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Dissolved Organic Carbon Fluxes in a Discontinuous Permafrost Subarctic Alpine Catchment

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ABSTRACT

The sources and fluxes of dissolved organic carbon (DOC) were investigated within a subarctic catchment with discontinuous permafrost (Granger Basin, Yukon) from 23 June 2001 to 22 June 2002. During spring freshet, stream DOC increased rapidly on the rising limb of the hydrograph, peaked prior to maximum discharge, then declined exponentially to pre-baseflow levels while flows remained high. During summer storms, a similar pattern was observed whereby DOC increased on the ascending hydrograph limbs and peaked prior to maximum flows. Suction lysimeter and well data indicate that most of the DOC was mobilized from within near-surface organic soils. Comparisons between permafrost and seasonal frost slopes indicate that permafrost slopes are a greater source of DOC due to their thicker organic soils and wetter antecedent conditions that promote lateral flow in the shallower soil layers of the active layer. In contrast, slopes with seasonal frost encourage percolation and sorption of DOC in deeper mineral layers. Mass balance estimates of DOC export using actual and extrapolated data from regressions of DOC versus discharge indicate that 1.64 g C m^{-2} was exported from Granger Basin during the study year, 69% of this occurred during the 13 May to 22 June snowmelt period. Copyright © 2003 John Wiley & Sons, Ltd.

KEY WORDS: hydrology; dissolved organic carbon; runoff; subarctic; permafrost; seasonal frost; active layer; Yukon

INTRODUCTION

Dissolved organic carbon (DOC) is an important part of ecosystem-scale carbon balances and in the transport of dissolved substances and trace metals (McDowell, 1985; Worrall *et al*., 1997). Two primary sources of DOC to headwater streams are leached DOC from plants in throughfall and DOC derived from the decomposition of organic matter and plants within the soil (Thurman, 1985). Of these, DOC concentrations are typically greatest in water within organic-rich upper layers of the soil profile and decline with depth (Boyer *et al*., 1997; Worral *et al*., 2002). Low concentrations of DOC in groundwater are typically explained through chemical adsorption in mineral soils and biological degradation (Jardine *et al*., 1989; Qualls and Haines, 1991).

Estimates of DOC export vary widely depending upon catchment properties (see Fraser *et al*., 2001: Table 1). On an annual basis, large export terms (>20 g C m^{-2} yr^{-1}) result when precipitation greatly exceeds evapotranspiration and water yields are high (*e.g.* Moore, 1989; Collier *et al*., 1989) or upland area greatly exceeds wetland area (Niaman, 1982; Urban *et al*., 1989). Conversely, DOC export is smaller (<10 g C m^{-2} yr^{-1}) when the catchment is dominated by peatland, relief is negligible, and/or precipitation and evapotranspiration values are similar (McKnight *et al*., 1985; Moore, 1987; Koprivnjak and Moore, 1992).

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In the subarctic region of North America where precipitation and evapotranspiration are similar on an annual basis (Carey and Woo, 2001a), other factors such as the presence of frozen ground (both permanent and seasonal) and the widespread occurrence of organic soils likely act as a control on DOC export. Additionally, the role of snowmelt is of particular interest as approximately a third to half of the annual precipitation is released during a few short weeks in spring. Where permafrost is present, near-surface runoff pathways within organic soils predominate as perennial frozen ground and ice-rich layers act as a barrier to deep percolation (Carey and Woo, 2001b; Quinton and Marsh, 1999). During melt, the water table is at or near the surface and within the porous organic layer, rapidly delivering meltwater to the stream. As thaw progresses, runoff declines and the phreatic surface drops atop the frost table into less permeable organic and mineral layers, increasing subsurface residence time and decreasing runoff rates (McNamara *et al*., 1998; Carey and Woo, 2001b). By the end of summer and early fall prior to freeze-back, the water table can be several decimetres from the surface and completely within the mineral layers. During winter, lateral flows become negligible until spring thaw when meltwater infiltrates the frozen organic soils, raising the water table back to the surface and initiating runoff. This annual cycle likely controls DOC flushing to subarctic streams.

In the boreal forest zone of subarctic Alaska, MacLean *et al*. (1999) reported that a permafrost-dominated watershed had higher concentrations and fluxes of DOC, but lower concentrations and fluxes of solutes (Ca^{2+}, Mg^{2+} and Na^{+}) than an adjacent watershed nearly free of permafrost. In the permafrost-dominated watershed, water was restricted to the organic-rich active layer and enriched in DOC, yet in the catchment with low permafrost coverage, water infiltrated deeper into mineral soils where DOC was adsorbed and solutes were dissolved due to greater contact with soil exchange sites. Petrone *et al*. (2000) observed DOC and NO_3^- response during two summer storms for the high and low permafrost watersheds studied by MacLean *et al*. (1999) and an additional watershed that had 30% of its area burned. In all cases, DOC increased with increasing discharge during the storm event, and the catchment with the highest percentage of permafrost had the greatest DOC increase. The reason inferred for this increase in DOC is overland flow or subsurface flow through peat layers in the permafrost-underlain valley bottoms of each stream.

Despite the aforementioned research in central Alaska, there is scant information from discontinuous permafrost catchments evaluating the controls on DOC flushing from hillslopes to the stream. Furthermore, there has been no estimate of the annual DOC export from small subarctic alpine catchments. Using a small headwater catchment with discontinuous permafrost, the objective of this study was to: 1) investigate the mechanism whereby DOC is flushed to the stream during spring freshet and summer rainfall events, 2) evaluate what roles permafrost and frozen ground play in DOC flushing, and 3) provide a first-order estimate of annual DOC export.

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). Climate records from the Whitehorse airport (elevation 703 m a.s.l.) indicate that the study area has a subarctic continental climate characterized by large temperature range and low precipitation. The mean January and July temperatures are −21 °C and +15 °C. Mean annual precipitation is *ca.* 270 mm, half of which falls as rain (Wahl *et al*., 1987). Hydrological investigations carried out since 1996 suggest that Whitehorse airport precipitation may underestimate basin precipitation by *ca.* 25 to 35% (Pomeroy and Granger, 1999).

Granger Basin drains an area of *ca.* 6 km^2 and ranges in elevation from 1310 to 2250 m a.s.l.

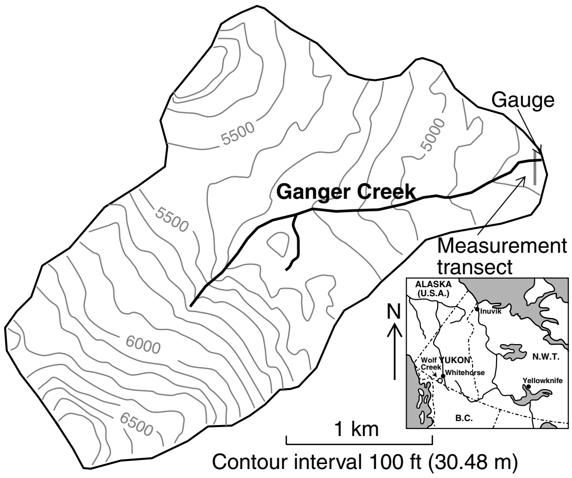

Figure 1 Study catchment (Granger Basin) within the Wolf Creek Research Basin and location of the well/tension lysimeter transects. Inset shows location in Canada.

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. The basin is overlain with 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. Permafrost is found under much of the north-facing slopes and higher elevation areas, whereas seasonal frost predominates on southerly exposures. In permafrost zones 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 above treeline (*ca.* 1200 m a.s.l.). Vegetation consists predominantly of assorted willow shrubs (*Salix*) and Labrador tea (*Ledum groenlandicum*). A small perennial snowpack exists on the upper reaches of Mt Granger on the western edge of the catchment.

Two slopes separated by the river valley were selected to compare catchment areas with and without permafrost. A permafrost-underlain north-facing (Nf-slope) slope has a gradient *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 ± 0.09 ($n = 30$)) and declines in thickness upslope from the riparian areas.

FIELD AND ANALYTICAL METHODS

The study period was defined as the water year from 23 June 2001 to 22 June 2002. During this year, two intensive study periods occurred during the summer (24 June to 30 July, 2001), and snowmelt (20 April to 7 June, 2002). Discharge was calculated using a stage-discharge relationship for the open-water period 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. During the snowmelt period when flows are beneath ice, salt dilution was used to determine discharge (Dingman, 1994). Salt dilution was continued into the open-water season whereby measurements were compared to the stage-discharge relationship and current metering. Over-winter discharge was estimated by drawing a recession line between the final open-water measurement and the first salt dilution measurement in the spring.

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 to a depth of 0.75 m and four within the seasonal frost Sf-slope to a depth of 1 m. Wells were spaced *ca.* 40 m apart along the slope length and numbered sequentially upward from the riparian zone (*i.e.* well N3 was in well farthest from the stream on the permafrost-underlain Nf-slope). Wells were then purged for a 2-wk period prior to the 2001 measurement period and were left in place over the winter. 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 summer study period. Suction lysimeters were removed at the end of the 2001 study season to prevent freezing and cracking of the ceramic cup.

During the summer 2001 period, DOC concentrations were measured in the stream, suction lysimeters and groundwater wells two to three times per week. During storm events, stream water was sampled every 2 hr using an ISCO water sampler. Samples were removed from the sampler within 24 hr. To obtain suction lysimeters samples, the instruments were sealed under a vacuum as 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. Rainfall and throughflow collectors consisting of plastic gutters were used to collect precipitation.

For the 2002 melt period, streamflow samples were collected several times weekly until the onset of freshet. Once freshet began, samples were collected a minimum of once daily. There were no suction lysimeters installed due to freezing conditions. Wells were sampled using the aforementioned method a minimum of twice weekly. Snowmelt lysimeters were installed at the base of the snowpack at three locations and sampled weekly to evaluate snowpack DOC.

All DOC samples were filtered through pre-combusted 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.

Methods of Calculating DOC Export

DOC export was calculated using two methods. For the 2002 snowmelt period, DOC concentrations were interpolated to make 15 min estimates using a nearest neighbour routine. Export was then calculated every 15 minutes using the stage-discharge relationship and the interpolated DOC concentration. For the 2001 summer and over-winter period, a regression equation between DOC concentration and stream discharge was combined with discharge values to provide an estimated DOC record for the entire discharge measurement period. Hinton *et al.* (1997) provides a detailed examination of the regression method for determining DOC export and the underlying assumptions and errors.

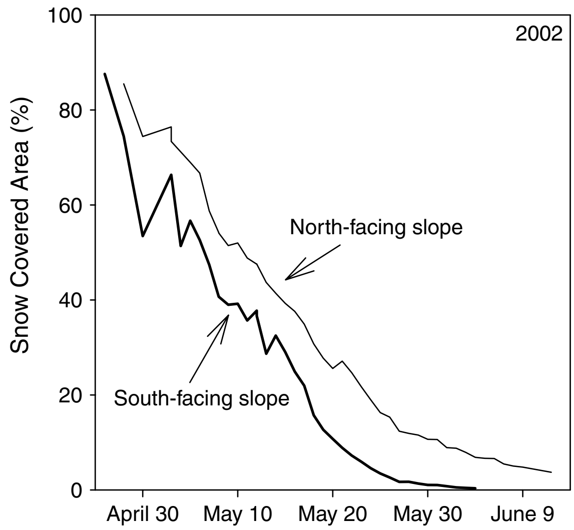

Figure 2 Snow covered area for the north- and south-facing study slopes during the 2002 snowmelt season.

RESULTS 1: SNOWMELT PERIOD

Snowpack

Pre-melt snow surveys on 19 April 2002 yielded a snow water equivalence of 297 ± 141 mm on the Nf-slope compared with 177 ± 0.62 mm on the Sf-slope. The greater snow accumulation on the Nf-slope is attributed to a large drift that formed just beneath the slope crest *ca.* 120 m from the river. Snow-covered areas (Figure 2) show that the Sf-slope depletes much faster than the Nf-slope due to increased radiation receipt; a trend that has been observed elsewhere within the Wolf Creek Basin (Carey and Woo, 1998).

DOC concentration in snowmelt water ranged from below 0.1 mg C L^{-1} to 1.9 mg C L^{-1}, with a mean of 0.24 mg C L^{-1}. Highest DOC concentrations were located at a melt lysimeter at the base of the Nf-slope where considerable shrub vegetation existed. There was no temporal trend in DOC concentration within snowmelt waters.

Table 1 Dissolved organic carbon (DOC) concentration from groundwater wells obtained during the snowmelt period, 2002. N are north-facing wells underlain with permafrost and S are south-facing wells with seasonal frost only.

	DOC Concentration (mg C L^{-1})						
Date	*N*1	*N*2	*N*3	*S*1	*S*2	*S*3	*S*4
9-May-02				33.1			
11-May-02					35.5		
12-May-02							
14-May-02							
15-May-02					21.4	15.5	
16-May-02	78.9			27.2			
18-May-02	50.1	37.3	42.7	18.9		20.1	7.3
21-May-02	30.9	22.0	36.4	13.4		15.8	7.7
25-May-02	20.9	16.6	22.6	10.9		17.5	5.6
29-May-02	13.9	16.5	20.2	5.3	23.8	13.1	3.1
1-June-02	17.7	22.7	16.2	5.3		10.1	5.1
4-June-02	13.2	22.7	19.5	4.7	15.6	9.1	4.5
8-June-02				5.2	13.0	8.3	4.4

Subsurface

DOC variation was pronounced within hillslope soils as concentrations decreased rapidly during the spring melt period in all near-surface sampling wells (Table 1). Initial sampling date varied based upon when wells became snow free and/or when water appeared within the wells that were cleared of snow cover. Wells S1 to S4 in the Sf-slope had high DOC concentrations immediately following the disappearance of the snowpack when water tables were at or near the surface, averaging 25.8 ± 9.7 mg C L^{-1} between 10 and 15 May. Following this, water tables slowly fell and concentrations declined to an average of 7.8 ± 4.4 mg C L^{-1} between 1 and 5 June. There was some relation between DOC and hillslope position as the concentrations in the riparian zone declined more rapidly compared with upslope positions. A notable exception was site S4 that had low DOC levels throughout melt, likely due to the absence of an appreciable organic layer ($<$0.05 m). The development of a saturated zone in the permafrost-underlain Nf-slope was delayed by several weeks due to slower melt. DOC concentrations were significantly higher throughout the duration of melt, averaging 55.4 $\pm$ 21.3 mg C L^{-1} between 15 and 20 May and declined to 19.1 $\pm$ 4.5 mg C L^{-1} between 1 and 5 June despite water table remaining near the surface (Table 1). Unlike the Sf-slope, there was no apparent correspondence among DOC concentration, water table, and topographic position.

Stream

The 2002 snowmelt freshet period lasted from 13 May to 1 June (Figure 3). Prior to the onset of freshet, flows were their lowest annual level at *ca.* 10 L s^{-1}. On 13 May, discharge slowly began to rise until mid-day on 16 May when a sudden increase occurred. Discharge again rose abruptly to *ca.* 400 L s^{-1} on 17 May and stayed at that approximate level until 24 May when a rapid increase to a peak freshet value of 1480 L s^{-1} occurred over 8 hr. Following this peak, the daily minimum flows began to gradually decline until 1 June. Superimposed atop the seasonal melt pattern are large daily cycles caused by the diurnal variability in snowmelt. Following 1 June, daily melt cycles were small and flow returned to post-freshet summer levels.

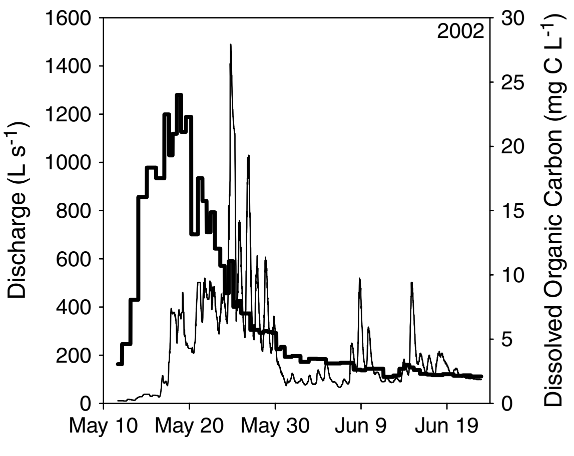

Figure 3 Discharge (thin line) and dissolved organic carbon concentration (heavy line) measured at the gauge for the spring freshet period, 2002.

Prior to the beginning of freshet on May 13, DOC concentrations remained stable between 2 and 3 mg C L^{-1}. After streamflow began to slowly increase, DOC concentrations rose rapidly to a maximum of 24 mg C L^{-1} on 18 May, 6 days before peak discharge (Figure 3). Following this DOC peak, concentrations declined exponentially, reaching pre-freshet concentrations in early June whereafter DOC responded much less to changes in discharge. The relation between DOC and discharge exhibited large hysteresis during the melt period as values on the rising limb were significantly greater than those on the receding limb at equivalent discharges.

RESULTS 2: SUMMER PERIOD

Precipitation

Precipitation samples above the canopy were collected on six occasions, and in each case, DOC concentrations were below 0.1 mg C L^{-1}, eliminating precipitation as a significant source of DOC to the catchment. Two rainfall collectors placed below the birch-willow shrub canopy approximately equidistant between the slopes had a mean DOC concentration of 0.7 $\pm$ 0.4 mg C L^{-1} ($n = 6$).

Subsurface

Interstitial waters sampled using suction lysimeters within the Nf-slope showed a sharp transition in DOC concentration at the organic/mineral interface (Table 2). Pore water obtained at N2 and N3 within the organic layer (0.1 and 0.2 m level) had an average DOC concentration of 39.7 $\pm$ 7.1 mg C L^{-1} on 24 June and declined gradually over the summer period

Table 2 Dissolved organic carbon (DOC) concentrations in soil water within the permafrost-underlain north-facing slope, summer 2001.

	DOC Concentration (mg C L^{-1})							
	Site N2				Site N3			
Depth (m)	0.10	0.20	0.30	0.40	0.10	0.20	0.30	0.40
24-Jun-01	42.4	46.5	7.2		29.9	39.8	6.2	
3-Jul-01	39.3	38.2	6.1		26.2	42.4	5.5	
10-Jul-01	24.7	38.4	6.2		21.1	32.3	5.7	
15-Jul-01	19.9	30.2	4.9	2.9		30.4	5.9	3.3
21-Jul-01		29.6	8.2	4.2		27.8	4.4	3.4
30-Jul-01		24.2	4.3	4.1		23.2	5.2	3.3

to 23.7 ± 0.7 mg C L^{-1} on 30 July. As summer progressed and near-surface soils dried, samples could not be obtained from the 0.1 m level. DOC concentrations within the upper mineral soils (0.3 and 0.4 m level) were significantly lower, averaging 5.1 ± 1.4 mg C L^{-1} for all samples taken during the summer study period. Unlike the upper organic soils, there was no apparent temporal trend in DOC concentrations within the mineral substrate. Shallow wells on the Nf-slope had gradually declining DOC concentrations throughout the summer period from 22.0 ± 4.4 mg C L^{-1} on 24 June to 13.4 ± 3.2 mg C L^{-1} on 30 July (Table 3).

DOC concentrations within the Sf-slope were lower both within the upper organic and mineral soils compared with the Nf-slope (Table 4). At the riparian site S1, DOC concentrations within the upper organic soils (0.1 and 0.2 m) declined from a maximum of 7.7 ± 0.6 mg C L^{-1} on 2 July to 3.7 ± 0.6 mg C L^{-1} on 30 July. Differences in DOC obtained from suction lysimeters in the mineral substrate were less variable, averaging 2.3 ± 0.8 mg C L^{-1} for the study period. Site S3 had greater contrast between the organic and mineral soils, yet no apparent temporal trend in DOC concentration. For the summer study period, DOC concentration averaged 12.9 ± 2.3 mg C L^{-1} for the organic soil samples compared with 2.4 ± 0.6 mg C L^{-1} for those obtained from the mineral soils. Within the near-surface wells, DOC concentrations averaged 9.8 ± 2.8 mg C L^{-1} on 24 June and declined to 5.2 ± 1.9 mg C L^{-1} by 30 July (Table 3). Unlike the Nf-slope, there was an apparent trend in DOC concentrations related to hillslope position. Water obtained from the riparian area at the slope base had lower DOC concentrations compared with upslope wells. However, at well S4, a water table was not present within the top 1 m by 15 July.

Table 3 Dissolved organic carbon (DOC) concentration from groundwater wells obtained during the summer period, 2001. N are north-facing wells underlain with permafrost and S are south-facing wells with seasonal frost only.

	DOC Concentration (mg C L^{-1})						
Date	N1	N2	N3	S1	S2	S3	S4
24-Jun-01	17.2	25.1	24.0	6.6	10.1	14.2	8.6
29-Jun-01	22.3	21.0	18.6	5.9	11.2	8.2	8.5
3-Jul-01	15.6	24.0	7.9	4.2	12.1	6.5	7.0
6-Jul-01	16.0	19.9	14.4	3.9	7.7	3.8	7.4
10-Jul-01	14.4	19.3	16.1	4.5	11.3	4.4	7.1
15-Jul-01	15.4	12.5	17.8	2.9	7.7	7.2	
20-Jul-01	9.1	18.2	16.5	3.7	6.6	6.3	
25-Jul-01	10.8	15.4	13.3	2.2	7.2	8.0	
30-Jul-01	10.4	16.3	14.0	2.6	6.7	6.4	

Stream

During the summer study period (24 June to 29 July, 2001), streamflow DOC was sampled 103 times; a minimum of once daily and at 2 hr intervals during three stormflow events (Figure 4). Baseflow DOC concentrations were much lower than freshet values and showed only a small decline during the study period, ranging from 2.4 to 2.0 mg C L^{-1} (Figure 4). During the three monitored stormflow events, increasing DOC concentrations to values above 3 mg C L^{-1} were observed.

A positive trend between DOC and streamflow was observed (Figure 5). As during snowmelt, a hysteretic relation between DOC concentration and discharge occurred whereby DOC increased rapidly on the ascending hydrograph limb, typically peaking prior to discharge. Once reaching a maxima, DOC concentrations declined despite continued increase and fluctuations in the stormflow discharge.

Table 4 Dissolved organic carbon (DOC) concentrations in soil water within the south-facing slope, summer 2001.

	DOC Concentration (mg C L^{-1})									
	Site S1					Site S3				
Depth (m)	0.10	0.20	0.30	0.40	0.50	0.10	0.20	0.30	0.40	0.50
24-Jun-01	6.2	7.6	3.1	2.9	2.0	12.2	13.1	2.8	2.2	1.6
3-Jul-01	7.3	8.1	2.4	3.3	1.6	14.5	17.2	3.4	2.1	1.9
10-Jul-01	6.6	5.9	3.3	2.7	1.9	10.7	15.6	3.3	2.4	2.0
15-Jul-01	5.6	5.2	4.1	1.5	1.8	12.2	14.4	2.9	1.9	2.1
21-Jul-01	4.2	4.4	2.1	1.4	1.8	10.2	13.7	2.9	2.6	1.8
30-Jul-01	3.3	4.1	1.4	1.8	1.8	9.6	12.0	3.1	2.7	1.9

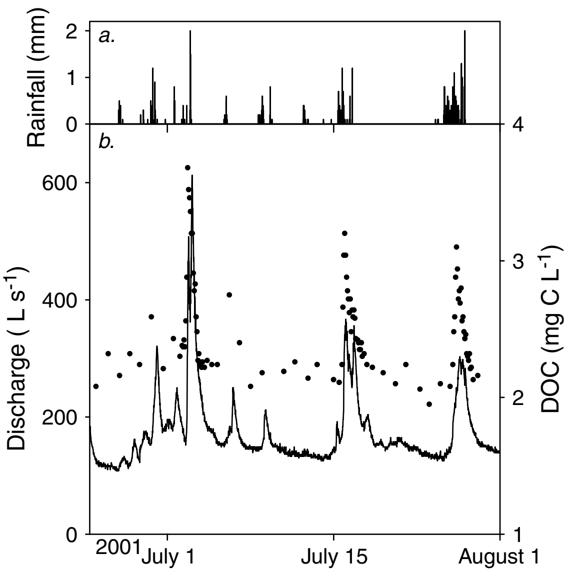

Figure 4 (a) Rainfall amounts and (b) streamflow discharge (solid line) and dissolved organic carbon (DOC) concentration (dots), summer 2001.

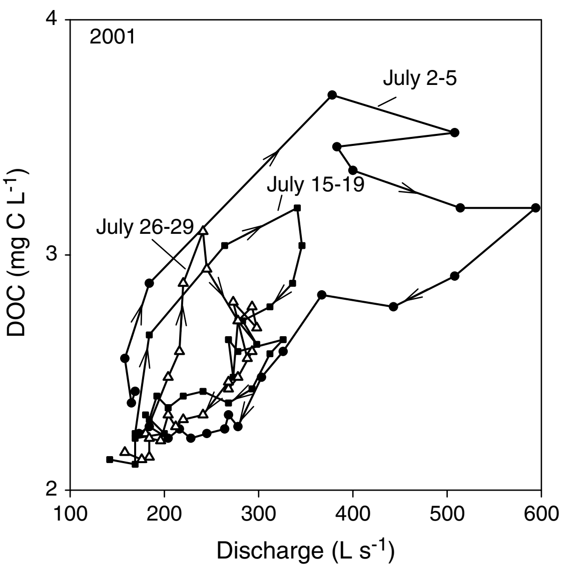

Figure 5 Dissolved organic carbon (DOC) versus discharge for three summer rainstorm events. Arrows indicate the clockwise trend of the DOC versus discharge relationship during the event.

For the 5.4 mm 2–3 July storm, DOC values rose from 2.2 mg C L^{-1} to 3.7 mg C L^{-1} over 6 hr, cresting 2 hr before the first hydrograph peak. Following the first hydrograph peak (508 L s^{-1}), DOC declined continuously despite a second peak 8 hr later of greater magnitude (594 L s^{-1}) when DOC concentrations reached 3.2 mg C L^{-1}. On the descending limb of the hydrograph, DOC values returned to baseflow levels prior to the cessation of the stormflow event (Figure 5). Similarly, for the 8.2 mm 16–17 July event, DOC rose rapidly on the ascending limb from 2.2 mg C L^{-1} to 3.2 mg C L^{-1} and crested 2 hr prior to the first hydrograph peak (346 L s^{-1}). Following this peak, DOC declined to 2.6 mg C L^{-1}during the second hydrograph peak (326 L s^{-1}) 20 hr later. Following the second hydrograph peak, DOC declined steeply along the receding hydrograph limb. The third storm was the greatest in magnitude, depositing 24.1 mm between 26 and 29 July. DOC rose from a baseflow concentration of 2.1 mg C L^{-1} to 3.1 mg C L^{-1} in 10 hr on the ascending hydrograph limb, peaking 8 hr before the hydrograph peak at 298 L s^{-1}. Following the peak DOC concentration, values declined steeply despite a continued increase and then a gradual decrease of the stormflow discharge. However, the decline in DOC during the receding hydrograph limb was more protracted than the two previous summer storms, potentially due to the effects of the increased storm magnitude. An interesting observation is, despite the increase in storm magnitude among the three storms, there is a corresponding decline in the volume of stormflow from the runoff hydrograph. This may in part be explained by declining contributing areas as the catchment dries throughout the summer.

DOC EXPORT

Regression equations between DOC and discharge for the three summer stormflow events show considerable variability yet were not significantly different to the pooled estimates of DOC versus discharge for all 103 values that was used to construct 15-min DOC

Table 5 Regression between DOC concentrations and stream discharge during the summer sampling season. DOC concentrations in mg L^{-1} and stream discharge in L s^{-1}.

Period	Regression	r^2	*n*
2 July–5 July	[DOC] = 0.003 Q + 1.824	0.54	23
15 July–19 July	[DOC] = 0.004 Q + 1.622	0.65	28
26 July–29 July	[DOC] = 0.004 Q + 1.539	0.45	25
Entire Record	[DOC] = 0.003 Q + 1.795	0.61	103

concentrations from 23 June 2001 to 12 May 2002 (Table 5). For this 322 day period, total runoff was 252 mm and organic carbon export is estimated at 0.54 g C m^{-2}. During the snowmelt period, estimates of interpolated 15 min DOC concentration using a nearest neighbour function provided a more precise method of estimating DOC export than regression does, as discharge versus DOC during this period was poor (Figure 3). For the period of 13 May to 22 June 2002, the total DOC export is calculated as 1.10 g C m^{-2} and runoff was calculated at 131 mm. The total organic carbon export for the water year 24 June 2001 to 23 June 2002 is therefore estimated at 1.64 g C m^{-2} and total runoff for this period is estimated at 383 mm. Although there is considerable error in this estimate based upon the strength of the regression equation, the limited collection period and the over-winter flow interpolation, it does provide a first-order approximation of DOC loss from a headwater catchment with discontinuous permafrost.

DISCUSSION

In Granger Basin, flow through porous near-surface organic soils is the primary source of DOC to streamflow during both the snowmelt freshet and summer rainstorms. Concentrations of DOC within snowmelt waters are low and not considered a significant contributor to the stream. Snowmelt readily infiltrates porous organic soils, typically creating a zone of saturation above impermeable mineral or ice-rich layers deeper within the profile (Carey and Woo, 2001b). This water becomes enriched with DOC as near-surface soils have accumulated large stores of soluble carbon since their last flushing event, which is potentially as long as the previous spring for upslope areas. This water is then rapidly conveyed to the stream where a relatively large increase in streamflow DOC concentration is observed at the onset of runoff. DOC concentrations reach a peak soon after snowmelt freshet begins, and then decline exponentially as the catchment flushes soluble carbon from the organic layer. This pattern of DOC is typical in snowmelt-dominated catchments (Lewis and Grant, 1979; Denning *et al*., 1991; McKnight and Bencala, 1990; Boyer *et al*., 1997) and is accounted for by the finite terrestrial source of DOC that is flushed as meltwater moves through the organic soils.

The presence of permafrost influences DOC flushing during melt as slopes underlain with permafrost have thicker organic soils with higher pore-water DOC concentrations and restrict infiltration into deeper mineral layers, encouraging near-surface flow pathways (Slaughter and Kane, 1979; Carey and Woo, 1998; Quinton and Marsh, 1999). In contrast, slopes with southern exposures and seasonal frost are smaller contributors of DOC and near surface wells had significantly lower concentrations as organic layers are thinner and infiltration and percolation typically occurs unimpeded (Kane and Stein, 1983; Carey and Woo 1998) allowing meltwater to percolate into deeper mineral soils, where DOC immobilization by sorption occurs (McDowell and Wood, 1984; Koprivnjak and Moore, 1992).

For the summer period, baseflow provides the majority of flow and background DOC concentrations are similar to groundwater concentrations within the riparian zone. During rainstorms, increases in DOC within the stream indicate that near-surface pathways within porous organic soils become active, transporting DOC from the slopes to the stream. Patterns of summer stormflow DOC response are similar to those observed by Petrone *et al.* (2000) in Alaska and researchers in more temperate environments (Hinton *et al*., 1997). The hysteretic behaviour of discharge and DOC, with greater concentrations on the ascending hydrograph, support the concept that permafrost-underlain organic soils are flushed of accumulated soluble organic carbon as the water table rises into zones of aeration (Boyer *et al*., 1997). Once this organic carbon is flushed, concentrations decline, explaining the lower levels with similar corresponding discharge on the descending hydrograph. Despite increased rainfall volume for each progressive summer storm, discharge and DOC response became less. This is particularly notable for the 24.1 mm 26–29 July event that had the smallest hydrograph and DOC response of the three summer storms. Likely explanations for this pattern of runoff and DOC are: 1) declining contributing source throughout the summer as the catchment dries, 2) a greater emphasis on deeper flow pathways in mineral soils as thaw progresses, enhancing sorption and immobilization of DOC, and 3) depletion of soluble organic carbon in soils due to flushing from prior events.

Sampling DOC soil water indicates the near-surface organic layer is the primary source of terrestrial DOC to the stream. DOC concentrations decline sharply with depth on both slopes, although pore water was only obtained within the top 0.5 m on each slope. This decay in DOC concentration implies sorption was occurring within the top layers of the mineral soil and that near-surface flow explains increase in stream DOC concentrations during stormflow events. DOC concentrations within the permafrost-underlain Nf-slope are greater than the Sf-slope during the summer period, indicating that organic soils are the primary terrestrial source of DOC to the stream. Both rainfall and throughfall occur in concentrations much lower than streamflow.

Topographic position and differences in DOC dynamics between the riparian zone and the hillslopes did not show any conclusive patterns. Within the Sf-slope, the slope base and riparian zone had DOC concentrations decline more rapidly than upslope locations, suggesting near-stream areas flush more rapidly during melt (Boyer *et al.*, 1997). In contrast, the permafrost-underlain slope did not show a relation between DOC and topography.

The importance of snowmelt and near-surface flow within organic soils in flushing DOC and nutrients from terrestrial to aquatic systems has been previously reported (Hornberger *et al.*, 1994; Boyer *et al.*, 1997). The snowmelt period dominates DOC export, with *ca.* 67% of total DOC exported in a 6 wk period. This has important implications for estimates of annual DOC export using discharge versus concentration relations as they are poor during the snowmelt period when DOC is flushed prior to peak freshet. Annual DOC export is low compared with temperate wetland and forested-wetland (2.5 to 43.8 g C m^{-2} yr^{-1}) catchments reported by Fraser *et al.* (2001), and are also considerably lower than 9.6 g C m^{-2} yr^{-1} estimated for Deer Creek, a snowmelt-dominated alpine catchment in Colorado, USA (Boyer *et al.*, 2000). However, values are similar to those reported for a subarctic peatland (1.1 to 1.9 g C m^{-2} yr^{-1}) (Moore, 1987) and fen (1.2 g C m^{-2} yr^{-1}) (Koprivnjak and Moore, 1992).

In a paired catchment study, MacLean *et al.* (1999) showed that a forested permafrost-dominated catchment had greater DOC concentrations, but low dissolved minerals and conductivity compared with a predominantly seasonal frost catchment. A conceptual model for the effect of permafrost on nitrogen and DOC flushing (their Figure 8) was presented whereby permafrost reduces the passage of water though mineral soils and speeds its passage through soil/stream ecotones in the valley bottoms. In contrast, permafrost-free deciduous uplands have slow flow through mineral horizons and across valley bottoms, providing significant opportunity for adsorption and nitrogen mineralization. This conceptualization is applicable for the alpine catchment in this study, and despite their being much smaller vegetation differences between the slopes, the confining permafrost layer, the development of thick organic layers and rapid delivery of event water to the stream exert the greatest influence on catchment and streamflow DOC dynamics.

Sources of Error

Due to the limited spatial network of DOC sampling wells, uncertainty remains in how different areas of the catchment combine to influence DOC export. Boyer *et al.* (2000) modelled the effect of asynchronous melting on DOC flux, indicating that melting from different zones aggregate to control the stream DOC signal. In Granger Basin, permafrost increases with elevation, yet organic soils become thinner. However, in comparison with Deer Creek, Colorado, DOC freshet response in Granger Basin is much faster and declines while much of the catchment still has residual snow cover, suggesting that the lower-elevation zones monitored in this study are the principal zones responsible for DOC flushing. Additionally, the limited temporal extent of stream DOC discharge for mass balance reconstruction and only one year of data collection make the results presented here a preliminary estimate as significant inter-annual variability in DOC production can occur (Brooks *et al.*, 1999).

SUMMARY

The majority of allochtonous DOC to the stream in high-elevation subarctic catchment is controlled by the snowmelt flush of the soil DOC pool. Permafrost plays an important role in DOC flushing by inhibiting deep percolation and sustaining near-surface water tables during melt and throughout the summer. Additionally, suction lysimeter and well data indicate the presence of thick organic soils on permafrost slopes provides a large DOC source compared with slopes underlain with seasonal frost. An estimate of 1.64 g C m^{-2} yr^{-1} is low compared with more temperate catchments, likely reflecting lower heterotrophic processing of soil carbon in permafrost and cold environments.

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