Evaluating runoff generation during summer using hydrometric, stable isotope and hydrochemical methods in a discontinuous permafrost alpine catchment

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Abstract:

Research on runoff generation in catchments with discontinuous permafrost has focused primarily upon the role of surface organic layers and frozen soils (both permanent and seasonal). Much of this work has been hydrometric, with isotope and hydrochemical methods receiving only limited application in delineating old and new water contributions and chemically inferred hydrological pathways. In a small subarctic alpine catchment within the Wolf Creek Research Basin, Yukon, runoff generation processes were studied in the summer of 2001 using a mixed method approach to evaluate the mechanisms and pathways of flow from the hillslopes to the stream during rainfall events. Two storms had δ^{18} O isotopic ratios that differed significantly from baseflow and water within hillslopes, allowing for two-component hydrograph separation to infer new and old water contributions. Event water contributions ranged between 7 and 9%, exhibiting little variability despite the large differences in event water and stormflow volume. Utilizing δ^{18} O-dissolved organic carbon and δ^{18} O-specific conductance data, two tracer three-component hydrograph separations were attempted to isolate rainfall, water within the organic layer and mineral layer contributions to stormflow. Three-component separations suggest that water from the mineral soil dominates the stormflow hydrograph, yet the contribution of organic-layer water varies greatly depending upon the choice of tracers. Hydrometric data indicate that slopes with permafrost likely supply much of the stormflow water due to near-surface water tables and transmissive organic soils. However, this signal was not clearly discernable in the streamflow hydrochemistry. More integrated studies are required to establish a greater understanding of hillslope processes in mountainous discontinuous permafrost catchments. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS runoff generation; permafrost; organic soils; hydrograph separation; $\delta^{18}O$; dissolved organic carbon; specific conductance

INTRODUCTION

The physical mechanisms responsible for streamflow and identifying the flow pathways that generate runoff have received much attention in temperate and humid environments (e.g. McDonnell, 1990; Bonell, 1993; Gibson *et al.*, 2000; Shanley *et al.*, 2002). Over the past 30 years, hydrometric, isotopic and geochemical methods have been used alone or in combination to elucidate runoff processes by identifying the sources, residence times and pathways that water takes from hillslopes to the stream (e.g. Maulé and Stein, 1990; Maloszewski and Zuber, 1992; Bonell, 1993; Buttle, 1994; Rodhe *et al.*, 1996; Brown *et al.*, 1999). Mass balance, end-member mixing analysis, and numerical convolution approaches predominate the literature as a means to establish flow pathways and residence times. Typically, differences in isotopic ratios are used to establish the sources of water, whereas chemical constituents provide information on flow pathways (Hooper

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and Shoemaker 1986; Maulé and Stein, 1990; Rice and Hornberger, 1998; Hoeg *et al.*, 2000; Ladouche *et al.*, 2001). Using this information, conceptual models of runoff generation have been constructed for a wide variety of environments (e.g. McDonnell, 1990; Bonell *et al.*, 1998; Gibson *et al.*, 2000; McGlynn *et al.*, 2002).

Runoff generation studies in regions with permafrost using hydrochemical methods are scarcer, yet conceptual models of runoff generation do exist that are largely based on hydrometric observations (Dingman, 1971; Kane *et al.*, 1981; Hinzman *et al.*, 1993; McNamara *et al.*, 1997; Quinton and Marsh, 1999; Carey and Woo, 2001a). Several factors distinguish runoff generation in permafrost regions from more temperate zones: (1) snowmelt dominates the hydrological cycle, as a third to half of annual precipitation is released during a few weeks (McNamara *et al.*, 1998; Carey and Woo, 2001b); (2) where permafrost is present, deep drainage is restricted, and runoff is enhanced due to near-surface water tables (Slaughter and Kane, 1979; Kane *et al.*, 1989; Quinton and Marsh, 1999; Carey and Woo, 2001a); (3) the ubiquitous presence of capping organic soils allows rapid translocation of water along near-surface pathways when water tables reside within this upper soil layer (Quinton *et al.*, 2000; Carey and Woo, 2001a); (4) bypass flow mechanisms, such as soil pipes (Gibson *et al.*, 1993; Carey and Woo, 2000) and interhummock flow (Quinton and Marsh, 1998), can predominate during certain wetness conditions.

Few studies have employed the application of stable isotopes and hydrochemistry for hydrograph separation in permafrost environments Typically, water stored within the catchment dominates the stream hydrograph, except during certain periods of snowmelt, when large volumes of water are released and rapidly reach the stream via near-surface pathways (Obradovic and Sklash, 1986, Gibson et al., 1993; Cooper et al., 1993; McNamara et al., 1997). In the subarctic, understanding the link between hillslope and runoff hydrology is complicated by the presence of discontinuous permafrost, as catchment areas with permafrost have a very different hydrological response than areas without (Carey and Woo, 2001b). This variability affects water chemistry, as demonstrated in subarctic Alaska by MacLean et al. (1999), who reported that permafrostdominated catchments had higher concentrations of dissolved organic carbon (DOC), but lower concentrations and fluxes of solutes than an adjacent watershed nearly permafrost free. In the permafrost-dominated catchment, water was restricted to the organic-rich active layer and was, therefore, enriched in DOC. In the catchment with low permafrost coverage, water infiltrated deeper into the mineral soils, where DOC was adsorbed and solutes were dissolved due to greater contact time with mineral soil exchange sites. Petrone et al. (2000) observed DOC and NO₃ response during two summer storms for the high and low permafrost watersheds studied by MacLean et al. (1999) and found that DOC increased with discharge during rain events and that the catchment with the highest percentage of permafrost had the greatest DOC increase. The mechanism cited for this increase in DOC is overland flow or subsurface flow through peat layers in the permafrost-underlain valley bottoms of each stream. Carey (2003) reported DOC fluxes from the subarctic catchment utilized in the present study and showed that, although snowmelt resulted in the largest DOC fluxes from the catchment, summer rainstorms increase stream DOC by increasing the proportion of hillslope drainage derived from the organic layer.

Considering the lack of research on runoff generation in subarctic environments, the objective of this study is to obtain an improved understanding of sources and pathways of runoff in a discontinuous permafrost catchment. To this end, a mixed-method approach utilizing hydrometric, isotopic and hydrochemical data will be used to evaluate runoff generation during summer rainstorms. The snowmelt period will not be considered in this study.

STUDY AREA

Granger basin (60°32′N, 135°18′W) is located within the Wolf Creek research basin, 15 km south of Whitehorse, Yukon Territory, Canada (Figure 1). The study area has a subarctic continental climate characterized by a large temperature range and low precipitation. Mean annual January and July temperatures from the

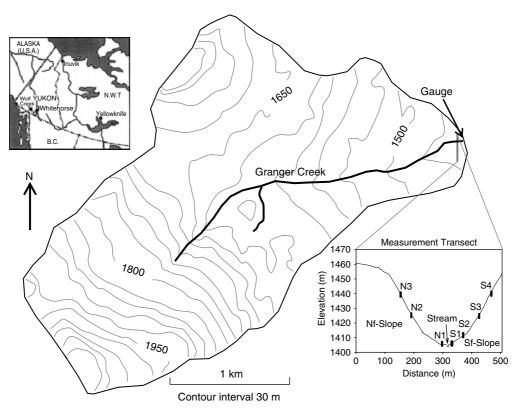


Figure 1. Study catchment (Granger basin) within the Wolf Creek research basin and location of the well/tension lysimeter transects. Insets show location in Canada and position of measurement sites along transect

Whitehorse airport (elevation 703 m a.s.l.) are $-21\,^{\circ}$ C and $+15\,^{\circ}$ C respectively. Mean annual precipitation is 260 mm, half of which falls as rain (Wahl *et al.*, 1997), yet precipitation at the Whitehorse airport may underestimate basin precipitation by ca 25 to 35% (Pomeroy and Granger, 1999).

Granger basin drains a *ca* 6 km² area and ranges in elevation from 1310 to 2250 m. The main river valley trends west to east at lower elevations, resulting in predominantly north- and south-facing slopes. The geological makeup is primarily sedimentary, comprised of limestone, sandstone, siltstone and conglomerate, and is overlain by a mantle of glacial till ranging from a thin veneer to several metres in thickness. Fine-textured alluvium covers most of the valley floor, whereas upper elevations have shallow deposits of colluvial material with frequent bedrock outcrops present (Mougeot and Smith, 1994). Permafrost is found under much of the north-facing slopes (Nf-slopes) and higher elevation areas, whereas seasonal frost predominates on southerly exposures. In permafrost areas and the riparian zones, soils are capped by an organic layer up to 0.4 m thick consisting of peat, lichens, mosses, sedges and grasses. Only a few scattered white spruce (*Picea glauca*) occur within the basin, which is considered to be above the treeline. Vegetation consists predominantly of assorted willow shrubs (*Salix*) and Labrador tea (*Ledum groenlandicum*).

Two slopes separated by the river valley were selected to compare catchment areas with and without permafrost. A permafrost-underlain Nf-slope has a gradient of ca 0.35 and is underlain by till soils predominantly sandy in texture capped by an organic layer consisting of peat, lichens and mosses. The thickness of this organic layer varies, averaging 0.26 ± 0.10 m (n = 30). The active layer ranges from several decimetres to >1 m near the slope base. A south-facing slope (Sf-slope) with a ca 0.34 gradient is underlain by seasonal frost only. Organic layer thickness is typically less $(0.12 \pm 0.09 \text{ m} (n = 30))$ and

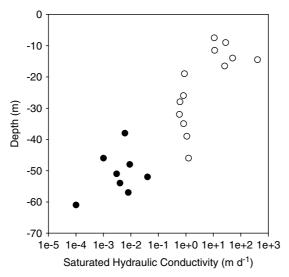


Figure 2. Saturated hydraulic conductivity of organic soils (open circles) and mineral soils (closed circles). Values for the organic soils were determined from tracer tests, whereas the mineral soil values were determined from head-recovery tests

declines in thickness upslope from the riparian areas. Saturated hydraulic conductivity declines with depth in the organic layer and then exhibits a sharp reduction in the mineral substrate (Figure 2; Quinton and Gray, 2001). Between the slopes is a thin riparian zone that ranges from 10 to 30 m across, being is wider at the base of the permafrost-free Sf-slope.

FIELD AND ANALYTICAL METHODS

The study period can be considered as July 2001, during which two rainfall-runoff events were intensively studied. Discharge was calculated using a stage—discharge relationship consisting of a stilling well with a float connected to an electronic logger. A stable stage—discharge relationship has existed for this catchment since 1998. In August 2000, seven shallow groundwater wells were constructed from PVC pipe (35 mm internal diameter) with a screen section along the entire subsurface length and placed down augured holes the same size as the pipe diameter. Three wells were placed within the permafrost-underlain Nf-slope and four within the seasonal frost Sf-slope. Wells were spaced along the slope length and numbered sequentially upward from the riparian zone (Figure 1). In addition, water level was monitored continuously in a water-filled, natural depression located approximately 110 m upslope of the stream channel. These measurements were made with pressure transducers (Druck PDCR 950) connected to a data logger for continuous measurement. Readings were taken every 60 s and averaged and recorded every 30 min. Suction lysimeters were installed every 0·1 m to depths of 0·4 m at sites N2 and N3 and to 0·5 m at sites S1 and S3 for the study period by coring a hole with a same diameter coring device and placing the porous cup down the hole.

Water samples were obtained in the stream, suction lysimeters and groundwater wells at least twice weekly. During storm events, stream water was sampled every 2 h using an ISCO water sampler. Samples were removed from the sampler within 24 h. To obtain suction lysimeters samples, the instruments were sealed under a vacuum as the water was drawn from the soil through the ceramic cup and into the sampler. Both wells and lysimeters were purged once prior to sample collection. Two rainfall and two throughflow collectors consisting of plastic gutters were used to collect precipitation and evaluate differences in waters collected above and below the willow shrub canopy.

Isotope samples were collected in 60 ml vials sealed with airtight caps. Analyses for $\delta^{18}O$ were performed at the Department of Geological Sciences, University of Saskatchewan, by CO_2 equilibrium. Accuracy of the analysis based on replicate samples was 0.1%. Isotope compositions are expressed as δ (per mil) ratio of the sample to the Vienna standard mean ocean water standard. DOC samples were filtered through precombusted Whatman GF/F glass-fibre filters and acidified with H_2SO_4 to 0.035 M prior to storage in sterilized 50 ml vials. Samples were kept cool until analysis, which occurred within 2 months of sample collection. There was no evidence of precipitate within the vials prior to analysis. Samples were run on a Technicon Autoanalyzer and DOC concentrations were determined using an automated persulphate–UV digestion with a phenolphthalein colour reagent. Accuracy of carbon content of DOC samples based on replicate analysis was 0.1 mg 1^{-1} .

A Hydrolab 4a Datasonde placed near the outlet gauge was used for continuous measurement of specific electrical conductivity (SpC), stream temperature and other water quality parameters not used in this study (pH, dissolved oxygen, oxidation/reduction potential). SpC from soil waters was determined soon after collection using a portable Hydrolab Quanta sensor.

Hydrograph separation techniques

Hydrograph separations are based on the steady-state mass balance equations that describe the contributions of various water sources to streamflow under a simple batch mixing-model with conservative tracers (Sklash and Farvolden, 1979). In the case of n runoff components and n-1 observed tracers, $t_1, t_2, \ldots, t_{n-1}$ the following n linear mixing equations can be written:

$$Q_{\mathrm{T}} = Q_1 + Q_2 + \dots + Q_n \tag{1}$$

$$c_{\mathrm{T}}^{t_i}Q_{\mathrm{T}} = c_1^{t_i}Q_1 + c_2^{t_i}Q_2 + \dots + c_n^{t_i}Q_n \tag{2}$$

where Q_T is the total runoff, Q_1, Q_2, \ldots, Q_n are the runoff components and $c_1^{t_i}, c_2^{t_i}, \ldots, c_n^{t_i}$ are the respective concentrations of the observed tracer t_i . The application of Equations (1) and (2) is based on the following assumptions (Hinton *et al.*, 1994; Hoeg *et al.*, 2000): (1) there is a significant difference between tracer concentrations of the different components; (2) tracer concentrations are constant in space and time, or any variations can be accounted for; (3) contributions of an additional component must be negligible, or the tracer concentrations must be similar to that of another component; (4) the tracers mix conservatively; and (5) the tracer concentrations of the components are not collinear.

Using Equations (1) and (2), two-component separations to evaluate the fractional contribution of a runoff component can be determined from

$$\frac{Q_1}{Q_T} = \frac{(c_T^{t_1} - c_1^{t_1})}{(c_2^{t_1} - c_T^{t_1})} \tag{3}$$

where the event component $(Q_1 = Q_e)$ is defined as the fraction of total runoff that entered the hydrological system during the rainfall event, whereas the pre-event component $(Q_2 = Q_p)$ is defined as that part of total runoff stored within the catchment prior to runoff. Q_2/Q_T can be solved in an analogous manner. The event fraction isotopic ratio is calculated as the incremental weighted mean of event water as (McDonnell *et al.*, 1990)

$$\delta^{18}O = \sum_{i=1}^{n} P_i \delta_i / \sum_{i=1}^{n} P_i$$

$$\tag{4}$$

where P_i and δ_i denote fractionally collected precipitation depth and δ ratio respectively.

Three-component hydrograph separation with two tracers, as confined by Equations (1) and (2), can be used to calculate the fractional component of the first component of the total streamflow (Q_1/Q_T) following the method of Gibson *et al.* (2000):

$$\frac{Q_1}{Q_T} \left[\frac{(c_T^{t_1} - c_3^{t_1}) - (c_T^{t_2} - c_3^{t_2})(c_2^{t_1} - c_3^{t_1})/(c_2^{t_2} - c_3^{t_2})}{(c_1^{t_1} - c_3^{t_1}) - (c_1^{t_2} - c_3^{t_2})(c_2^{t_1} - c_3^{t_1})/(c_2^{t_2} - c_3^{t_2})} \right]$$
(5)

where Q_2/Q_T and Q_3/Q_T can be solved in an analogous way and sum to unity as confined by Equation (1). In this study, $\delta^{18}O$ was used as t_1 , and DOC and SpC each as t_2 for different separation scenarios. For the three-component separations, c_1 , c_2 and c_3 refer to event water Q_e , soil water from the organic layer Q_{ol} and mineral layer Q_{ml} respectively. The applicability of using DOC and SpC as conservative tracers is discussed later.

Uncertainty analysis

To estimate uncertainty associated with the pre-event Q_p and event Q_e fractions of total discharge associated with systematic errors in the isotopic signatures, the Gaussian standard error method of Generaux (1998) was applied:

$$W_{f_{pe}} = \sqrt{\left[\frac{c_{e} - c_{T}}{(c_{p} - c_{e})^{2}} W_{c_{p}}\right]^{2} + \left[\frac{c_{T} - c_{p}}{(c_{p} - c_{T})^{2}} W_{c_{e}}\right]^{2} + \left[\frac{1}{(c_{p} - c_{e})} W_{c_{T}}\right]^{2}}$$
(6)

where W is uncertainty, c is the tracer concentration, f is the mixing fraction, and the subscripts p, e and T refer to the pre-event, event and stream water components respectively. Analytical errors were liberally assumed equal to 0.2%, and an error of 2% was used to account for spatial and temporal variability in rainfall δ^{18} O ratio. To evaluate the error associated with the three-component separations, the values of all end members were varied by one standard deviation and the subsequent maximum and minimum contributions reported.

RESULTS

Of five rainstorm events where water samples were collected for hydrograph separation in 2001 and 2002, only two had $\delta^{18}O$ ratios that were significantly different than pre-event waters within the soils and stream. Event isotopic ratios were considered significantly different when the mean event signature was greater or less than two standard deviations from the mean stormflow isotopic ratio. Coincidentally, both storms occurred in July 2001: (1) an 8·2 mm event between 16 and 17 July (termed Storm 1) and (2) a 24·1 mm event between 26 and 29 July (termed Storm 2).

Hillslope waters

Nf-slope. Interstitial water sampled using suction lysimeters within the Nf-slope did not show a strong $\delta^{18}O$ transition with depth for July 2001 (Table I). Pore waters at N2 and N3 within the organic layers were slightly enriched compared with water deeper in the profile. However, the overall similarity between near-surface and deeper waters suggests that soil water is well mixed from snowmelt, which supplied water into the soil profile until early June. As summer progressed and near-surface soils dried, samples could not be obtained from the 0·1 m level. DOC exhibited a sharp transition within the Nf-slope at the organic/mineral interface, with carbon averaging 29.9 ± 7.0 mg 1^{-1} and 4.9 ± 1.4 mg 1^{-1} for the organic and mineral layers respectively (Table I). Pore water DOC declined gradually over July, yet elevated levels within the organic layer persisted. SpC was approximately double within the mineral layer (89 ± 7 μS cm⁻¹) and open wells (80 ± 10 μS cm⁻¹) compared with organic-layer pore water (35 ± 6 μS cm⁻¹) (Tables I and III). Throughout July 2001 the water tables showed a general decline, and depth increased with distance upslope from the stream.

Sf-slope. There was no significant difference (p < 0.05) in $\delta^{18}O$ between the Sf-slope and the Nf-slope (Table II). Pore water within the Sf-slope had a mean $\delta^{18}O$ of $-21.2 \pm 0.3\%$, and again only slight enrichment at the surface. There was no apparent trend in $\delta^{18}O$ with slope position or between sampling dates. DOC within the Sf-slope was lower than the Nf-slope, both within the thin upper organic layer and the mineral layer (Table III). There was a decline in organic-layer DOC concentration at the S1 riparian site from 2 July

Table I. DOC, δ^{18} O and SpC variation with depth in soil water within the permafrost-underlain north-facing slope, July 2001

		0.10 1	m		0.20 1	m		0.30 r	n		0.40 r	n
	DOC (mg l ⁻¹)	δ ¹⁸ Ο (‰)	SpC (µS cm ⁻¹)	DOC (mg l ⁻¹)	δ ¹⁸ Ο (‰)	SpC (µS cm ⁻¹)	DOC (mg l ⁻¹)	δ ¹⁸ Ο (‰)	SpC (μS cm ⁻¹)	DOC (mg l ⁻¹)	δ ¹⁸ Ο (‰)	SpC (μS cm ⁻¹)
Site N2												
3 Jul 01	39.3	-21.1	30	38.2	-21.3	27	6.1	-21.4	89			
10 Jul 01	24.7		28	38.4		31	6.2		88			
15 Jul 01	19.9	-21.0	33	30.2	-21.2	31	4.9	-21.2	98	2.9	-21.6	87
21 Jul 01				29.6		32	8.2		94	4.2		98
30 Jul 01				24.2	-21.0	29	4.3	-21.3	101	4.1	-21.4	94
Site N3												
3 Jul 01	26.2	-21.0	40	42.4	-21.6	44	5.5	-21.4	83			
10 Jul 01	21.1		44	32.3		37	5.7		77			
15 Jul 01				30.4	-21.1	43	5.9	-21.6	94	3.3	-21.7	80
21 Jul 01				27.8		41	4.4		85	3.4		84
30 Jul 01				23.2	-21.0	34	5.2	$-22 \cdot 1$	86	3.3	-21.4	82

 $(7.7\pm0.6~mg~l^{-1})$ to 30 July $(3.7\pm0.6~mg~l^{-1})$. DOC within the mineral substrate averaged $2.3\pm0.7~mg~l^{-1}$ for July 2001. Within the near-surface wells, DOC concentrations averaged $7.5\pm3.3~mg~l^{-1}$ on 3 July and declined to $5.2\pm2.3~mg~l^{-1}$ by 30 July (Table II). Unlike the Nf-slope, there was an apparent trend in DOC related to slope position as water obtained from the riparian area (S1) had lower DOC concentrations than upslope wells. As with the Nf-slope, there was a discontinuity in SpC between the organic and mineral soils (Table III). SpC within the organic layer was approximately 58 μ S cm⁻¹ less than mineral soils for all samples. Water table within the riparian zone (S1) showed little variability, always occurring between 0·1 and 0·2 m from the surface (Table II). At upslope wells, water tables declined more rapidly throughout July due to the absence of permafrost and late-lying snow, and at well S4 the water table fell below 1 m by 15 July (Table II).

Storm 1

Between 16 and 17 July, 8·2 mm of isotopically distinct rain precipitated on the catchment (Figure 3a). The antecedent wetness T_{5d} (defined as the rainfall during the 5 days prior to the storm event) was $13\cdot2$ mm. The isotopic and chemical composition of rainfall was measured twice during the storm at two locations above and below the canopy. After 10 h and 4·4 mm of rain, the δ^{18} O ratio of collected water (both rainfall and throughflow) was $-12\cdot2\pm0\cdot8\%$ (n=4) and became slightly depleted to $-13\cdot1\pm0\cdot9\%$ (n=3) after 16 h and an additional 2·5 mm. DOC concentrations in above-canopy rainfall were below the analytical detection limit of 0·1 mg l⁻¹, whereas throughfall mean DOC concentration was $0\cdot6\pm0\cdot4$ mg l⁻¹ (n=3). SpC of rainfall and throughfall was 25 ± 9 µS cm⁻¹ (n=7).

There were two distinct peaks in the runoff hydrograph (Figure 3b). Flows first increased from ca 160 to 350 l s⁻¹ after 6 mm of rain over 11 h. Flows declined and then rose in response to a high-intensity 1·3 mm event 20 h later. Following this, stormflow receded over 48 h, although there was a small increase observed on 19 July not associated with any measured rainfall. Discharge was separated into stormflow and baseflow by projecting a straight line across the hydrograph from the time of hydrograph rise to the point where discharge returns to within 10% of the pre-storm level. This method provides a conservative estimate of baseflow, yet has been cited as appropriate considering the high hydraulic conductivity of the surface organic mat (McNamara *et al.*, 1997). For Storm 1, approximately 3·5 mm of stormflow occurred, giving a runoff ratio of 0·43.

Table II. DOC, δ^{18} O and SpC from groundwater wells, July 2001. WT refers to water table depth. N are north-facing wells underlain with permafrost and S

					a	re south-1	are south-facing wells with seasonal frost only	s with se	easonal fro	st only						
Date			N1					1	N2					N3		
	DOC (mg l ⁻¹)		ο%) Ο%)	SpC (μS cm ⁻¹)	WT (m)	-	DOC (mg l ⁻¹)	(%) O ₈₁ 8	${\rm SpC} \\ (\mu {\rm S~cm}^{-1})$	1-1)	WT (m)	DOC (mg I ⁻¹)	(%) O ₈₁ 8		${\rm SpC}_{(\mu {\rm S~cm}^{-1})}$	WT (m)
3 Jul 01 6 Jul 01	15.6		-21.2	78	0.08		24.0 19.9	-21.5	80 79		0.11 0.14	7.9	-22.0		86 64	0.20
10 Jul 01 15 Jul 01	14:4 15:4		-21.2	72	0 0		19.3 12.5	-21.3	89 104		0.16 0.22	16·1 17·8	-21.9		77 88	0.24 0.27
20 Jul 01 25 Jul 01	9.1	- ~		69	0 0		18·2 15·4		88 46		0.19 0.21	16·5 13·3			84 72	0.26
30 Jul 01	10.4	·	-20.7	78	0		16.3	-21.2	93		0.20	14.0	-21.5		77	0.32
Date		S	S1			S2	2			S3				S4		
	DOC 8 (mg 1 ⁻¹) (8 ¹⁸ O (%)	SpC (µS cm ⁻¹)	WT (m)	DOC (mg l ⁻¹)	δ ¹⁸ Ο (%ο)	$\begin{array}{c} \mathrm{SpC} \\ \mathrm{(\mu S~cm^{-1})} \end{array}$	WT (m)	DOC (mg l ⁻¹)	δ ¹⁸ Ο (%ο)	$\begin{array}{c} \mathrm{SpC} & \mathrm{V} \\ (\mu \mathrm{S} \ \mathrm{cm}^{-1}) & (\end{array}$	WT m)	$DOC \\ (mg \ l^{-1})$	8 ¹⁸ O (%0)	SpC (µS cm ⁻¹)	WT (m)
3 Jul 01 6 Jul 01 10 Jul 01	4.2 3.9 4.5	-21.2	88 84 87	0.10 0.13 0.17	12·1 7·7 11·3	-21.4	90 87 97	0.19 0.17 0.17	6.5 8.8 4.4	-21.3	92 94 88	0.27 0.28 0.28	7.0 7.4 7.1	-21.4	88 89	0.76 0.88 0.89
15 Jul 01 20 Jul 01 25 Jul 01	2.9 2.2	-21.3	79 88 88	0.18 0.14 0.16	7.7 6.6 7.2	-21.5	88 84 84	0.22 0.18 0.27	7.2 6.3 8.0	-21.4	86 90 85	0.29 0.27 0.39				7 7 7
30 Jul 01	2.6	-20.9	81	0.14	6.7	-21.0	88	0.26	6.4	-21.1	84	0.42				>1

Table III. DOC, 8¹⁸O and SpC variation with depth in soil water within the south-facing slope, July 2001

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			0.10 m			0.20 m			0.30 m			0.40 m			0.50 m	
7.3 -21.2 30 8.1 -21.3 33 2.4 -22.0 96 3.3 -21.3 94 1.6 -21.2 6.6 36 5.9 3.3 2.4 -22.0 96 3.3 -21.3 94 1.6 -21.2 5.6 -21.4 37 5.2 -21.2 32 4.1 -21.6 99 1.5 -20.9 92 1.8 -21.4 4.2 31 4.4 21.0 32 1.4 -21.4 98 1.8 -21.0 91 1.8 -21.4 3.3 -21.0 30 4.1 -21.0 32 1.4 -21.4 98 1.8 -21.0 91 1.8 -21.5 10.7 46 15.6 80 3.3 97 2.4 109 2.0 101 2.1 -21.2 101 1.9 -21.3 101 2.1 -21.3 101 2.1 -21.3 101 1.9 -21.3 101 1.9 -21.5 101 1.9 -21.5 101 1.9 -2		DOC (mg l ⁻¹)	(%) O ₈₁ 8		DOC (mg l ⁻¹)	δ ¹⁸ Ο (%ο)		DOC (mg l ⁻¹)	δ ¹⁸ Ο (%)	SpC (µS m ⁻¹)	DOC (mg l ⁻¹)		SpC (µS m ⁻¹)	DOC (mg I ⁻¹)) (%) O818	SpC µS m ⁻¹)
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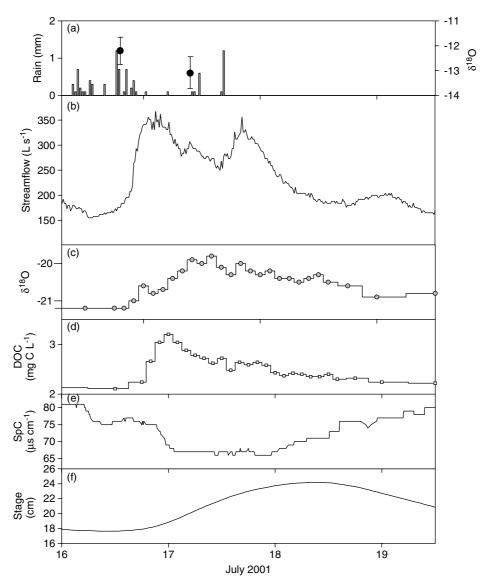


Figure 3. Time series of (a) rainfall and $\delta^{18}O$ ratio of rainfall (circles), (b) streamflow, (c) streamflow $\delta^{18}O$ ratio, (d) streamflow DOC, (e) streamflow SpC, and (f) stage in standing water location on Nf-slope between 16 July (00:00) and 19 July (12:00) 2001

An increase in stream $\delta^{18}O$ from baseflow levels of $-21\cdot2\%$ began on the rising limb of the hydrograph, and was enriched by $1\cdot4\%$, $22\cdot5$ h after stormflow began and $5\cdot5$ h after the first hydrograph peak (Figure 3c). Following this, there was no $\delta^{18}O$ peak associated with the second hydrograph peak as values gradually receded to pre-event levels over 36 h. DOC concentrations rose rapidly on the ascending limb from $2\cdot2$ mg l⁻¹ to $3\cdot2$ mg l⁻¹ and crested 2 h following the first hydrograph peak (Figure 3d). Following this peak, DOC declined to $2\cdot6$ mg l⁻¹ during the second hydrograph peak and then fell steeply along the receding hydrograph limb. SpC declined from $82~\mu\text{S}$ cm⁻¹ to $66~\mu\text{S}$ cm⁻¹ with increasing stormflow, whereupon values stabilized between the two hydrograph peaks (Figure 3e). Following the second stormflow peak, SpC increased steadily along the recession limb. It is of interest to note that SpC values

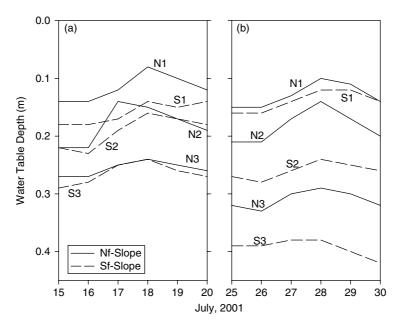


Figure 4. Water table position (m) during Storm 1 (a) and Storm 2 (b). Nf-slopes are north-facing wells underlain with permafrost and Sf-slopes are south-facing wells with seasonal frost only. Measurements were taken between 13:00 and 14:00

declined only after the second hydrograph peak, whereas DOC and δ^{18} O values declined earlier within the event.

The single continuous and seven daily water table measurements are presented in Figure 3f and Figure 4 respectively. Prior to Storm 1 the Sf-slope was frost-free, whereas the Nf-slope had a mean frost table position of 0.41 ± 0.10 m (n=15), with the lower slope locations having a greater depth to frozen ground. Between 16 and 17 July, water tables rose within the Nf-slope, and more noticeably at the mid-slope position (N2) compared with the slope base (N1) and upslope (N3) positions (Figure 4a). On the Sf-slope, water tables increased again, most notably in mid-slope positions (S2, S3), whereas the riparian site (S1) had smaller rises (Figure 4b). There was no water within the top 1 m at well S4 at this time. Following the cessation of rainfall, water tables declined, although the degree of this decline varied depending upon slope position and aspect. The standing water on the Nf-slope (Figure 3f) receded more slowly than streamflow recession and water levels measured in wells at a similar slope position (N2). There was some observational evidence to suggest that this standing water may have restricted drainage. Hillslope waters were not specifically monitored for chemical constituents prior and after the storm event, yet their changes throughout July 2001 are reported in Tables I–III. It appears that the 8·2 mm precipitation event had no notable affect on the δ^{18} O ratio of water within the saturated and unsaturated zone.

Storm 2

The second rain event deposited $24\cdot 1$ mm of precipitation between 26 and 29 July (Figure 5a). This was the greatest summer rainfall event and represented ca 15% of annual rainfall for 2001. After 12 h and 5·9 mm of rain, δ^{18} O was $-15\cdot 3\pm 0\cdot 6\%$ for rainfall and throughfall (n=4). A second precipitation sampling event after an additional 12·3 mm, 36 h after the beginning of the event, had a δ^{18} O value of $-14\cdot 0\pm 1\cdot 6\%$ (n=4). Throughfall DOC concentration was $0\cdot 6\pm 0\cdot 2$ mg 1^{-1} (n=4) and SpC was 23 ± 8 μ S cm⁻¹ (n=8) for both rain and throughflow.

The stormflow hydrograph exhibited a simple single hydrograph peak, yet significant increase in flows did not occur until after ca 6 mm of precipitation (Figure 5b). Streamflow increased from below 150 l s⁻¹ to ca

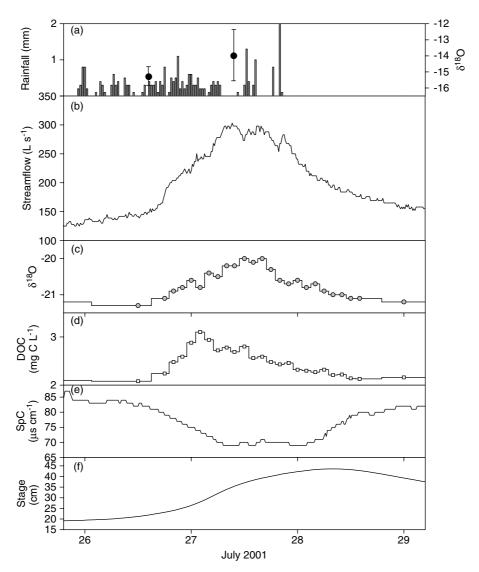


Figure 5. Time series of (a) rainfall and $\delta^{18}O$ ratio of rainfall (circles), (b) streamflow, (c) streamflow $\delta^{18}O$ ratio, (d) streamflow DOC, (e) streamflow SpC, and (f) stage in standing water location on Nf-slope between 25 July (19:30) and 29 July (05:00) 2001

 $300 \ l\ s^{-1}\ 13$ h after rainfall began and gradually declined over the following 52 h despite two intermittent rainfall events that caused minor peaks. Stormflow runoff was calculated as 2.7 mm, providing a runoff ratio of 0.12, which is markedly less that Storm 1 and is unexpected considering the greater precipitation volume. However, antecedent wetness for Storm 2 ($T_{5d} = 10.7$ mm) and the mean water table depths at all sites prior to the event were lower than Storm 1, suggesting a greater catchment storage capacity.

An increase in stream $\delta^{18}O$ from baseflow levels of $-21\cdot3\%$ did not begin until $10\cdot4$ mm of rain had fallen (Figure 5c). $\delta^{18}O$ rose slowly with the ascending hydrograph and peaked at a value of $-20\cdot0\%$, $8\cdot5$ h after the hydrograph peak. $\delta^{18}O$ then declined swiftly on the descending limb and achieved consistent levels 16 h after the isotopic peak. There does appear to be a slight isotopic enrichment of streamwaters from this storm, as levels did not drop to pre-event values. DOC rose from a baseflow concentration of $2\cdot1$ mg 1^{-1} to

 3.1 mg I^{-1} in 10 h on the ascending limb, peaking 8 h before the hydrograph peak and 16.5 h before the $\delta^{18}\text{O}$ peak (Figure 5d). Following the DOC maxima, values declined steadily despite a continued increase then gradual decrease in stormflow. SpC declined from ca 85 μS cm⁻¹ to 67 μS cm⁻¹ over 24 h along the ascending hydrograph, remained steady for 19 h during the period of maximum flow and then declined to pre-event levels along the recession limb (Figure 5e).

The Nf-slope had a mean frost table position of 0.53 ± 0.14 m (n=15) prior to the storm. Between 25 and 28 July, water tables rose within the Nf-slope, again with a more evident rise at mid-slope locations compared with base and upslope positions (Figure 4b). Within the Sf-slope, water tables had a less pronounced increase, and there was significant within slope variation (Figure 4b). Water tables on both slopes declined gradually over the following several days, which was slightly longer than the period streamflow recession. Considering the greater precipitation of Storm 2, water table responses were more subdued than Storm 1. Again, the standing water on the Nf-slope receded much more slowly than wells within the slope (Figure 5f). The 24·1 mm of precipitation did not have a clear influence on δ^{18} O in hillslope wells (Table II), although there was some enrichment observed from water extracted at the 0·1 and 0·2 m levels from the two slopes (Tables I and III).

Hydrograph separations

Two-component separations. Concentrations of event water $\delta^{18}O$ (c_e) were determined from Equation (4) and pre-event $\delta^{18}O$ water (c_{pe}) was taken as baseflow $\delta^{18}O$ prior to the storm, which is not an unreasonable assumption considering that the $\delta^{18}O$ values within the slopes are similar to baseflow values. Results of the two-component hydrograph separations using $\delta^{18}O$ showed total event water of 7% and 9% of stormflow for Storms 1 and 2 respectively (Figure 6a and b). Maximum contributions (17% and 18% for Storms 1 and 2 respectively) occurred after the hydrograph peak for both storms and did not correspond with precipitation intensity. Storm 1 had a slightly longer period during the recession when event water was contributing to the stormflow hydrograph, likely due to wetter antecedent conditions within the catchment prior to the event. Standard error applied for two-component separations based on analytical uncertainties ranges between 2.3 and 3.7% for all periods of separation.

Three-component two-tracer separations. Two end members were obtained from the saturated zone of the soil, one representing the water of the organic layer and the other representing water from the underlying mineral sediment. These organic and mineral end members were used to evaluate the contributions from both regions of the soil to stormflow as they bound the δ^{18} O-DOC and δ^{18} O-SpC mixing diagrams and are not collinear in their stormflow response (Figure 7a and b). Concentrations of water from the organic (c_{ol}) and mineral $(c_{\rm ml})$ layers were taken as the mean values obtained from all lysimeters for July 2001. The event water isotopic ratio was calculated from Equation (4). DOC has not seen widespread application as an end member in hydrograph separation, yet it has been used successfully to separate organic horizon contributions in humid temperate environments (Brown et al., 1999). It may be a particularly useful tool in permafrost regions, as near-surface organic-rich soils leach DOC into the stream when water tables rise into these layers (MacLean et al., 1999; Petrone et al., 2000; Carey, 2003). SpC has been used more frequently as a tracer in hydrograph separation (e.g. Pilgrim et al., 1979; Matsubayashi, et al., 1993; McNamara et al., 1997). The difficulty in using rainfall SpC as a new-water end member is detailed by Pilgrim et al. (1979), who showed that SpC of dilute water changes with soil contact time and, therefore, is not a reliable new-water end member. SpC can change dramatically during the early stages, and then approach equilibrium more slowly. However, SpC levels in the organic layer are much lower than those in the mineral soil, suggesting that event water travelling to the stream within the organic layer does not become enriched with dissolved minerals compared with waters that pass through the mineral substrate.

Flow contributions from the δ^{18} O-DOC and δ^{18} O-SpC three-component analyses are shown in Figure 6c-f and summarized in Table IV. The mineral layer component $Q_{\rm ml}$ dominated the hydrograph for both storms,

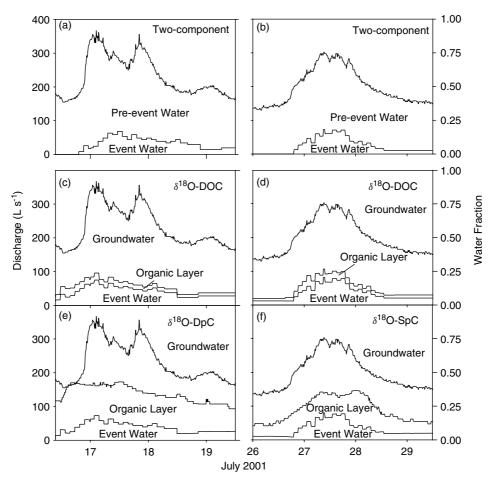


Figure 6. Two-component hydrograph separations using $\delta^{18}O$ for Storm 1 (a) and Storm 2 (b). Fraction of event water Q_e is represented by the dashed line. Three-component hydrograph separations using $\delta^{18}O$ and DOC for Storm 1 (c) and Storm 2 (d) and three-component hydrograph separations using $\delta^{18}O$ and SpC for Storm 1 (e) and Storm 2 (f)

yet the organic horizon contribution $Q_{\rm ol}$ had dramatically different contributions based on the $\delta^{18}{\rm O}\text{-DOC}$ and $\delta^{18}{\rm O}\text{-SpC}$ separations. For both storms, separations using $\delta^{18}{\rm O}\text{-DOC}$ resulted in low estimates of $Q_{\rm ol}$ (3·1% and 2·7% for Storm 1 and Storm 2 respectively); an expected result considering the modest increases in streamflow DOC compared with the high concentration of DOC within the organic soils (Figure 7b). In contrast, the $\delta^{18}{\rm O}\text{-SpC}$ separations provide organic-layer contributions of 23·9% and 14·9% for Storms 1 and 2 respectively. Event water contributions $Q_{\rm e}$ were between 7·5 and 8·9% for both separations and both storms (Table IV). Their relative contributions and timing during the storm were similar to the two-component separations. $Q_{\rm ml}$ dominated the stormflow hydrograph, contributing between 68·0 to 88·3% depending upon the storm and the tracers utilized (Table IV).

The errors associated with varying end members one standard deviation are reported in Table IV. Considering the $\delta^{18}\text{O-DOC}$ separations, even if DOC concentrations were at the low end of the observed range (typical of the riparian areas), Q_{ol} only reached 6·1% of stormflow, a value still considerably less than the minimum Q_{ol} (12·3%) calculated from the $\delta^{18}\text{O-SpC}$ separations. $\delta^{18}\text{O-SpC}$ separations were particularly sensitive to groundwater SpC values, which resulted in the maximum sensitivity to Q_{ol} and Q_{ml} estimates. Changes in rainfall $\delta^{18}\text{O}$ by $\pm 2\%$ affected Q_{e} to a maximum range of $\pm 5\%$ of the mean value.

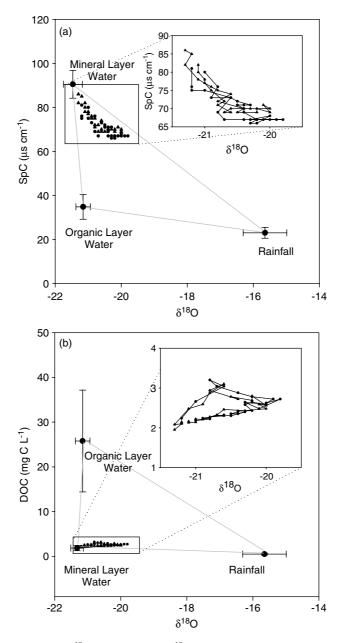


Figure 7. Component mixing diagrams for (a) $\delta^{18}O$ and SpC and (b) $\delta^{18}O$ and DOC. Mean values of the end-members for all samples are combined and plotted with plus/minus one standard deviation error bars. Streamflow trends from Storm 1 (circles) and Storm 2 (triangles) are represented on the diagram and in the inset

DISCUSSION

Hydrograph separations

Event-water contributions were low compared with more temperate humid environments (Buttle, 1994; Generaux and Hooper, 1998). Despite the presence of permafrost, which restricts drainage, this low fraction of event water is expected considering the large storage capacity of organic soils and modest precipitation

Table IV. Three-component, two-tracer (δ^{18} O-SpC and δ^{18} O-DOC) hydrograph separations showing percentage contribution of event water $Q_{\rm e}$, water from the organic layer $Q_{\rm ol}$ and mineral layer $Q_{\rm ml}$ of total streamflow for Storm 1 and Storm 2. Maximum and minimum contribution values were obtained by varying all tracer components by plus/minus one standard deviation

		δ ¹⁸ O-SpC			$\delta^{18}\text{O-DOC}$	
	Mean	Max.	Min.	Mean	Max.	Min.
Storm 1 (16–20 June 2001)						
$Q_{ m e}$	7.9	10.4	6.3	8.6	11.3	7.0
$\widetilde{Q}_{ m ol}$	23.9	30.8	12.3	3.1	6.1	2.1
$Q_{ m ml}$	68.0	79.2	61.5	88.3	92.5	86.0
Storm 2 (26–30 June 2001)						
$Q_{ m e}$	7.5	12.0	6.3	8.9	12.6	4.9
$\widetilde{Q}_{ m ol}$	14.9	24.1	12.9	2.7	5.4	1.9
$\widetilde{Q}_{ m ml}$	77.6	88.0	68.9	88.2	92.5	84.3

events that occur in the subarctic, where evapotranspiration exceeds rainfall during the summer (Carey and Woo, 2001b). Considering the hydrograph separations, overland flow and precipitation on saturated areas were minimal in extent, and precipitation directly on the stream channel area was insufficient to account for event-water contributions for both two- and three-component separations. The delayed timing of the peakevent contribution and the lack of correspondence with precipitation intensity suggests an alternate delivery mechanism other than overland flow on saturated areas. In the subarctic, porous organic soils allow for rapid delivery of rainwater to the stream, and bypass flow, either through soil pipes (Carey and Woo, 2000) and other preferential pathways (Quinton and Marsh 1998), does exist. However, the premise that event water can reach the stream channel from areas within the catchment without altering its hydrochemical or isotopic composition is considered unlikely (Bazemore et al., 1994). Both two- and three-component separations indicate that approximately 8% of event-water contributes to stormflow and that the remaining mix is dominated by mineral water. Application of the three-component hydrograph separation provided some ambiguity in evaluating the relative importance of the organic-layer contribution, which is likely due to: (1) potentially non-conservative nature of DOC and SpC; (2) their variability within the catchment; (3) obtaining end members from suction lysimeters can overestimate DOC and SpC, as tightly bound pore water, not leachate water, may be sampled (Swistock et al., 1990). There is also uncertainty regarding the degree to which water sampled from the saturated zone, especially at slope-base locations, represents the water from the organic or mineral layer. In a study conducted at several arctic and alpine sites, including Granger basin, Quinton and Gray (2001) demonstrated that both the depth to the frost table and the thickness of the organic soil can vary by more than 200% within 1 m. As water drains down a hillslope through the saturated layer, it encounters a wide variation of depth positions within the soil profile, including different soil layers. Therefore, water sampled in riparian zones may have a mixed chemical and isotopic signature. With regard to the present study, an isotopically representative water sample of each soil layer may be difficult, as samples obtained from dip-wells are potentially affected by both soil layers, even though the saturated layer within the well might be entirely within one layer or the other.

There are significantly lower DOC concentrations within riparian zone and waters at the hillslope base (S1 and N1), suggesting that water reaching the stream via saturated flow in the organic layer is depleted in DOC in relation to the values from the suction lysimeters. However, even using values at the minimum range of DOC within the organic layer, the stream shows only a slight rise in DOC during summer storms, and both δ^{18} O-DOC and δ^{18} O-SpC three-component separations indicate flow through the organic soils is a minor component of summer stormflow generation. This conflicts with conceptual models developed from hydrometric work in similar subarctic settings, which suggest that summer rainfall reaches the stream rapidly via quickflow in

the organic layer (Dingman, 1971; MacLean *et al.*, 1999; Carey and Woo, 2001a). It is important to note that most successful applications of three-component hydrograph separations were performed for small basins with areas less than 1 km² (Bazemore *et al.*, 1994; Hinton *et al.*, 1994; Rice and Hornberger, 1998) and that the method has provided inconclusive results in larger catchments (Hoeg *et al.*, 2000). Furthermore, Rice and Hornberger (1998) showed that the combination of different tracers often leads to inconsistent results, making additional hydrometric data necessary to develop an accurate understanding of runoff processes. At the scale of Granger basin ($ca \ 6 \ \text{km}^2$), there may be other sources of water that were not identified due to the limited spatial sampling that complicates the application of three-component hydrograph separation. Spatial variability of δ^{18} O within upper soils is potentially large due to evaporative enrichment, which likely varies significantly in this topographically complex basin. Furthermore, the presence of late-lying snowdrifts may impart certain areas with a distinct isotopic ratio. However, the similarity in isotopic ratio among the different soil horizons, slopes and baseflow suggests the catchment is well mixed, likely due to the large snowmelt inputs that typically finish by early to mid June. Finally, despite low observed intrastorm variability in δ^{18} O, there is some error associated with the infrequent temporal sampling of event water, as McDonnell *et al.* (1990) clearly show the impact of event sampling frequency on hydrograph separations.

Summer runoff mechanisms

The stormflow response for both events was similar hydrochemically and isotopically, suggesting like mechanisms are controlling runoff generation during the summer. However, the fact that the runoff ratio declined from 0.43 for Storm 1 to 0.12 for Storm 2, despite Storm 2 having three times the rainfall of Storm 1, indicates a strong soil water and/or frost control on the total volume of lateral water movement. The small surface-saturated area of the catchment cannot explain event water contributions of ca 8% indicated by hydrograph separations. Well data show that the water tables reside in near-surface organic layers, especially at lower slope locations, indicating that rapid flow within the organic layer provides water for streamflow by nature of its higher hydraulic conductivity (Figure 2), allowing some event water (possibly through preferential or bypass flow) to reach the stream with little mixing. Both two- and tree-component separations indicate an overwhelming portion of stormflow water exists within the catchment prior to the event. Three-component hydrograph separations show that flow through the mineral substrate, not the organic layer, dominates stormflow response. Whether significant mixing between mineral- and organic-layer water occurs during storms, thus reducing the apparent organic flow contributions, is unclear. The hydrological and hydrochemical interaction between the riparian zone and the hillslope is an area of considerable uncertainty, and the extent to which the riparian zone modifies hillslope DOC and water chemistry is potentially large. McGlynn and McDonnell (2003) found no evidence that riparian zones exhibit DOC flushing in a temperate catchment, and that the temporally dynamic mixing of spatial sources of runoff controlled the observed patterns of runoff at both the slope and small catchment scale.

The near-surface position of the phreatic surface controls the larger volumes of runoff observed in Storm 1, as the concept of transmissivity feedback (Bishop, 1991) applies to organic-covered permafrost slopes (Quinton *et al.*, 2000). As summer progresses and water tables fall deeper within the porous organic soil, more precipitation must be applied to raise water tables and increase runoff rates and ratios. The descent of the frost table on permafrost-underlain slopes moderates water table positions, encouraging enhanced drainage compared with permafrost-free slopes (Carey and Woo, 2001a). On the permafrost-free Sf-slope, the water table was significantly lower at upslope locations, indicating reduced runoff, yet remained near the surface in riparian zones. Using hydrochemical and isotopic methods, it was not possible to distinguish between slopes with seasonal frost and permafrost.

Future research direction

Whereas hydrometric evidence appears to confirm concepts of runoff generation developed for permafrost and subarctic slopes (Dingman, 1971; Quinton and Marsh, 1999; Carey and Woo, 2001a), water chemistry and

hydrograph separation complicate previous perceptions of runoff processes. Both two- and three-component hydrograph separations confirmed that approximately 8% of event water reached the stream during the stormflow hydrograph and that the mineral layer dominates the remaining fraction. However, issues of spatial variability in source water, end members and the conservative behaviour of tracers must be more rigorously evaluated before more precise contributions from the organic layer can be determined. The interaction between the hillslopes and riparian zone is of particular interest, and is an area that remains largely unexplored in permafrost settings. Literature from more-temperate zones suggests moisture-controlled connections and disconnections between hillslopes and riparian zones and within-storm dynamics of chemical signatures (Branfireun and Roulet, 1998; McGlynn and McDonnell, 2003). Whether these processes occur within permafrost slopes is unclear, although Carey and Woo (2001a) do show declining contributing areas at the slope scale from changes in stormflow recession characteristics.

SUMMARY

Stable isotope (δ^{18} O) and hydrochemical (DOC, SpC) data were used in combination with hydrometric data to evaluate the sources and pathways of summer stormflow generation in a mountainous subarctic catchment with discontinuous permafrost. Results from two- and three-component hydrograph separations indicate that event water contributes less than 10% of stormflow. Utilizing δ^{18} O-DOC and δ^{18} O-SpC data, two-tracer three-component hydrograph separations were performed to isolate rainfall, water within the organic layer and water within the mineral layer contributions to stormflow. Three-component separations suggest that flow from the mineral layer dominates the stormflow hydrograph, yet the contribution of organic-layer water varies based on the selection of tracers. Water table data suggest that flow within organic layers, particularly from permafrost slopes, supplies stormflow. However, streamflow DOC concentrations do not increase as would be expected if rapid flow through the organic layer occurs. More integrated studies are required to establish a greater understanding of hillslope processes in this environment.

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