 12 collectors each (Figure 1). Transects were located in an upland hardwood zone, an upland conifer zone, and a wetland zone [i.e., Ohrui *et al.*, 1999]; these areas also corresponded to the following landscape positions: ridge top, midslope, and valley bottom, respectively. The collectors were constructed from 160 mm diameter plastic funnels attached to 1.9 L plastic bottles with 6.4 mm diameter Tygon[®] tubing. Snowmelt was collected daily during melt from three $1 \times 0.5 \text{ m}$ snowmelt lysimeters. Meltwater was collected

in 19 L plastic buckets that were rinsed with deionized water each time they were sampled. The volume of melt was recorded at the time of sampling. Soil water was sampled biweekly at depths of 0.15 and 0.5 m using porous cup tension lysimeters. Forty pairs of lysimeters were located in four transects of 10 pairs each. Three transects were colocated with throughfall collectors, and an additional transect was located where the hillslope met the valley bottom. Lysimeters were evacuated to 275 kPa one day prior to sampling. During the same period of this study, Ohrui *et al.* [1999] measured net mineralization and nitrification rates on the same hillslope that throughfall collectors and soil lysimeters were located. Lysimeter transect 1 was located in what Ohrui *et al.* [1999] defined as the upland hardwood ridge zone, and transects 2 and 3 were located in what Ohrui *et al.* [1999] defined as the upland hillslope zone.

[13] Near-stream riparian groundwater was sampled approximately biweekly from 11 piezometer nests within one valley bottom wetland from 1 March 1996 through 31 July 1996 (Figure 1). Piezometers were constructed from 12.7 mm diameter PVC pipe screened 0.10 m at the bottom. Each piezometer nest consisted of two to three piezometers installed to depths of 0.5, 1.5, and 2.5 m. One 12.7 mm diameter sampling well that was screened for its entire depth (3.0 m) was installed in the wetland. The piezometers and well were pumped dry and allowed to recharge before sampling. Piezometer nests and wetland sampling well G9 were located in what Ohrui *et al.* [1999] defined as the wetland zone.

[14] All water chemistry samples were collected in opaque, brown polyethylene bottles and stored at 1°C until analyzed using suppressed ion chromatography (NO_3^- , SO_4^{2-} , and Cl^-), ion coupled plasma injection (Ca^{2+} and Mg^{2+}), atomic adsorption spectroscopy (K^+ and Na^+), a Wescan ammonium analyzer (NH_4^+), and persulfate digestion for total N. Dissolved organic nitrogen was calculated by subtracting NO_3^- and NH_4^+ from total nitrogen. Nitrate is reported as NO_3^- rather than $\text{NO}_3\text{-N}$.

3.2. Storm NO_3^- Flux and the Hydrologic Budget

[15] Storm NO_3^- flux from the watershed was calculated by multiplying water flux by concentration at 15 min intervals (corresponding to the frequency of stream discharge measurements) and dividing by watershed area. Concentrations were linearly interpolated between sample intervals, which ranged from 1 to 3 hours.

[16] A hydrologic budget was calculated from the 2 years of data available for the watershed to relate periods of hydrologic recharge and discharge to stream water NO_3^- characteristics [Burns *et al.*, 1998]. Change in storage of the groundwater and soil water reservoirs was calculated as

$$\Delta S = P - Q + ET, \quad (1)$$

where Q is watershed discharge, ET is evapotranspiration, and P is incoming precipitation. The water equivalence of the snowpack was measured biweekly during snow cover. The monthly change in the water equivalence of the snowpack was added to (snowpack loss) or subtracted from (snowpack additions) the P term. We assumed that surface water and groundwater divides were coincident because of the steepness of the watershed (relief of 225 m), particularly at the divides. Changes in the storage term indicate storage recharge when ΔS is positive and storage discharge when ΔS is negative. Discharge was measured at the HL flume at the watershed outlet, and precipitation was measured with a weighing rain gauge 1.5 km from the watershed. Evapotranspiration (ET) was calculated using the evapotranspiration subroutine included in the BROOK 90 hydrologic model [Federer, 1992] that uses the Shuttleworth and Wallace [1985] modification of the Penman-Monteith approach.

Table 1. Mean Solute Concentrations For Archer Creek, Stream Sample Points 1–7, and Sources of Streamflow in Archer Creek Watershed 1 January 1995 to 31 December 1996^a

Source	Solute								
	Na ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	K ⁺	NH ₄ ⁺	NO ₃ ⁻	DON	Cl ⁻
Archer Creek (outlet) ^b	37(±10)	101(±16)	23(±5)	69(±9)	6(±3)	2(±2)	23(±18)	15(±7)	12(±4)
Stream sample point SW1 ^b	43(±13)	113(±25)	25(±6)	69(±11)	4(±3)	1(±1)	24(±12)	11(±7)	11(±4)
Stream sample point SW2 ^b	39(±8)	131(±26)	25(±5)	72(±8)	4(±2)	1(±1)	30(±18)	10(±5)	
Stream sample point SW3 ^b	44(±16)	74(±49)	18(±12)	82(±11)	6(±3)	2(±1)	17(±13)	11(±19)	13(±2)
Stream sample point SW4 ^b	37(±10)	91(±33)	26(±6)	69(±9)	9(±7)	3(±2)	17(±12)	15(±17)	11(±3)
Stream sample point SW5 ^b	36(±10)	75(±11)	22(±4)	72(±8)	4(±3)	2(±1)	15(±10)	10(±10)	11(±3)
Stream sample point SW6 ^b	53(±14)	133(±28)	32(±7)	75(±11)	3(±2)	1(±1)	25(±11)	9(±7)	11(±2)
Stream sample point SW7 ^b	48(±14)	93(±75)	23(±7)	68(±19)	4(±2)	1(±1)	10(±12)	14(±17)	11(±4)
Soil water (15 cm) ^c	21(±12)	39(±20)	17(±10)	53(±25)	22(±27)	2(±3)	3(±15)	44(±17)	15(±10)
Soil water (50 cm) ^c	32(±9)	43(±2)	21(±7)	70(±15)	11(±8)	2(±2)	^d	15(±12)	14(±5)
Wetland groundwater ^e	105(±86)	176(±73)	100(±46)	34(±36)	18(±7)	56(±24)	^d	34(±55)	25(±11)
Groundwater well G14 ^f	255(±149)	220(±18)	70(±7)	144(±14)	19(±8)	13(±25)	21(±6)	18(±27)	23(±13)
Groundwater spring SS1 ^g	70(±27)	185(±87)	49(±23)	108(±27)	7(±4)	2(±1)	24(±8)	9(±22)	12(±1)
Groundwater spring SS2 ^g	32(±3)	428(±83)	40(±4)	113(±25)	5(±5)	1(±1)	63(±15)	10(±18)	12(±2)
Throughfall ^b	5(±9)	32(±25)	14(±10)	39(±24)	69(±56)	15(±32)	38(±50)	28(±32)	17(±14)
Snowmelt ^h	5(±9)	14(±21)	6(±14)	15(±20)	8(±15)	11(±7)	31(±29)	7(±7)	10(±13)

^a Sampling locations are shown in Figure 1. All values are in $\mu\text{mol L}^{-1} \pm 1$ standard deviation.

^b Sources were sampled from 1 January 1995 to 31 December 1996.

^c Soil lysimeters were sampled from July 1995 to December 1996.

^d Samples were below the limit of quantification.

^e Wetland groundwater was sampled from 1 March 1996 to 31 August 1996.

^f Groundwater well G14 was sampled from 1 April 1996 to 31 December 1996.

^g Groundwater springs SS1 and SS2 were sampled from 1 June 1995 to 31 December 1996.

^h Snowmelt was sampled during the 1995 and 1996 melt seasons.

Groundwater flux to the stream was not measured; consequently, no error estimate of the hydrologic budget was possible.

3.3. Hydrograph Separations and Antecedent Precipitation Index

[17] Hydrograph separations were completed for three storms using H_2^{18}O and Cl^- as conservative tracers. Samples for isotopic analyses were collected in 20 mL glass polyseal vials and sealed with paraffin. The $^{18}\text{O}/^{16}\text{O}$ ratios of the samples were determined by mass spectrometry at the U.S. Geological Survey (USGS) Isotope Laboratory in Menlo Park, California. Values are reported as per mil difference relative to Vienna standard mean ocean water (VSMOW) with a precision of 0.1‰. Both one-tracer two-component and two-tracer three-component hydrograph separations were completed [Kendall and McDonnell, 1998].

[18] The antecedent precipitation index (API) was calculated for rainstorms to determine the antecedent moisture conditions prior to each storm (not including snowmelt). The API was calculated as [Viessman et al., 1989]

$$\text{API}_i = K(\text{API}_{i-1}) + P_i, \quad (2)$$

where the antecedent precipitation index on any given day (API_i) is equal to a recession constant K normally reported in the range 0.85–0.98 (0.9 was used for our calculations) multiplied by the API on the previous day (API_{i-1}) plus the total daily precipitation P_i .

3.4. End-Member Mixing Analysis

[19] End-member mixing analysis (EMMA) [Christopherson and Hooper, 1992] was completed using four solutes (Na^+ , Ca^{2+} , Mg^{2+} , and SO_4^{2-}). EMMA was completed for the entire data set and for six storms during the study period. Although EMMA has been used as a hydrograph separation tool in previous studies [Brown et al., 1999], on the timescale of a single storm the

accuracy of the calculated percentages of end-member contributions to streamflow is questionable because on short timescales, end-member chemical compositions can vary substantially [Elsenbeer et al., 1995]. In our study, EMMA was used as an investigative tool to identify end-members that contribute to streamflow and to indicate the relative contributions of end-members to streamflow during different seasons and with different antecedent moisture conditions. EMMA was also used to corroborate the selection of streamflow components for the conservative tracer hydrograph separations.

4. Results

4.1. Spatial Variability of End-Members

[20] The aerial extent of throughfall, soil water, and groundwater sampling was necessarily limited owing to the logistical constraints of sampling a 135 ha watershed. Throughfall and soil water sampling was conducted within the intensive research hillslope, and although collectors were installed from the ridge top to the valley bottom, this encompassed only ~20 m of relief. Nonetheless, considerable variability was measured for many of the solutes for both throughfall and soil water (Table 1). During this study, mean throughfall and soil water NO_3^- concentration increased with increasing elevation within the intensive research hillslope (Table 2). The highest non-volume weighted mean throughfall NO_3^- concentration was measured in the ridge zone as was the highest soil water mean NO_3^- concentration. Both throughfall and soil water NO_3^- concentrations decreased with elevation (Table 2).

[21] Groundwater piezometers and wells were installed in a wetland that bordered Archer Creek close to the watershed outlet to provide a measure of near-stream riparian groundwater chemistry. Many studies have shown near-stream riparian groundwater to be a significant source of streamflow [Jenkins et al., 1994; Waddington

Table 2. Non-Volume Weighted Mean NO_3^- Concentrations of Soil Water at 0.15 and 0.5 m Depths and Throughfall Across Elevation Gradients Within the Intensive Research Hillslope in the Archer Creek Watershed^a

Elevation Zone	Soil Water (15 cm)	Soil Water (50 cm)	Throughfall
Ridge zone	19 ± 35	6 ± 13	51 ± 66
Hillslope zone	^b	^b	33 ± 35
Wetland zone	^b	^b	31 ± 36

^aSampling was conducted from 1 January 1995 to 31 December 1996. All concentrations are in $\mu\text{mol L}^{-1} \pm 1$ standard deviation.

^bConcentrations were below the limit of quantification ($3 \mu\text{mol L}^{-1}$).

et al., 1993; Hooper *et al.*, 1990]. The grid of piezometers nests was focused in the near-stream zone to sample this potentially significant source of streamflow.

[22] All first-order perennial streams within the watershed were sampled approximately biweekly. This sampling was completed to test whether the soil water lysimeters were representative of soil water throughout the catchment (whether the chemistry of soil lysimeter water was expressed in surface water throughout the catchment). End-member mixing analysis indicated that the intensive research hillslope soil lysimeter water was indeed representative of water throughout the catchment in that all of the first-order streams plot roughly on a mixing line between the soil lysimeters and the groundwater springs SS1 and SS2 (Figure 2). This analysis suggests that both soil lysimeter water and the water from groundwater spring SS2 (deeper till groundwater) were representative of end-members that were present throughout the watershed. All first-order streams were mainly composed of a mixture of these two end-members (Figure 2).

4.2. Annual Analyses

[23] Hydrologic budgets calculated for the 1995 and 1996 calendar years showed that the principal time of recharge was from September through December (Figure 3). Recharge also occurred during February and March in 1995, April in 1996, and

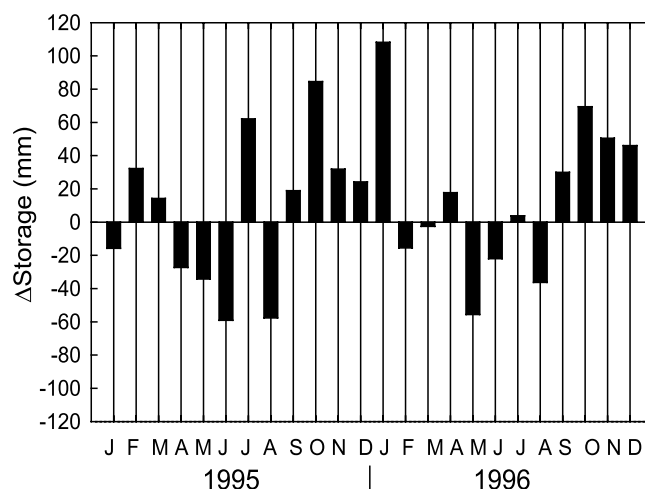


Figure 3. Monthly change in soil water and groundwater storage in the Archer Creek Watershed 1995–1996.

during July of both years, most notably in 1995. The July 1995 recharge was due to the large amount of rainfall (189 mm) during that month.

[24] Snowmelt and season affected annual patterns of NO_3^- concentration within the watershed (Figures 4a–4f). Peak outlet NO_3^- concentrations occurred during winter and spring snowmelt (Figure 4f). Stream water NO_3^- concentrations declined markedly during the growing season of both years. The flow-weighted mean NO_3^- concentration during the growing season (June–September) was $5.4 \mu\text{mol L}^{-1}$ for 1995 and 1996. All NO_3^- concentrations exceeded the limit of quantification ($3 \mu\text{mol L}^{-1}$). Nitrate concentrations at groundwater spring SS1 were similar to concentrations at the outlet; however, during outlet base flow periods, NO_3^- concentrations were higher, and concentrations during snowmelt were lower at SS1 than at the outlet (Figure 4a). Groundwater spring SS2 had higher NO_3^- concentrations than either SS1 or the outlet during outlet base flow and a seasonal pattern similar to SS1; however, growing season NO_3^- concentrations were consistently higher at SS2 (Figures 4a and 4b). With the exception of transect 1,

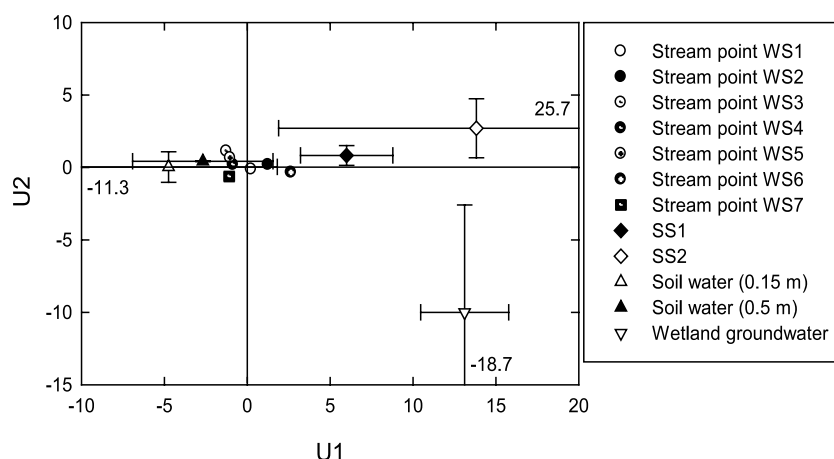


Figure 2. End-member mixing analysis (EMMA) of stream water sampling points within Archer Creek watershed and selected end-members (soil water at 0.15 and 0.5 m depths, near-stream wetland groundwater, and groundwater springs SS1 and SS2). The 25th and 75th quartiles are included for each end-member. Locations of all points are shown in Figure 1.

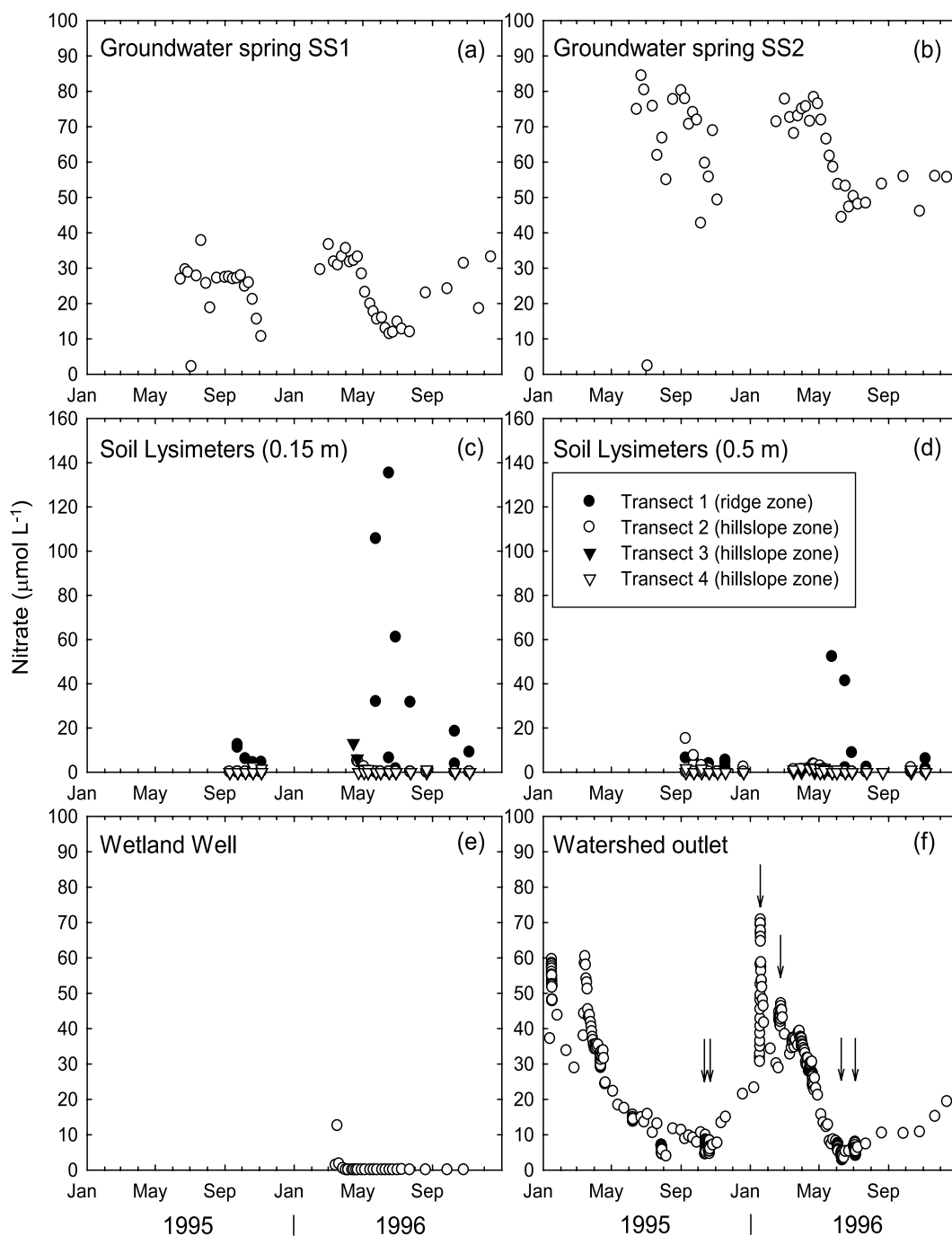


Figure 4. Nitrate concentration of (a) groundwater spring SS1, (b) groundwater spring SS2, (c) soil water at 0.15 m, (d) soil water at 0.5 m, (e) near-stream wetland groundwater, and (f) streamflow throughout the study period. Arrows in Figure 4f indicate periods that storms were sampled.

located in the upland hardwood zone, soil water NO_3^- concentrations at both 0.15 and 0.5 m depths were close to the limit of quantification throughout the study (Figures 4c and 4d). Near-stream groundwater was sampled from a valley bottom wetland well (Figure 1, well G9) from March 1996 through October 1996 during which time NO_3^- concentrations were close to or below the limit of quantification (Figure 4e).

[25] The means and standard deviations of solutes used for EMMA as well as other solutes measured during the study period for stream water and stream water end-members are shown in Table 1. Archer Creek is the outlet of the watershed at the flume;

SW1, SW2, and SW3 are longitudinal stream sampling sites along Archer Creek (Figure 1). Stream sampling points SW4, SW5, SW6, and SW7 are additional sampling sites on first-order streams within the watershed. The mean non-volume weighted NO_3^- concentration of Archer Creek at SW3 was $17 \mu\text{mol L}^{-1}$ during the study (Table 1). The groundwater springs SS1 and SS2 joined Archer Creek between stream sampling points SW3 and SW2, and the mean NO_3^- concentration was close to twice as great at SW2. Calcium and magnesium concentrations also increased from SW3 to SW2. From SW2 to the watershed outlet, NO_3^- concentrations decreased (Table 1).

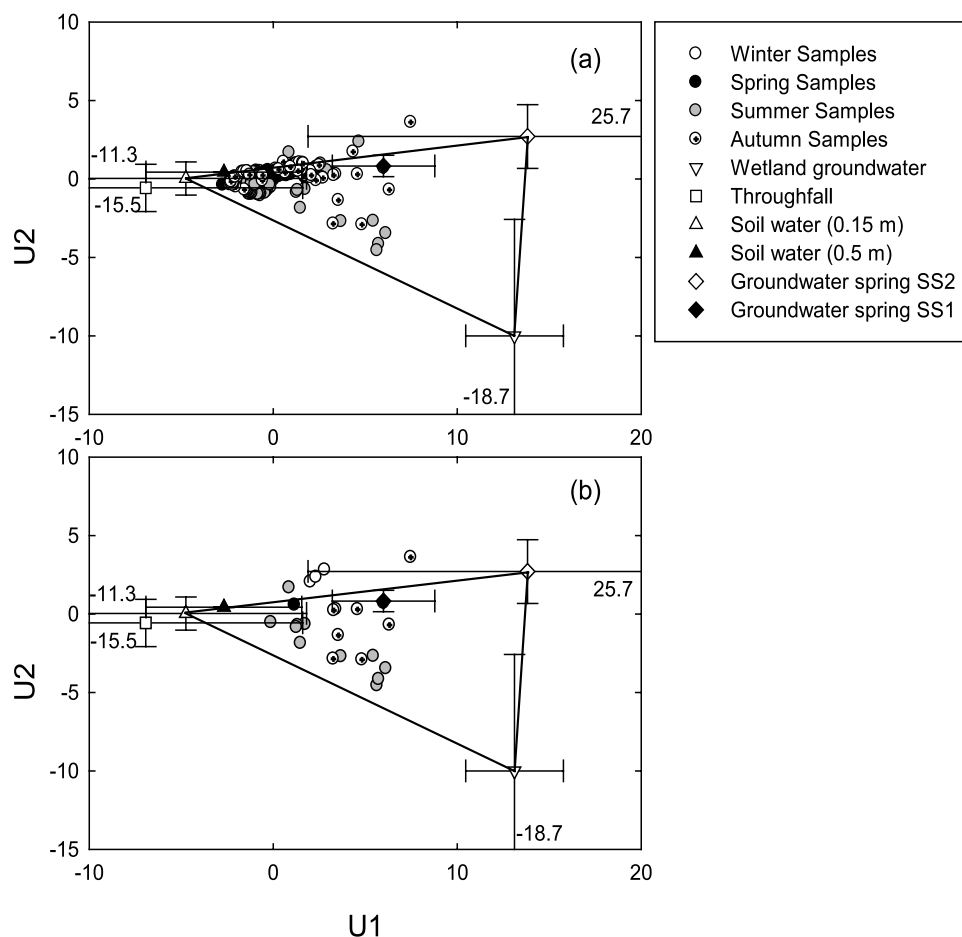


Figure 5. EMMA of (a) all outlet water sample data and (b) outlet water samples at flow $< 0.05 \text{ mm h}^{-1}$. Possible end-members include throughfall, soil water (0.15 and 0.5 m depths), near-stream wetland groundwater, and groundwater springs (used to represent till groundwater). Lines are used to define the mixing diagram by the proposed end-members shallow soil water, near-stream wetland groundwater, and groundwater spring SS2. The 25th and 75th quartiles are included for each end-member.

[26] The results of a principal components analysis of the four solutes used for EMMA (Na^+ , Ca^{2+} , Mg^{2+} , and SO_4^{2-}) indicate that 91% of the variability in Archer Creek outlet stream chemistry could be accounted for by two principal components, indicating that for most conditions, stream water could be accounted by three end-members: soil water, wetland groundwater, and deeper till groundwater. Stream water was principally a mixture of soil water and deeper till groundwater (as represented by groundwater springs SS1 and SS2) (Figure 5a). During very low flow in the summer and fall, wetland groundwater contributed appreciably to streamflow (Figure 5b). All end-members exhibited a large amount of spatial (in the case of soil water) and temporal chemical variability (Figures 5a and 5b). A greater spatial distribution of soil lysimeters in the watershed might have produced an even greater amount of variability in the end-member. However, as discussed in section 4.1, including all first-order perennial streams in EMMA suggests that the soil water end-member, as sampled, was representative of soil water throughout the watershed (Figure 2).

[27] A combination of stable isotopic (H_2^{18}O) and NO_3^- concentration data supports the selection of stream water end-members suggested by EMMA (Figure 6). Results from H_2^{18}O and NO_3^- data also suggest that during winter and spring snowmelt, when stream water NO_3^- concentrations were highest, the majority of

stream water NO_3^- was contributed by groundwater, rather than directly from snowmelt (Figure 6). Soil water was a major source of stream water when stream water NO_3^- concentrations were low during the summer and fall (Figure 6). The mixing diagram in Figure 6 indicates that the highest summer and fall stream water NO_3^- concentrations coincided with periods when the contribution of stream water from SS1 and SS2 was the greatest. These results suggest that till groundwater was the principal source of stream water NO_3^- .

4.3. Storm and Snowmelt Analyses

[28] Six storms were sampled during the study (Table 3). Storms 1 and 2 occurred during the fall of 1995, storms 3 and 4 were 1996 winter melt events, and storms 5 and 6 occurred during the summer of 1996.

4.3.1. Fall storms. [29] Storm 1 occurred after a dry period reflected by the low 7 day API and low prestorm daily mean runoff values (Table 3). Storm 2 occurred 1 week after storm 1 during much wetter antecedent conditions. Wetland water table depth was monitored during all storms; however, because of equipment failure, data from storms 1 and 2 were not available. Visual observations were made of the extent of saturation within watershed valley bottom wetlands during storms 1 and 2. There was no standing water in the wetlands at peak flow during storm 1.

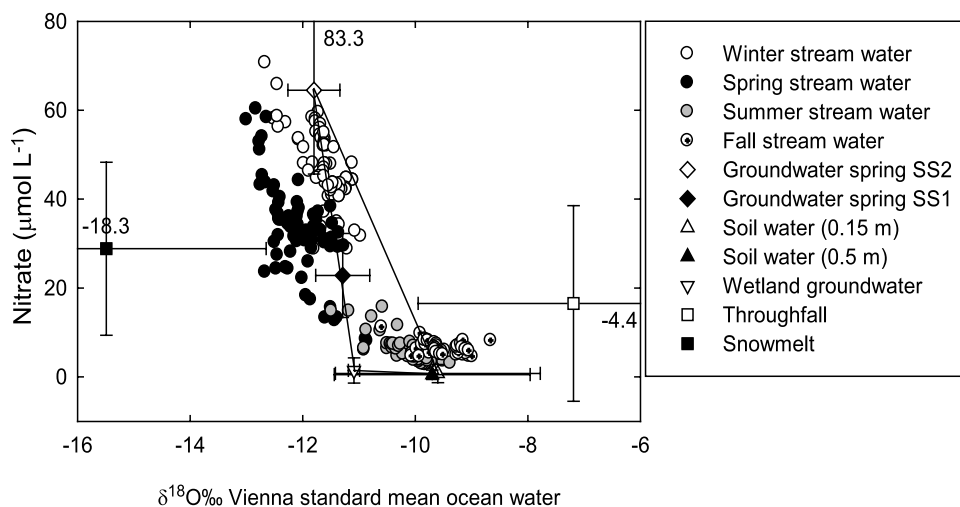


Figure 6. Stream water $\delta^{18}\text{O}$ relative to Vienna standard mean ocean water (VSMOW) versus NO_3^- concentrations ($\mu\text{mol L}^{-1}$) including stream water end-members. Lines are used to define the mixing diagram defined by the proposed end-members.

During the falling limb of the storm 2 hydrograph, there was 0.25 m of standing water in the near-stream zone, and extensive surface saturation was observed in all watershed wetlands.

[30] Storms 1 and 2 produced peak stream NO_3^- concentrations of 9.8 and 8.2 $\mu\text{mol L}^{-1}$, respectively (Table 3). Although stream water NO_3^- concentrations were higher during storm 1, storm 2 exported more NO_3^- owing to the large volume of storm flow. During storm 1 the highest NO_3^- concentration preceded peak discharge whereas during storm 2, the highest NO_3^- concentration occurred after peak discharge (Figures 7 and 8). The pattern for storm 1 is consistent with the notion of NO_3^- flushing [Creed *et al.*, 1996] following accumulation of soil NO_3^- during dry antecedent conditions; this same pattern was also exhibited by Cl^- during the storm. Storm 2 did not exhibit a NO_3^- flushing response.

[31] Hydrograph separations using $\delta^{18}\text{O}$ and Cl^- were completed for storms 1, 2, and 4 (H_2^{18}O samples were not collected for other storms) (Figure 7). Chloride exhibited a flushing response during storm 1 (data not shown) that may have been associated with Cl^- accumulation in near-stream soils during evaporative conditions and the general dry period preceding the storm. For these reasons we did not use Cl^- as a tracer for storm 1. A one-tracer two-component separation using H_2^{18}O identified discharge during storm 1 as a mixture of 57% soil water and 43% water from

the groundwater springs. There was no evidence of a significant contribution of throughfall (contributed by direct channel precipitation or as precipitation onto saturated areas) to discharge during the storm. Water from groundwater springs was most dominant early in the storm and accounted for ~60% of the discharge when stream water NO_3^- concentration was greatest (Figure 7a). After peak discharge, the amount of groundwater in discharge decreased to ~50%, and stream water NO_3^- concentrations also declined (Figure 7a).

[32] A two-tracer three-component hydrograph separation was completed for storm 2 using H_2^{18}O and Cl^- (Figure 7b). Discharge was estimated as a mixture of 48% soil water, 14% groundwater, and 38% throughfall. Throughfall was contributed by direct channel precipitation and precipitation onto the extensive saturated area that developed in near-stream wetlands during the storm. The highest NO_3^- concentrations occurred after peak discharge (Figures 7 and 8). The contribution from groundwater was as high as 48% when the event started but quickly declined to 10%. The groundwater contribution peaked again at 18% at the maximum discharge. Soil water contributed 45–50% of discharge throughout storm 2. The throughfall contribution was highest at 41% and preceded maximum discharge. For storms 1 and 2, EMMA supports the selection of streamflow sources used for

Table 3. Storm Characteristics^a

	Storm 1	Storm 2	Storm 3	Storm 4	Storm 5	Storm 6
Date	14 Oct. 1995	21 Oct. 1995	18 Jan. 1996	21 Feb. 1996	10 June 1996	4 July 1996
7 day API ^a	0.47	7.9	—	—	17.9	21.0
7 day mean runoff, mm d ^{-1b}	0.71	2.7	0.15	1.1	3.5	1.1
30 day API ^b	7.64	12.0	—	—	30.1	32.6
30 day mean runoff, mm d ^{-1b}	0.65	1.2	0.22	2.7	4.8	3.0
Quickflow, mm	9.6	60.7	44.9	21.0	4.7	6.8
Highest NO_3^- concentration, $\mu\text{mol L}^{-1}$	9.8	8.2	70.1	47.0	5.1	7.8
Peak runoff, mm hr ⁻¹	0.44	3.3	2.5	0.58	0.56	0.41
NO_3^- export, mol ha ⁻¹ d ⁻¹	0.36	1.9	5.8	3.3	0.27	0.33
Rainfall, mm	34.3	70.9	—	—	13.5	13.0
Runoff:rainfall ratio	0.26	0.49	—	—	1.04	0.91

^a Quickflow, as defined by Hewlett and Hibbert [1967], is a measure of a watershed's responsiveness to rainfall.

^b The 7 and 30 day API and mean runoff values are for the period immediately preceding the storms.

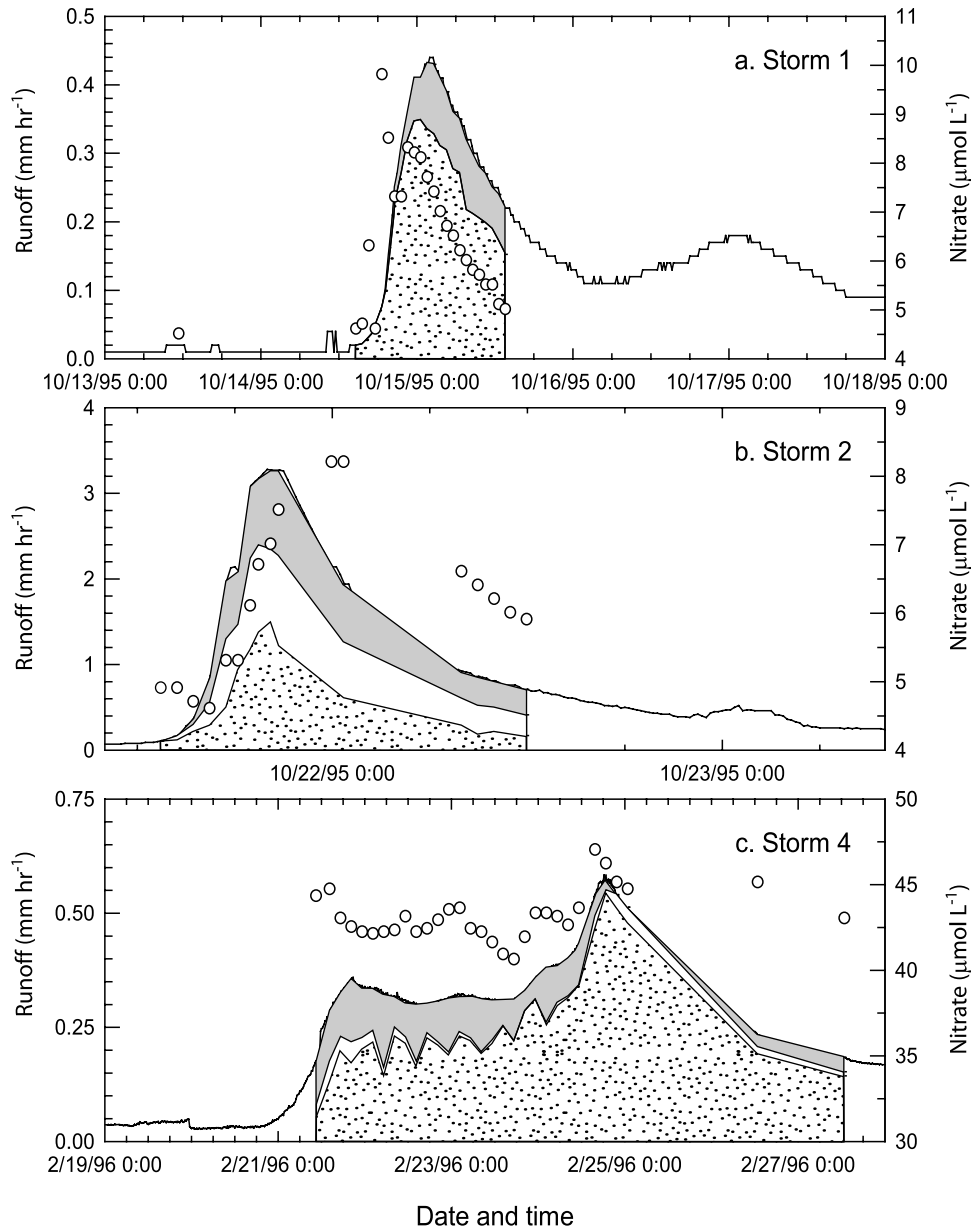


Figure 7. Graphical representations of (a) the two-component hydrograph separation for storm 1, 14 October 1995, and the three-component hydrograph separations for (b) storm 2, 21 October 1995, and (c) storm 4, 21 February 1996. The stippled pattern represents the groundwater contribution, the white area represents the event contribution, and the shaded pattern represents the soil water contribution. Nitrate concentrations are shown as circles.

isotopic and chemical hydrograph separations. EMMA indicates that discharge during the two storms was composed of soil water and till groundwater, though throughfall also contributed to streamflow during storm 2 (Figure 9). Although a two-component separation of storm 2 could be completed for comparison with storm 1, the comparison would not be appropriate for the two storms. Storm 1 was composed of mainly “old” water the two-component separation distinguishes between soil water and groundwater. A two-component separation for storm 2 would distinguish between “new” throughfall water and “old” soil water and groundwater combined. Therefore no comparison is made.

[33] An error analysis was completed for both separations using the method described by *Genereux* [1998]. The combined error estimate for all water sources at a 70% confidence level (≈ 1 standard deviation) for the two-component separation of storm 1

was $\pm 0.03\%$; the error estimate for the three-component separation of storm 2 was $\pm 11\%$. As storm 2 progressed, throughfall became increasingly depleted in H_2^{18}O , such that later in the storm, there was only a 1.3‰ difference between throughfall and groundwater concentration, which caused the large amount of uncertainty. The large difference in error estimates between the two storms was due mainly to how uncertainty in the storm flow component concentrations was estimated. Ideally, the uncertainty for each storm flow component should account for both the spatial and temporal variability throughout the storm. In the absence of data encompassing the spatial and temporal variability of any component, the analytical uncertainty is used in its place. For storm 1 the analytical uncertainty (0.1‰) was used as an estimate of the uncertainty associated with the groundwater concentration, and the spatial variability of the soil water component was low (0.38‰). There

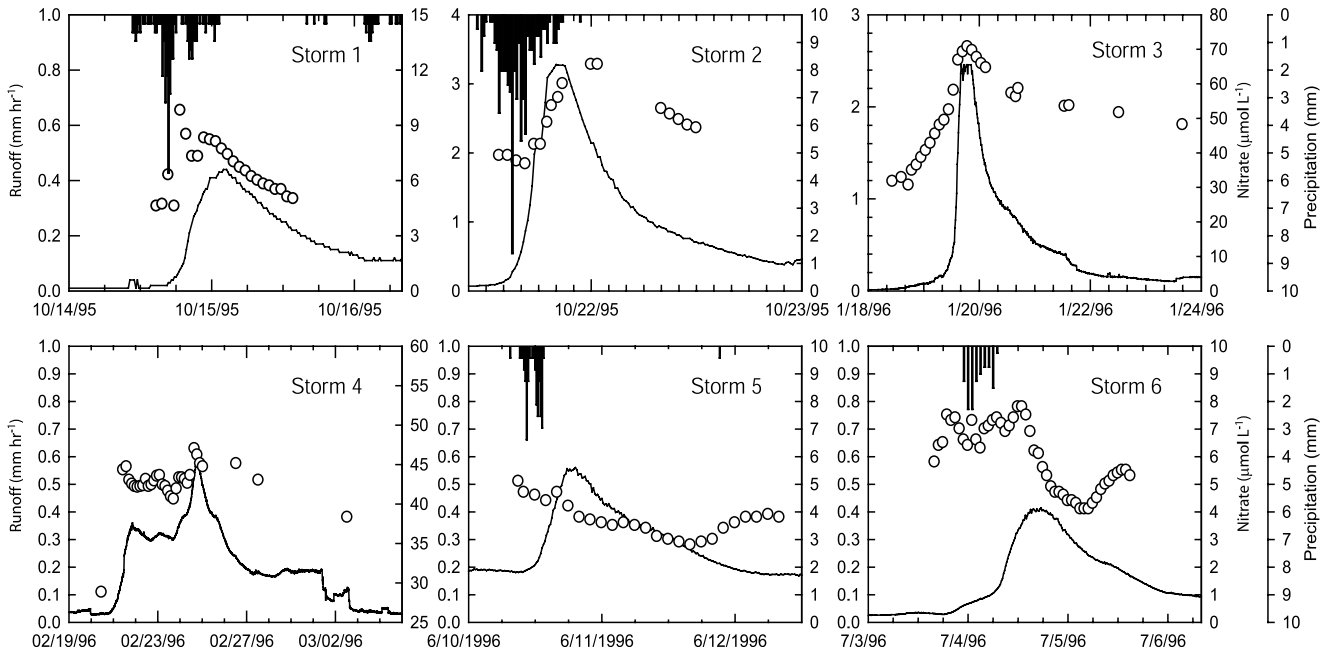


Figure 8. Hydrographs and NO_3^- chemographs for individual storms. Bars show precipitation in millimeters, circles show nitrate concentration in micromoles per liter, and lines show runoff at the watershed outlet (mm h^{-1}).

was no estimate of the temporal variability for either component. As a result, it is likely that this error estimate was underestimated.

4.3.2. Winter melt events. [34] The 7 and 30 day mean daily runoff values show that runoff rates were lower before storm

3 than before any of the other storms sampled (Table 3). Discharge before storm 4 was similar to that before storm 2 (Table 3). At the peak of storms 3 and 4, there was 0.56 and 0.37 m of standing water in the near-stream zone (monitoring well 1) and 0.44 and

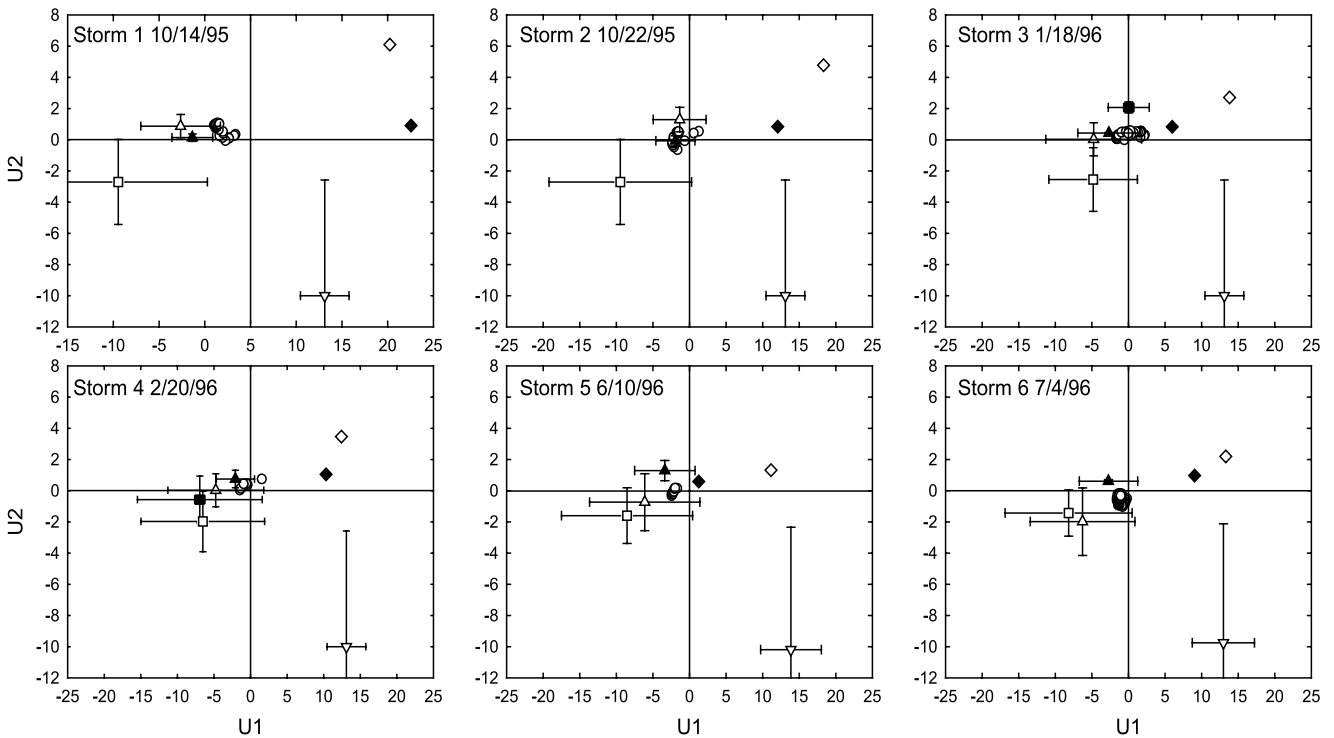


Figure 9. EMMA for individual storms. Stream water samples are shown as open circles, stream SS1 is shown as a solid diamond, stream SS2 is shown as an open diamond, throughfall is shown as an open square, soil water from a depth of 0.15 m is shown as an open triangle, soil water from a depth of 0.5 m is shown as a solid triangle, snowmelt is shown as a solid square, and wetland groundwater is shown as an inverted open triangle. For storms 1–4 the wetland groundwater composition is represented by the composition for the entire study period because wetland groundwater was not sampled prior to those storms.

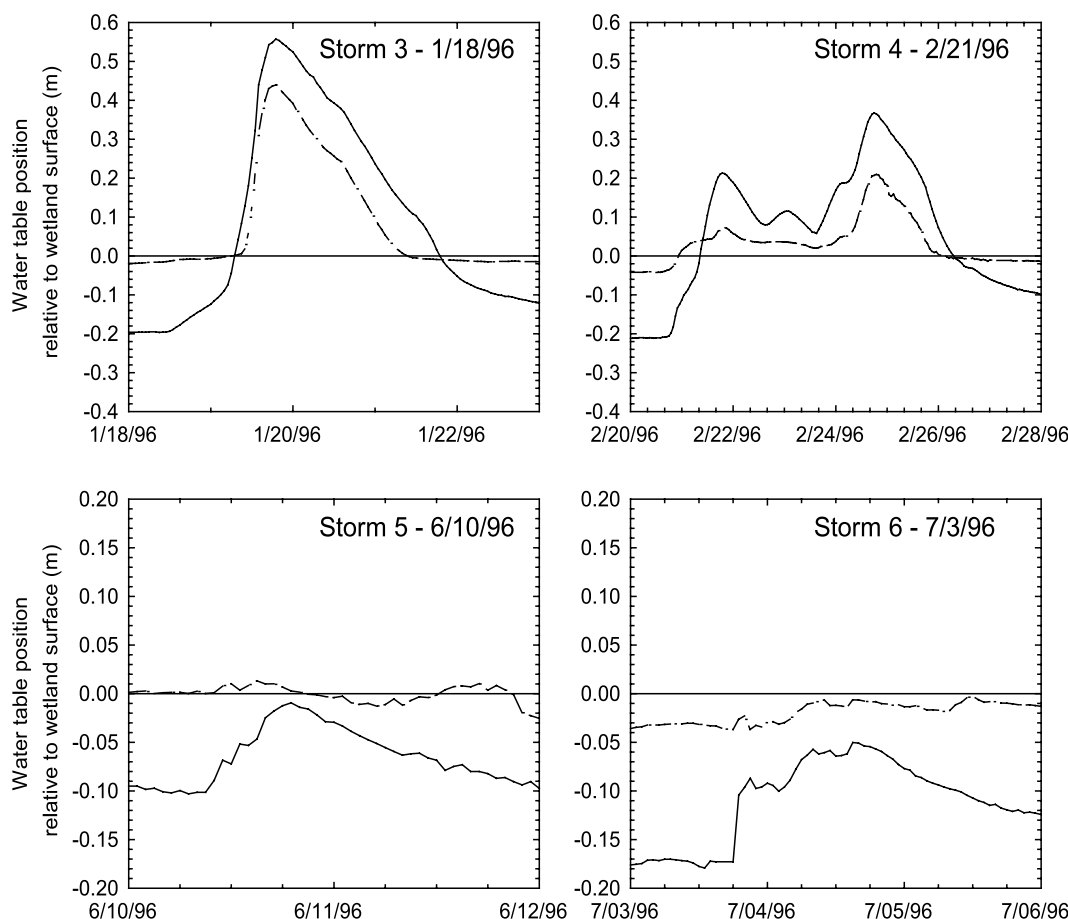


Figure 10. Wetland recording well hydrographs for storms 3–6. Solid line is the well hydrograph for the near-stream monitoring well (M1), and the dashed line is the well hydrograph for the hillslope-wetland interface monitoring well (M2).

0.21 m of standing water at the hillslope-wetland interface (monitoring well 2), respectively (Figures 10 and 1). Extensive saturated areas were observed in valley bottom wetlands during both of these storms.

[35] The highest stream water NO_3^- concentrations during storms 3 and 4 (the two snowmelt events) were 70.7 and $47.0 \mu\text{mol L}^{-1}$, respectively, and coincided with peak runoff (Table 3 and Figure 8). Stream NO_3^- concentrations were 8 times greater during these storms than during storms in the fall and summer (Table 3). Storms 3 and 4 also exported the most NO_3^- of any of the storms sampled (5.8 and $3.3 \text{ mol ha}^{-1} \text{ d}^{-1}$ for storms 3 and 4, respectively). According to EMMA, as many as four end-members contributed to discharge during storms 3 and 4 (snowmelt, throughfall, soil water, and till groundwater) (Figure 9). A two-tracer three-component hydrograph separation for storm 4, using H_2^{18}O and Cl^- as conservative tracers, provided a clearer picture of the sources of discharge than EMMA. Snowmelt contributed 5%, soil water contributed 15%, and till groundwater contributed 75% of streamflow during storm 4 (Figure 7c). The error estimate for storm 4 was $\pm 2.01\%$. The greatest groundwater contribution (96%) coincided with peak discharge and was within 3 hours of the highest NO_3^- concentration ($47 \mu\text{mol L}^{-1}$).

4.3.3. Summer storms. [36] API values were similar for storms 5 and 6 and greater than storms 1 and 2; however, the 7 and 30 day mean daily runoff values indicate that base flow was higher preceding storm 5 than before storm 6 (Table 3). The runoff:rainfall ratios for storms 5 and 6 indicate that there were

wetter antecedent moisture conditions before those two storms than before storms 1 and 2 (Table 3). The wetland water table was at or near the wetland surface during storms 5 and 6 at the hillslope-wetland interface (monitoring well M2) but did not reach the wetland surface close to the stream (monitoring well M1), likely because of the small amount of rainfall (Figure 10).

[37] Stream water NO_3^- concentrations were lowest for storms 5 and 6 (Table 3). Although storm 1 had a higher peak NO_3^- concentration than storms 5 and 6, the greater export of water during the summer storms resulted in similar amounts of NO_3^- export (Table 3). During storm 5, there was a decrease in stream NO_3^- concentrations through most of the storm and a small increase as the stream returned to base flow (Figure 8). At the beginning of storm 6, stream water NO_3^- concentrations were variable and then began to decline before the hydrograph peak; concentrations increased as the stream returned to base flow (Figure 8).

[38] During storms 5 and 6, shallow soil water and throughfall were similar in chemical composition (Figure 9). Storm flow was a mixture of throughfall-shallow soil water and water from groundwater springs. Near-stream wetland groundwater was sampled before each of these storms but did not appear to contribute significantly to storm flow (Figure 9).

4.4. Sources of Stream Water NO_3^-

[39] Groundwater springs SS1 and SS2 had the highest NO_3^- concentrations of the various stream water sources (Tables 1 and 4). The NO_3^- concentrations of these springs were greatest during

Table 4. Nitrate Concentration of Potential Stream Water Sources During Storms^a

	Date	NADP Precipitation	Throughfall	Soil Water 0.15 m	Soil Water 0.5 m	SS1	SS2	Base Flow	Snowmelt	Wetland Ground- water
Storm 1	14 Oct. 1995	7.3 (10–17 Oct. 1995)	^b (8–22 Oct. 1995)	^b (7)	^b (7)	25.8 (1)	59.9 (1)	4.5 (1)	^c	^c
Storm 2	21 Oct. 1995	1.5 (8–24 Oct. 1995)	^b (8–22 Oct. 1995)	^b (1)	^b (1)	21.1 (1)	55.7 (1)	5.4 (1)	^c	^c
Storm 3	18 Jan. 1996	^b	^b	^b	^b	^b	^b	23.3 (10)	43.6 ± 21 (22 Jan. 1996)	^b
Storm 4	21 Feb. 1996	^b	^b	^b	^a (0)	29.5 (4)	71.3 (4)	30.0 (1)	43.3 ± 19 (21–22 Feb. 1996)	^b
Storm 5	10 June 1996	1.3 (4–11 June 1996)	8.6 ± 8 (29 May to 11 June 1996)	^a (9)	^a (9)	12.9 (0)	43.3 (0)	5.1 (1)	^b	^a (1)
Storm 6	4 July 1996	0.7 (2–9 July 1996)	14.1 ± 7 (25 June to 9 July 1996)	5.7 ± 18 (6)	^a (6)	14.7 (3)	50.2 (3)	6.7 (3)	^b	^a (3)

^a All concentrations are in $\mu\text{mol L}^{-1} \pm 1$ standard deviation for means. The range of dates for samples collected during several days is included. Values in parentheses after the sample means indicate the number of days before the storm the sample was collected. NADP precipitation, SS1, SS2, and base flow concentrations represent one sample each before storm. Throughfall is a mean of 36 collectors. Soil water is a mean of 40 lysimeters at each depth. Snowmelt was from one snowmelt lysimeter for storm 3 and a mean of three lysimeters for storm 4. Wetland groundwater is from one wetland well.

^b Value was below the limit of quantification ($3 \mu\text{mol L}^{-1}$ for NO_3^- , does not include NADP chemistry).

^c No sample was taken.

snowmelt, relatively high before the fall storms, and lowest during the summer (before storms 5 and 6). Soil water NO_3^- concentrations were always low before storms (Tables 1 and 4) and showed little variability between storms with a range of $5.7 \mu\text{mol L}^{-1}$ at 0.15 m and $2.2 \mu\text{mol L}^{-1}$ at 0.5 m depth. We did not sample soil water throughout storms and therefore were unable to characterize within storm variability of soil water NO_3^- . Throughfall was a minor potential source of NO_3^- during the fall and had the second highest NO_3^- concentrations for storms 5 and 6 (Table 4). Snowmelt had high NO_3^- concentrations during both of the winter events (storms 3 and 4) (Table 4).

5. Discussion

5.1. Where Does the High NO_3^- Water Originate?

[40] We expected that streamflow in the Archer Creek watershed would be a mixture of hillslope soil water, throughfall, and near-stream groundwater following the classic observations of *Dunne and Black* [1970] in the nearby Sleepers River watershed. After constructing bivariate plots of stream water solutes (Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , K^+ , and Cl^-) as a preliminary step to EMMA (using soil water, throughfall, and near-stream groundwater as potential end-members), we were confronted with two problems: (1) the end-members sampled did not encompass the majority of the stream water samples (i.e., an end-member was missing), and (2) none of the end-members sampled had sufficiently high NO_3^- concentrations to account for the NO_3^- measured in the stream.

[41] All first-order perennial streams were sampled biweekly to characterize the composition of surface water throughout the watershed. When the median concentrations of each of these streams were included in EMMA, streams SS1 and SS2 allowed prediction of outlet stream water chemistry in combination with soil water and throughfall/snowmelt or near-stream groundwater, making them the most likely missing stream water source (Figure 5). A more careful investigation of streams SS1 and SS2 revealed that they emerged from the ground at the soil-till interface and were sampled ~50 m downstream from these seepage positions. In addition, streams SS1 and SS2 were concentrated in many solutes including NO_3^- and base cations (Table 1). These data and observations suggested that this water originated from an older groundwater source. After these observations were made, midway through the study, a groundwater

well (G14) was installed adjacent to stream SS1 and developed into the till layer. Groundwater springs SS1 and SS2 are used as end-members for this study rather than well G14 because samples were only collected from the well during the latter half of the study. Stream SS1 chemical concentrations were similar to those of well G14, though the groundwater was more concentrated than stream water from SS1 (Table 1). Mean Ca^{2+} concentrations from 1 April 1996 through 31 December 1996 (the period of time that well G14 was sampled) were 220 and $142 \mu\text{mol L}^{-1}$ for G14 and SS1, respectively, suggesting that SS1 was probably also influenced by soil water. This hypothesis is supported by storm EMMA plots where SS1 was more similar to the composition of soil water during wet antecedent moisture conditions (Figure 9). The composition of groundwater spring SS2 showed little variation (Figure 9). The chemical and isotopic composition of springs SS1 and SS2 and their high NO_3^- concentrations together suggested that till groundwater was the missing source of streamflow and stream water NO_3^- (Figure 6).

[42] The high stream water NO_3^- concentrations measured at Archer Creek watershed outlet, particularly during the growing season, might be indicative of a watershed in stage 2 of N saturation [Stoddard, 1994]. The results from our study show that the majority of stream water NO_3^- was contributed by deeper till groundwater that does not necessarily indicate a source of N in excess of biotic demand. Previous investigations have found high NO_3^- concentrations during spring snowmelt in the Adirondacks [Rascher et al., 1987; Schaefer et al., 1990; Schaefer and Driscoll, 1993]. Till groundwater NO_3^- may have originated as high NO_3^- snowmelt that recharged groundwater during the dormant season and thus was never available to watershed vegetation. This NO_3^- draining mechanism has been described previously for the Turkey Lakes watershed [Creed et al., 1996] as well as the Neversink River watershed in the Catskill Mountains of New York State [Burns et al., 1998].

[43] Another possible source of groundwater NO_3^- could have been higher nitrification rates in ridge top watershed soils. *Ohrui et al.* [1999] reported higher net N mineralization and net nitrification rates in a ridge top hardwood stand in the intensive research hillslope within the Archer Creek watershed than in the lower elevation stands included in their study. These higher rates appeared to be linked to higher soil pH and lower C:N ratios. Groundwater springs SS1 and SS2 were located at a greater elevation than the ridge top hardwood stand studied by *Ohrui*

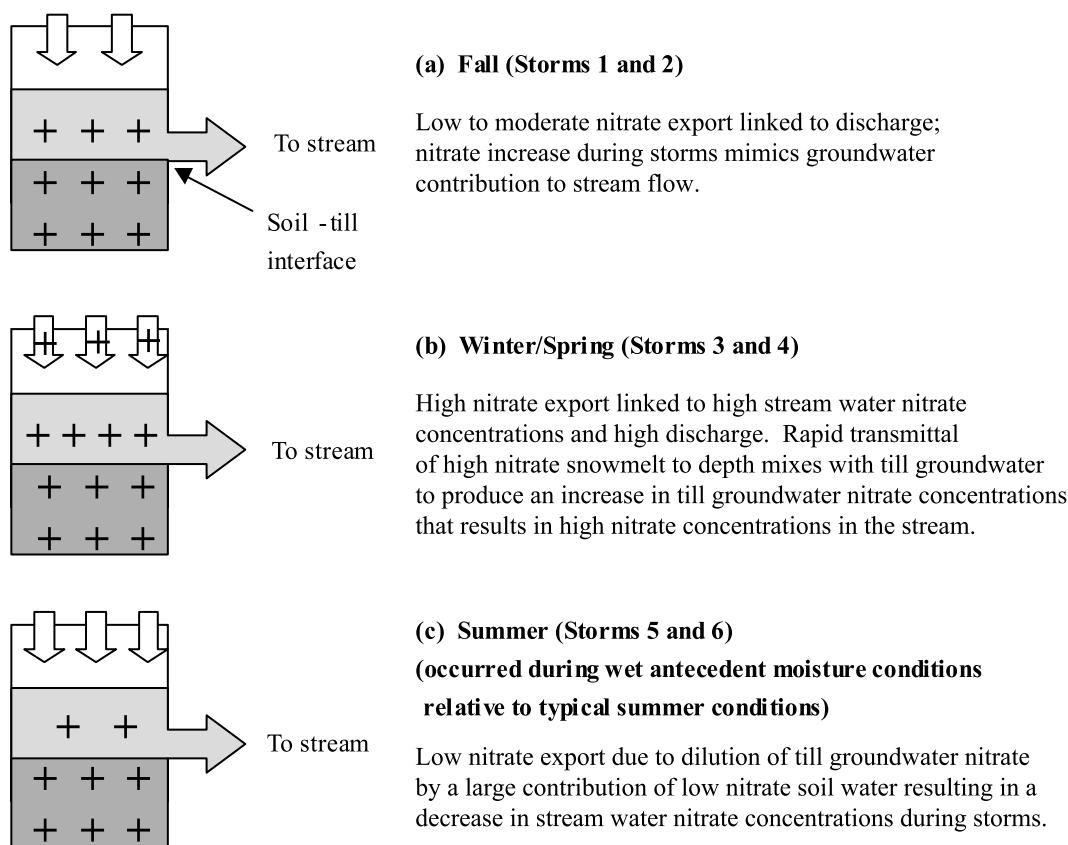


Figure 11. Conceptual model of streamflow generation and NO_3^- release in the Archer Creek watershed during (a) fall, (b) winter, and (c) summer. Nitrate concentration is represented by pluses.

et al. [1999] (~600 m at SS1 and SS2 and 540 m at the hardwood mineralization plots). Our study suggests that soil water NO_3^- recharged deeper till groundwater in the ridge top areas of the watershed rather than being flushed to the stream as described by *Creed et al.* [1996]. The importance of groundwater as a stream NO_3^- source has been suggested by other studies [*Burns et al.*, 1998; *Ohrui and Mitchell*, 1998]. The source of the till groundwater NO_3^- was likely a combination of snowmelt and greater nitrification potential in the ridge top areas of the watershed that supplied NO_3^- to groundwater.

[44] By using EMMA, stream water chemical analyses, and field reconnaissance we were able to identify a water source we had not suspected of contributing to streamflow and identify a significant source of NO_3^- to the stream. The source of the groundwater NO_3^- is not clear at this time; however, it is likely that either high NO_3^- snowmelt, high rates of soil nitrification, or a combination of the two supplied NO_3^- to deep till groundwater. These results show the value of linking geochemical models with field measurements to interpret the results of stream water chemical studies.

5.2. Conceptualization of NO_3^- Release

[45] Our results differ from other studies that have concluded near-stream groundwater contributes significantly to streamflow and that its relative contribution increases as drainage from hillslope soils decreases [*Dunne and Black*, 1970]. In the Archer Creek watershed, streamflow generation and NO_3^- release are concentrated in hillslope hollows that appear to provide the primary mixing zone for soil water and deeper till groundwater. The watershed has landscape features that are typical of the hydrologically complex

Adirondack Mountains. The watershed was glaciated as recently as 10,000–15,000 years ago and therefore has a relatively immature drainage system that is exemplified by several hillslope hollows that contain no stream channels but where water rushing beneath the ground surface was audible. Water appears to flow along the soil-till interface between rocks and boulders that line the hollows. These rocks are overlain by a thin layer of soil, but there is little soil between the rocks at the till surface. We hypothesize that soil water in and near hillslope hollows was mobilized by infiltrating event water and by a rising water table and then rapidly transmitted to the stream along the soil-till interface (Figures 11a–11c). The soil-till interface is typically characterized by an abrupt reduction in hydraulic conductivity in the till. Soil water mixed with deeper till water that flowed into the hollows from upslope groundwater springs or rose into the soils as the water table elevation increased during storms (Figure 11). At the break in slope in the valley bottom this well-mixed soil water and groundwater was transmitted to the stream through rivulets and wetland stream channels during base flow and small storms or across the wetland surface during larger storms when the wetland water table intersected the ground surface. These pathways through the near-stream zone allowed little interaction with wetland groundwater and therefore soil water and till groundwater reached the channel with little chemical alteration [*McHale*, 1999]. Draining soil water mixed with groundwater to sustain base flow after storms. During dry conditions, as soil water became less important to streamflow, till groundwater (and in very low flow conditions, near-stream wetland groundwater) began to dominate streamflow.

[46] Nitrate release from the watershed appears to have been controlled mainly by groundwater springs SS1 and SS2 that drain

ridge top areas of the watershed where nitrification potentials were greater than in other areas of the watershed. Although our data suggest that the till groundwater source represented by SS1 and SS2 was representative of deeper groundwater throughout the watershed (Figure 2), the high NO_3^- concentrations in till groundwater appear only to have been present in ridge top areas of the watershed (Table 1). Nevertheless, we currently do not have the data needed to characterize the groundwater chemistry throughout the watershed.

5.3. Do the Hydrometric, Chemical, and Isotopic Data Support the Conceptualization?

[47] This conceptualization of streamflow generation and NO_3^- release was supported by the detailed storm event findings. During the dry antecedent moisture conditions before storm 1, soil water NO_3^- levels were low, probably as a result of microbial immobilization and root uptake in the forest floor [Mitchell *et al.*, 1992b; Hill *et al.*, 1999; Ohrui *et al.*, 1999]. The peak stream water NO_3^- concentration coincided with the maximum groundwater contribution to storm flow during storm 1. During storm 2, the NO_3^- peak did not coincide with the peak groundwater contribution, but its timing was close to a secondary rise in the groundwater contribution. The NO_3^- peaks for both storms were similar (Table 4); however, during storm 2 fivefold more NO_3^- was exported from the watershed than during storm 1 (Table 4). Two storms with very different antecedent moisture conditions but producing similar NO_3^- concentrations implies a consistent source of NO_3^- . This conclusion was also supported by H_2^{18}O - NO_3^- analysis (Figure 6). During the fall, streamflow was dominated by soil water, and stream water NO_3^- concentrations were consistently low. When stream water NO_3^- concentrations increased, the H_2^{18}O composition of stream water moved toward that of till groundwater (Figure 6). Storms 5 and 6 occurred during much wetter antecedent moisture conditions than storms 1 and 2 (Table 4). Consequently, the runoff:rainfall ratios were much greater for storms 5 and 6, although the amount of rainfall during the summer storms was less than half that from storm 1 (Table 4). Stream water NO_3^- concentrations decreased during storms 5 and 6.

[48] For storm 1 our conceptualization would suggest that groundwater was mobilized early in the storm owing to increased flow from groundwater springs and a rising water table in hillslope hollows (Figure 11a). This interpretation accounts for the early stream water NO_3^- peak. As the storm continued, there was mobilization of soil water in and near hillslope hollows that acted to dilute stream water NO_3^- concentrations throughout the remainder of the storm. The peak stream water NO_3^- concentration generally followed the groundwater contribution to storm flow during storm 2, but the large amount of streamflow during the storm and the large soil water contribution kept stream water NO_3^- concentrations low throughout the event. During storms 3 and 4, NO_3^- was likely contributed from till groundwater. Figure 6 indicates that snowmelt did not contribute directly to streamflow but rather that till groundwater was the major source. The results from a three-component hydrograph separation of storm 4 also support this conclusion (Figure 7). The chemical and isotopic composition of snowmelt was obscured when snowmelt mixed with the large groundwater reservoir. The large amount of NO_3^- present in groundwater and the importance of groundwater as a stream water source during the two winter events accounted for the high NO_3^- concentrations measured at the watershed outlet (Figure 11b). For storms 5 and 6 the large amount of soil water present in the watershed, due to very wet antecedent moisture

conditions, diluted stream water NO_3^- concentrations supplied by groundwater (Figure 11c).

5.4. Implications for NO_3^- Flushing Hypotheses

[49] These results suggest the importance of hydrology in regulating the temporal and spatial distribution of NO_3^- within a watershed. Nonetheless, as Creed *et al.* [1996] emphasize, both source and transport factors must be present to allow NO_3^- -flushing to occur. In Archer Creek watershed the NO_3^- source appears to be confined to ridge topsoils that recharge till groundwater with high NO_3^- water (in conjunction with high NO_3^- snowmelt) rather than delivering the NO_3^- directly to the stream. This high NO_3^- groundwater then acts as the primary source of stream water NO_3^- throughout the year and across antecedent moisture conditions, similar to the draining mechanism described by Creed *et al.* [1996]. This mechanism constitutes a third mechanism for watershed NO_3^- release that combines the flushing and draining mechanisms of Creed *et al.* [1996].

[50] We also found evidence for rapid transmittal of throughfall to the stream due to precipitation onto saturated areas following the classic observations of Dunne and Black [1970] in the nearby Sleepers River catchment in St. Johnsbury, Vermont. During large storms and snowmelt this provided an additional source of NO_3^- to the stream. These results emphasize the influence of antecedent moisture conditions on stream water end-member contributions. For example, during storm 1 when antecedent moisture conditions were low the throughfall contribution to streamflow was confined to direct channel precipitation. During storm 2, which occurred during much wetter antecedent moisture conditions, throughfall accounted for 38% of streamflow.

[51] The results from this study show the importance of including soil water NO_3^- measurements in watershed NO_3^- release studies and the need to link soil water NO_3^- flux to stream water chemistry to interpret the mechanisms of NO_3^- release in watersheds and to relate the results of studies conducted at different scales, like those of Creed *et al.* [1996] and Hill *et al.* [1999], to one another. In addition, these results underscore the variability of N cycling within watersheds. Our results suggest that lower elevation soils within Archer Creek watershed behaved as a sink for atmospheric N inputs similar to those at Plastic Lake watershed [Hill *et al.*, 1999] but ridge topsoils, with greater nitrification potentials, acted as a source of NO_3^- similar to, though not as great as, those at TLW [Creed *et al.*, 1996].

6. Conclusions

[52] This research was conducted to identify sources of stream water NO_3^- and the mechanisms that deliver NO_3^- to the stream. Using a combination of isotopic, chemical, and hydrometric data, we developed a conceptualization of the mechanisms of NO_3^- loss during base flow and storm runoff. Soil water NO_3^- concentrations were not greatly affected by changes in antecedent moisture conditions and season. According to EMMA, soil water and till groundwater dominated both stream base flow and storm flow. These results were supported by stable isotopic hydrograph separations. Therefore our results do not support our first hypothesis; soil water NO_3^- concentrations were not highest after dry periods and subsequently lower with each storm. On the contrary, soil water NO_3^- concentrations remained low throughout the study except in the ridge top hardwood zone. In contrast to previous studies, near-stream groundwater only contributed significantly to streamflow during very low base flow conditions. Of the major sources of streamflow (soil water, till groundwater, snowmelt, and

throughfall), only till groundwater had sufficiently high NO_3^- concentrations and a sufficient streamflow contribution to account for the NO_3^- concentrations measured at the watershed outlet. Isotopic hydrograph separations using H_2^{18}O identified peaks in the till groundwater contribution to streamflow as being coincident with peak stream water NO_3^- concentrations. Consequently, our results do not fully support our second hypothesis; stream water NO_3^- concentrations were not controlled by soil water during the dormant season and during storms and by groundwater during growing season low flows. Rather, stream water NO_3^- concentrations were controlled by till groundwater during most conditions.

[53] Soil chemistry and nitrification potential controlled NO_3^- availability in the watershed; however, high NO_3^- soil water was confined to ridge top areas where nitrification potential was high. This high NO_3^- soil water in conjunction with high NO_3^- snowmelt acted to recharge till groundwater in ridge top areas rather than contribute directly to the stream. The steady supply of NO_3^- to till groundwater has caused the ridge top area of the watershed to become a relatively constant source of NO_3^- to the stream during storms and base flow. These results emphasize the need for NO_3^- release studies to be conducted at a watershed scale and to include soil water, stream water, and groundwater chemistry in combination with hydrometric data. Although this research has led to a detailed conceptualization of NO_3^- release, a better characterization of the nitrification potential and soil water movement in ridge top areas is required to test this conceptualization. Additional research is also needed to characterize the till groundwater chemical composition throughout the watershed. Confining soil and throughfall measurements to the intensive research hillslope was necessary given the logistical constraints of conducting research in a 135 ha watershed. Locating the collectors from the valley bottom to the ridge top helped to identify differences in soil water and throughfall concentrations with elevation; however, greater variability may have been measured if these collectors encompassed the entire range of watershed elevations.

[54] Archer Creek watershed has a stand age about half that of TLW. The nitrification potential in lower elevation soils appears to be similar to those in Plastic Lake watershed. While the nitrification rates in the ridge topsoils are likely much lower than those at TLW, they do appear to be of sufficient magnitude to have caused high concentrations of NO_3^- in till groundwater in that area of the watershed. These results indicate that before an entire watershed reaches the stand age or nitrification potentials (i.e., N saturation status) present at TLW, elevated base flow NO_3^- and high storm NO_3^- concentrations may occur. This study also shows the danger of inferring N saturation status or watershed N cycling based only on outlet stream chemistry.

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