
The impact of storm events on solute exports from a glaciated forested watershed in western New York, USA

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Abstract:

This study analysed the importance of precipitation events from May 2003 to April 2004 on surface water chemistry and solute export from a 696 ha glaciated forested watershed in western New York State, USA. The specific objectives of the study were to determine: (a) the temporal patterns of solutes within individual storm events; (b) the impact of precipitation events on seasonal and annual export budgets; and (c) how solute concentrations and loads varied for precipitation events among seasons as functions of storm intensity and antecedent moisture conditions. Analysis of solute trajectories showed that NH_4^+ , total Al and dissolved organic nitrogen (DON) peaked on the hydrograph rising limb, whereas dissolved organic carbon (DOC) concentrations peaked following the discharge peak. Sulphate and base-cations displayed a dilution pattern with a minimum around peak discharge. End-member mixing analysis showed that throughfall contributions were highest on the rising limb, whereas valley-bottom riparian waters peaked following the discharge peak. The trajectories of NO_3^- concentrations varied with season, indicating the influence of biotic processes on the generation, and hence flux, of this solute. Storm events had the greatest impact on the annual budgets for NH_4^+ , K^+ , total dissolved Al, DON and DOC. Storm events during summer had the greatest impact on seasonal solute budgets. Summer events had the highest hourly discharges and high concentrations of solutes. However, NO_3^- and DOC exports during a spring snowmelt event were considerably more than those observed for large events during other periods of the year. Comparisons among storms showed that season, precipitation amount, and antecedent moisture conditions affected solute concentrations and loads. Concentrations of solutes were elevated for storms that occurred after dry antecedent conditions. Seven of the largest storms accounted for only 15% of the annual discharge, but were responsible for 34%, 19%, 64%, 13%, 39% and 24% of the annual exports of NH_4^+ , K^+ , Al, NO_3^- , DON and DOC respectively. These results suggest that the intense and infrequent storms predicted for future climate-change scenarios will likely increase the exports of solutes like DOC, DON, NH_4^+ , Al and K^+ from watersheds. Copyright © 2006 John Wiley & Sons, Ltd.

KEY WORDS storm events; solute budgets; dissolved organic carbon; dissolved organic nitrogen; watershed; hydrochemistry; season

INTRODUCTION

There is increasing recognition that high-frequency sampling of stream chemistry, especially during storm events, is critical for quantifying solute export patterns from watersheds and for identifying the processes responsible for the release of solutes (Hinton *et al.*, 1997; Swistock *et al.*, 1997; McHale *et al.*, 2000; Inamdar *et al.*, 2004; Kirchner *et al.*, 2004). Kirchner *et al.* (2004) argued that high-frequency sampling conducted over longer time periods is certain to yield new insights into hydrologic and biogeochemical processes regulating stream chemistry (processes that occur over time-scales of minutes to hours in small watersheds). Through

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detailed storm-event monitoring, Hinton *et al.* (1997) found that 10% of the stream discharge accounted for 41 to 57% of dissolved organic carbon (DOC) export in the autumn, with one large event contributing 31%. McClain *et al.* (2004) referred to such events as 'hot moments', i.e. short periods of time that have a disproportionate influence on catchment hydrologic and solute response. Swistock *et al.* (1997) found that storm events were important contributors to solute budgets, especially for solutes that were strongly correlated to stream discharge. Storm events were also responsible for most of the annual dissolved organic nitrogen (DON) export from a forested watershed in the Adirondack Mountains of New York (McHale *et al.*, 2000). The importance of storm events in acidification of surface waters has also been shown (Wigington *et al.*, 1990). However, the impact of storm events on surface water acidification or other changes in solute chemistry may vary with event size, season, and antecedent moisture conditions. Wellington and Driscoll (2004) found that events following wet conditions produced more severe acid episodes than events following drier conditions. Biron *et al.* (1999) studied solute concentrations during a sequence of fall storms for 2 years with contrasting moisture regimes and found that concentrations during the drier year were higher than those during the wetter year.

Information on temporal patterns within storms is needed not only in developing models of discharge versus solute concentrations for computing solute flux budgets (Swistock *et al.*, 1997), but will also provide insights into the hydrologic flowpaths responsible for solute export. NO_3^- (Creed and Band, 1998a) and DOC (Boyer *et al.*, 1997) concentrations were observed to increase with increasing discharge and were attributed to the 'flushing' of the solutes from near-surface layers by the rising water table. Inamdar *et al.* (2004) were able to identify a clear separation in NO_3^- and DOC concentration trajectories for a large summer event that suggested NO_3^- and DOC were exported via different hydrologic flow paths. Mitchell *et al.* (2006) studied a sequence of four summer–fall storms after an extended dry period and found that there was a clear change in surface water chemistry. Differences in solute concentrations among events suggested that wetlands contributed more to solute export as the catchment moisture regimes increased.

We explored the role of storm events in influencing the surface water chemistry of a 696 ha glaciated, forested, watershed in western New York State through an intense high-frequency sampling campaign conducted over 1 year. A total of 32 rainfall events and a large snowmelt event were sampled. Sampling for rain events was conducted at frequencies as low as 15 min, whereas the snowmelt event was sampled on a daily basis. Concentrations of cations (total Al, Ca^{2+} , Mg^{2+} , K^+ , Na^+), anions (SO_4^{2-} , NO_3^-), DOC, and DON were determined. Using Mg^{2+} , Si, and DOC in an end-member mixing analysis (EMMA), Inamdar and Mitchell (2006) identified throughfall, shallow groundwater (SGW) and valley-bottom riparian water (VBRW) as the three controlling end-members for stream chemistry during rainfall events. Throughfall contributions were high on the rising limb, whereas VBRW contributions were found to dominate the receding limb of the streamflow hydrograph (Inamdar and Mitchell, 2006). Our interest in this study was to investigate the impact of storm events and these runoff components on the temporal pattern and amounts of solutes exported from the watershed. Specific questions that were addressed in our study were:

1. How do solute concentrations vary temporally within storm events and how are they influenced by sources of runoff in the watershed? Do event solute patterns vary with seasons and event size?
2. What is the impact of storm events on annual and seasonal solute export budgets?
3. How do solute concentrations and loads vary for storms as a function of storm size, antecedent moisture and season?

METHODS

Site description

This study was conducted in the 696 ha Point Peter Brook watershed (Figure 1), located in Cattaraugus County and 55 km southeast of Buffalo, NY (42°26'30"N; 78°55'30"W). Mean annual winter temperature is -3°C and the mean summer temperature is 21°C . Annual precipitation averages 1006 mm, of which

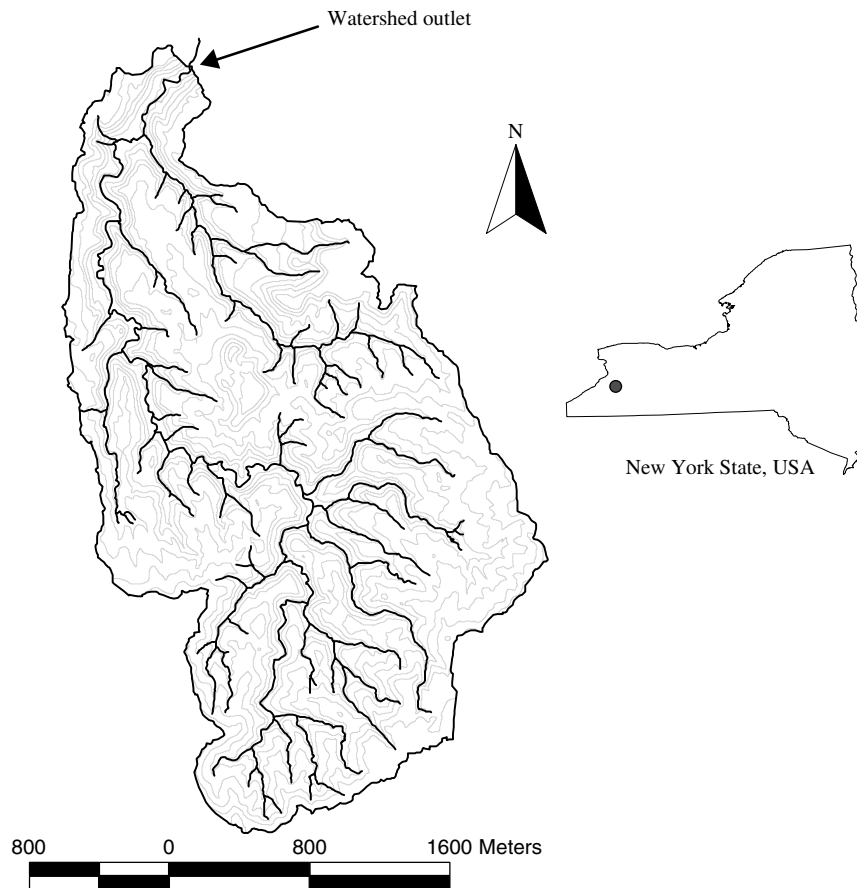


Figure 1. The 696 ha Point Peter Brook watershed and its location in New York State, USA (indicated by filled circle)

200–250 mm occurs in the form of snow (20-year average based on the National Atmospheric Deposition Program (NADP) weather station at Chautauqua, NY, 35 km southwest of the watershed; NADP, 2004). The parent material was derived from glacial till (Kent Drift of Woodfordian, formed 19 000 years BP) (Phillips, 1988). Soils in the watershed belong to the Volusia–Mardin–Erie association (Phillips, 1988). Vegetation on ridgetops and hillslopes is dominated by deciduous trees, including sugar maple (*Acer saccharum*), black maple (*Acer nigrum*), American beech (*Fagus grandiflora*), yellow birch (*Betula alleghaniensis*), with larger proportions of conifers, including hemlock (*Tsuga canadensis*) and white pine (*Pinus strobus*) in valley bottoms.

The topography of the entire watershed is fairly distinct, with wide ridgetops, steep hillslopes, and narrow valley bottoms. Slope gradients in the watershed range from 0 to 69%, with a mean gradient of 14%. Elevation values range from 252 to 430 m above mean sea level. The soils are underlain by a low-permeability clay layer that generates perched water tables and forces water to move as shallow subsurface flow on the steep hillslopes. The depth to the clay/till measured using soil cores varies from 1.2–1.7 m in the valley-bottom locations, 0.3–0.5 m along the side slopes and 0.6 m at the ridgetops.

Watershed monitoring, sampling, and analysis

Hydrologic and surface water chemistry monitoring in the watershed was initiated in November 2002 and intensive storm-event sampling started in May 2003 and continued through May 2004. Precipitation

was recorded using a tipping-bucket rain gauge located near the watershed outlet. Stream flow stage at the watershed outlet was recorded every 15 min using a pressure transducer (Global Water Inc., WL15 water level logger). A stage–discharge relationship was developed for the 3 m wide stream channel. Groundwater elevations were recorded using pressure transducers (Global Water Inc.) nested within logging wells that were constructed of 5 cm (ID) PVC tubing. The logging wells were cored to the depth at which an impeding clay or gravel layer was intersected (between 1.5 and 3 m). Three logging wells were located in the valley-bottom positions and two wells were located on hillslope benches.

Grab sampling was performed on a biweekly basis to characterize the spatial water chemistry in the watershed and included valley-bottom riparian wells, hillslope seeps, zero-tension lysimeters located in valley-bottom and hillslope-bench saturated areas and streams. Riparian sampling wells were constructed of 5 cm (ID) PVC tubing and were cored to the depth at which an impeding clay or gravel layer was intersected (between 1.5 and 3 m). The wells were screened from 30 cm below the soil surface to the bottom. Groundwater seeps were observed to discharge water on hillslopes where the glacial till was exposed. These seeps were typically located halfway up the valley and were assumed to discharge SGW. Zero-tension lysimeters were constructed of 5 cm (ID) PVC tubing and were inserted at a 45° angle to a depth of 30 cm from the soil surface. The lysimeters were screened such that they collected soil waters from the O (forest floor) and A horizons. Lysimeters were installed in valley-bottom riparian and wetland areas and hillslope-bench saturated areas.

Storm-event sampling was conducted using an ISCO sampler, which was triggered for event sampling when the rainfall amount exceeded a threshold of 2.8 mm. The sampler was programmed on the ‘variable time’ mode so as to sample more frequently on the hydrograph rising limb than on the recession limb. Composite precipitation samples were collected in a collector placed in the open; throughfall samples were collected from two collectors, one placed under a coniferous canopy and one placed under a deciduous canopy. Precipitation and throughfall collectors were 3.8 l plastic containers connected to funnels that had a plastic mesh on the mouth to prevent entry of debris. The plastic containers were cleaned frequently to prevent debris build-up and contamination. All samples were collected in 250 ml Nalgene bottles within 24 h of an event.

Water samples were analysed for DOC on a Tekmar–Dohrmann Phoenix 8000 TOC analyser, and cations (total Al, Ca²⁺, Mg²⁺, K⁺, Si, Na⁺) were analysed on a Perkin–Elmer ICP-AEC Div 3300 instrument. Total dissolved nitrogen (TDN) was determined using persulphate oxidation (Ameel *et al.*, 1993) followed by colorimetric analysis on an autoanalyser. Ammonia was also determined on an autoanalyser using the Berthelot reaction followed by colorimetric analysis. Anion concentrations (SO₄²⁻, NO₃⁻) were determined on a Dionex IC. Concentration of DON was estimated by subtracting NH₄⁺ and NO₃⁻ from TDN. The laboratory is a participant in the United States Geological Survey performance evaluation programme, which ensures data quality. A system of calibration quality control, detection quality control, analytical blanks and replicates is used with every set of samples (Mitchell *et al.*, 2001).

Data selection and analysis

Hydrological and chemistry data are provided from November 2002 to April 2004, with more detailed analyses for storms events being obtained from May to April 2004. The calendar year was divided into four seasons: spring (March, April and May); summer (June, July, and August); fall (September, October and November); and winter (December, January and February). Mean concentrations in discharge and precipitation were volume weighted. Sample concentrations were linearly interpolated for sampling intervals within events to calculate solute fluxes.

A total of 32 rainfall events were monitored for stream chemistry, with 9, 15, and 8 events being sampled in spring, summer, and fall respectively. A large snowmelt event (1–6 March) was sampled during the first week of spring (Figure 2). Most of the winter snowpack melted during this event. No events were sampled during the winter period. Six of the largest rainfall events (24 and 27 July, 15 October, 19 and 28 November 2003, 12 April 2004) and the snowmelt event were further evaluated to investigate the impact of storm-event sizes and antecedent conditions on solute flux and on solute chemistry (Figure 2). Water and solute budgets,

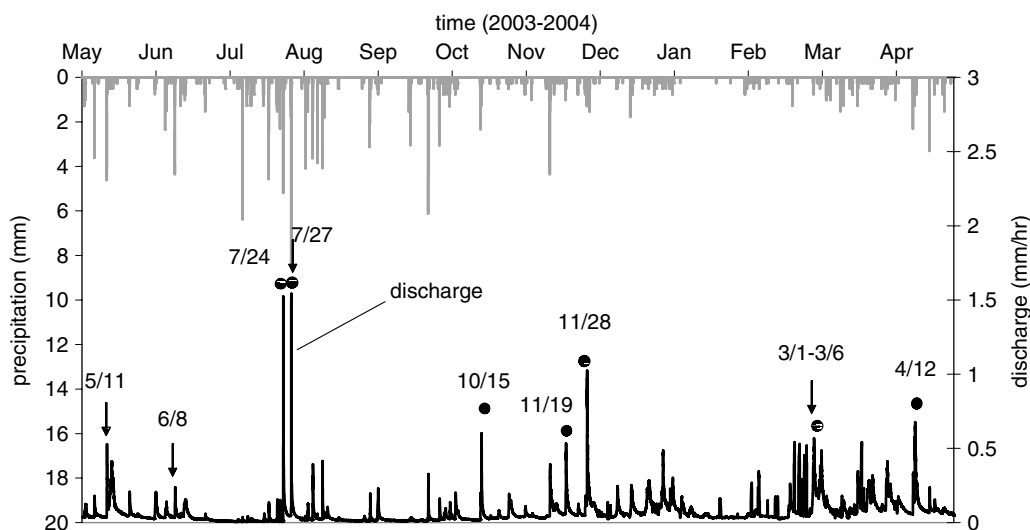


Figure 2. Precipitation and streamflow discharge for the study period of May 2003 to April 2004. A total of 32 storm events and a snowmelt event were sampled and analysed. Filled circles indicate the seven large events for which detailed analyses were performed, and events for which EMMA separations were performed are indicated by arrows

flow-weighted concentrations, and the maximum percentage change in concentrations during the events (from pre-storm values) were computed for these events. In addition to 7-day antecedent precipitation index (API7), an antecedent wetness index (AWI) was also developed. The AWI was a 7-day running average of groundwater elevations measured from the soil surface for a groundwater logging well located on a hillslope bench.

End-member mixing analysis and hydrograph separations

End-member mixing analysis (EMMA) (Burns *et al.*, 2001; Christopherson *et al.*, 1990; McHale *et al.*, 2002) for this watershed was performed by Inamdar and Mitchell (2006). A complete description of the methods and the resulting model is provided in Inamdar and Mitchell (2006). Three solutes, namely Mg^{2+} , Si, and DOC, were selected to characterize the storm-event mixing regime. Streamflow concentrations for the selected solutes were then standardized and a correlation matrix was developed. Eigenvectors for the correlation matrix were computed using Mathematica (Wolfram, Inc.). The first two components, U_1 and U_2 , of the eigenvector matrix were then used to project the stream and all potential end-members into the U -space. Selection of the two principal components implied a three-component mixing model. For the U -space mixing diagrams for individual events, stream concentrations for the event were used, and the potential end-members were represented by an average of baseflow solute concentrations recorded before and after the event. Throughfall, SGW discharged at seeps, and VBRW bounded the streamwater concentrations across most events. For the snowmelt event of 1–6 March, snowpack replaced throughfall as the constraining end-member. Three-component hydrograph separations were performed to identify the contributions of the selected end-members to streamflow discharge. Hydrograph separations indicated that SGW amounts were high at the start of the event, followed by high throughfall values on the hydrograph rising limb, whereas the receding limb was dominated by throughfall and VBRW (Inamdar and Mitchell, 2006). The contribution of VBRW on the receding limb was independently confirmed by groundwater elevations (Inamdar and Mitchell, 2006). Groundwater elevations in valley-bottom riparian wells reached a peak (closest to the surface) at or after the discharge peak and remained elevated through streamflow recession.

To allow comparisons of solute concentrations with end-member contributions for this study, we performed EMMA separations for four events: 27 July, 11 May, 8 June (all in 2003) and 1–6 March 2004 (indicated by arrows on Figure 2). These four events were selected to characterize end-member and solute responses across

varying event conditions. The event of 1–6 March was a large snowmelt episode (total discharge 33.7 mm). The event of 27 July produced the highest peak discharge during the study period (total rainfall of 24 mm, event discharge of 6.6 mm, peak discharge of 1.54 mm h⁻¹); the event of 11 May was a medium-sized event (total rainfall of 14 mm, event discharge of 3.3 mm, peak discharge of 0.52 mm h⁻¹); and the event of 8 June was a small event (total rainfall of 12 mm, event discharge of 2.8 mm, peak discharge of 0.23 mm h⁻¹).

RESULTS

Solute concentrations in various watershed compartments

Concentrations of solutes varied widely between the different watershed compartments (Table I). The highest concentrations for NH₄⁺ were recorded in throughfall, followed by rainfall and near-surface waters measured by lysimeters. NH₄⁺ concentrations were lowest in SGW discharged at seeps. Base cations (Na⁺, Mg²⁺, and Ca²⁺) were highest in VBRWs and near-surface waters measured in lysimeters. High concentrations for total Al and K⁺ concentrations were recorded in throughfall. However, total Al concentrations measured in stream baseflow exceeded those measured in any of the watershed compartments.

The highest NO₃⁻ concentrations were recorded in SGW discharged at seeps, followed by conifer throughfall. High NO₃⁻ concentrations in groundwater seeps have also been previously reported in the Catskills (Burns *et al.*, 1998) and Adirondack Mountains (McHale *et al.*, 2002) of New York State. The lowest NO₃⁻ concentrations were observed in near-surface waters. SO₄²⁻ concentrations were most elevated in VBRWs and near-surface waters, i.e. locations of high moisture in the catchment. Mitchell *et al.* (2006) also observed high SO₄²⁻ concentrations in riparian wetlands and attributed this to reoxidation of accumulated sulphide, which had previously been reduced from SO₄²⁻ under more saturated soil conditions. The distribution of DON concentrations in watershed compartments was similar to NH₄⁺, with elevated concentrations in surficial waters like throughfall, snowpack, rainfall, and near-surface soil waters. DOC concentrations were highest in throughfall, followed by near-surface waters and VBRWs.

Although NH₄⁺ was higher below the deciduous canopy, K⁺, DON and DOC were higher below the coniferous canopy. Conifer throughfall was especially high in DOC, with values an order of magnitude greater than those measured under the deciduous canopy. Similar observations of high solute concentrations for conifer canopies have been made by Mitchell *et al.* (2006) and Mollitor and Raynal (1982) for stands in the Adirondack region of New York State.

Table I. Mean concentrations (standard deviations in parentheses) of solutes in various watershed compartments in the Point Peter Brook watershed

Solute	Rainfall	Snowpack	Throughfall		VBRW (wells)	SGW from seeps	Near-surface waters (lysimeters)	Stream
			Deciduous	Conifer				
<i>n</i>	37	10	35	38	62	41	28	221
NH ₄ ⁺ (μmol _c l ⁻¹)	17 (24)	14 (14)	30 (46)	17 (21)	11 (10)	2 (2)	15 (28)	5 (7)
Na ⁺ (μmol _c l ⁻¹)	5 (7)	16 (10)	4 (6)	9 (14)	389 (284)	133 (44)	101 (33)	317 (88)
Mg ²⁺ (μmol _c l ⁻¹)	14 (12)	17 (15)	19 (9)	41 (29)	1210 (132)	987 (122)	1080 (250)	978 (208)
K ⁺ (μmol _c l ⁻¹)	2 (2)	51 (124)	31 (20)	82 (44)	29 (7)	41 (27)	30 (15)	41 (14)
Ca ²⁺ (μmol _c l ⁻¹)	39 (36)	91 (134)	57 (27)	105 (88)	2570 (450)	2190 (349)	2790 (642)	1930 (402)
Total Al (μmol l ⁻¹)	0.4 (0.4)	0.5 (0.2)	1 (1.5)	3 (4)	1 (8)	0.1 (0.4)	0.4 (1.6)	9 (30)
NO ₃ ⁻ (μmol _c l ⁻¹)	25 (23)	42 (42)	37 (25)	46 (73)	4 (6)	58 (30)	1 (3)	26 (9)
SO ₄ ²⁻ (μmol _c l ⁻¹)	61 (28)	26 (18)	73 (32)	131 (75)	910 (309)	442 (70)	664 (320)	795 (134)
DON (μmol l ⁻¹)	10 (12)	24 (21)	19 (13)	33 (17)	13 (13)	7 (7)	16 (22)	14 (20)
DOC (μmol l ⁻¹)	207 (78)	242 (395)	366 (200)	1200 (612)	275 (147)	44 (19)	682 (941)	322 (122)

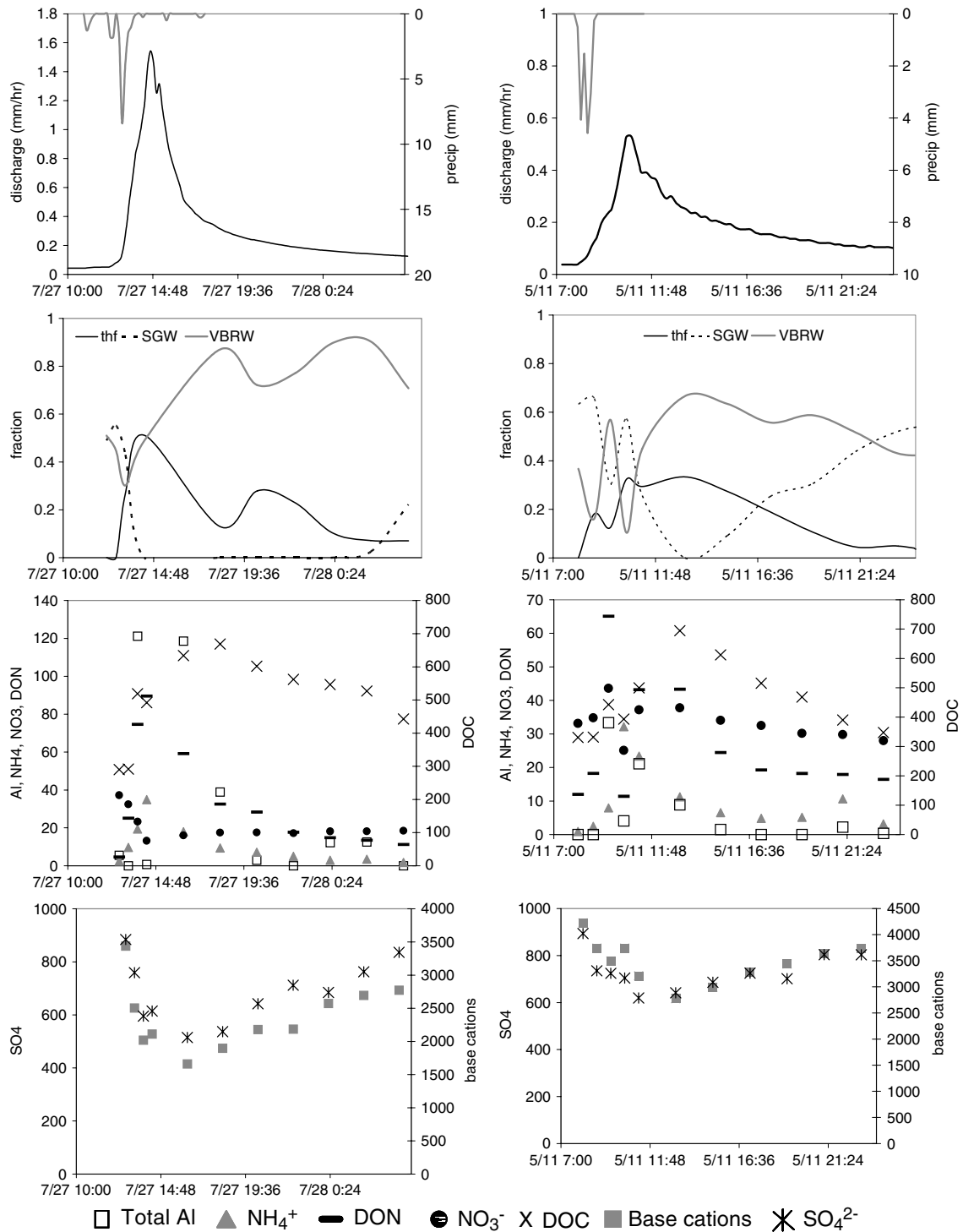


Figure 3. Precipitation, discharge, end-member contributions (fraction) and solute concentrations for events of 27 July 2003 (left) and 11 May 2003 (right). All solute concentrations are $\mu\text{mol}_c \text{ l}^{-1}$, except for total Al, DON and DOC ($\mu\text{mol l}^{-1}$)

Within-event patterns of end-member contributions

At the start of the 27 July event (Figure 3), streamflow discharge was primarily composed of SGW (49%) and VBRW (51%). SGW contributions declined rapidly as the event proceeded, reaching negligible values around peak discharge. Throughfall contributions increased through the rising limb, reaching a peak just before peak in discharge. VBRW amounts showed an initial drop, then steadily increased with a peak following the peak in discharge, and remained high during hydrograph recession. The first third of the rising limb was primarily composed of SGW and VBRW, the contributions from all three end-members were comparable during the second third, and throughfall fractions exceeded VBRW values during the last third of the hydrograph rising limb. VBRW dominated hydrograph recession, with a simultaneous decline in throughfall amounts during this period. Over the full duration of the event, throughfall, SGW, and VBRW contributions to streamflow amounted to 31%, 4%, and 65% respectively.

For the 11 May event (Figure 3), streamflow at the start of the event was again composed of SGW and VBRW. SGW and VBRW amounts fluctuated at the start of the event, but they stabilized as the event proceeded. Throughfall contribution reached a peak at discharge peak, and remained high through the early part of the recession curve. VBRW amounts reached a maximum after the throughfall peak. Total throughfall, SGW, and VBRW contributions to streamflow for the event were 22%, 29% and 49% respectively.

For the 8 June event (Figure 4), throughfall and VBRW amounts both reached peak values after discharge peak and during the recession period. The first-half of the recession limb was dominated by SGW, with about equal contributions of the three end-members during the second-half of the rising limb. Similar to the events of 27 July and 11 May, the major portion of the hydrograph recession was composed of VBRW and throughfall. Total event contributions for throughfall, SGW, and VBRW were 33%, 23%, and 45% respectively.

For the snowmelt event (Figure 4), SGW contributions were again highest at the start of the event and declined and reached a minimum during the peak discharge. In contrast, snowpack and VBRW amounts increased and peaked with the first discharge peak. Both snowpack and VBRW amounts then simultaneously declined and reached steady values through event recession. The 6-day snowmelt event displayed multiple discharge peaks. It is likely we could also have observed multiple peaks in snowpack and VBRW contributions if sampling had been performed at a higher frequency than the daily rate for the event. Over the duration of the event, the snowpack, SGW, and VBRW contributions to streamflow amounted to 31%, 38%, and 31% respectively.

Within-event patterns of solutes

Solute patterns for NH_4^+ , DON, and total Al were similar across the events of 27 July and 11 May. For both events (Figure 3), NH_4^+ and DON values quickly increased and reached peak concentrations on the rising limb prior to the peak in discharge. The peak in NH_4^+ and DON concentrations matched the peak in throughfall contributions. Concentrations of total Al also peaked on the rising limb and when throughfall contributions were high. For the 27 July event, NO_3^- concentrations declined at the outset of the event, reached a minimum close to the time when throughfall contributions were highest, and then steadily recovered through recession. NO_3^- concentrations for the 11 May event displayed a different pattern, with an increase in NO_3^- at the outset of the event, followed by drop in concentrations and a subsequent recovery. DOC concentration patterns for 27 July and 11 May were similar, with a steady increase through the rising limb and a delayed peak in values during hydrograph recession. The peak in DOC concentrations occurred between the peaks in contributions of throughfall and VBRW. Since DOC was one of the solutes used in EMMA, and since DOC was high in throughfall and VBRW, the close correspondence between DOC and throughfall/VBRW was expected. Both SO_4^{2-} and the sum of base cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+) followed a dilution trajectory for the 27 July and 11 May events, with a minimum concentration around the time when DOC concentrations were at their maximum.

Solute patterns for the small 8 June event (Figure 4) were not as pronounced as they were for the larger 27 July and 11 May events. Similar to the 27 July and 11 May events, the NH_4^+ , DON, and total Al concentrations were at their maximum on the hydrograph rising limb; but, unlike those two events, the maximum

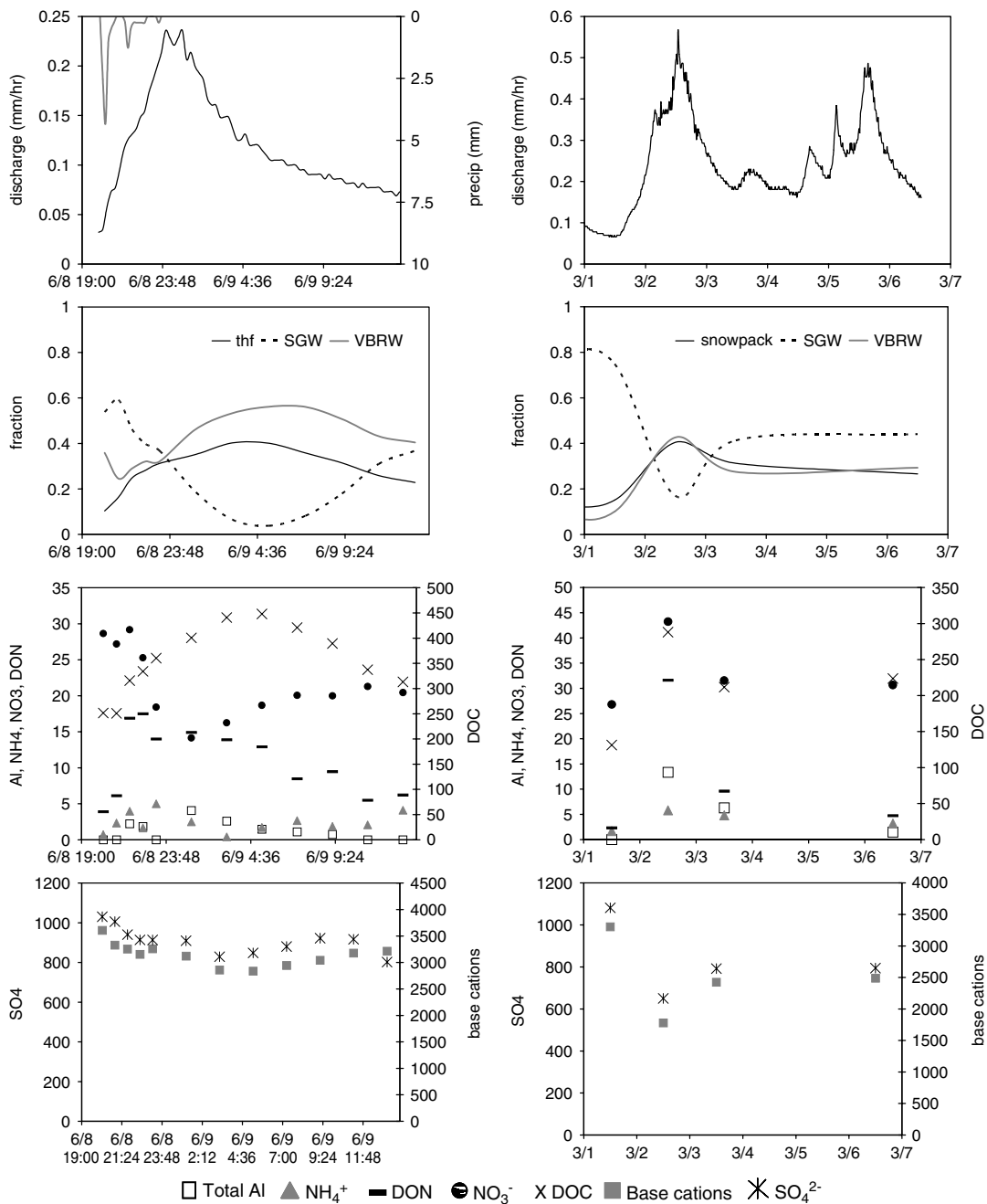


Figure 4. Precipitation, discharge, end-member contributions and solute concentrations for events of 8 June 2003 (left) and 1–6 March 2004 (right). All solute concentrations are in $\mu\text{mol}_c \text{ l}^{-1}$, except for total Al, DON and DOC ($\mu\text{mol l}^{-1}$)

concentrations for these solutes peaked before the peak in throughfall contributions. Similarly, NO₃⁻ concentrations followed a dilution trajectory, but the minimum concentrations occurred before the throughfall maxima. The patterns in DOC, SO₄²⁻, and base cations for the 8 June event were similar to those observed for the 27 July and 11 May events.

The major difference in solute patterns between the rainfall and snowmelt events was for NO_3^- . NO_3^- concentrations (1–6 March, Figure 4) increased through the rising limb and peaked with the first peak in discharge and then decreased through the recession period. Concentrations of NH_4^+ , DON, and Al followed the temporal pattern of NO_3^- concentrations and the peak values of all these solutes coincided with maximum contributions from the melting snowpack and VBRW. Concentrations for base cations and SO_4^{2-} followed the same temporal pattern as those observed for the rainfall events.

Annual and seasonal mass balances for water and solutes

We measured 895 mm of precipitation at Point Peter Brook from 1 May 2003 to 30 April 2004. Total precipitation measured at the nearest NADP weather station at Chautauqua, NY, for the same period was 872 mm. Seasonal precipitation totals for spring, summer, fall, and winter were 262 mm, 244 mm, 274 mm, and 115 mm respectively. This indicates that about 13% of the total precipitation for the study period was in the form of snow (115 mm). The average rainfall amounts for the sampled events during spring, summer, and fall were 13 mm, 11 mm and 18 mm respectively. The greatest 10 min rainfall intensities for these events averaged 2.1 mm, 3.0 mm and 2.0 mm for spring, summer and fall respectively. Storm events in spring and fall were larger than in summer, but summer events were more intense.

Total stream discharge measured at the watershed outlet during the 12 month period was 609 mm, of which 24% (146 mm) occurred during the 32 rain events (112 mm) and the large snowmelt event (34 mm). The sampled storm events contributed to 32%, 41%, and 32% of the discharge during spring, summer and fall, respectively. Although highest hourly streamflow discharge peaks were observed in summer, daily discharge totals were higher in spring (Figure 2).

Ca^{2+} had the greatest export of any solute from the Point Peter Brook watershed, followed in order of importance by Mg^{2+} , SO_4^{2-} , Na^+ , and DOC (Table II). Seasonal patterns of export were closely linked with discharge, with generally the highest export in the spring and the lowest exports in the summer. Storm events clearly had a major impact on solute budgets for total Al, DON, NH_4^+ , DOC, and K^+ , with contributions to the annual budget being 81%, 49%, 48%, 36%, and 28% respectively (Table III). Seasonally, summer storm-event contributions were the highest for solutes, except for NH_4^+ (higher in fall) and NO_3^- (higher in spring) (Table III). After summer, storm-event percentages for some solutes were higher in spring (DON), whereas for others the contributions were higher in the fall (K^+ , Al, and DOC). Storm events did not contribute much to the annual and seasonal budgets of Na^+ , Mg^{2+} , Ca^{2+} , and SO_4^{2-} . Spring events clearly had a greater

Table II. Variation in stream solute fluxes and discharge during (S) and between storms (NS) in the Point Peter Brook watershed during the study period of May 1, 2003 through April 30, 2004. Includes all 32 rain events and the large snowmelt event

	Spring			Summer			Fall			Winter total	Full period		
	S	NS	Total	S	NS	Total	S	NS	Total		S	NS	Total
Discharge (mm)	76	163	239	33	46	79	37	78	115	176	146	463	609
NH_4^+ ($\text{mol}_c \text{ ha}^{-1}$)	4	5	9	3	1	4	3	1	4	5	10	12	21
Na^+ ($\text{mol}_c \text{ ha}^{-1}$)	169	514	683	85	186	271	95	329	424	573	349	1600	1950
Mg^{2+} ($\text{mol}_c \text{ ha}^{-1}$)	547	1650	2190	273	533	806	319	1000	1330	1790	1140	4980	6120
K^+ ($\text{mol}_c \text{ ha}^{-1}$)	24	46	71	15	16	31	21	32	53	60	61	155	216
Ca^{2+} ($\text{mol}_c \text{ ha}^{-1}$)	1270	3400	4670	548	937	1480	663	1700	2360	3290	2480	9330	11800
Total Al ($\text{mol}_c \text{ ha}^{-1}$)	7	2	9	10	0	10	3	0	3	3	21	5	26
NO_3^- ($\text{mol}_c \text{ ha}^{-1}$)	21	39	60	7	16	23	5	17	23	43	34	115	149
SO_4^{2-} ($\text{mol}_c \text{ ha}^{-1}$)	513	1380	1890	225	401	626	271	750	1020	1590	1010	4120	5130
DON ($\text{mol}_c \text{ ha}^{-1}$)	14	8	23	9	2	11	8	8	16	12	30	31	61
DOC ($\text{mol}_c \text{ ha}^{-1}$)	200	308	507	136	88	224	161	153	314	317	497	866	1360
DON (%)	36	15	25	47	11	29	50	31	37	20	41	20	26

Table III. Percent contributions of storms events (32 rain events and one snowmelt event) to solute budgets during spring, summer, fall, and the full period from May 2003 to April 2004

Parameter	Contribution (%)			
	Spring	Summer	Fall	Full period
Discharge	32	42	32	24
NH ₄ ⁺	41	74	78	48
Na ⁺	25	31	22	18
Mg ²⁺	25	34	24	18
K ⁺	34	48	40	28
Ca ²⁺	27	37	28	21
Total Al	82	100	100	81
NO ₃ ⁻	36	31	23	23
SO ₄ ²⁻	27	36	27	20
DON	62	79	49	49
DOC	39	61	51	36

impact on NO₃⁻ than events during other seasons. The percentage of nitrogen exported in DON form was higher during storms than non-storm periods, and especially during the fall season (Table II).

Impact of selected large events on water and solute flux

Hydrologic data and solute data are presented in Tables IV and V respectively for six rain events and the 6-day snowmelt event. These storm events produced a total of 89 mm of streamflow, which amounted to 15% of the discharge measured during the study period. The largest event discharge (33.7 mm) was generated during the long snowmelt event. Water yields associated with the rain events ranged from a low of 19% after a dry period (AWI = 29.7 cm) in early fall (15 October) to a high of 52% (19 November) during wet (AWI = 4.5 cm) fall conditions. The highest streamflow discharge totals associated with rain events were generated during the spring and late-fall events of 12 April 2004 (16 mm) and 28 November 2003 (11.9 mm). And the two consecutive summer events of 24 and 27 July 2003 produced the highest hourly discharge peaks (1.49 mm h⁻¹ and 1.54 mm h⁻¹ respectively).

Budgets for selected solutes (NH₄⁺, K⁺, NO₃⁻, DON and DOC) were computed for the storm events. Although the events made up only 15% of the total streamflow discharge, their contributions to solute budgets were substantial. Combined, these seven events contributed to 64% of the annual total Al, 39% of the DON, 34% of the NH₄⁺, 24% of the DOC, and 19% of the K⁺. However, contribution of NO₃⁻ load during the seven events was just 13%, i.e. lower than the discharge contribution.

The 6-day snowmelt produced the largest event export of NH₄⁺, K⁺, NO₃⁻ and DOC of any event (1.4 mol_c ha⁻¹, 11.3 mol_c ha⁻¹, 11.4 mol_c ha⁻¹ and 77 mol ha⁻¹ respectively). NO₃⁻ export, especially,

Table IV. Selected large storm events and their hydrologic parameters

Season	Date	Rain (mm)	API7 (mm)	AWI (cm)	Discharge (mm)	Water yield (%)	Peak discharge (mm h ⁻¹)
Spring	1–6 March 2004	—	0	8.0	33.7	—	0.57
	12 April 2004	39.6	0.25	2.1	16	40	0.67
Summer	24 July 2003	17.5	39.1	31.2	7.4	42	1.49
	27 July 2003	21.1	47.5	12.6	6.6	31	1.54
Fall	15 October 2003	32.1	0	29.7	6.1	19	0.6
	19 November 2003	15.0	27.1	4.5	7.7	52	0.53
	28 November 2003	33.3	15.2	10.5	11.9	36	1.02

Table V. Solute loads and concentrations for the selected storm events

	1–6 Mar 04	12 Apr 04	24 Jul 03	27 July 03	15 Oct 03	19 Nov 03	28 Nov 03	Total	% of annual
Discharge (mm)	33.7	16	7.4	6.6	6.1	7.7	11.9	89.4	15
NH ₄ ⁺ (mol _c ha ⁻¹)	1.4	1	1.2	1	0.5	0.4	1.4	6.9	34
K ⁺ (mol _c ha ⁻¹)	11.3	5.8	4.2	3.5	4.9	4.3	6.4	40.4	19
Total Al (mol ha ⁻¹)	2	4.2	4.9	2.6	0	0.8	2.1	16.6	64
NO ₃ ⁻ (mol _c ha ⁻¹)	11.4	3.3	1.6	1.2	0.4	1	1.8	20.7	13
DON (mol ha ⁻¹)	4.2	6.4	4.1	3.1	2.1	1.5	2.5	23.9	39
DOC (mol ha ⁻¹)	77	51	40	36	35	30	52	321	24
<i>Flow-weighted concentrations</i>									
NH ₄ ⁺ (μmol _c l ⁻¹)	4	7	17	16	9	5	12		
K ⁺ (μmol _c l ⁻¹)	33	36	56	53	81	56	54		
Total Al (μmol l ⁻¹)	6	26	67	39	0	11	18		
NO ₃ ⁻ (μmol _c l ⁻¹)	34	21	21	18	6	13	15		
DON (μmol l ⁻¹)	13	40	55	47	36	19	21		
DOC (μmol l ⁻¹)	229	319	547	540	584	392	439		
<i>Maximum change^a from pre-storm values</i>									
NH ₄ ⁺ (%)	240	260	3200	2100	1600	1200	1900		
K ⁺ (%)	29	52	250	100	120	90	81		
Total Al (%)	36 000	170 000	1 000 000	330 000	n.a.	92 000	130 000		
NO ₃ ⁻ (%)	61	-16	-86	-71	-92	-57	-34		
DON (%)	1200	30 000	6300	2200	1700	1200	760		
DOC (%)	120	170	370	350	210	170	170		

^a Change (%) = (peak event value – pre-storm value) × 100/pre-storm value; n.a.: not available/measured.

during this snowmelt event was considerably more (8% of annual total) than for the other events. The snowmelt event also contributed the largest combined flux of nitrogen species (Table V). Excluding the event of 12 April, exports of total Al and DON were largest from the intense summer events. The highest exports of NH₄⁺, K⁺, and DOC for rainfall events were associated with the fall event of 28 November 2003.

The largest percentage difference between pre-storm and peak event solute concentrations were observed for total Al and DON (Table V). Total Al values before storms were always below non-detect levels (set at non-detect levels for these computations), resulting in the high percentages in Table V. The largest increase for NH₄⁺, total Al, and DOC was seen for the summer events. A dramatic increase in DON concentrations was seen for the 12 April event, with high percentage increases for the summer events. Summer and the early-fall (15 October) event registered the largest drop in concentrations for NO₃⁻.

DISCUSSION

How do solute patterns vary within storm events and what are the likely sources and mechanisms responsible for solute export? Do event solute patterns vary with seasons and event size?

The EMMA results showed that streamflow was composed of three sources of runoff, each of which contributed at specific periods during the storm event. Prior to an event, streamwater was a mixture of SGW and VBRW; throughfall contributions were elevated on the latter half of the rising limb, whereas VBRW amounts dominated the receding limb. This conceptual model was confirmed by Inamdar and Mitchell (2006) by comparing the timing of VBRW contributions against groundwater elevations measured in valley-bottom riparian areas. Groundwater elevations reached a peak (closest to the surface) after the discharge peak and were sustained at elevated levels through the hydrograph recession, supporting our EMMA observations of delayed VBRW contributions. The quick expression of throughfall water on the rising limb was attributed

to the interception of rainfall/throughfall on channel and riparian saturated areas and rapid delivery along surficial flow paths (Inamdar and Mitchell, 2006). The delayed expression of VBRW on the recession limb was attributed to the displacement of VBRW by subsurface hillslope flux initiated by infiltrating rain waters (Inamdar and Mitchell, 2006). Results for the three rainfall events also show that events with the larger discharge peaks (27 July > 11 May > 8 June) had greater contributions of VBRWs. However, a consistent pattern for throughfall amounts was not apparent across the three events.

The temporal patterns of solutes showed some consistent differences, and when compared with the runoff source contributions provide some important insights into how runoff sources are likely influencing the exports of solutes during storm events. The difference between the solute trajectories was more pronounced for the larger events (e.g. 27 July). Across all three rain events, NH_4^+ , DON and total Al concentrations increased and reached peak concentrations prior to DOC. For the events of 27 July and 11 May these solute patterns also matched the rise and peak in throughfall concentrations. Watershed concentrations of solutes in Table I also indicate that the highest concentrations of NH_4^+ , DON, and total Al were recorded for throughfall, rainfall and near-surface waters. DOC concentrations were also high in throughfall, VBRW, and near-surface waters (Table I), but the peak DOC concentrations always lagged behind the peak in NH_4^+ and DON values. Observations made for smaller subcatchments in this watershed indicated a consistent sequence in peak concentrations for the two nitrogen species: the NH_4^+ peak was followed by DON and later by DOC (Inamdar and Mitchell, In preparation). Furthermore, the rise and peak in DOC concentrations was found to be in agreement with the rise in groundwater elevations recorded in valley-bottom riparian wells (Inamdar and Mitchell, 2006). Based on these observations, we hypothesize that NH_4^+ concentrations in this watershed are being regulated primarily by throughfall, whereas DOC concentrations are influenced by contributions of both throughfall and near-surface soil waters from valley-bottom riparian areas. The match between valley-bottom groundwater elevations and DOC concentrations suggest that elevated DOC exports occur when groundwater rises up in the valley-bottom riparian areas and displaces-out the DOC from the near-surface horizons at these landscape positions. We believe the control/influence of throughfall and VBRW on DON concentrations is somewhere between that observed for NH_4^+ and DOC. It is likely that the forest floor or litter layer also has a role to play in the exports of DON.

Vanderbilt *et al.* (2003) reported the highest DON concentrations preceding the discharge peak for fall storms and attributed it to the flushing of solutes generated by partially decomposing litter. The importance of forest floor or the litter layer as a source for DON has also been reported elsewhere (Yavitt and Fahey, 1984; Qualls *et al.*, 1991). However, Hagedorn *et al.* (2000) observed that both DOC and DON concentrations reached peak values following the discharge peak, attributing this to the delayed expression of solute-rich topsoil waters. Furthermore, Hagedorn *et al.* (2000) performed EMMA separations in their study and found that rainfall contributions occurred on the rising limb of the hydrograph whereas topsoil waters were expressed later during the recession limb. Hill (1993) observed NH_4^+ peaks on the rising limb and attributed this to the high concentrations measured in throughfall.

The pattern of total Al concentrations during events was similar to that observed for DON. We believe the mechanisms that regulate the DON release in our watershed also influence the exports of total Al. The forest floor has been identified as an important contributor to total Al (Palmer *et al.*, 2005) and could be a likely factor influencing the total Al concentrations we observed in this study. However, in contrast to our observations, Soulsby (1995) reported Al peaks following the discharge peaks.

NO_3^- concentrations displayed varying patterns across the rainfall and snowmelt events. Within watershed compartments, NO_3^- was highest in SGW, throughfall and the snowpack (Table I). We hypothesize that the increase in NO_3^- concentrations and the peak in concentrations close to discharge peak was due to high NO_3^- contribution from the melting snowpack (Table I) and the flushing of NO_3^- accumulated in the soil over the dormant winter period. Creed and Band (1998b) also found a NO_3^- peak on the rising limb of the hydrograph and attributed this pattern to flushing of NO_3^- from surface soils by rising water tables. In contrast to the snowmelt event, NO_3^- concentrations during the large 27 July rain event showed a clear dilution trend from the outset of the event, with a minimum on the rising limb followed by a subsequent

recovery in concentrations. The dilution trend in NO_3^- was not that apparent for the smaller two rain events. Rather, both events showed slight increases in NO_3^- concentrations at the outset of the event. We attribute this behaviour to the relative trends and mixing of throughfall and SGW amounts. SGW had the highest NO_3^- concentrations across all watershed compartments, followed by throughfall (Table I). When the relative contributions of SGW to streamflow were high and when there was a slight increase in SGW amounts at the start of the event, a slight rise in NO_3^- concentrations was observed. In contrast, for large events (like 27 July), where SGW amounts dropped rapidly and large contributions of VBRW occurred (low in NO_3^-), the streamflow NO_3^- concentrations followed a distinct dilution curve. Inamdar *et al.* (2004), working on a watershed in the Adirondack Mountains of New York State, also observed an NO_3^- peak early on the rising limb and attributed the peak to the displacement of NO_3^- -rich till waters by infiltrating precipitation. Increases in NO_3^- concentrations at the outset of the event were also observed by Hill (1993), who attributed this to the mixing of NO_3^- -rich throughfall and local groundwaters.

The sum of base cations and SO_4^{2-} showed consistent and similar dilution trends across all events. Concentrations for these solutes were lowest in throughfall and highest in VBRW and SGW. Hence, the relative proportions of these end-members dictated the event concentrations, with values reaching a minimum when throughfall amounts were at their maximum.

What is the impact of storm events on annual and seasonal solute exports? Which solutes are impacted the most?

Storm events clearly had a large impact on the exports of some solutes. Storm-event concentrations of NH_4^+ , K^+ , total Al, DON and DOC, were always greater than the corresponding baseflow values, resulting in high exports of these solutes during the year's largest storms. On an annual basis, large proportions of the total Al (81%), DON (49%), NH_4^+ (48%), DOC (36%), and K^+ (28%) were exported during storms. Furthermore, the seven largest storm events combined for only 15% of the year's discharge, but produced 64% of the year's exports of total Al, 39% of the annual DON, 34% of the year's exports of NH_4^+ and one-fourth of the year's exports of DOC.

Summer storms contributed more to the seasonal budget than storms in any other season. However, spring snowmelt also produced very high solute loads, mostly due to the elevated discharges associated with snowmelt. Similar to Lawrence (2002), our observations highlight the importance of storm-event sampling, particularly during large events, in developing solute mass balance studies. Hinton *et al.* (1997) also found storms to be very important contributors to export budgets, even though their durations were short. In their study, large proportions of DOC export occurred during high discharge conditions, and the contribution of DOC export by stormflow sometimes exceeded that exported during baseflow. The impact of storm events on DOC has been noted in several studies: Butturini and Sabater (2000) observed that storm events contributed to only 39% of the annual water export, but generated 52% of the DOC export; Buffam *et al.* (2001) reported that storms contributing to 36% of the discharge were responsible for greater than 50% of the DOC budget; Hinton *et al.* (1997) found that 10% of the stream discharges were responsible for 41 to 57% of the total autumn DOC export. Our result of 24% of the storm-event discharge generating 36% of the annual DOC is further support of the importance of storms in the export of DOC. In terms of total seasonal flux, DOC contributions during spring were highest of all seasons.

Storm events had a greater impact on DON than on DOC export. Storms had a major impact on the export of DON (26% of total nitrogen budget; Table III), with 40% and 20% (Table III) being exported during storm and non-storm periods respectively. For Gleysol-dominated catchments in Switzerland, Hagedorn *et al.* (2000) found that DON contributed to 60% of the total nitrogen export, and the contribution of DON increased when storm events were included in the analysis. McHale *et al.* (2000), monitoring a forested catchment (135 ha) in the Adirondack Mountains of New York State, found that DON contributed to 36% of the annual nitrogen flux. However, they found that the DON budget was reduced by $18 \text{ mol ha}^{-1} \text{ year}^{-1}$ when budgets were computed using event-based sampling versus using only biweekly sampling. These results vary from the current study, which clearly showed that DON contributions are higher during storm events.

How do solute patterns vary across storms occurring in different seasons and with varying magnitude and antecedent conditions?

Spring (including snowmelt) and late-fall events with wet antecedent conditions generated the highest discharge volumes, whereas the high-intensity summer events produced the highest hourly discharge values. Although the spring and fall events were responsible for a larger proportion of annual solute exports, high solute concentrations, especially for DON, DOC, Al, K⁺, and NH₄⁺, were associated with intense summer and early-fall events.

The snowmelt event, which produced the highest NH₄⁺, K⁺, NO₃⁻ and DOC loads for the study period, underscores the need for monitoring such melt events closely. The elevated exports of NO₃⁻ and DOC during spring snowmelt events resulted from two key conditions: the elevated wetness conditions and the availability of NO₃⁻ and DOC in the snowpack and surficial soil layers following the dormant winter period. However, the spring snowmelt did not yield the highest total Al and DON loads, both of which were generated during high-discharge summer and fall events. The high concentrations of DON, DOC, Al, K⁺, and NH₄⁺ with summer/early-fall events can be attributed to two factors. First, the high intensity of the summer/fall events resulted in greater surface runoff (as seen in the high proportions of VBRW for these events) and, therefore, more leaching of forest-floor humic material and a greater delivery of sediment and forest-floor humic materials to streamflow. Second, there were larger fluctuations in groundwater elevations, and therefore antecedent conditions, during summer and early-fall periods. Thus, during the summer and fall, soils were subjected to more cycles of 'accelerated drying and wetting' (quicker drying of soils by high evapotranspiration and quicker rewetting because of rain intensity). These rapid changes in soil moisture status would enhance mineralization rates, e.g. the event of 15 October, which with the driest antecedent conditions produced the highest concentrations of DOC. A similar pattern of higher solute concentrations after dry antecedent conditions has been reported by Biron *et al.* (1999).

The response of solutes to antecedent conditions may differ across solutes. The intense sequential summer events of 24 and 27 July produced high concentrations of DOC (547 $\mu\text{mol l}^{-1}$ and 540 $\mu\text{mol l}^{-1}$ respectively; Table V), but lower than those for the storms of 15 October. Despite the high discharge peaks that occurred within 3 days of each other, DOC concentrations were similar, suggesting that the watershed had a fairly large reservoir of DOC. In comparison, some depletion was observed in DON for the two storms (55 to 47 $\mu\text{mol l}^{-1}$), suggesting that DON storage in the watershed was lower than DOC or that the flowpaths differed between these two solutes.

The most intense events with high peak discharges yielded the highest solute concentrations, although the actual patterns differed among solutes. For example, DON concentrations showed a much sharper rise with increasing peak discharge than DOC. Ito *et al.* (2005) have also found different relationships for DOC and DON, suggesting that different flowpaths may be affecting how these solutes enter surface waters (Ito *et al.*, 2005).

CONCLUSIONS

The results from this study show that within-event temporal patterns of solute concentrations vary between solutes. Moreover, the same solute (e.g. NO₃⁻) can produce very different patterns for events occurring in different seasons. These observations have important implications for solute exports from watersheds and need to be accounted for when developing discharge–concentration regression relationships (Arheimer *et al.*, 1996) or equations used for budget computations (Swistock *et al.*, 1997).

Storm events had a greater impact on the exports and budgets of some solutes (NH₄⁺, K⁺, total Al, DON and DOC). Concentrations for all of these solutes were high in surficial watershed compartments (throughfall, near-surface and riparian water), indicating that solutes from these sources are more vulnerable and are preferentially exported during storm events. Even within this group, storm events had a disproportionately greater impact on the exports and concentrations of total Al and DON.

The response of solutes to storm intensity and antecedent conditions observed in this study has important implications for the long-term exports of these solutes from watersheds, especially under future climate-change scenarios. More intense and infrequent rain events, especially during the summer and fall seasons (associated with Atlantic and Gulf Coast hurricanes and tropical depressions), have been predicted as a part of the future climate-change scenarios (USGCRP, 2000). Considering our results, such climate-change-induced shifts in storm events will likely increase the exports of solutes like DOC, DON, NH_4^+ , Al and K^+ from watersheds.

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