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The Concentration and Fluorescence of Dissolved Organic Carbon (DOC) in Glacial and Nonglacial Catchments: Interpreting Hydrological Flow Routing and DOC Sources

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Abstract

The concentration and fluorescence characteristics of dissolved organic carbon (DOC) from surface waters in glacial and nonglacial catchments were used to investigate the provenance of DOC and flow routing of runoff from glacial and nonglacial environments. Seasonal trends in DOC concentration and fluorescence in the Bow River indicate that DOC in nonglacial runoff originates primarily from soil and plant organic matter that is flushed to the stream by shallow subsurface flow at the onset of snowmelt. Snowmelt in ice-free areas of the glacial catchment also appears to be routed through the shallow subsurface, but this snowmelt runoff has much less contact with organic soils or litter, than snowmelt runoff from the nonglacial catchment. The fluorescence of DOC in the Glacial stream in summer (when most runoff originates from ice-covered areas), suggests that DOC from glaciated regions is more “microbial” in character than that derived from ice-free areas. Summer rainstorms in the Glacial catchment flushed DOC derived from catchment soils and plants by displacing concentrated pre-event waters from the shallow subsurface to the stream.

Introduction

The chemical composition of surface waters reflects their hydrological pathway and their source. The concentration of dissolved organic carbon (DOC) and its spectrofluorometric properties have proven to be useful tools for investigating the flow routing of snowmelt, and the sources of DOC in runoff (Boyer et al., 1997; McKnight et al., 2001; Newson et al., 2001). In this study we examine the concentration and the fluorescence of DOC in the surface waters (snowmelt, soil, and stream waters) of adjacent glacial and nonglacial catchments. Our goal is to investigate differences in the provenance (and abundance) of DOC in runoff from glacial and nonglacial environments and their implications for hydrological flow routing.

Snowmelt runoff may be routed through the soil profile or as overland flow (where the saturation or impermeability of soils limits infiltration, or where the snowpack is underlain by glacier). In alpine streams, DOC consists primarily of carbon that is leached from plant litter and soils by infiltrating snowmelt, and flushed to streams by shallow subsurface flow (Hornberger et al., 1994; Boyer et al., 1997). During a typical flushing event, stream DOC concentrations ([DOC]) increase dramatically at the onset of snowmelt, peak prior to maximum stream discharge, and then decrease to near premelt values by the end of the summer (Lewis and Grant, 1979; Hornberger et al., 1994; Boyer et al., 1997; Hood et al., 2003). Conversely, soil pore waters display a decrease in [DOC] during snowmelt, and begin to recover to higher values towards the end of the summer (Boyer et al., 1997), which is likely due to heterotrophic decomposition of soil organic matter as soil temperatures increase (Savage and Davidson, 2001).

On glaciers, snowmelt percolates downwards through snow and firn until it reaches the underlying ice surface. It then flows down slope

until it either leaves the glacier surface or encounters a crevasse or moulin (Fountain and Walder, 1998). Most meltwater intercepted by crevasses and moulins drains via major englacial or subglacial conduits and has little interaction with subglacial sediments (Hubbard and Nienow, 1997). Some surface-derived runoff and meltwaters produced by basal melting may, however, drain by a more extensive distributed drainage system (consisting of thin water films, linked cavities, and/or permeable subglacial sediments) that allows more significant water-sediment interaction. Waters routed through this component of the subglacial drainage system may make a significant contribution to runoff under recession flow conditions and early in the melt season before major drainage channels have developed. Although, subglacial environments can support bacterial populations, subglacial sediments typically contain very low amounts of organic carbon (Sharp et al., 1999; Skidmore et al., 2000). This organic carbon is probably derived from glacially overridden soils, bedrock kerogen, or inwash from the glacier surface and valley walls (Sharp et al., 1999; Skidmore et al., 2000; Margesin et al., 2002; Säwström et al., 2002; Takeuchi, 2002). Although, we are not aware of any published reports of [DOC] in glacial runoff, we expect [DOC] to be relatively low, since most runoff probably has limited contact with organic matter.

It is possible to qualitatively differentiate DOC that is derived primarily from terrestrial precursor material (from soil or plant organic matter) from DOC that is of microbial origin (either from algal and bacterial precursor material and/or the by-products of microbial activity) using spectrofluorometric techniques (McKnight et al., 2001). The fluorescent properties of DOC vary with the aromatic carbon content of fulvic acids (Chin et al., 1994; McKnight et al., 2001). In rivers and alpine streams fulvic acids generally account for 30 to 70% of the DOC (Thurman, 1985; Hood et al., 2003). DOC derived from terrestrial sources contains fulvic acids from plant litter and soil organic matter, which are generally more aromatic (because of aromatic components such as lignin) than fulvic acids formed from the components of microbial cells and by-products of microbial activity

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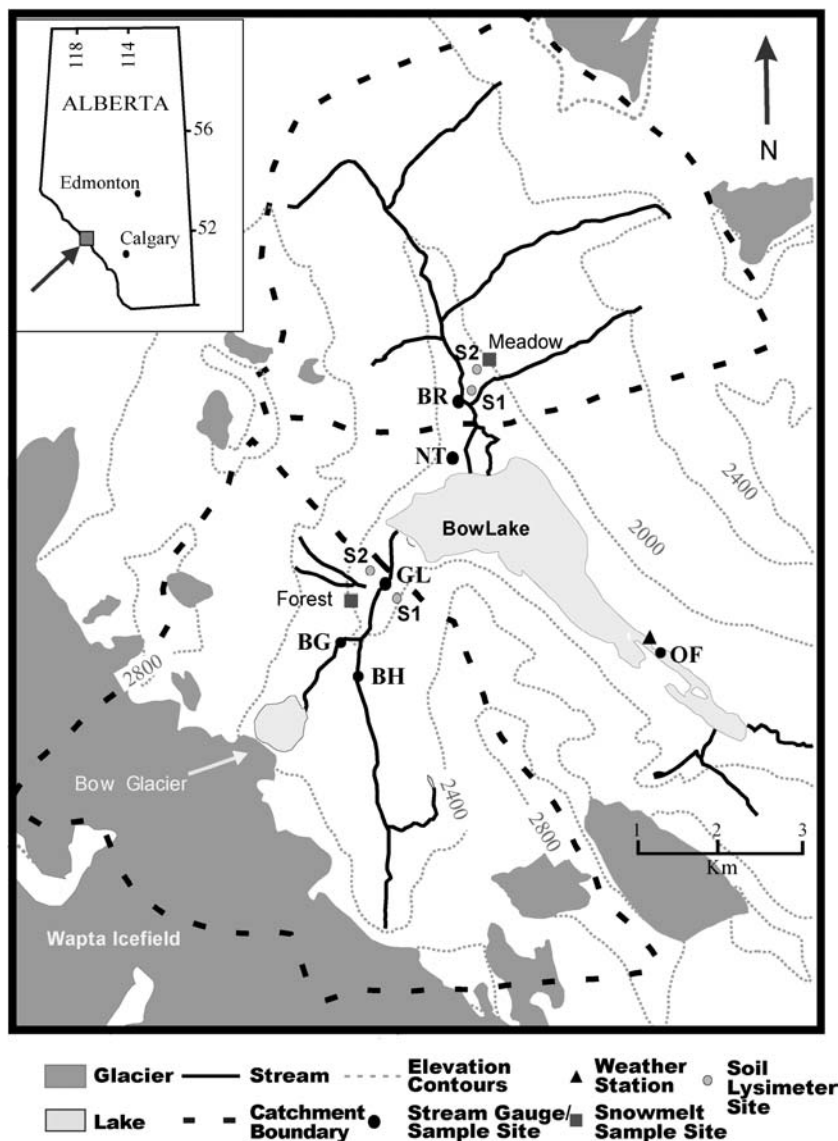


FIGURE 1. Map of Bow Lake, showing the stream sampling (and gauging) locations for the Glacial stream (GL), the Bow River (BR), the Bow Glacier tributary (BG), the Bow Hut tributary (BH), Numtjihah Lodge well water (NT), and the lake outflow (OF). Snowmelt and soil lysimeter sites are also shown.

(Harvey et al., 1983; Visser, 1983; Chin et al., 1994; McKnight et al., 1994; Wagner and Wolf, 1999). The spectrofluorometric character of DOC can therefore help to determine the flow routing of runoff by indicating the general source of the fulvic acid fraction of the DOC in different catchments. DOC in streams fed by snowmelt runoff from vegetated areas of both glacial and nonglacial catchments will likely be composed of fulvic acids derived primarily from plant litter and soil organic matter. Most fulvic acid from the surface of a glacier will likely be primarily of microbial origin (e.g., primary productivity of algae and bacteria in cryoconites or snow; Margesin et al., 2002; Takeuchi, 2002). Old plant-derived carbon may provide an energy source for microbial populations in subglacial soils and sediments (Welker et al., 2002), but its characteristics are likely changed considerably over time due to recycling within the microbial ecosystem. In absence of continued inputs of terrestrially derived organic matter, microbial biomass may become an important component of the organic carbon reservoir within subglacial sediments (Wetzel, 1992; Wagner and Wolf, 1999). Thus, glacial runoff may contain DOC derived primarily from microbial activity (i.e. from the decomposition of microbial biomass, by-products of microbial metabolism, and/or primary productivity). To our knowledge, this is the first paper to examine

the concentration and fluorescence of DOC in glacial runoff, and to compare the patterns of seasonal variation in these parameters in runoff from adjacent glacial and nonglacial catchments.

Site Description and Instrumentation

The study was conducted at Bow Lake, Banff National Park, Alberta, Canada (51°40'N, 116°27'W). Two main catchments feed Bow Lake; one is substantially glaciated, the other is virtually unglaciated (<1.5% ice cover) (Fig. 1). The principal inflow to the lake is the Glacial stream (GL), fed primarily by meltwater from the Wapta Icefield. This catchment is approximately 27 km², with a mean elevation of 2560 m a.s.l. Twelve percent of the catchment is forested and overlain by soils with developed mineral horizons (brunisols and podsoles) and some organic matter accumulation (Holland and Coen, 1982). The rest consists of glacier ice (41%, 11 km²), till, and moraines on which soils are absent or poorly developed (i.e. regosols). The Glacial stream is a secondary stream with two tributaries, the Bow Hut (BH, 37% glaciated; 42% rock, till, and moraine; 21% forested) and the Bow Glacier (BG, 75% glaciated; 24% rock, till, and moraine; <1% forested). The source of the tributaries is the Wapta Icefield (Fig. 1).

From the snout of Bow Glacier, the BG stream falls approximately 100 m down a cliff into a proglacial lake, the outflow from the lake then falls another 120 to 150 m, from here the stream flows over bedrock until it encounters till a short distance from the base of the cliff. The residence time of water in the proglacial lake is estimated to be ~40 d. The BH stream originates in the valley southeast of Bow Glacier and flows over glacial till and bedrock. The GL stream also flows through glacial till. This stream was gauged and sampled approximately 800 m away from the canyon where the tributaries merge (Fig. 1). The secondary nonglacial inflow, the Bow River (BR), flows through a subalpine meadow and drains into the north side of Bow Lake. This catchment has a mean elevation of 2310 m a.s.l.. Its area is approximately 17 km², of which 67% consists of subalpine meadow and spruce-fir forests. The remaining area is sparsely vegetated (29%) or unvegetated (2%). The soils are primarily developed mineral soils with some organic horizons (63% of the catchment is overlain by brunisols, podsols, and gleysols). Soils are absent or poorly developed in the rest of the catchment (Holland and Coen, 1982).

DOC samples were collected from the Glacial stream and the Bow River approximately every 3 to 7 d during the spring and summers of 1998, 1999, and 2000 (the stream sampling locations are the same as the stream gauging stations, as shown in Fig. 1). Occasionally, multiple samples (up to 5) were collected in a single day (between approximately 0800 h and 2100 h) to monitor diurnal variability. In 1998 and 1999 the Bow Hut and Bow Glacier streams were also sampled every 3 to 7 d. In 1999 and 2000 well-water samples were collected from Numtjih Lodge (NT), located on the north side of Bow Lake (Fig. 1). During the 2000 snowmelt period (April–July 2000), DOC samples were collected from the snow, snowmelt, and soil lysimeter sites (Fig. 1).

The discharge of the Glacial and Bow River streams was also monitored during the summers of 1998, 1999, and 2000. Gauging stations on each stream recorded hourly and daily averages of 10-s measurements of stage using a Keller 169 pressure transducer and Campbell CR10 datalogger. The stage records were converted to discharge using rating curves based on discharge measurements made by the velocity area method. The error associated with the discharge measurements is estimated to be ±10% (Dingman, 1993).

Eight tension soil lysimeters were installed at four sites in August 1999. Sites were chosen in order to sample a range of soil types in the lake catchment that might have different flow regimes during snowmelt. There were two sites (S1 and S2) in each of the Glacial and Bow River catchments (Fig. 1). Two lysimeters were installed at each site, one at 24 cm depth and one at 12 cm depth. Tension lysimeters consisted of a PVC tube fixed to a porous ceramic cup. The top of the tube was sealed with a rubber cap fitted with an extraction tube. Lysimeters were soaked overnight in deionized (DI) water and then rinsed in DI water prior to installation in the field. Each lysimeter was evacuated once prior to sampling in spring 2000. Samples were extracted using a hand-held vacuum pump and HDPE tubing that was cleaned by rinsing with 30% hydrogen peroxide and DI water. To minimize contamination and disturbance of the surrounding snowpack, soil lysimeters were not sampled until the snowpack at each site was very thin (<25 cm).

Two snowmelt collectors were installed in October 1999 (Fig. 1). One was installed in an area surrounded by mixed spruce/fir forest (Forest), the other was installed in the subalpine meadow, where nearby vegetation consists of grass, willows, and sedges that are snow covered until late spring (Meadow). The collectors consisted of Plexiglas “troughs” installed on a fixed base at a slight angle. These troughs collected meltwater that drained through an outlet directly into a covered plastic 10-L bucket. The wood base was sunk a few centimeters into the ground, and the bucket was housed in an insulated box in a hole below the ground surface. The troughs and plastic

buckets were soaked and rinsed in DI water, then covered and sealed in clean plastic until field installation was complete. Snowmelt was sampled by carefully digging out the box and dispensing the contents of the bucket into sample bottles. Solid snow samples were collected from pits dug near the snowmelt collector.

Sampling and Analytical Methods

Stream, snowmelt, and soil water samples were filtered on-site using glass filtration apparatus and Whatman GF/F glass fiber filters. The filtrate was transferred to amber glass EPA vials, acidified to pH 2 with HCl, and refrigerated until analysis. Prior to sampling, vials were rinsed with DI water and combusted overnight at 550°C. The filtration apparatus was soaked and rinsed with 30% hydrogen peroxide, DI water, and sample between each use. Snow was collected by inserting clean wide-mouth glass jars (rinsed in DI water and combusted overnight at 550°C) into the face of a snowpit. Snow samples were stored frozen, and melted, filtered, and acidified just prior to analysis.

[DOC] was measured as nonpurgeable organic carbon (NPOC) by high temperature combustion (680°C) with a Shimadzu TOC 5000A analyzer equipped with high a sensitivity platinum catalyst. The detection limit (Miller and Miller, 1988) for the analysis of snow and stream samples was 0.19 ppm, based on the analysis of sample blanks (DI water that was filtered, stored, and analyzed as field samples, $n = 6$). Based on duplicate determinations of similar samples, the uncertainties in the precision of the measurements ($P < 0.05$) were ±0.07 ($n = 7$), ±0.02 ($n = 9$) and ±0.03 ppm ($n = 5$), for 1998, 1999, and 2000 samples, respectively (Kretz, 1985). Soil solution samples from the tension lysimeters were diluted to [DOC] < 3 ppm with DI water (1:5 or 1:10 dilutions) before DOC analysis. DOC concentrations reported for soil solutions were corrected for the concentration of DOC in DI water used in the dilution. The uncertainty for soil water DOC was ±0.21 ppm ($P < 0.05$), based on duplicate determinations ($n = 13$) (Kretz, 1985).

The fluorescence of the DOC was measured using a Shimadzu RF-1501 scanning spectrofluorometer with a xenon lamp. Samples were scanned in an optically clear quartz cuvette (path length = 1.000 cm). Scans were performed at an excitation wavelength of 370 nm, for emission wavelengths between 370 and 700 nm at 1-nm increments. Scans of sample blanks of DI water were performed, and the blank fluorescence values were subtracted from the raw scans of the samples in order to remove the effects of Raman scattering (Donahue et al., 1998; McKnight et al., 2001; Wolfe et al., 2002). After subtracting the blank, the fluorescence index (FI—the ratio of emission intensity at 450 nm to 500 nm for an excitation of 370 nm), the peak intensity of fluorescence, and wavelength of peak fluorescence (λF_{\max}) were determined. The FI has values of ~1.9–2.0 for predominantly microbial DOC, and values of ~1.4 for DOC with predominantly terrestrial sources (Donahue et al., 1998; McKnight et al., 2001; Newson et al., 2001). The λF_{\max} also varies according to provenance, with microbial DOC peaking at lower wavelengths (~445 nm) than soil/vegetation derived DOC (~455 nm) (McKnight et al., 2001). Uncertainties for FI and λF_{\max} were 0.03 and 4.7 nm ($P < 0.05$, $n = 24$), respectively, based on the analyses of duplicate samples (Kretz, 1985). McKnight et al. (2001) indicate that, in general, a change in FI of at least 0.1 is necessary to suggest a difference in source of fulvic acids.

The oxygen isotopes ($\delta^{18}\text{O}$) of water were measured on a VG MM 903 triple Faraday cup collector mass spectrometer at the Environmental Isotope Laboratory (EIL) at the University of Waterloo, Ontario, Canada. The EIL uses the standard procedure for oxygen isotopes (Epstein and Mayeda, 1953). All $\delta^{18}\text{O}$ results are reported as per mille (‰) VSMOW (Vienna Standard Mean Ocean Water). The uncertainty in the measurements is ±0.1‰ based on 11 duplicate analyses. Cation concentrations were determined by ion chromatography

TABLE 1

[DOC] sample statistics by site: Bow River (BR), the Glacial stream (GL), the Bow Glacier tributary (BG), Bow Hut tributary (BH), Numtjih Lodge well water (NT). Soil sites are identified by catchment (BR or GL), site (S1 or S2, as in Fig. 1), and lysimeter depth (12 or 24 cm). All concentrations are in ppm.

1998	BR	GL	BH	BG					
Mean	0.91	0.44	0.53	0.44					
SD	0.36	0.14	0.45	0.18					
N	11	10	9	13					
Min	0.50	0.32	0.29	0.24					
Max	1.63	0.71	1.09	0.95					
1999	BR	GL	BH	BG	NT				
Mean	1.18	0.36	0.37	0.23	0.34				
SD	0.46	0.14	0.07	0.11	0.06				
N	22	22	11	11	2				
Min	0.36	0.15	0.26	0.14	0.30				
Max	1.95	0.77	0.45	0.52	0.38				
2000	BR	GL	BH	BG	NT	Meadow Snow	Meadow Melt	Forest Snow	Forest Melt
Mean	1.41	0.39			0.44	0.28	0.57	0.41	1.70
SD	0.37	0.12			0.07	0.12	0.42	0.18	1.54
N	24	29			6	6	7	6	6
Min	0.44	0.17			0.37	0.14	0.22	0.26	0.75
Max	2.12	0.71			0.56	0.46	1.38	0.68	4.69
2000	BR S1-12	BR S1-24	BR S2-12	BR S2-24	GL S1-12	GL S1-24	GL S2-12	GL S2-24	
Mean	40.3	9.9	30.5	17.7	11.3	11.0	15.7	12.9	
SD	22.5	7.9	7.9	9.9	8.6	8.2	10.8	9.9	
N	8	11	7	9	9	9	5	6	
Min	20.1	4.8	17.5	10.1	4.9	4.5	6.2	6.2	
Max	83.5	23.4	39.0	31.6	24.9	24.1	32.2	25.8	

on a Dionex DX500 ion chromatograph equipped with a CRSR-Ultra self-regenerating suppressor, and CS-12A analytical and guard columns. The uncertainties in the ion concentrations ($\mu\text{eq}\cdot\text{L}^{-1}$) were estimated using analyses of 16 duplicate samples run on separate days (Kretz, 1985). The uncertainties were (SE $\mu\text{eq}\cdot\text{L}^{-1}$, CV% in brackets, $P < 0.05$): $\text{Mg}^{2+} \pm 19$ (2%), $\text{Ca}^{2+} \pm 25$ (2.0%).

TABLE 2

Statistics (mean \pm SD) for DOC concentration and fluorescence properties by site: Bow River (BR), Glacial (GL), Numtjih Lodge well water (NT), soils (BR S1-24 cm), and snowmelt. The Suwannee River fulvic acid (FA) and aquatic natural organic matter (NOM) are reference materials obtained from the International Humic Substances Society (IHSS).

Site	N	[DOC] (ppm)	FI	λF_{max} (nm)
BR	16	1.25 \pm 0.59	1.47 \pm 0.03	453 \pm 3
GL	17	0.35 \pm 0.15	1.64 \pm 0.13	440 \pm 13
NT	6	0.44 \pm 0.08	1.66 \pm 0.02	443 \pm 8
BR S1 -24cm	6	5.17 \pm 0.36	1.49 \pm 0.01	453 \pm 2
GL S1 -24cm	7	10.67 \pm 8.95	1.48 \pm 0.04	454 \pm 2
Meadow Melt	6	0.43 \pm 0.25	1.71 \pm 0.22	431 \pm 14
Forest melt	6	1.70 \pm 1.54	1.45 \pm 0.21	454 \pm 6.2
Suwannee River				
Fulvic Acid	1	19.0	1.26	464
Suwannee River NOM	1	14.7	1.24	464

Results

VARIABILITY BETWEEN SITES

In the Bow River, [DOC] ranged from ~ 0.4 to 2.1 ppm, and the mean [DOC] was usually more than double that found in the other streams (Table 1). In the Glacial stream and its tributaries (BH and BG) [DOC] was always < 1 ppm (Table 1). In 1999, the mean [DOC] for these three streams were similar to that in groundwater sampled at the lodge (NT). The mean [DOC] in snow was also similar to the mean [DOC] of the glacial streams. Snowmelt was, however, enriched in DOC relative to the snow samples. [DOC] in the soil lysimeter samples was 5 to 10 times higher than [DOC] in other surface waters (Table 1).

The mean values for fluorescent properties (FIs and λF_{max}) and [DOC] for each sampling site are listed in Table 2; reference material for Suwannee River fulvic acid (FA) and aquatic natural organic matter (NOM) are also listed. The Suwannee River reference materials have much lower FIs (1.26 for FA and 1.24 for NOM) and higher λF_{max} (464 nm) than any other samples in this study (Table 2). However, the FI and λF_{max} of the Suwannee River reference materials are similar to those of the Suwannee River fulvic acid cited in McKnight et al. (2001).

TABLE 3

The fluorescent properties of DOC in the GL, BG, and BH streams.

	FI	λF_{max} (nm)
BH 05/21/99	1.56	448
BG 05/21/99	1.53	448
GL 10/12/03	1.63	450
BH 10/12/03	1.66	453
BG 10/12/03	1.69	453

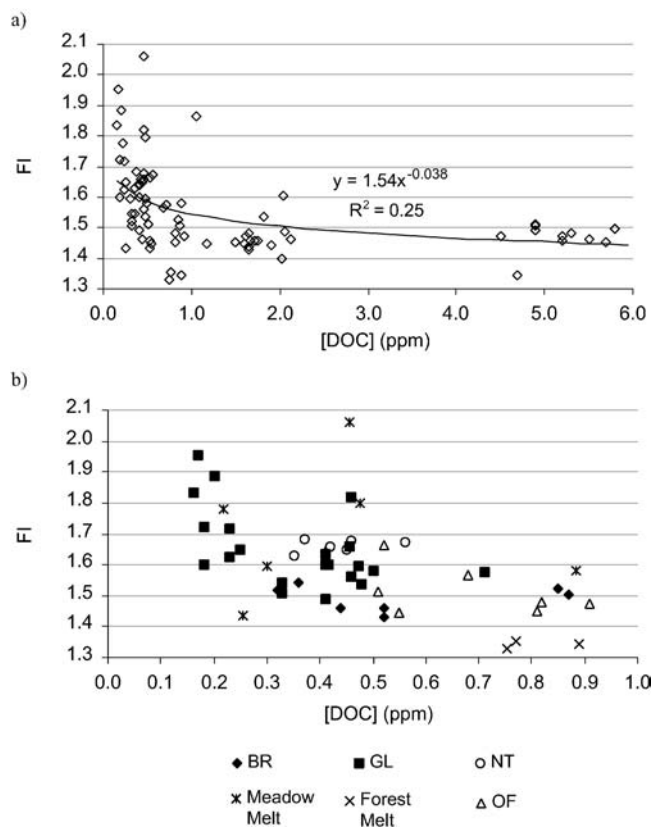


FIGURE 2. (a) FI vs. [DOC] for all samples grouped together. The two soil solutions with DOC > 20 ppm are not shown on the graph, but they were included in the derivation of the regression equation shown ($FI = a*[DOC]^b$). (b) FI vs. [DOC] by sample site (excluding soils).

The Glacial stream, the groundwater, and the Meadow snowmelt had the highest mean FIs (1.64–1.71) and lowest mean values for λF_{max} (~440–443 nm). The FI and λF_{max} for DOC from BG and BH streams were determined for samples collected in May 1999 and November 2003 (Table 3). On both occasions the fluorescent properties of DOC in the BG and BH streams were very similar to each other and to the GL sample in November 2003 (Table 3). The Bow River water, the soil pore waters from both sites, and the snowmelt from the Forest lysimeter defined the low end of the FI range (1.45–1.49) and the high end of the range for λF_{max} (~453–454 nm). In general, FI was inversely related to [DOC] (Fig. 2a). The regression (a power function) defining the relationship is significant at $P < 10^{-5}$, but weak ($R^2 = 0.25$). Thus, [DOC] does not account for a large proportion of the variability in FI. For example, even when [DOC] is similar in the Glacial stream and the Bow River, FI is usually higher in the Glacial stream samples than in the Bow River samples (Fig. 2b). Also, [DOC] in the soil solutions is significantly higher than in the Bow River, but the FI values are similar (Table 2).

The statistical significance of the differences in [DOC], FI, and λF_{max} between and within the various sampling sites was evaluated using a one-way analysis of variance (ANOVA). For all variables, there was more between site variability (for the two streams, groundwater, the two soils lysimeters, and the two snowmelts), than within site variability ($P < 0.01$). Post-hoc analysis was performed to determine which sites were significantly different from each other. Duncan's multiple range test (StatSoft, 1997) revealed that the fluorescent properties of DOC (FI and λF_{max}) from the Bow River were significantly different from those of the Glacial stream, the groundwater, and the Meadow snowmelt (FI was significantly lower,

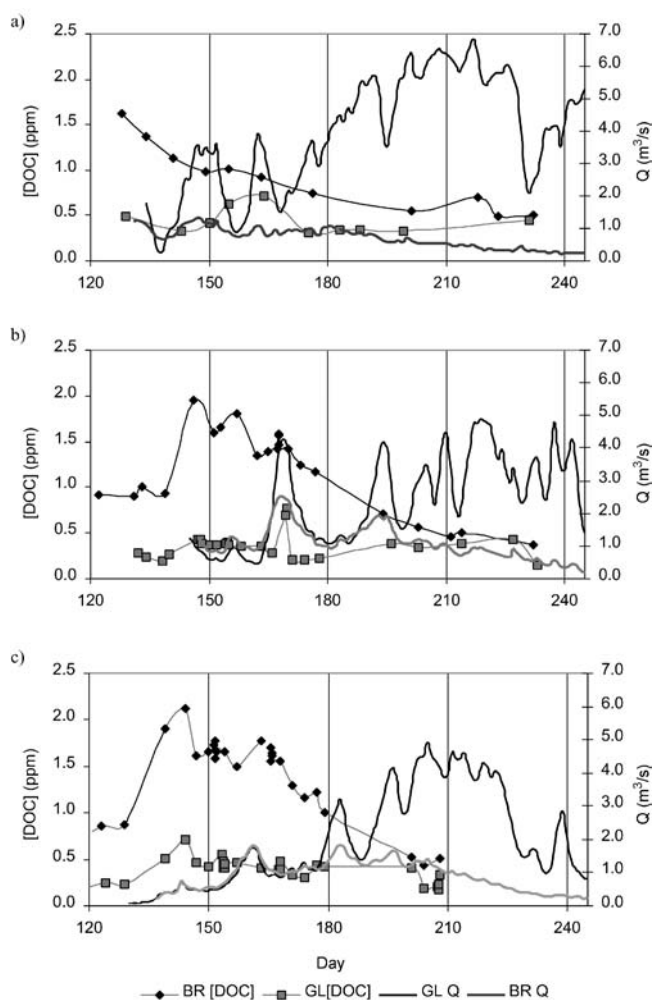


FIGURE 3. Stream [DOC] and discharge (Q) in the Bow River and Glacial stream May–August (a) 1998, (b) 1999, and (c) 2000.

and λF_{max} was significantly higher, $P < 0.05$). The Glacial stream DOC was significantly different from that from the Bow River, soil waters, and Forest snowmelt (FI was significantly higher, and λF_{max} was significantly lower). The fluorescence properties of Bow River DOC were therefore similar to those of the soils, while the fluorescence properties of the Glacial stream DOC were similar to those of DOC from the groundwater and Meadow snowmelt.

SEASONAL AND INTERANNUAL VARIABILITY OF STREAM [DOC]

Except for very late in the summer, [DOC] was much higher in the Bow River than in the Glacial stream (Fig. 3). In the Bow River, [DOC] showed a clear and consistent seasonal pattern every year, peaking at the start of the melt, prior to the peak in stream discharge (Fig. 3). For this stream, linear regressions of [DOC] against time for the period between the seasonal maximum and minimum are virtually identical for 1999 and 2000 ($DOC_{1999} = -0.022 * \text{days} + 5.10$, $r^2 = 0.94$, $P < 0.001$; $DOC_{2000} = -0.023 * \text{days} + 5.21$, $r^2 = 0.89$, $P < 0.001$). The pattern in 1998 was somewhat different, probably because snowmelt began before our sampling that year due to a thin winter snowpack and warm spring temperatures (Lafrenière and Sharp, 2003).

The Glacial stream showed a small increase in [DOC] coincident with the initial increase in stream discharge, but the magnitude and timing of the seasonal changes in [DOC] were inconsistent and ill

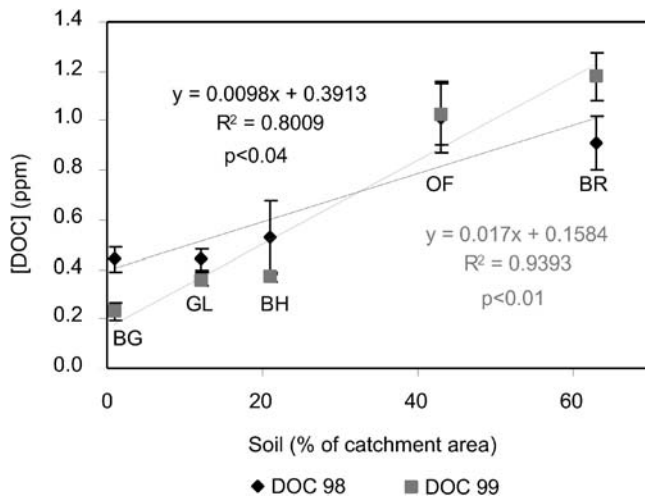


FIGURE 4. Relationship between mean [DOC] in stream waters (1998 and 1999) and the soil-covered area in each catchment. Error bars are the standard error of the means. The regression equations, correlation coefficients (R^2), and level of significance (p) are indicated.

defined (Fig. 3). The Glacial stream [DOC] always remained low in late summer despite the significant increase in runoff (Fig. 3). It is, however, difficult to estimate the degree of uncertainty associated with the last statement, given the low number of samples collected in late summer. The [DOC] in the Bow Hut tributary (BH) was usually marginally higher than in the Glacial stream, while [DOC] in the Bow Glacier tributary (BG) was slightly lower than in the Glacial stream (Table 2). There is a strong relationship between the mean stream [DOC] and the abundance of developed soils in the catchment drained by the stream (Fig. 4). This suggests that the mean [DOC] in a stream may be controlled by the availability of terrestrial carbon in its catchment, or by the fraction of the catchment that is overlain by developed soils (i.e. soils other than regosols).

[DOC] AND DOC FLUORESCENCE IN THE STREAMS

Although the Bow River has a much larger seasonal variation in [DOC] than the Glacial stream, the fluorescence of the DOC in the Glacial stream (as indicated by FI), is much more variable (both seasonally and diurnally) than that of DOC in the Bow River (Fig. 5). In the Bow River, FI was highest in the winter (1.50–1.54). FI in this stream decreased slightly (1.44–1.48) as [DOC] rose at the start of snowmelt, and then remained essentially constant through the rest of the summer (Fig. 5a). There was no diurnal variability in FI (1.46–1.45) in the Bow River despite relatively large changes in the [DOC] (1.75–1.59 ppm, day 151, Fig. 6a).

In the Glacial stream, the initial increase in [DOC] (from 0.23 to 0.71 ppm) coincident with the early snowmelt discharge (between days 123 and 143) was associated with a decrease in FI (from 1.72 to 1.58, Fig. 5b). The Glacial stream also displays significant variability in DOC fluorescence over diurnal and 2- to 3-d timescales (Fig. 5b). These variations in [DOC] and DOC fluorescence are examined in more detail and in conjunction with variations in discharge, Ca^{2+} , and $\delta^{18}\text{O}$ to try to understand their causes. The large decrease in FI (from 1.82 to 1.54) between days 153.50 (1200 h) and 153.63 (1500 h) was associated with decreases in both [DOC] and $[\text{Ca}^{2+}]$, and an increase in discharge (Fig. 6b). The decrease in FI at 1500 h, however, preceded the decreases in [DOC] (from 0.48 to 0.41 ppm) and $[\text{Ca}^{2+}]$ (from 1425 to 1333 $\mu\text{eq L}^{-1}$), which were not noticeable until the sample collected at 1800 h (day 153.75, Fig. 6b). There was no rain on day 153, so the

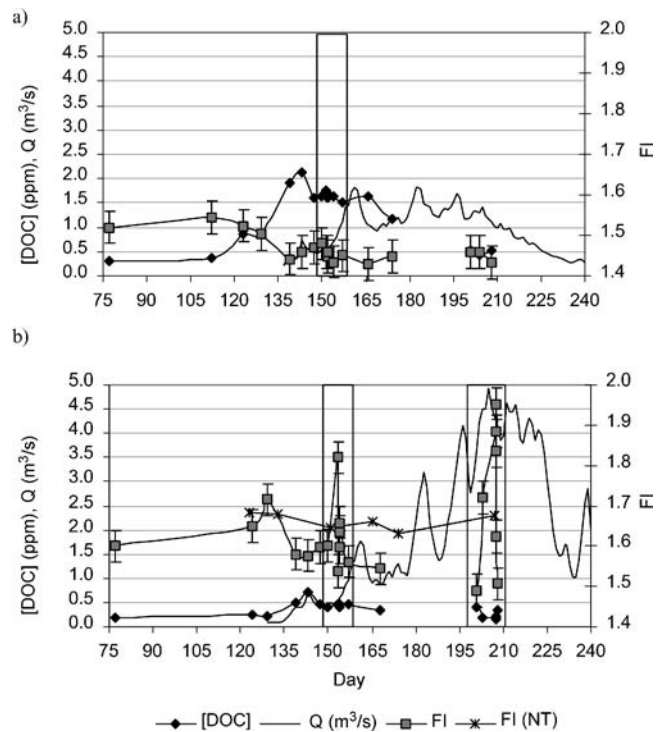


FIGURE 5. Seasonal trends in [DOC], discharge ($Q \text{ m}^3/\text{s}$) and fluorescence index (FI) in 2000 for (a) the Bow River and (b) the Glacial stream. The FI for groundwater (NT) is also included in (b). Error bars are the uncertainty (± 0.03) in the measurement of the FI as shown in Table 2. The boxed areas indicate the time series highlighted in Figures 6 and 7.

increase in discharge could only have been due to snowmelt runoff. This indicates that the afternoon snowmelt waters diluted the more concentrated “baseflow” water (as indicated by the decrease in $[\text{Ca}^{2+}]$ and [DOC]), but also provided enough terrestrial DOC to shift the FI towards lower values (1.82 to 1.54) despite decreasing the [DOC] (Fig. 6b).

Another dramatic change in the FI of the Glacial stream DOC occurred between days 201 and 207 of 2000 (19–25 July, Fig. 7a). During the first part of this period (between days 201 and 203, 19–21 July), discharge and FI increased, while [DOC] and $[\text{Ca}^{2+}]$ decreased (Fig. 7a). This discharge increase was likely due to snowmelt at higher elevations in the catchment and/or on the glacier surface, since there was no significant rain or snow at low elevations during this period. The increase in FI from terrestrial (FI = 1.49, day 201) to significantly more microbial values (FI = 1.72, day 203) at this time was opposite to that seen on day 153 (18 May), when $[\text{Ca}^{2+}]$ and [DOC] decreased with the increase in discharge, but FI shifted towards more “terrestrial” values (compare Figs. 7b and 8a).

On day 207 (25 July), when discharge increased as a result of a rainstorm late in the day, there was a corresponding increase in [DOC] and $[\text{Ca}^{2+}]$, but a decrease in FI of the DOC (Fig. 7b). There was also a dramatic increase in the stream suspended sediment load (field observations). This event differed from the previous ones in that the increase in discharge was associated with a slight increase in [DOC] and a significant increase in $[\text{Ca}^{2+}]$ rather than a dilution. This might suggest that the rain dissolved DOC from plant and soil organic carbon sources, and Ca^{2+} from fine sediments in the proglacial part of the catchment, and that the solutes, sediment, and DOC were probably delivered to the stream via overland flow. However, the stream chemistry also shows that following the rain (between 1700 and 2100

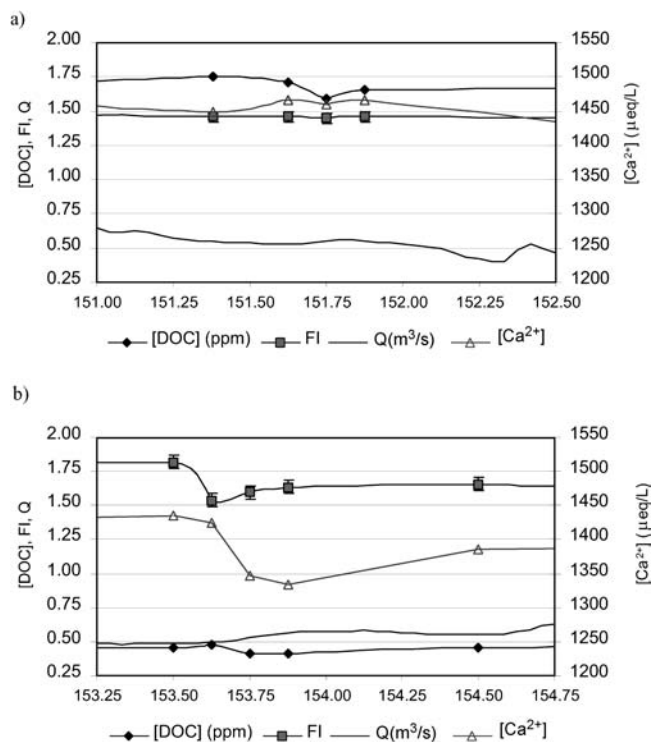


FIGURE 6. Diurnal variations in [DOC], FI, [Ca²⁺], and discharge (Q m³/s) in 2000 for (a) the Bow River (days 151–152) and (b) the Glacial stream (days 153–154).

h, day 207.71–207.88), there was an increase in the Mg²⁺:Ca²⁺ ratio (from 0.56 at 1700 h to 0.67 at 2100 h, Lafrenière, unpublished data). In addition, there was only a slight increase in the δ¹⁸O of stream runoff (from –20.8 at 1700 h to –20.5 at 2100 h), even though the δ¹⁸O composition of the rainwater collected at the weather station near the lake outflow (OF, Fig. 1) at 1900 h was much heavier (–13.4‰ VSMOW) than that of the stream runoff (mean = –20.7, SD ± 0.4‰, n = 21).

DOC IN SNOW AND SNOWMELT

The means for [DOC] in snow and snowmelt samples at the Forest site were higher than for snow and snowmelt samples at the Meadow site (Table 1). Snowmelt was enriched in DOC relative to the snowpack at both sites (Fig. 8a, b). The enrichment was usually greatest in the first fraction of the melt, but a very high [DOC] was also recorded near the end of the melt season at the Forest site (Fig. 8b). The fluorescent properties of snowmelt DOC were also very different at each site (Fig. 8c). FIs of snowmelt at the Meadow site were extremely variable (1.43–2.06), and there was no apparent seasonal trend, or relationship with [DOC] (Fig. 8c). The average FI and λF_{max} of the Meadow snowmelt suggest that DOC in snow at this site was primarily microbially derived (Table 2). In contrast, FIs of DOC from snowmelt at the Forest site were usually low (1.33–1.49) and relatively constant, with the exception of the last sample (day 154), when FI reached 1.87 (Fig. 8c).

DOC OF SOIL SOLUTIONS

With the exception of site BR S1-12cm, most of the soil waters had similar [DOC] (Table 1) and displayed the same seasonal trends (Fig. 9a, b). This lysimeter was disturbed over the winter, re-installed in the spring of 2000, and then flushed once prior to sampling. The differences in the trend and concentrations of DOC observed at this site

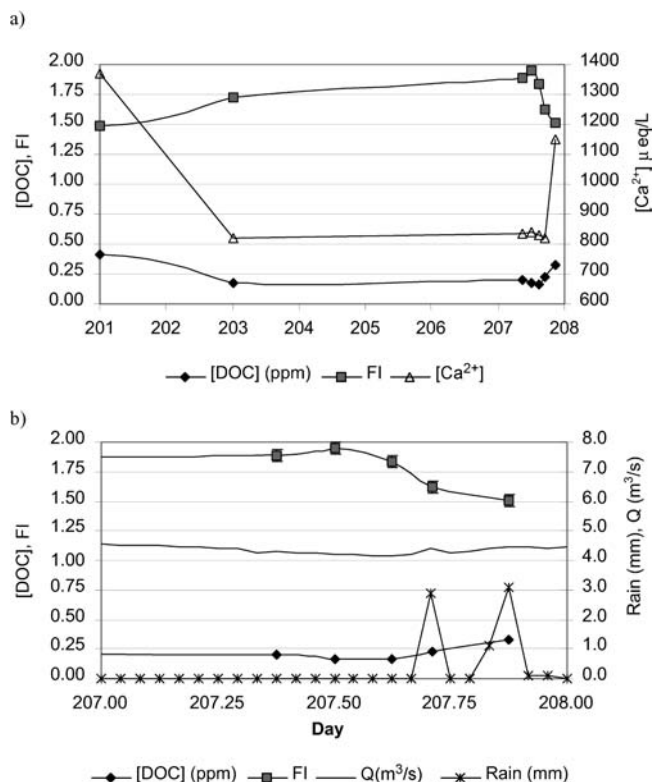


FIGURE 7. DOC in the Glacial stream, 2000. (a) [DOC], FI and [Ca²⁺] between days 201–208 (19–26 July) (b) Diurnal variations in [DOC], FI, rain (mm) and discharge (Q m³/s) on day 207 (25 July)

are, therefore, most likely due to this disturbance. Hence, the results from BR S1-12cm are not included in the subsequent interpretation and analysis.

The soil solutions from BR S2 had the highest [DOC], with minimum concentrations approximately twice those at other sites (Table 1). For all locations, the 12-cm lysimeter had higher mean [DOC] than the 24-cm lysimeter at the same site (Table 1). The higher [DOC] in the shallow soil layers is expected, since [DOC] normally decreases with increasing depth in the soil (Thurman, 1985). At all sites, [DOC] in soil solutions were low in June (5–10 ppm), and higher in July (20–40 ppm). Only a limited number of soil solution samples were available for fluorescence analysis because sample volumes were small (<8 ml) and most of the sample was required for [DOC] measurements. FIs for soil water DOC were relatively low and constant at both sites in mid summer (Fig. 9c). At lysimeter GL S1-24cm, FI increased at the end of summer, coincident with the increase in [DOC] (Fig. 9c). There was not enough sample to determine the fluorescence of the late summer samples from BR S1-24cm (Fig. 9c).

Discussion

There are significant differences in both the quantity and fluorescence of DOC exported by the Glacial stream and the snowmelt fed Bow River (Table 2). Compared to the Bow River, in which [DOC] can exceed 2.0 ppm in early spring, [DOC] in the Glacial Stream is low (0.2–0.8 ppm) and displays minimal seasonal variability (Fig. 3). However, the fluorescence of the DOC in the Glacial stream (as indicated by FI), is much more variable (both seasonally and diurnally) than that of DOC in the Bow River (Fig. 6). Values of FI and λF_{max} for the DOC in the Bow River runoff (Table 2) were very similar to those found in Deer Creek in the Colorado Rocky Mountains (FI 1.40–1.48, λF_{max} 452–454 nm, McKnight et al., 2001), but the FIs were higher

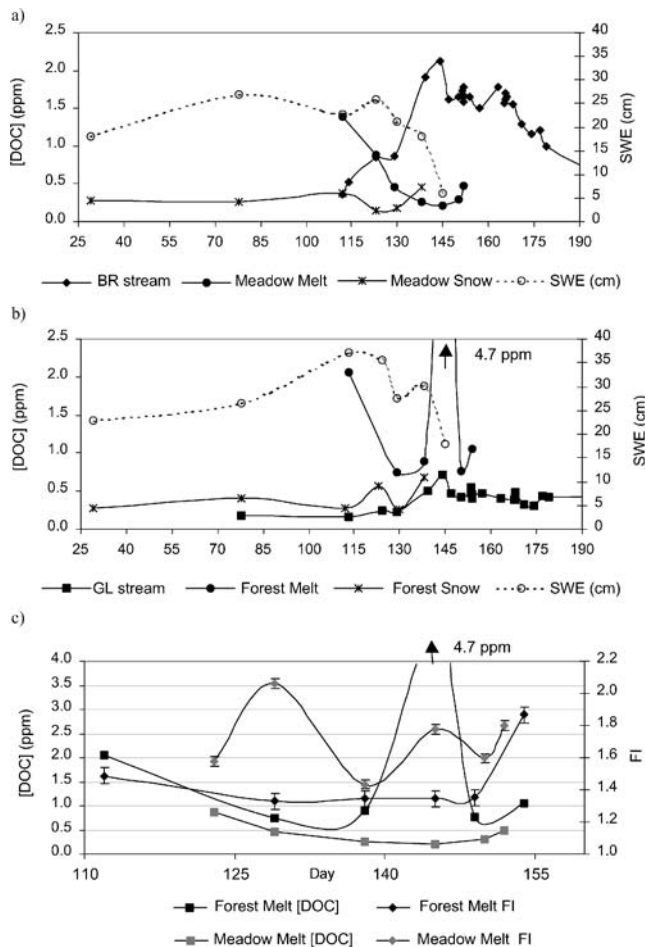


FIGURE 8. February–June 2000 (a) [DOC] for the Meadow snow, snowmelt, and stream [DOC] for the Bow River, with snow depth in SWE (cm); (b) [DOC] for the Forest snow, snowmelt, and stream [DOC] for the Glacial stream, with snow depth in SWE (cm); (c) Seasonal trends in [DOC] and FI for snowmelt.

and the λF_{\max} higher than the Suwannee River reference material (FI ~ 1.25 and λF_{\max} 464 nm, Table 2). FI values for DOC from the Glacial stream were, on average, relatively low (Table 2) compared to those of microbially derived DOC from lakes in the Antarctic (FI 1.7–2.2; McKnight et al., 2001). λF_{\max} values for most of the Glacial stream DOC samples are, however, in the same range as values for DOC from water samples from Antarctic Lakes (λF_{\max} 435–445 nm, McKnight et al., 2001) (Table 2).

The content and fluorescence of DOC in snow and snowmelt also vary significantly. It is likely that the higher [DOC] in the snow and snowmelt at the Forest site is a reflection of higher inputs of particulate organic carbon (POC) from surface litter and debris fall from the surrounding spruce/fir forest (Thurman, 1985; McKnight et al., 1993). The lower [DOC] in snow at the Meadow site can probably be explained by the fact that most of the vegetation (willows and sedges) is buried until near the end of the snowmelt period. Visual inspection of filter papers from snow DOC samples confirmed that there was substantially more particulate organic matter in snow from the Forest site. Although there was not enough material on the filters to quantify the inorganic and organic particulate fractions, the low pH of the snow (5.5–6.5) suggests that there was little inorganic (carbonate) particulate matter in the snow. The mean [DOC], FI and λF_{\max} also indicate that in areas where there is significant exposed vegetation, the DOC in snowmelt is likely derived from leaching of terrestrial POC contained within the snowpack (Table 2). In contrast, where vegetation is absent

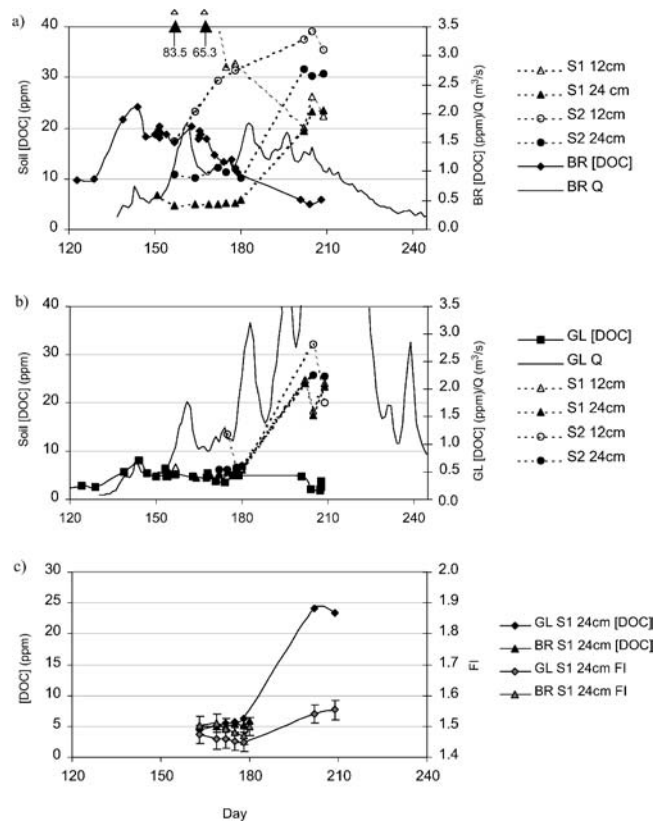


FIGURE 9. Soil water [DOC] and discharge (Q m^3/s) for (a) Bow River and (b) Glacial catchments (c) Soil water [DOC] and fluorescence index (FI)

or buried, snowmelt DOC appears to be predominantly of microbial origin (Table 2). The large variations in the FI in the snowmelt at the Meadow site suggest that, where vegetation is sparse, the input of plant derived organic matter to the snowpack is probably limited, heterogeneous, and intermittent, and that the variation in the fluorescence of the DOC is a reflection of frequent changes in the balance of DOC derived from plant matter and DOC of microbial origin.

The [DOC] in the Bow River displays a characteristic flushing response (Boyer et al., 1997) in all three years, reaching maximum values near the beginning of snowmelt, prior to the peak in stream discharge (Fig. 3). The decrease in FI at the start of the 2000 season indicates that the pulse of DOC in the Bow River at the onset of snowmelt was derived from terrestrial sources (Fig. 5a). However, the lowest FI of the Bow River DOC (Fig. 5a) is still significantly higher than that of the Suwannee River reference materials (Table 2). The higher FI (~ 1.52 – 1.55) for Bow River DOC prior to the onset of snowmelt suggests that groundwater (FI ~ 1.65) was a significant source of runoff and DOC at this time. The consistency in the amplitude of, and rate of recession from, the spring peak in [DOC] suggests that the flow routing and source of DOC do not vary appreciably from year to year, despite significant differences in the annual snowpack and spring air temperatures (Lafrenière and Sharp, 2003). Therefore, the seasonal trends in [DOC] and DOC fluorescence in the Bow River indicate that stream DOC originates primarily from soil and plant organic matter that is flushed to the stream by shallow subsurface flow.

The trend in [DOC] in the soil pore waters is also consistent with the flushing of DOC from soils during spring snowmelt (Boyer et al., 1997). The low [DOC] in June suggests that DOC is flushed from soils during spring snowmelt (Fig. 9a). The FIs of soil waters in the GL S1-24cm lysimeter indicate that, in the spring, DOC is derived primarily from leaching of plant litter and soil organic matter (Fig. 9c). The

increase in the FI of the soil water DOC in late summer is coincident with an increase in [DOC] (Fig. 9c). The observed increase in DOC in July may be partly due to evaporative concentration of DOC in the soil solutions as soils dry out over the summer. Nevertheless, an increase in DOC over the summer is also consistent with a build up of DOC in the soil water due to increases in soil temperature and the microbial decomposition of soil organic matter (Yano et al., 2000; Moore and Dalva, 2001). An increase in microbial activity in the soil should result in the production of plant derived fulvic acids (with low FI). However, in the absence of new inputs of plant derived substrates from surface soil horizons, the increase in microbial biomass (and fulvic acids from the decomposition of microbial cells and by-products of microbial activity) during the dry summer months could potentially cause the observed shift in the FI to higher values (from 1.45 to 1.54).

In the Glacial stream, the shifts in FI towards lower values during the first stages of snowmelt (day 139–143, Fig. 5b) and diurnal snowmelt events (day 153, Fig. 6b), indicate that snowmelt runoff generated in the lower reaches of the catchment flushes terrestrially derived DOC to the stream, similar to what is observed in the Bow River catchment during snowmelt. The FI of DOC in the Glacial stream is, however, high (1.58) relative to that of Bow River DOC, and the [DOC] is relatively low. This likely indicates that a much lower fraction of snowmelt runoff from the Glacial catchment has contact with soil and plant derived organic carbon than snowmelt runoff from the Bow River catchment. Only 12% of the Glacial catchment is covered in developed soils, compared to 63% in the Bow River catchment.

The dilution of [DOC] (from 0.41 to 0.18 ppm) and the shift in FI towards more microbial values (from 1.49 to 1.72) in the Glacial stream near the end of July (days 201, 203; Fig. 7b) indicate that meltwater from snow (and/or ice) in glaciated areas contains lower [DOC] than snowmelt from nonglaciated parts of the catchment, and that this DOC is derived primarily from microbial activity. This is consistent with the observation that the DOC in snow from the Meadow site (where there was little exposed vegetation) was, on average, less abundant and more microbial in character than DOC from snow at the Forest site (where there was a nearby source of plant debris). The microbial nature of DOC in the Glacial stream in summer could be the result of microbial and algal activity in snow on the glacier surface (Margesin et al., 2002; Sävström et al., 2002; Takeuchi, 2002), or in subglacial environments (Sharp et al., 1999; Skidmore et al., 2000). The more microbial nature of the DOC in the Glacial stream may also be due to runoff contributions from the proglacial lake (Fig. 1), which likely contains DOC produced from aquatic algae and bacteria. However, the similarity between the fluorescent properties of the DOC from the BG (downstream of the proglacial lake) and the BH (no proglacial lake) tributaries suggests that the proglacial lake does not significantly alter the properties of DOC in the BG stream. The recycling of a limited supply of terrestrially derived organic carbon over long periods of time by microbes in the subglacial environment (where organic residue is largely isolated from new inputs of terrestrially derived organic carbon) might also lead to a progressive change in the nature of DOC. The trend towards more microbial values of FI in glacial runoff could reflect evolution of the subglacial microbial community structure from one dominated by heterotrophs feeding on plant matter to one composed of a mixture of autotrophs and heterotrophs that utilise autotrophic biomass as a substrate for respiration (Wagner and Wolf, 1999). However, further examination of DOC from glacial systems in late summer is required in order to better constrain the range of concentrations and fluorescence of DOC from subglacial environments.

The response of stream DOC to the rainstorm on 25 July (day 207), 2000, shows that late season precipitation can flush terrestrial DOC to the Glacial stream (Fig. 7b). The increases in solute concentrations, [DOC], and discharge initially suggest that the rain

dissolved DOC from plant and soil organic carbon sources, and that the solutes, sediment and DOC were probably delivered to the stream via overland flow. The availability of fine sediment, and leaf and plant debris on the surface of the proglacial area could explain the input of terrestrial DOC and the increase in the suspended sediment load. However, the relatively constant $\delta^{18}\text{O}$ composition of the stream water indicates that the increase in discharge is not the result of overland runoff of rainfall. The lack of an increase in the $\delta^{18}\text{O}$ composition of the stream water and the higher $\text{Mg}^{2+}:\text{Ca}^{2+}$ ratio suggest that the discharge increase resulted from flushing of pre-event waters from tills and/or soils in the proglacial part of the catchment. The quick response of stream chemistry and discharge to the precipitation event requires that the infiltrating event water displaced water that could reach the stream via relatively fast (i.e. shallow) flow paths. Alternatively, the high concentration of solutes and suspended sediment could have resulted from re-arrangement and flushing of the subglacial drainage system. However, it seems unlikely that the subglacial environment could be a source for the higher concentrations of terrestrially derived DOC. Thus, the rain must have infiltrated the surface and flushed pre-event waters, DOC, sediments, and solutes from the shallow subsurface.

Conclusions

Trends in [DOC] and DOC fluorescence indicate that DOC in the Bow River is derived primarily from soil and plant organic matter, and that this terrestrially derived DOC is flushed to the stream by shallow subsurface flow at the onset of snowmelt. Snowmelt in ice-free areas of the glacial catchment also appears to be routed through the shallow subsurface, but DOC concentrations are relatively low since snowmelt runoff from this catchment has less contact with organic soils or litter. The fluorescence of DOC in the Glacial stream in summer (when most runoff originates from ice-covered areas), suggests that DOC from glaciated regions is more microbial in character than that derived from ice-free areas. Summer rain appears to have an effect similar to early season snowmelt runoff, in that it results in the flushing of organic carbon derived from plants and soils to the stream via shallow subsurface flow paths.

The FIs of DOC in environments where sources of terrestrially derived organic carbon are limited (e.g., snowmelt, summer soil water, glacial meltwater) suggest that, although the microbial community may initially be using plant or soil derived organic matter as a substrate, in the absence of continued inputs of terrestrial organic material, the composition of the DOC can evolve to one that is dominated by organic carbon derived from the by-products of the growing microbial community (i.e. the products of decomposition of microbial biomass and/or the products of microbial metabolic activity). Further study of changes in DOC and DOC fluorescence under these conditions is, however, required in order to confirm these interpretations.

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