Factors controlling nitrogen release from two forested catchments with contrasting hydrochemical responses[†]

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Abstract:

Quantifying biogeochemical cycles of nitrogen (N) and the associated fluxes to surface waters remains challenging, given the need to deal with spatial and temporal variability and to characterize complex and heterogeneous landscapes. We focused our study on catchments S14 and S15 located in the Adirondack Mountains of New York, USA, which have similar topographic and hydrologic characteristics but contrasting stream nitrate (NO_3^-) concentrations. We characterized the mechanisms by which NO_3^- reaches the streams during hydrological events in these catchments, aiming to reconcile our field data with our conceptual model of factors that regulate nutrient exports from forested catchments. Combined hydrometric, chemical and isotopic ($\delta^{18}O-H_2O$) data showed that the relative contributions of both soil and ground water sources were similar between the two catchments. Temporal patterns of stream chemistry were markedly different between S14 and S15, however, because the water sources in the two catchments have different solute concentrations. During late summer/fall, the largest source of NO_3^- in S14 was till groundwater, whereas shallow soil was the largest NO_3^- source in S15. NO_3^- concentrations in surface water decreased in S14, whereas they increased in S15 because an increasing proportion of stream flow was derived from shallow soil sources. During snowmelt, the largest sources of NO_3^- were in the near-surface soil in both catchments. Concentrations of NO_3^- increased as stream discharge increased and usually peaked before peak discharge, when shallow soil water sources made the largest contribution to stream discharge. The timing of peaks in stream NO_3^- concentrations was affected by antecedent moisture conditions. By elucidating the factors that affect sources and transport of N, including differences in the soil nutrient cycling and hydrological characteristics of S14 and S15, this study contributes to the overall conceptualization of NO_3^- release from temperate forested catchments. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS   catchment; nitrate; hydrology; storms; hydrograph; isotopes

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INTRODUCTION

Forest lands in most locations of the world are blanketed with inputs of nitrogen (N) resulting from emissions and long-range transport in the atmosphere. Rates of N deposition input to forests in the northeastern USA are the highest in the country, far exceeding natural N inputs (Boyer *et al.*, 2002; Driscoll *et al.*, 2003b). The fate of excess N in the terrestrial landscape is not well understood, though the possibilities include being taken up in forest vegetation, stored in forest soils or groundwater, converted and lost to atmospheric forms through denitrification, or exported from the system in streamflow (Van Breemen *et al.*, 2002). Elevated concentrations of nitrate (NO_3^-) in surface waters have been observed in numerous forested catchments in the UK (Burt and Haycock, 1992), Germany (Hauhs *et al.*, 1989), Canada

(Creed and Band, 1998; Spoelstra *et al.*, 2001), and many locations in the USA, such as the Adirondack Mountains (Driscoll *et al.*, 2003a), the Catskill Mountains (Murdoch and Stoddard, 1992), mid-Atlantic Appalachia (Smith *et al.*, 1987), the Great Smokey Mountains (Elwood *et al.*, 1991) and numerous high-elevation forests of the western states (Fenn *et al.*, 2003). Although atmospheric N has been considered to be a major source of stream NO_3^- (Driscoll *et al.*, 2003b; Galloway *et al.*, 2003), and in the northeastern USA, catchment export of N increases with atmospheric deposition, this factor only accounts for <38% of the spatial variation of NO_3^- in surface waters (Aber *et al.*, 2003). Furthermore, below a threshold deposition value of $[N] \approx 0.5$ to 0.6 kmol ha^{-1} year^{-1}, little export of NO_3^- occurs and no relation with atmospheric N deposition is evident. Hence, other factors, such as tree species composition (Lovett and Mitchell, 2004; Lovett *et al.*, 2004; Christopher *et al.*, 2006), land-use history (Compton and Boone, 2000; Goodale and Aber, 2001), climatic variables (Mitchell *et al.*, 1996; Groffman *et al.*, 2001; Goodale *et al.*, 2003; Park *et al.*, 2003) and hydrological regime (Creed and Band, 1998; Inamdar *et al.*,

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2000; Schiff *et al.*, 2002; Ito *et al.*, 2005), contribute to the heterogeneous spatial pattern of NO_3^- export in eastern catchments of North America and other temperate forested regions.

Researchers have developed conceptual models of hydrochemical responses in forested catchments with regard to NO_3^- export. Many researchers document that NO_3^- is released by a 'flushing' mechanism (Burns, 2005), as observed in temperate forests such as the Turkey Lakes region of Ontario, Canada (Creed *et al.*, 1996), and the Catskill Mountains of upstate New York, USA (Welsch *et al.*, 2001). In these systems, significant loadings of NO_3^- in streams originate from shallow landscape soils, whereby NO_3^- is flushed during hydrologic events when the water table rises into the upper soil profile, providing a connection to the stream (Burns, 2005). Variation in this response across the catchment is controlled largely by topography and its influence on the areal extent, location, and rate of change of saturation in the variable source areas (Creed and Band, 1998). Welsch *et al.* (2001) suggested that the variability of flushing responses is due to antecedent moisture and soil temperature, which influences the connectivity within the catchment and the microbial production of N respectively.

In some forested systems, deeper flow paths have also been shown to be significant in transporting NO_3^- from landscapes to streams. For example, Schiff *et al.* (2002) noted an order of magnitude difference in the NO_3^- export from two catchments within the Harp Lake watershed in Ontario, Canada. They attributed high NO_3^- concentrations in streamflow to very steep hillslope gradients that expedited the movement of NO_3^--enriched groundwater downslope to the stream. Similarly, studies in the Archer Creek catchment, USA, which encompasses the subcatchments that are the focus of this study, indicate that till groundwater may be enriched in NO_3^-, in locations where and at times when it is recharged from well-drained soils where high rates of nitrification occur (Ohrui *et al.*, 1999; McHale *et al.*, 2002). Groundwater NO_3^- from deep subsurface flow pathways is then delivered to the stream via displacement by infiltrating precipitation during summer/fall hydrologic events, as well as during snowmelt (McHale *et al.*, 2002; Inamdar *et al.*, 2004; Mitchell *et al.*, 2006).

Such previous investigations have shown that solute transport along various flow paths during hydrologic events is a function of complex factors affecting sources, transport, and transformations of N in the landscape and in the stream, including ecosystem-level interactions between microbial production of N, plant uptake, and N transport, as well as landscape heterogeneities (e.g. catchment wetness, topographic variables, soil depth, geology). Quantifying biogeochemical cycles of nutrients and the associated fluxes to surface waters remains challenging, given the need to deal with spatial and temporal variability and to characterize such heterogeneous landscapes.

Our overall objective was to characterize the water sources of NO_3^- and mechanisms by which NO_3^- reaches the streams from catchments, aiming to reconcile our field data with our conceptualization of factors that regulate nutrient exports from forested catchments. Here, we examine two catchments that are similar in terms of the topographic features, which earlier studies have shown to be most important in determining fluxes of NO_3^- to streamflow, yet with significant differences in streamflow NO_3^- export. The two paired subcatchments that are the subject of this study, named S14 and S15, both are located within the Archer Creek catchment in the Adirondack Mountains of New York State (Figure 1). The basins are nearly adjacent and set in similar topographic settings (with regard to geomorphic configuration, size, and elevation range), are completely forested, with little development of distinct riparian zones, and have no permanent wetlands. However, the tributary waters issuing from these two catchments have differing chemical responses, both in terms of NO_3^- concentrations and mass fluxes. For example, during June 2002–May 2003 S14 had twofold or greater means in annual stream NO_3^- concentration and export (73 μmol_c l^{-1} and 0·4 $kmol_c$ ha^{-1} respectively) than S15 (26 μmol_c l^{-1} and 0·2 $kmol_c$ ha^{-1} respectively), attributed to differences in soil NO_3^- production as a function soil base-status and tree species composition (Christopher *et al.*, 2006). Furthermore, S14 and S15 represent the extreme ranges (both low and high) of N exports that have been observed in the long-term record of monitoring throughout the network of subcatchments in the Archer Creek catchment (Christopher, 2004). Thus, these catchments provide an opportunity to study the range in regional sources of NO_3^- and flow paths that combine to yield the observed patterns of N release from landscapes to streams.

To approach this, we collected data during snowmelt and rainfall events throughout the seasons of the year. Examining catchments during rainfall and snowmelt events is important because the greatest export of solutes generally occurs during these periods (Mitchell *et al.*, 1996; Hinton *et al.*, 1997; Creed and Band, 1998; Frank *et al.*, 2000; Inamdar *et al.*, 2004; Inamdar *et al.*, 2006). In snow-dominated systems, a substantial proportion of annual solute export occurs during snowmelt (Baron and Campbell, 1997; Boyer *et al.*, 1997; Piatek *et al.*, 2005). Seasonal differences are also important, given utilization and uptake of nutrients by vegetation, particularly during the months of the growing season. We characterized these catchments using a combined hydrometric and tracer-based approach (Buttle, 1994; Bonell, 1998), and utilized these results combined with the findings of other investigators to expand the conceptual framework of responses in NO_3^- release in forested catchments. Given the similar environment and topographic characteristics (Christopher *et al.*, 2006), we hypothesized that relative proportions of surface and subsurface water sources were similar in the streams of S14 and S15, but that the loadings of NO_3^- from the various flow pathways would vary significantly between catchments due to higher soil NO_3^- production rates in S14. Key questions we addressed with our field-based dataset included:
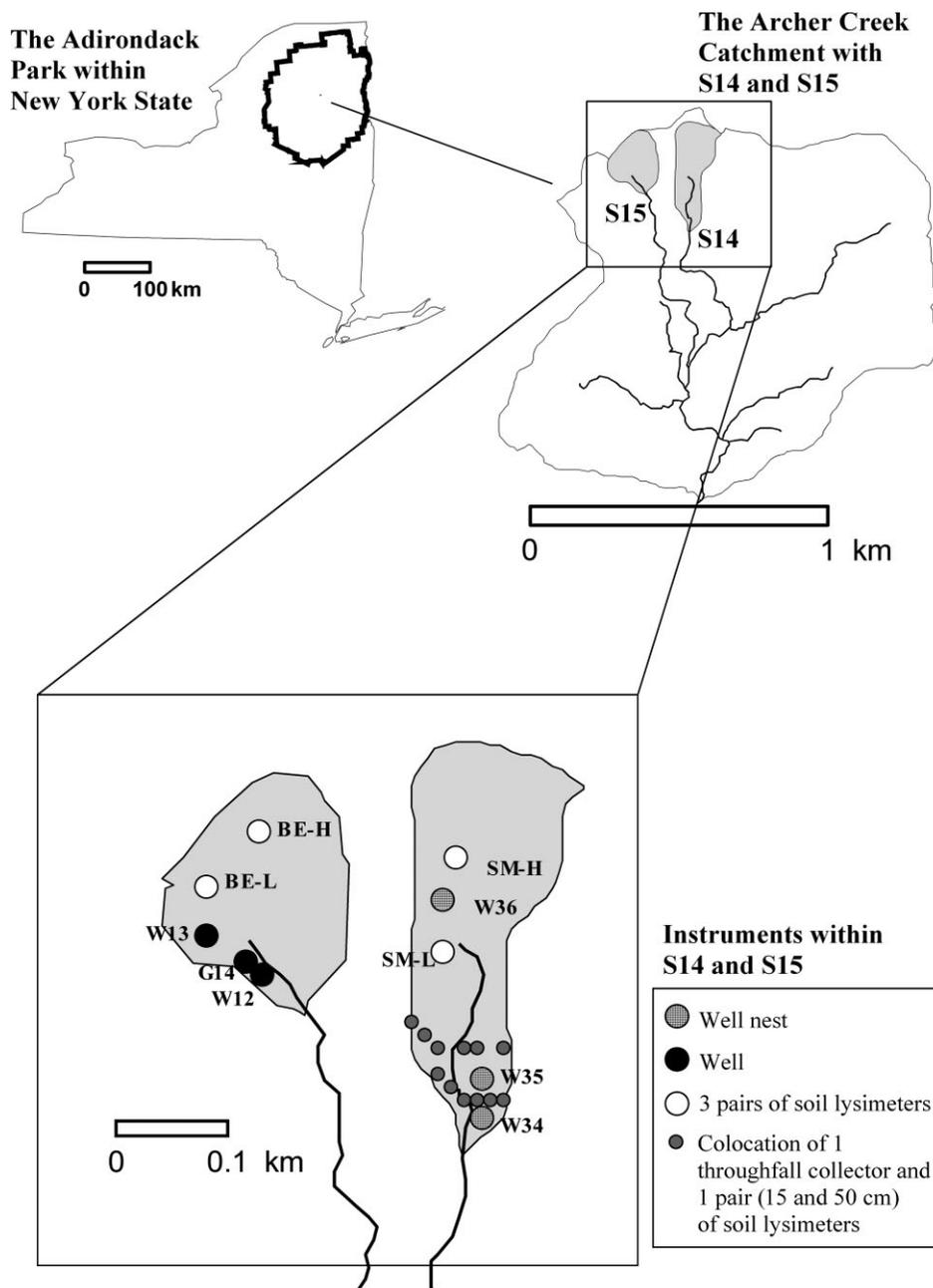
Figure 1. Catchments S14 and S15 in the Archer Creek catchment located in the Adirondack Park, New York

1. Are water sources similar between S14 and S15 and do differences in NO_3^- concentration in water sources control differences in within-event stream chemistry patterns?
2. How does antecedent moisture affect the timing of NO_3^- export during events?
3. Can a conceptual model be developed that explains NO_3^- release in S14 and S15?
4. How does our conceptual model of NO_3^- release in S14 and S15 compare with other models?

Our work sheds light on the couplings among hydrological and biogeochemical cycles that combine to control the variation of NO_3^- in streams.

SITE DESCRIPTION

S14 (3·0 ha) and S15 (2·4 ha) are located in the 135 ha Archer Creek catchment (43°58′N, 74°14′W) within the 6066 ha Huntington Forest near the centre of the Adirondack Park of New York State (Figure 1). Mean slopes are 16% in S14 and 10% in S15. S14 and S15 catchments have typical stair-step topography with flat hillslope hollows connected by steep side slopes. Soils are generally <1 m in depth, with deeper depths of ∼2 m observed in valley bottoms and hillslope hollows. Soils are Becket–Mundal series sandy loams (coarse-loamy, isotic, frigid, oxyaquic Haplorthods) with a 5 cm thick O-horizon, a Bs-horizon approximately 80 cm thick, and a C-horizon (Sommers, 1986). Similar soils are found throughout the Adirondack region and in other areas

of the northeastern USA (Sommers, 1986). Soil bulk densities in the mineral soil increase with depth from 0·41 to 1·24 g cm^{-3} and coarse fragment content (>2 mm) ranges from 5 to 32%. There are high concentrations of organic matter ([C] = 1·10 to 20·8 mol kg^{-1}) in the mineral horizons. The soils commonly contain a compacted layer at ~70 cm formed from the weight of the Wisconsin glacier, which recessed ~14 000 years ago. The soils are derived from a thin layer (<3 m) of glacial till, which has a high sand (~75%) and low clay (<10%) content, with an abundance of cobbles and boulders. The bedrock includes Precambrian materials of Panther gneiss, Goodnow gneiss, and biotite gneiss with isolated bodies and lenses of gabbro-amphibolite. Archer Creek is also located within the Adirondack Massif, a large metamorphosed igneous intrusion composed of up to 90% calcium-rich plagioclase feldspar (Isachsen *et al.*, 2000). Overstorey total basal area at S14 is dominated by, in decreasing order of abundance, *Acer saccharum* Marsh. (sugar maple), *Tilia americana* L. (American basswood), *Fraxinus americana* L. (white ash), and *Fagus grandifolia* Ehrh. (American beech) and S15 is dominated by sugar maple, white ash, *Pinus strobus* L. (eastern white pine), and American beech (Christopher *et al.*, 2006).

The climate at the Huntington Forest is cool and moist with a mean annual temperature and precipitation of 4·4 °C and 1010 mm respectively (1951–1980 means; Shepard *et al.*, 1989). During the period of study (June 2002–May 2003), annual precipitation was 972 mm and the mean temperature was 4·8 °C. Estimated total atmospheric N deposition values (~0·6 kmol ha^{-1} year^{-1}) for the study period (including dry and wet only compounds of NH_4^+-N, NO_3^--N, and dissolved organic N (DON)) at the two catchments were identical (Christopher *et al.*, 2006). A detailed description of how estimated total N deposition was calculated is given in Christopher *et al.* (2006).

METHODS

Field measurements

Catchments S14 and S15 were monitored from June 2002 to May 2003, with the most intensive sampling occurring for four hydrological events (Table I). Storms 2, 3, and 4 occurred during the late summer and fall of 2002 and spring snowmelt began in March 2003. Mitchell *et al.* (2006) investigated solute sources for storms 2, 3, and 4 (Table I) in the entire Archer Creek catchment.

Precipitation was measured hourly at a National Atmospheric Deposition Program/National Trends Network site located 2·5 km from the catchments. Stream stage height was monitored at 20 min intervals at the outlets of S14 and S15 using water-height capacitance probes (±1 mm resolution; Tru Track, New Zealand) housed in stilling wells. Stage height was related to discharge through a rating curve based on flow data collected over a range of stream stages. Stream samples were collected approximately biweekly during baseflow at the catchment outlets. Samples were collected approximately hourly during the late-summer/fall storms of 2002 and daily during snowmelt 2003 using automated water samplers that were programmed to sample at specified time intervals.

Water-table wells 12 and 13 (W12 and W13) were installed in S15 during the summer of 2000. Each water-table well consisted of 5·1 cm diameter PVC pipe with a screened interval of 114·3–173·1 and 44·0–90·2 cm below the ground surface in W12 and W13 respectively (Figure 1; Table II). W12 was located near the catchment S15 outlet and W13 was located in a hillslope hollow ~50 m upslope of W12. Well nests were installed in S14 during the fall of 2001 and consisted of one water-table well and two piezometers constructed from 3·8 cm diameter PVC attached to a 2 cm screened interval and open at the end. These well nests were installed at varying landscape positions (Figure 1; Table II). W36 was located in a hillslope hollow in the middle of S14, and W34 and W35 were located near the catchment outlet. W35 was often

Table I. Hydrological characteristics of each event in S14 and S15 (N/A: not applicable)

Hydrologic event	Dates	Total precip. [snow] (mm)	API (mm)		Discharge (mm)	Discharge (mm h^{-1})			% of annual discharge Jun 02–May 03	NO_3^- flux (mol ha^{-1})
			7-day	30-day		Peak	Min.	Mean		
S14										
Storm 2	21–24 Sep 2002	33 [0]	3·7	5·5	0·8	0·03	0·005	0·009	0·1	0·5
Storm 3	26–29 Sep 2002	43 [0]	6·2	8·7	1·1	0·04	0·005	0·01	0·2	0·6
Storm 4	16–20 Oct 2002	68 [0]	1·9	6·9	2·3	0·07	0·006	0·02	0·4	1·2
Snowmelt	12 Mar–30 Apr 2003	135 [60]	—	—	180·0	0·4	0·02	0·2	30·2	69·3
Annual	June 2002–May 2003	972 [365]	N/A	N/A	600·0	0·4	0·005	0·07	100·0	440·0
S15										
Storm 2	21–24 Sep 2002	33 [0]	3·7	5·5	2·2	0·04	0·02	0·02	0·4	0·4
Storm 3	26–29 Sep 2002	43 [0]	6·2	8·7	2·4	0·04	0·02	0·03	0·4	0·4
Storm 4	16–20 Oct 2002	68 [0]	1·9	6·9	4·5	0·08	0·02	0·04	0·7	0·7
Snowmelt	12 Mar–30 Apr 2003	135 [60]	—	—	173·8	0·7	0·03	0·1	29·0	66·5
Annual	June 2002–May 2003	972 [365]	N/A	N/A	600·0	0·7	0·01	0·07	100·0	156·0

Table II. Wells (W) and piezometers (P) in S14 and S15 (N/A: not available)

Piezometer	S15			Well nest 34			Well nest 35			S14 Well nest 36		
	G14	W12	W13	W34	P34s	P34d	W35	P35s	P35d	W36	P36s	P36d
Screened interval below ground[a] (cm)	130.0–150.0 (B)	114.3–173.1 (B)	44.0–90.2 (A)	89.0–91.0 (A)	39.4–41.4 (A)	89.2–91.2	40.6–71.6(A)	36.0–38.0	73.6–75.6	193.5–231.6 (B)	147.6–149.6	226.0–228.0
Topographic index (dimensionless)	N/A	5.9	7.5	6.2	6.2	6.2	6.8	6.8	6.8	10.5	10.5	10.5
Hydraulic head gradient	N/A	N/A	N/A	Discharge			Recharge			Recharge		

[a] A and B indicate the well being screened above or below the soil compacted layer respectively.

dry except during storms; therefore, data from this well were used primarily to assess contributions of shallow subsurface flow to stormflow. All wells and piezometers were instrumented with water-height capacitance probes and water levels were recorded at 1 h intervals. These probes were hung by string from the top of the well and/or piezometer casing, so the water table was not always measurable if the probe was not installed sufficiently deep under dry conditions when the water table was low. All wells were sampled approximately once per month for water chemistry. A previously established well (G14; McHale et al., 2002) near W12 was also sampled for chemistry in this study.

We delineated catchment boundaries using a 3 m resolution digital elevation model (DEM) and field-delineated boundaries. We also used the DEM to calculate the topographic index (TI) of each well location as described by $\ln(a/\tan \beta)$, where a is the upslope contributing area per unit contour length and $\tan \beta$ is the local slope angle (Beven and Kirkby, 1979; Wolock, 1993). Areas in the subcatchments that drain large upslope contributing areas or that are flat in slope give rise to high index values. One of the main assumptions of this index is that all points with the same value respond similarly hydrologically (Beven et al. 1995; Beven 1997), meaning that points with the same TI value will wet and dry (i.e. water table rise and fall) similarly. Points in a catchment having high index values tend to saturate first and will, therefore, indicate potential subsurface or surface contributing areas (i.e. source areas of solutes that would be carried to the stream).

S14 was also instrumented with throughfall/snow collectors. Two transects (one near the catchment outlet and one approximately 50 m upslope from the catchment outlet) of six collectors were installed in S14 (Figure 1). The throughfall collectors were affixed to fence posts and were constructed from 16·0 cm diameter funnels attached to 1·9 l sealed plastic bottles with coupled 1·0 and 1·6 cm outer diameter Tygon® tubing. Snow collectors, constructed from 18·9 l plastic buckets also were attached to fence posts. During the snow-free period, throughfall was collected approximately biweekly or immediately following large storms, whereas snowfall was collected monthly.

Porous-cup tension lysimeters (5 cm diameter) also were installed in S14 in pairs at 15 and 50 cm depths. Twelve pairs of lysimeters were installed along the two throughfall transects. Each pair was collocated with a throughfall collector for a total of six pairs in each transect (Figure 1). Lysimeters were evacuated to 276 kPa and sampled monthly. In addition, during the summer of 2002, two lysimeter plots were installed upslope of the upper transect of throughfall and lysimeters in S14 (plots SM-H and SM-L) and near the catchment divide in S15 (BE-H and BE-L). In each plot, there were three pairs of lysimeters at two depths (15 and 50 cm) for a total of six lysimeters in each plot. These lysimeters were sampled approximately monthly from November 2002 to June 2003.

Sample collection and analyses for chemistry and isotopes

All water chemistry samples were collected in polyethylene bottles and stored at $1\,°C$ until analysed. Stream samples were transported on ice to the Biogeochemistry Laboratory at SUNY-ESF and generally were analysed within 2 weeks. Samples were analysed for Cl^-, SO_4^{2-}, and NO_3^- by ion chromatography, for Ca^{2+}, Mg^{2+}, K^+, Na^+ and total Al by inductively coupled plasma atomic emission spectrometry, for NH_4^+ by continuous flow colorimetry, for total dissolved N (TDN) by persulphate oxidation, and for pH by glass electrode potentiometry. DON was calculated by subtracting dissolved inorganic N ($NH_4^+ + NO_3^-$) from TDN. Dissolved organic carbon (DOC) concentrations were determined by ultraviolet–persulphate oxidation after being filtered through a pre-combusted glass-fibre filter (Whatman GF/F, $0·7\,\mu m$). The sum of Ca^{2+}, Mg^{2+}, K^+ and Na^+ concentrations is described as the sum of base cations C_b. Laboratory quality assurance (QA)/quality control (QC) procedures include participation in the US Geological Survey (USGS) audit programme, calibration QC samples, detection-limit QC samples, analytical blanks, and analytical replicates. Samples with concentrations above calibration standards were diluted and rerun. See Mitchell *et al.* (2006) for further details.
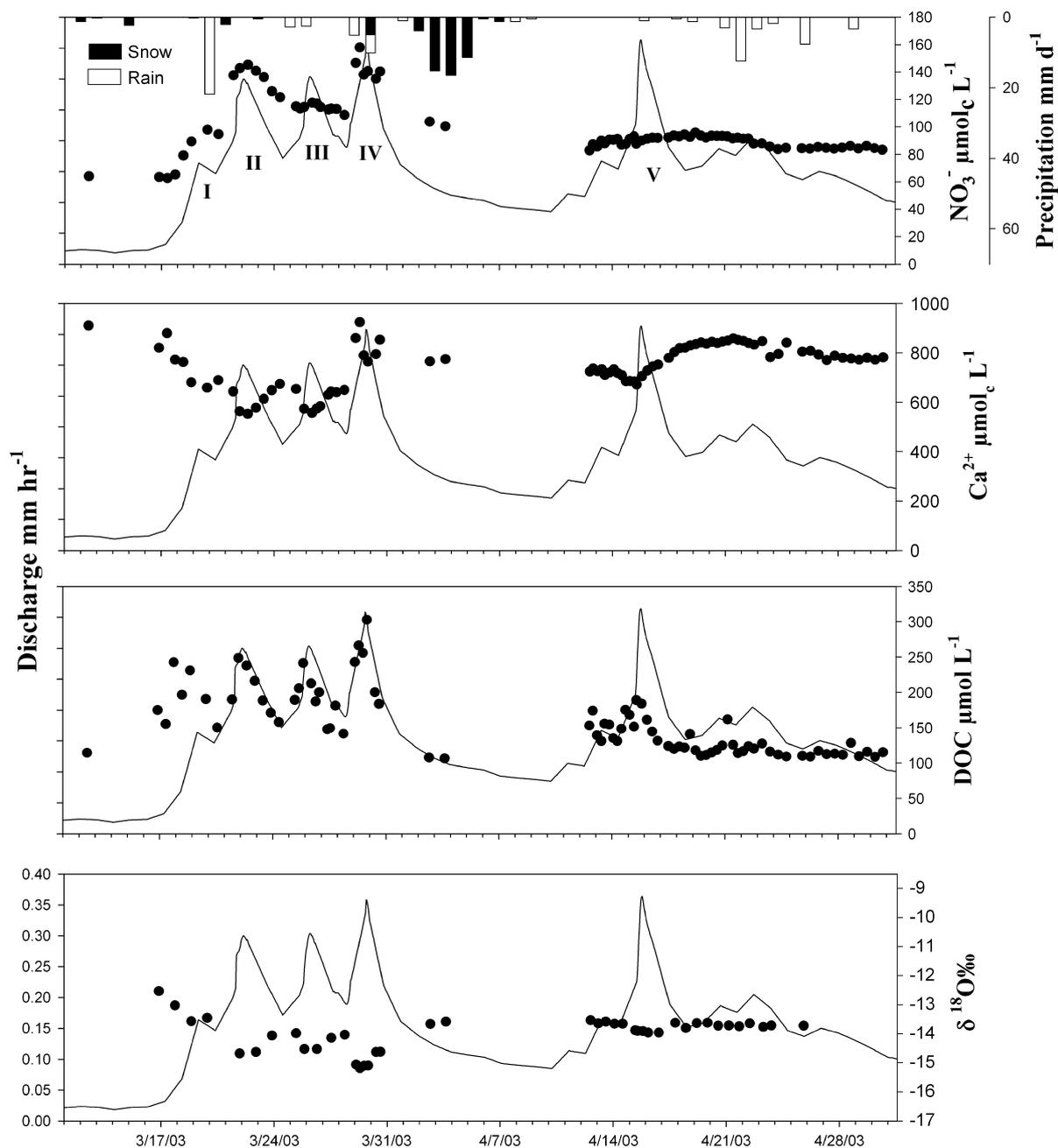

Figure 2. Precipitation, stream discharge, and stream solutes and isotopes in S14 during spring snowmelt 2003. Roman numerals indicate major peaks for this event. Bars show precipitation (mm day^{-1}); circles show stream $\delta^{18}O$ relative to VSMOW and solute concentrations (μmol_c l^{-1}); lines show stream discharge at the catchment outlet

The $^{18}O/^{16}O$ ratios of samples were determined at the USGS laboratory in Menlo Park, California, by mass spectrometry. Values are reported as the per mil difference relative to Vienna Standard Mean Ocean Water (VSMOW) with a precision of 0·1‰ using the standard definition:

$$\delta^{18}O = \left(\frac{^{18}O/^{16}O_x}{^{18}O/^{16}O_{VSMOW}} - 1 \right) \times 1000$$

where the subscript 'x' indicates sample.

Antecedent precipitation index

The antecedent precipitation index (API; McDonnell *et al.*, 1991) was calculated for fall storms in S14 and S15. Several researchers have used relative API values to compare antecedent moisture conditions among pre-storm conditions (e.g. McDonnell *et al.*, 1991; McHale *et al.*, 2002; Inamdar *et al.*, 2006). The API index is defined as

$$API_x = \sum_{i=1}^{x} \frac{P_i}{i} \tag{1}$$

where $x = 7$ or 30 days before an event and P_i (mm) is the total precipitation on the ith day before the event.
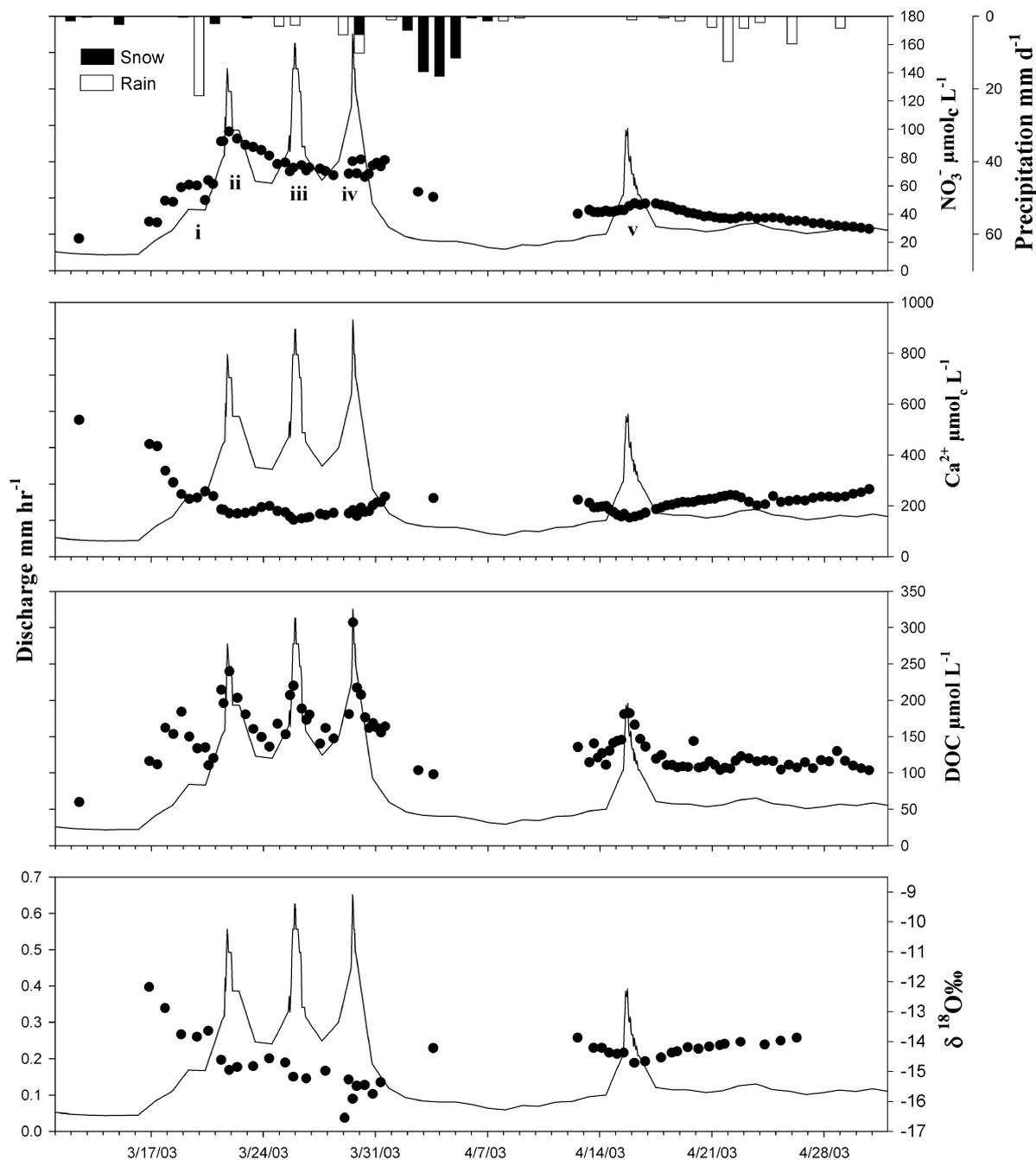

Figure 3. Precipitation, stream discharge, and stream solutes and isotopes in S15 during spring snowmelt 2003. Roman numerals indicate major peaks for this event. Bars show precipitation (mm day^{-1}); circles show stream $\delta^{18}O$ relative to VSMOW and solute concentrations (μmol$_c$ l^{-1}); lines show stream discharge at the catchment outlet

RESULTS

Hydrologic response

Snowmelt. The spring snowmelt occurred from 12 March to 30 April (Figures 2 and 3). Substantial melt began in the afternoon of 16 March in both catchments. By the end of March, the snow was nearly gone and stream discharge returned to near pre-melt rates. However, nearly 200 mm of snow fell between 2 and 7 April. About 1 week after this snow event, substantial snowmelt began on 14 April. About 34 mm of rain fell during snowmelt recession, with stream discharge showing a greater response in S14 than in S15.

Well nests in S14 were classified as being in recharge or discharge zones based on the direction of the hydraulic head gradient at each nest (Table II). Two of the three well nests in S14 were classified as recharge sites, including W36 (deep hillslope till groundwater) and W35 (shallow groundwater), whereas W34 (shallow discharging groundwater) was a discharging site located about 1 m from the stream. The wells in S15 could not be classified with respect to recharge or discharge zones since no well nests (greater than one piezometer in one site) were located in this catchment.

During snowmelt the water table surface in shallow discharging wells located in S14 (W34 and W35) and S15 (W13) rose rapidly from below the surface (40 cm, 66 cm, and 29 cm below respectively) and peaked 2 to 48 h before all stream discharge peaks (Figure 4). The

water table heights in the deep hillslope till ground-water wells W36 (S14) and W12 (S15) were far below the ground surface and detection of the water-height capacitance probes (>128 cm and 71 cm in W36 and W12 respectively) prior to the onset of snowmelt (Figure 4), but they peaked before or with all stream water discharge peaks. There was very little fluctuation in the water table height measured in W13 (S15) and W36 (S14) throughout snowmelt, except during a recession occurring between 30 March and 7 April, when temperatures were cold. By 30 April, water table height in W36 remained at or just below the ground surface, and values in W13 were within 14 to 22 cm of the ground surface. W13 and W36 were located in hillslope hollows (TI values of 7·5 and 10·5 for W13 and W36 respectively; Table II), which explains why high water table heights were sustained throughout the melt.

Late-summer/fall storms. Conditions were exceptionally dry prior to the late-summer/fall storms of 2002. Stream discharge ceased at the Archer Creek catchment outlet H-flume toward the end of summer (Mitchell *et al.*, 2006), a condition never observed since monitoring began in 1995. The 7- and 30-day APIs were lowest prior to storm 2 (Table I). This storm began with 5·0 mm of rain during 1 h on 21 September followed by 27·9 mm of rain during several hours starting at 16:00 on 22 September (Figures 5 and 6). Storm 3 had the highest 7- and 30-day APIs of all the storms (Table I). A total of 43 mm of rain fell during this storm from 27 September at 08:00 to
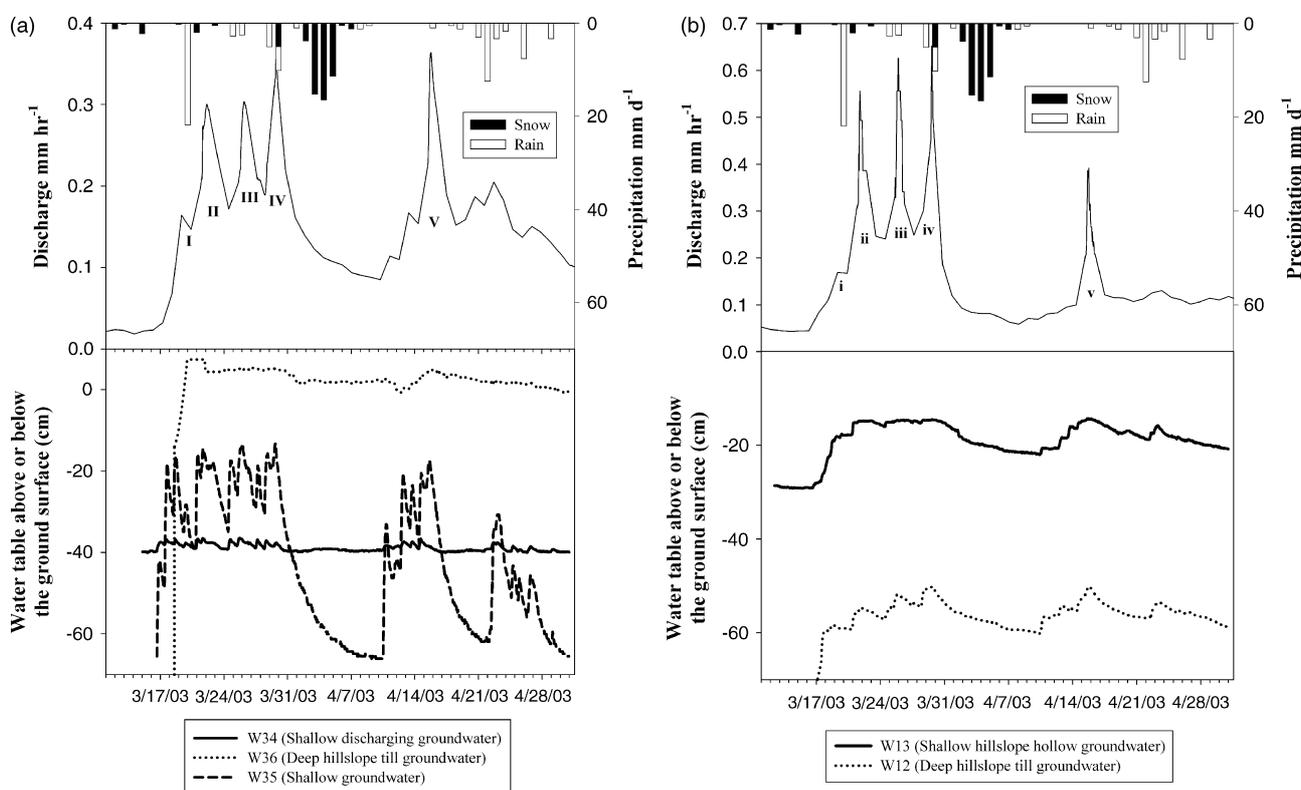

Figure 4. Water table elevations with precipitation and streamflow for spring snowmelt 2003 in S14 (a) and in S15 (b). Roman numerals indicate major peaks for this event
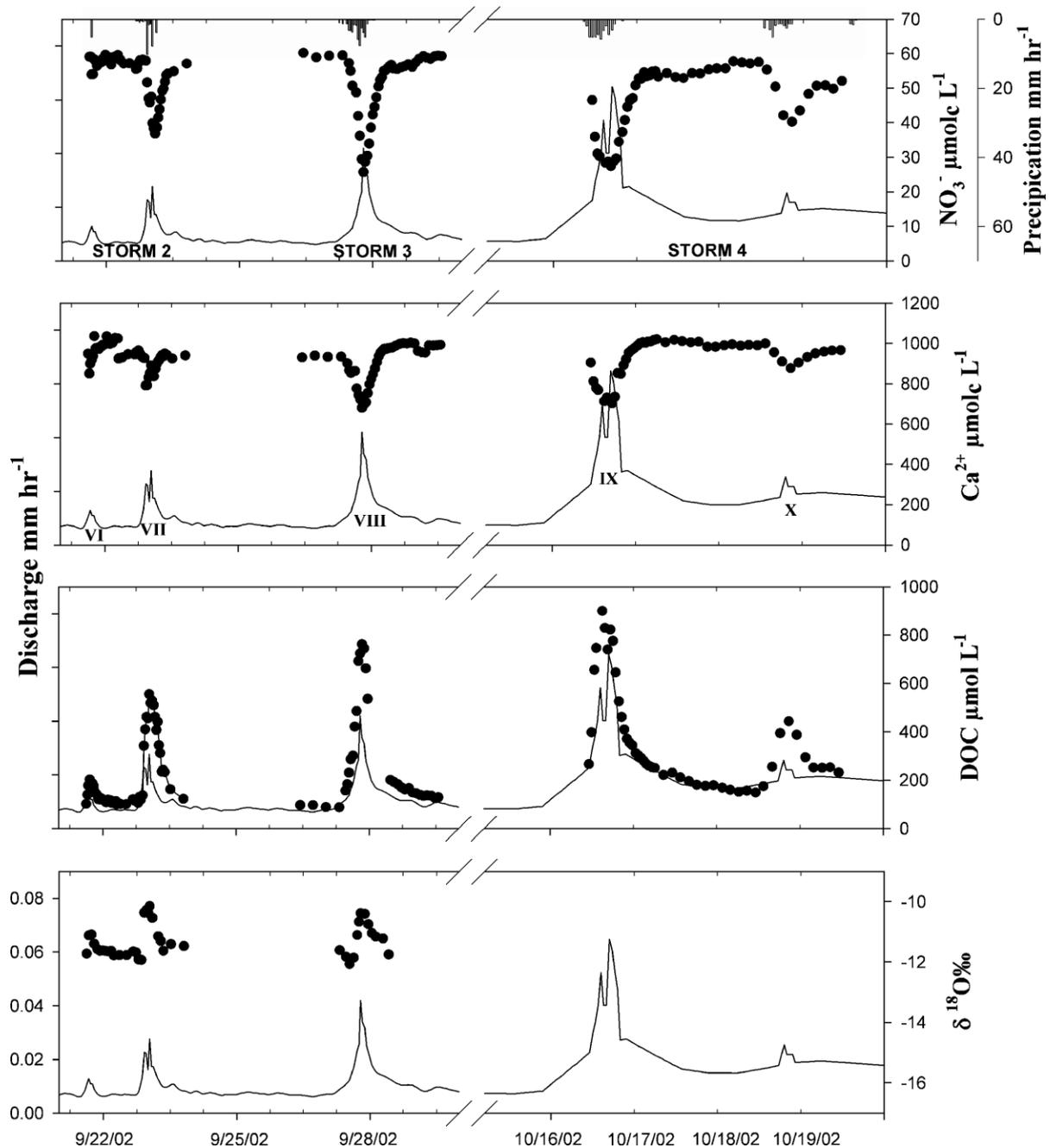
Figure 5. Precipitation, stream discharge, and stream solutes and isotopes in S14 during storms 2, 3, and 4 of 2002. Roman numerals indicate major peaks for each event. Bars show precipitation (mm day^{-1}); circles show stream δ^{18}O relative to VSMOW and solute concentrations (μmol$_c$ l^{-1}); lines show stream discharge at the catchment outlet

September 28 at 02:00 (Figures 5 and 6). Storm 4 consisted of two events: 43 mm of rain fell on 16 October (11:00–22:00) and 25 mm of rain fell between 19 and 20 October (Figures 5 and 6).

Although the 7- and 30-day APIs were lower for the 16 October storm than the 27 September storm, field observations indicated that the catchments were wetter than during the previous storms, with a greater number of 'patches' of saturated areas throughout the catchments. This greater wetness for storm 4 than storm 3 was likely due to lower transpiration rates, as deciduous foliage was becoming senescent in October. Mean discharge and water yield progressively increased

from storm 2 through to storm 4 in both catchments (Table I).

Prior to the late-summer/fall storms, the water table in W34 (S14) was close to the surface (41–42 cm below ground surface). At the onset of the events, the water table rose; but, unlike during snowmelt, it peaked 3 to 6 h after or coincident with the stream discharge peaks (Figure 7). W35 responded rapidly during storm 3, peaked 4 h after peak discharge, and receded below the detection of the water-height capacitance probe in W35 18 h after its peak (Figure 7b). The presence of water in W35 prior to storm 3 indicated that antecedent moisture was greater prior to storm 3 than prior to storm 2. During storm 4,
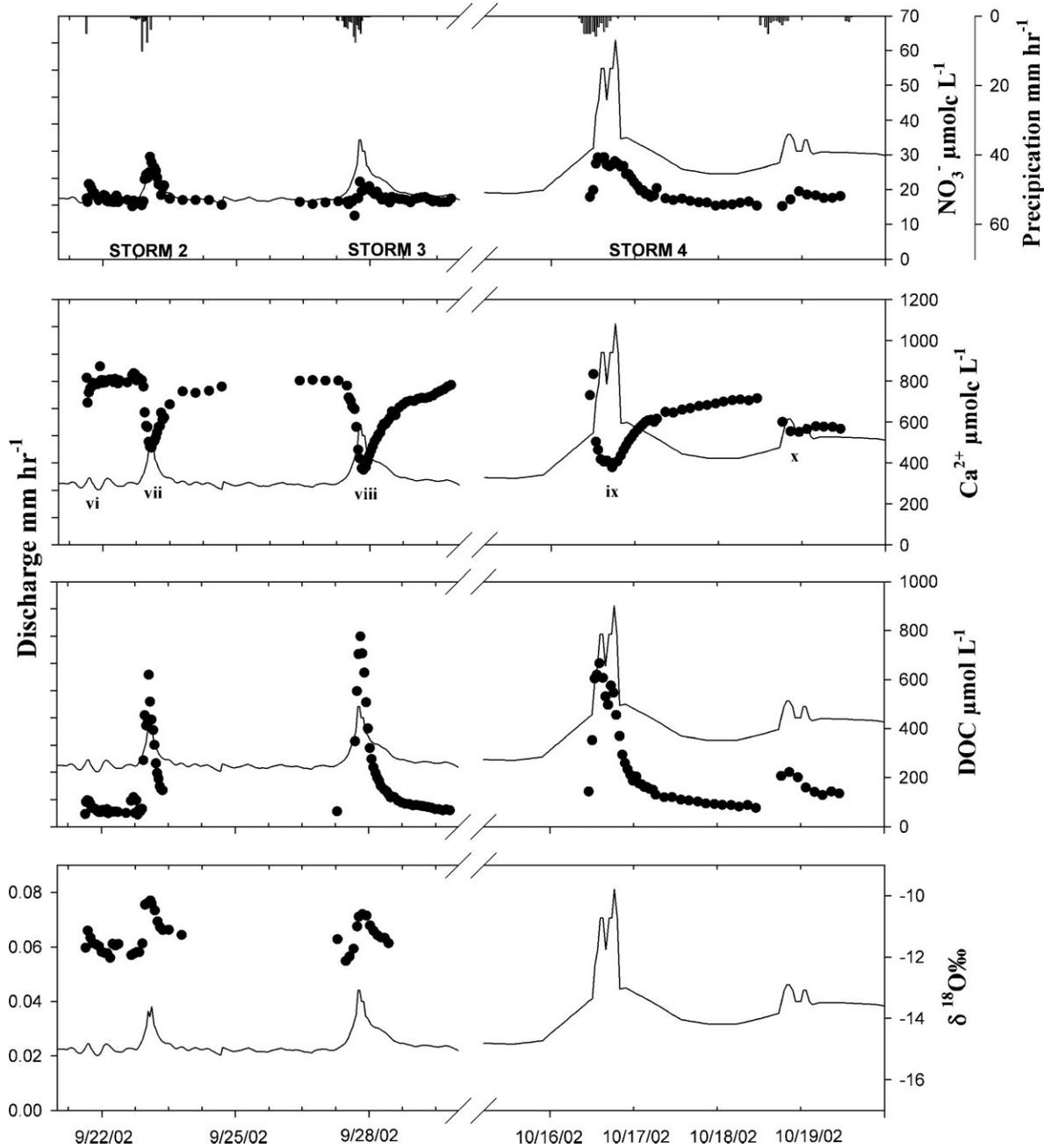
Figure 6. Precipitation, stream discharge, and stream solutes and isotopes in S15 during storms 2, 3, and 4 of 2002. Roman numerals indicate major peaks for each event. Bars show precipitation (mm day^{-1}); circles show stream $\delta^{18}O$ relative to VSMOW and solute concentrations (μmol_c l^{-1}); lines show stream discharge at the catchment outlet

W35 rose to 21 cm below the ground surface, which is the highest level observed for this well, reflecting the relatively high antecedent moisture conditions and precipitation associated with this event. During storms 2–4, W13 (S14) was dry and the capacitance rods in both W36 (S14) and W12 (S15) were not installed sufficiently deep to detect rises at these lower water table depths. The maximum detectable water table depths in W36 and W12 were respectively 132 cm and 167 cm below the ground surface.

Water chemistry and isotopes

Stream water sources. For all pools, S14 had higher NO$_3^-$ concentrations than S15 (Tables III and IV). During

the dormant period, the highest NO$_3^-$ concentrations were found in the near-surface soil (15 cm) water within the upper hillslopes of both catchments, whereas the highest $\delta^{18}O$ values were found in groundwater. In contrast, during the growing season, the highest NO$_3^-$ concentrations were found in deep hillslope till groundwater in S14 and the highest $\delta^{18}O$ values were found in soil water. Mean annual C_b (sum of the base cations) concentrations were lowest in soil water and highest in groundwater during both seasons, indicating that relatively high stream water C_b in surface waters are derived from groundwater sources. Concentrations of DOC were highest in near-surface soil water and decreased with depth for both S14
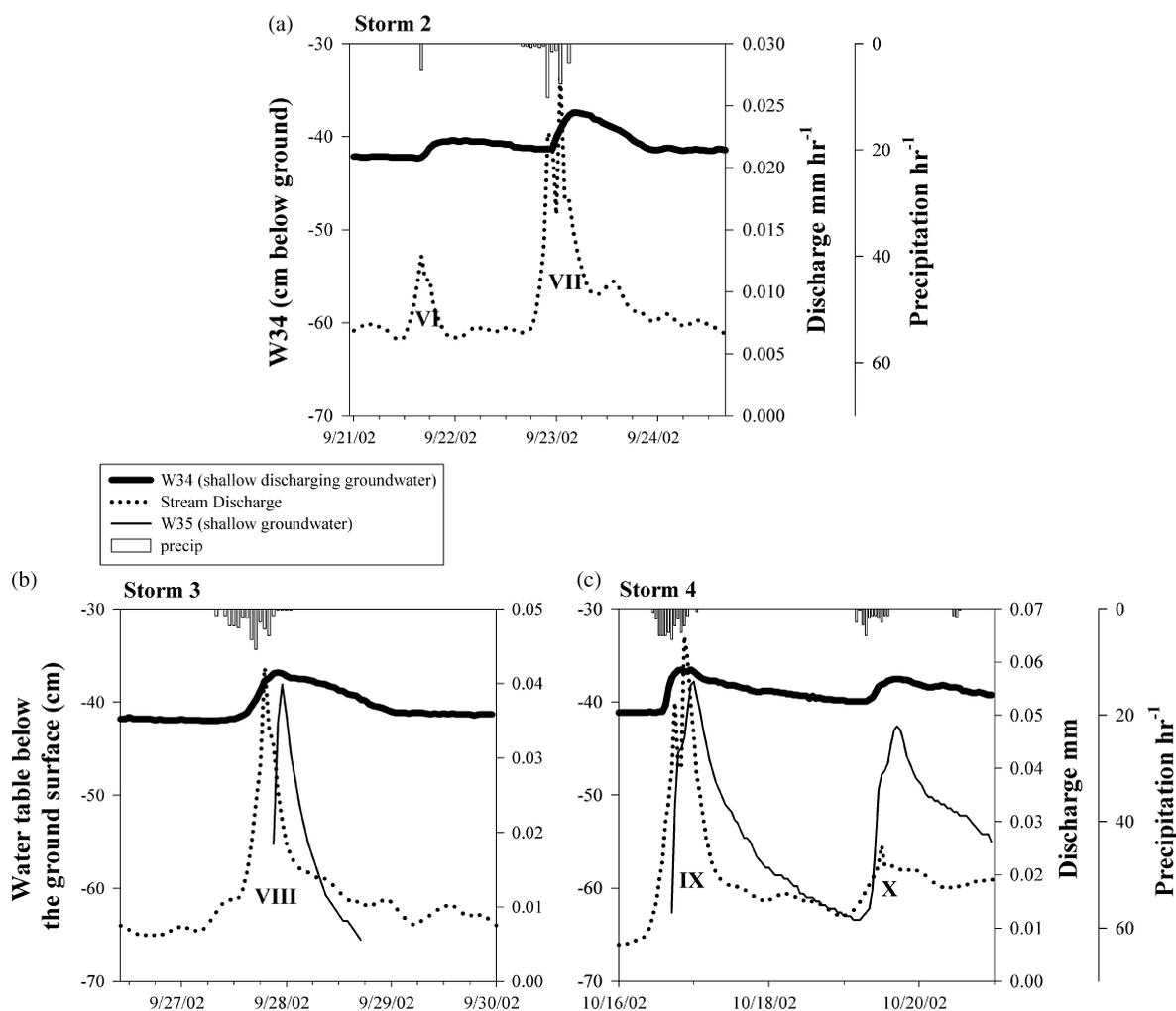
Figure 7. Water table elevations in S14 with precipitation and stream flow for the late-summer/early fall storms 2, 3, and 4 of 2002. Roman numerals indicate major peaks for each event

and S15 during the entire study period, suggesting that elevated DOC concentrations observed in surface waters are derived from the shallowest soil water sources (e.g. forest floor).

Snowmelt. Temporal patterns of stream water chemistry and water isotopes ($\delta^{18}O$) were similar in S14 and S15 during snowmelt. Concentrations of Ca^{2+} and $\delta^{18}O$ values were relatively high before snowmelt: 911 μmol_c l^{-1} and 538 μmol_c l^{-1} for Ca^{2+} in S14 and S15 respectively and $-12 \cdot 5‰$ and $-12 \cdot 2‰$ for $\delta^{18}O$ in S14 and S15 respectively (Figures 2 and 3). Concentrations of Ca^{2+} and $\delta^{18}O$ values generally decreased during snowmelt to minima of 553 μmol_c l^{-1} and $-15 \cdot 2‰$ respectively for S14 and to 58 μmol_c l^{-1} and $-16 \cdot 6‰$ respectively for S15. These values increased during hydrograph recessions but did not return to pre-melt concentrations by 30 April.

Concentrations of NO_3^- and DOC in both streams exhibited similar temporal patterns during snowmelt (Figures 2 and 3). Before melt, baseflow concentrations of NO_3^- and DOC were 64 μmol_c l^{-1} and 115 μmol l^{-1} respectively in S14 and 23 μmol_c l^{-1} and 60 μmol l^{-1} respectively in S15. Concentrations of NO_3^- increased

as discharge increased during the onset of snowmelt and were highest during or just before the first major stream discharge peak. Peaks in NO_3^- concentrations ranged from 118 to 158 μmol_c l^{-1} for S14 and 47 to 98 μmol_c l^{-1} for S15, whereas those for DOC ranged from 189 to 303 μmol l^{-1} in S14 and from 181 to 307 μmol l^{-1} in S15. Maximum NO_3^- and DOC concentrations on 15 April (stream discharge peaks 'V' and 'v') were lower than those observed during late March.

Late-summer/fall storms. Stream water NO_3^- and Ca^{2+} concentrations were highest before the late-summer/fall storms at the outlet of S14: 52–60 μmol_c l^{-1} NO_3^- and 905–951 μmol_c l^{-1} Ca^{2+} (Figure 5). NO_3^- and Ca^{2+} concentrations decreased and reached their lowest values during stream discharge peaks: 26–54 μmol_c l^{-1} NO_3^- and 682–852 μmol_c l^{-1} Ca^{2+}. As the hydrograph receded, NO_3^- and Ca^{2+} concentrations returned to baseflow values. In contrast, concentrations of DOC and $\delta^{18}O$ values increased monotonically during the late-summer/fall storm events, with highest values just before or at peak stream discharge (444–901 μmol l^{-1} DOC and $10 \cdot 1$–$10 \cdot 4‰$ $\delta^{18}O$), after which they returned to baseflow values during the hydrograph recessions.

Table III. Mean concentration of NO_3^-, DOC, and C_b (K^+, Na^+, Mg^{2+}, Ca^{2+}) during the growing season (May–October 2002) and the dormant season (November 2002–April 2003) in various pools of two catchments of Archer Creek. Standard error is in parentheses and sample number is in brackets (N/A: not available)

Water source	Growing season			Dormant season		
	NO_3^- ($\mu mol_c\ l^{-1}$)	DOC ($\mu mol\ l^{-1}$)	C_b ($\mu mol_c\ l^{-1}$)	NO_3^- ($\mu mol_c\ l^{-1}$)	DOC ($\mu mol\ l^{-1}$)	C_b ($\mu mol_c\ l^{-1}$)
Bulk throughfall	42·9 (21·3) [15]	753 (107) [15]	173 (29) [15]			
	47·2 (2·9) [60]	244·8 (26·6) [60]	29 (9) [60]			
S14						
Lower hillslope soil						
15 cm	75·8 (23·0) [19]	3618 (431) [7]	504 (42) [15]	126 (37·4) [35]	2513 (222) [24]	561 (60) [32]
50 cm	49·9 (11·3) [19]	1304 (207) [12]	534 (79) [18]	28·1 (2·5) [55]	1255 (141) [41]	336 (22) [45]
Upper hillslope soil						
15 cm	N/A	N/A	N/A	581 (113) [13]	870 (102) [22]	780 (90) [31]
50 cm	N/A	N/A	N/A	186 (16·9) [14]	310 (22·0) [28]	504 (53) [34]
Shallow discharging groundwater (W34)	1·5 (1·5) [6]	727 (169) [6]	1398 (63) [6]	3·6 (2·3) [7]	315 (40·6) [7]	813 (17) [9]
Deep hillslope till groundwater (W36)	109 (29·3) [2]	168 (72·4) [2]	1333 (48) [2]	99·6 (4·3) [3]	165 (8·5) [3]	1429 (22) [3]
Stream	55·7 (0·4) [413]	186 (7·6) [385]	1029 (6·4) [330]	102 (3·5) [88]	164 (7·6) [88]	877 (17·5) [87]
S15						
Upper hillslope soil						
15 cm	N/A	N/A	N/A	426 (96·9) [13]	1134 (171) [18]	290 (37) [22]
50 cm	N/A	N/A	N/A	49·0 (7·2) [26]	277·3 (18·1) [43]	111 (13) [47]
Deep hillslope till groundwater (G14)	22·3 (4·7) [6]	187 (15·5) [6]	779 (36) [6]	19·7 (2·0) [3]	192 (5·5) [3]	720 (56) [3]
Stream	18·9 (0·3) [312]	144 (8·6) [285]	895 (14·7) [147]	54 (2·1) [94]	144 (4·6) [94]	327 (14·7) [147]

Table IV. The $\delta^{18}O–H_2O$ (‰) in water sources before hydrologic events. Unless indicated otherwise, data were collected from one instrument. Standard error is in parentheses and sample number is in brackets

	Bulk throughfall	S14				S15 deep hillslope till groundwater (G14)
		15 cm soil	50 cm soil	Deep hillslope till groundwater (W36)	Shallow discharging groundwater (W34)	
Storm 2	−8·0(0·04) [4]	−7·3	−8·9	N/A	−11·0	−11·6[a]
Storm 3	−11·2(0·09) [3]	−7·3	−8·9	N/A	−11·0	−11·6[a]
Storm 4	−15·5(0·1) [4]	−7·3	−8·9	N/A	−11·1	−11·6[a]
Snowmelt	−16·5 0·2 [4]	−12·7	−14·0(0·4) [4]	−11·6	−12·3	−11·7[b]

[a] Sampled 21 July 2000.
[b] Sampled 27 February 2000.

The temporal patterns of Ca^{2+}, DOC, and $\delta^{18}O$ values in stream discharge at S15 were similar to those observed for S14 during fall storms, whereas the patterns for NO_3^- were markedly different between the two catchments. Highest Ca^{2+} concentrations (732–818 $\mu mol_c\ l^{-1}$) were observed before the storms (Figure 6) and decreased to their lowest values (368–553 $\mu mol_c\ l^{-1}$) during stream discharge peaks. Differing from the response of S14, DOC, $\delta^{18}O$, and NO_3^- values followed similar trajectories during late-summer/fall storms. NO_3^-, DOC, and $\delta^{18}O$ values increased with discharge, decreasing to pre-storm levels during hydrograph recessions.

DISCUSSION

Are water sources similar between S14 and S15 and do differences in NO_3^- concentration in water sources control differences in within-event stream chemistry patterns between these two catchments?

Snowmelt

Stream water NO_3^- concentrations exhibited similar patterns during snowmelt in S14 and S15. Concentrations of NO_3^- in deep hillslope till groundwater were relatively low compared with other water sources during the dormant season in S14 and S15, whereas C_b concentrations

and $\delta^{18}O$ values were relatively high. Low stream water NO_3^- concentrations and high C_b and $\delta^{18}O$ values were also observed at the inception of snowmelt, suggesting that deep hillslope groundwater was the dominant stream water source at this time. As the melt progressed, the catchments became wetter (Figure 4). The water table reached a maximum just before or coincident with each peak in stream discharge during snowmelt (Figure 4), increasing the potential contribution of shallower water sources. Indeed, concentrations of Ca^{2+} and $\delta^{18}O$ values in stream water in both catchments were lowest during peaks in stream discharge, whereas NO_3^- and DOC concentrations were greatest just before or at peak discharge (Figures 2 and 3), indicating that the maximum contribution of soil water occurred at the hydrograph peak during snowmelt.

Following snowmelt, by 30 April, the water table in most wells had not yet reached pre-event levels in either catchment. In addition, concentrations of Ca^{2+} and $\delta^{18}O$ values were increasing but had not reached pre-melt concentrations. Therefore, NO_3^- in the stream was a mixture of soil water and groundwater as snowmelt ended. A decrease in both NO_3^- and DOC with each successive discharge peak also occurred during snowmelt. This pattern was also observed in catchments in Ontario, Canada, and was attributed to the decreasing source of N as the event progressed (Creed *et al.*, 1996; Hinton *et al.*, 1998).

Late-summer/fall storms

During the growing season, deep hillslope till groundwater had high NO_3^- concentrations in S14 and low values in shallow soil water and shallow discharging groundwater (Table III), suggesting that deep hillslope till groundwater was the main source of NO_3^- at the beginning of each of the late-summer/fall storms. With each late-summer/fall storm of 2002, the catchments became wetter (Figure 7). When the groundwater was closest to the ground surface, DOC and $\delta^{18}O$ values peaked and NO_3^- Ca^{2+} and Mg^{2+} concentrations were lowest, suggesting shallower water sources with relatively high DOC and $\delta^{18}O$ values and low NO_3^- and Ca^{2+} concentrations were contributing to stream discharge. The temporal patterns in stream NO_3^- concentration in S14 and S15 differed during late-summer/fall storms. These differences were not due to variation in water sources between the two catchments, but rather to differences in the NO_3^- concentrations of those sources. Because there was little NO_3^- in groundwater in S15 during the growing season (Table III), low baseflow NO_3^- concentrations were observed in the stream prior to the late-summer/fall storms. As the catchment wetted during these late-summer/fall storms, Ca^{2+} stream water concentrations decreased to minimal values with peak discharge. In S15, during these late-summer/early fall storms, NO_3^- and DOC concentrations occurred at maximum discharge with these maximum values coinciding with the high concentrations of DOC and NO_3^- in the soil surface during this period (Table III), suggesting that these solutes were flushed from near-surface soil horizons via shallow flow-paths.

How does antecedent moisture affect the timing of NO_3^- export during events?

Antecedent moisture conditions affect the catchment wetness, the contribution of different source components, and hence the export of solutes. Flushing of NO_3^- and DOC sources (during all storms in S15 and melt in S14) from shallow soil sources generally occurred during peak discharge when antecedent conditions were dry, especially during late-summer storms (storm 2; Figures 5 and 6). In contrast, flushing under wetter conditions (storm 4 and spring snowmelt) occurred before peak discharge (Figures 2, 3, 5 and 6). This latter pattern has been commonly observed for other forested catchments (Murdoch and Stoddard, 1992; Boyer *et al.*, 1997; Creed and Band, 1998). During dry conditions, as was the case before storm 2, the water table peaked slightly after peak discharge, suggesting that the catchment wetted slowly and shallower flow paths did not contribute substantially to stream flow. During wet conditions (storm 4 and snowmelt), groundwater responded sooner and rose higher than during dry conditions, suggesting a contribution from shallow soil. Other investigators have stressed the importance of antecedent wetness on the overall export of solutes. Mitchell *et al.* (2006) also investigated the mechanisms of solute transport during the late-summer and fall 2002 storms within the entire Archer Creek catchment and attributed the marked difference in responses of hydrology and surface water chemistry to differences in antecedent moisture conditions and precipitation amount with progressive storms during this period. A delayed peak in DOC concentrations observed in Archer Creek during a fall (1999) storm associated with Hurricane Floyd was attributed to the disconnection of isolated saturated areas that became connected under conditions of maximum water content (Inamdar *et al.*, 2004).

Can a conceptual model be developed that explains NO_3^- release in S14 and S15?

A conceptual model considering the interaction of water sources and the relative magnitude of solutes in soil reservoirs can illustrate the dominant factors controlling the temporal variation in stream water chemistry across markedly different sites (Figure 8). During the dormant season, shallow soil water sources had high NO_3^- concentrations, whereas NO_3^- concentrations in groundwater sources were relatively low in S14 and S15. Prior to snowmelt, we hypothesize that deep groundwater flow paths travelling through deep soils carried relatively low concentrations of NO_3^- to the streams in S14 and S15 (Figure 8a and b). As the subcatchments became wetter, the water table rose into shallow soil horizons and, in some cases, above the ground surface (often at hillslope hollows) and shallow water sources dominated the stream hydrograph. Just before peak stream water discharge,
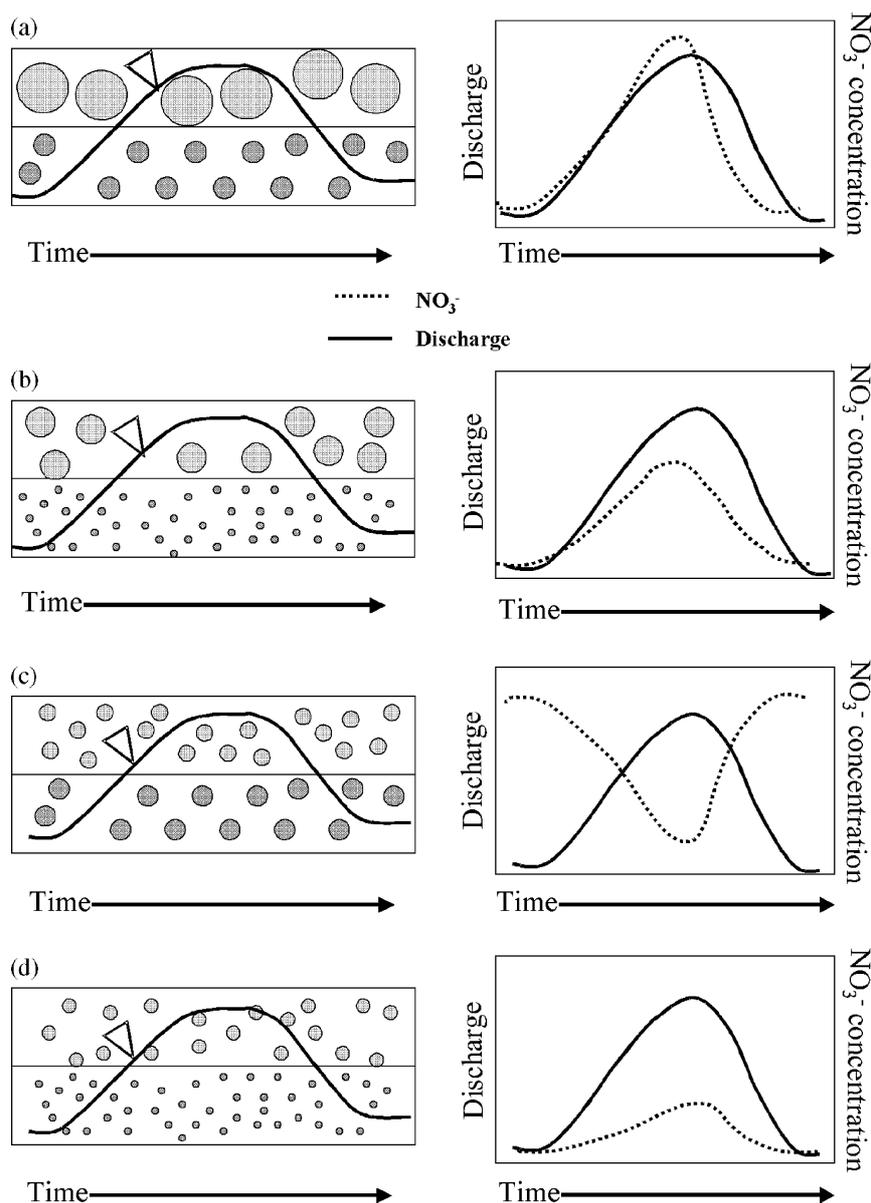
Figure 8. Conceptual model indicating the dominant factors controlling the concentration of stream water NO_3^- during snowmelt in S14 (a) and S15 (b) and late-summer/fall storms in S14 (c) and S15 (d). Size of the circles represents the relative concentration of NO_3^- in the shallow versus deep water source. The triangle represents the position of the water table

shallow soil sources carried relatively high concentrations of NO_3^- to the stream. Although water sources were similar between the subcatchments, S14 had greater NO_3^- concentration in all water sources compared with S15.

During the late-summer and early-fall storms, NO_3^- concentrations in S14 deep groundwaters were relatively high compared with other water sources (Figure 8c). Groundwater was the major source to drainage waters during the baseflow of this period. The contributions of these groundwater concentrations were diluted during these storms by shallower sources with lower NO_3^- concentrations. In contrast, the groundwater of S15 had lower NO_3^- compared with the groundwater and other water sources in the upper soil of S14. Therefore, during baseflow, stream water NO_3^- concentrations were lower in S15 than in S14. During the fall storms, stream water NO_3^- concentrations increased as shallower flow paths

contributed relatively higher NO_3^-, resulting in increased NO_3^- during storm events in S15 (Figure 8d).

How does our conceptual model of NO_3^- release in S14 and S15 compare with other models?

The conceptual model of NO_3^- release during snowmelt in S14 and S15 closely resembles Creed *et al.*'s (1996) flushing hypothesis, whereby the water table rises into shallow soil during hydrological events and carries NO_3^- to the stream. Piatek *et al.* (2005), conducting a study using NO_3^- $\delta^{15}N$ and $\delta^{18}O$ to determine sources of NO_3^- during snowmelt in the entire Archer Creek catchment, also found that groundwater was the main source of NO_3^- before melt, with increasing amounts of NO_3^- flushed from shallow soils as the melt increased.

NO_3^- release during spring snowmelt in S14 and S15 can be controlled by biotic and/or abiotic processes. For

example, the delivery of NO_3^- during snowmelt in some catchments is controlled by the balance of microbial assimilation versus mineralization beneath the snowpack (Brooks and Williams, 1999; Brooks *et al.*, 1999; Sickman *et al.*, 2003). A deeper, consistent snowpack resulted in higher microbial assimilation of NO_3^- relative to the flushing of mineralized N in Colorado (USA) catchments (Brooks and Williams, 1999). In contrast, the majority of NO_3^- exported in catchments located in the Sierra Nevada Mountains (USA) was not from flushing of overwintered soil N (Sickman *et al.*, 2003). Instead, snowmelt N was incorporated into microbial biomass during the active snowmelt and released gradually 2 weeks before peak stream discharge. NO_3^- release was controlled by redox potential, soil moisture, and pH in catchments. Another study, conducted in the White Mountains of New Hampshire (USA), indicated that snowpack N is retained abiotically in the soil and is not biologically available until later in the spring or summer when conditions such as temperature are more favourable (Campbell *et al.*, 2007). NO_3^- flushing of the Sierra Nevada catchments, as well as catchments located in Alberta, Canada, increased with greater snowpack depth/runoff by reducing net biological uptake (Sickman *et al.*, 2001; Lafreniere and Sharp, 2005) or by reducing the proportion of runoff that had come in contact with biologically active microbes in the soil that remove NO_3^- (Lafreniere and Sharp, 2005).

The mechanism of NO_3^- release in S15 most closely resembles the flushing hypothesis put forth by Creed *et al.* (1996) during late-summer/early fall storms. The results describing both the concentrations and temporal patterns of solutes in S14 during late-summer/fall storms are consistent with previous studies conducted within the larger Archer Creek catchment and another catchment in New York State. These previous studies have found that groundwater is an important source of NO_3^- during late-summer/fall storms (McHale *et al.*, 2002; Inamdar *et al.*, 2004; Inamdar and Mitchell, 2006; Mitchell *et al.*, 2006). Inamdar *et al.* (2004) observed a clear separation of DOC response compared with those of NO_3^-, Mg^{2+}, and Ca^{2+} in Archer Creek while observing the evolution of solutes during a 1999 fall storm, suggesting stream NO_3^- concentrations were derived from till groundwater whereas DOC was derived from near-surface soil water. Inamdar *et al.* (2004) attributed the early rise in NO_3^- concentrations in stream water to the displacement of till groundwater by infiltrating precipitation. McHale *et al.* (2002) suggested that the highest NO_3^- concentrations coincided with peaks in the till groundwater contribution to storm hydrographs in the Archer Creek. Similarly, Inamdar and Mitchell (2006) suggested that steep gradients expedited the movement of high-NO_3^- seep and shallow groundwater to the stream in a catchment located in southern New York. Both Inamdar and Mitchell (2006) and McHale *et al.* (2002) suggested that soil nitrification located on the ridge tops of the catchment recharged NO_3^- to groundwater, which was subsequently carried to the stream. S14 is located in the upland ridge tops of the Archer Creek catchment and its stream outlet is

the groundwater spring SS1 that accounted for the major source of NO_3^- to Archer Creek in the McHale *et al.* (2002) study. Soil water in S14 may be a major source of NO_3^- to the entire Archer Creek watershed due to the high rates of nitrification in this catchment, which contributes to high concentrations of NO_3^- in groundwater throughout the year, even during late-summer/fall storms in S14.

Source-chemistry-controlled stream water chemical response

Inorganic N supplies in S14 may have exceeded biologic demand, resulting in an accumulation of nitrified N in various pools. This excess NO_3^- would be transferred to groundwater, especially during periods of recharge in the dormant season, and would be subsequently transported to stream water. A study conducted in the Turkey Lakes watershed of Ontario, Canada (Creed and Band, 1998), suggested a draining mechanism whereby recharge of groundwater during spring snowmelt transfers N solutes from the upper soil layers into deeper hydrological flow paths that are released later in the year. Similarly, elevated stream water NO_3^- in Catskill, NY, perennial streams during the summer was attributed to recharge of NO_3^- to groundwater from the previous spring (Burns *et al.*, 1998). Many studies using NO_3^- $\delta^{15}N$ and $\delta^{18}O$ have indicated that nitrification continues under the snowpack in snow-dominated forested catchments, and it is now widely accepted that NO_3^- produced from nitrification, and not NO_3^- flushed from the melting snowpack, is the dominant source of NO_3^- exported during snowmelt (Kendall *et al.*, 1995, 1996; Kendall, 1998; Spoelstra *et al.*, 2001; Burns and Kendall, 2002; Campbell *et al.*, 2002; Piatek *et al.*, 2005). The greater soil water Ca^{2+} concentrations in S14 than in S15 in part explains: (1) the greater abundance of sugar maple in S14 (and other tree species that are found on base-rich sites) than in S15; (2) litter inputs that are probably more rapidly mineralized and nitrified in S14 than in S15 due to lower C : N ratios (Christopher *et al.*, 2006).

CONCLUSIONS

In this study, we explored the sources of NO_3^- and the mechanisms by which NO_3^- reaches the stream in two adjacent headwater catchments, with an aim of explaining the large differences in NO_3^- concentrations and export between the two catchments. Using combined hydrometric, hydrochemical, and isotopic data, we developed a conceptual model of NO_3^- release during baseflow, storm flow, and snowmelt that is consistent with the various types of data collected. Although the two catchments had similar hydrologic responses and similar relative contributions of water sources to stream flow during fall storms and snowmelt, the temporal patterns of stream chemistry varied markedly among these two streams due to differences in the N production and N availability and resulting differences in concentrations of solutes in the

mixing waters. The timing of the NO_3^- peaks during all hydrologic events not only depended on the relative magnitude of NO_3^- in water sources in S14 and S15, but also on the antecedent moisture conditions, with flushing occurring before the peak during wetter conditions but at peak discharge following the driest antecedent conditions. Although the late-summer/early fall storms did not contribute substantially to the overall annual hydrologic response for these catchments (Table I), these events had distinct chemical responses, the understanding of which provides new information on N processing and transport in forested watersheds.

Our study highlights the complexity of elucidating the heterogeneous temporal and spatial patterns of NO_3^- export in temperate forested catchments. The factors that affect sources and transport of N vary both within and among watersheds and include differences in species composition, soil nutrient cycling rates, land use, and hydrological characteristics (e.g. antecedent moisture and magnitude, duration, and intensity of storms), as well as atmospheric deposition and climate change.

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