

A comparison of solute fluxes and sources from glacial and non-glacial catchments over contrasting melt seasons

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Abstract:

Solute and runoff fluxes from two adjacent alpine streams (one glacial and one non-glacial) were investigated to determine how the inorganic solute chemistry of runoff responded to seasonal and interannual changes in runoff sources and volume, and to differences in physical catchment properties. Intercatchment differences in solute composition were primarily controlled by differences in catchment geology and the presence of soils, whereas differences in total solute fluxes were largely dependent on specific discharge. The glacial stream catchment had higher chemical denudation rates due to the high rates of flushing (higher specific discharge). The non-glacial Bow River had higher overall concentrations of solutes despite the greater prevalence of more resistant lithologies in this catchment. This is likely the result of both longer average water–rock contact times, and a greater supply of protons from organic soils and/or pyrite oxidation. Increases in snowpack depth/snowmelt runoff reduced the retention of nitrate in the Bow River catchment (i.e. increased nitrate export), probably by reducing net biological uptake, or by reducing the proportion of runoff that had contact with biologically active soil horizons that tend to remove nitrate.

The two streams exhibited opposite solute flux responses to climate perturbations over three melt seasons (1998, 1999, and 2000). The 1998 El Niño event resulted in an unusually thin winter snowpack, and increased runoff and solute fluxes from the glacial catchment, but decreased fluxes from the Bow River catchment. Solute fluxes in the Bow River increased proportionally to discharge, indicating that increased snowmelt runoff in this catchment resulted in a proportional increase in weathering rates. In contrast, the proportional variation in solute flux in the glacial stream was only ~70–80% of the variation in water flux. This suggests that increased ablation of glacier ice and the development of subglacial channels during the 1998 El Niño year apparently reduced the average water–rock contact time in the glacial catchment relative to seasons when the subglacial drainage system was primarily distributed in character. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS snowmelt and glacial hydrochemistry; inorganic solutes; weathering; solute flux–runoff relationships

INTRODUCTION

Weathering processes and the fluxes of solutes in rivers play important roles in the cycling of chemicals between the atmosphere, lithosphere, biosphere, and the oceans. Both exhibit climatically driven temporal variability, the extent and form of which may depend upon the balance of water sources and hydrological flow routing in a catchment, and on the catchment geology, soil, and vegetation characteristics. In alpine areas, glacial and snowmelt-fed rivers may show opposite runoff responses to climate changes (Lafrenière and Sharp, 2003), but the consequences of this for weathering processes and solute fluxes have received little study. The problem is, however, of considerable interest given that predicted anthropogenic climate warming (Houghton *et al.*, 2001) is likely to result in large changes in the magnitude and duration of seasonal snow cover and substantial shrinkage of glaciers in many of the world's mountainous regions (Braithwaite and Zhang, 1999; Fyfe and Flato, 1999; Dyurgerov, 2003).

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To assess the impact of short-term El Niño–southern oscillation (ENSO)-related climate variability on alpine chemical weathering processes and solute transport in glacier-fed and snowmelt-fed alpine streams, we measured solute fluxes into Bow Lake in the Canadian Rocky Mountains over three summer melt seasons: 1998, 1999, and 2000. This period included a strong El Niño event (1998), and two relatively strong La Niña years (1999 and 2000) (NOAA, 2004). Significant interannual variations were recorded in runoff from both catchments, but the two catchments displayed opposite discharge responses to the same climatic forcing (Lafrenière and Sharp, 2003). The lower snowfall and higher mean air temperatures in 1997–98 resulted in early removal of the winter snowpack from both catchments, and in early and extensive exposure of glacier ice in the glacial catchment. These conditions produced maximum summer runoff from the glacial catchment and minimum runoff from the snowmelt-fed catchment. It also seems likely that the high summer runoff in 1998 resulted in unusually extensive development of major subglacial drainage channels during that summer. In contrast, ice exposure and subglacial drainage development were more limited in 1999 and 2000, when the winter snowpack was more substantial (Lafrenière and Sharp, 2003). In both the glacial and snowmelt-fed streams, runoff responded more rapidly to air temperature changes in 1998 than in 1999–2000, indicating that the flow routing of meltwater was faster/more efficient (Lafrenière and Sharp, 2003). The aim of this paper is to determine how these hydrological changes affected the nature and quantity of inorganic solutes removed from the two catchments, and to identify the major factors controlling the relationships between climate, runoff, and solute flux in alpine settings.

SITE DESCRIPTION

Bow Lake, in Banff National Park, Alberta, Canada (51°40'N, 116°27'W) is fed by two main catchments. One is largely glaciated and the other is virtually unglaciated (<1.5% ice cover, Figure 1). The principal inflow to the lake is the glacial stream (GL), fed primarily by meltwater from the Wapta Icefield. The glacial catchment is approximately 27 km² (as measured from the point of gauging, 3 km away from and approximately 400 m below the snout of Bow Glacier) and has a mean elevation of 2560 m a.s.l. It consists primarily of glacier ice (41%, 11 km²), till, and moraines on which soils are absent or poorly developed (~40%). Only 12% is forested and/or overlain by soils with developed mineral horizons (brunisols and podsols) and some organic matter accumulation (Holland and Coen, 1982). The non-glacial inflow to the lake is the Bow River (BR). Its catchment (17 km²) consists mainly (67%) of subalpine meadow and spruce–fir forests, though the remaining areas are sparsely vegetated (29%) or unvegetated (2%). The mean elevation of the catchment is 2310 m a.s.l.

The geology of the Bow Lake catchment consists of Upper and Middle Cambrian carbonates and Lower Cambrian and Upper Proterozoic clastics (Price and Mountjoy, 1978). In the Bow Lake area, the Miette Group (part of the Upper Proterozoic Windermere Supergroup; Hein and McMechan, 1994) consists predominantly of slate and siltstone, feldspathic quartz sandstone and pebble conglomerates, as well as limestone and sandy limestone conglomerates (Price and Mountjoy, 1978). The Lower Cambrian Gog Group is mainly quartzite and quartzose sandstone (Price and Mountjoy, 1978), but in this area it likely contains the carbonate Peyto Formation, which is a unit of varied limestone, with some dolomite, sandstone and shale (Aitken, 1997). The Upper and Middle Cambrian carbonates include numerous limestone, dolomite and shale formations (Aitken, 1997; Price and Mountjoy, 1978). The glacial stream catchment is underlain entirely by Upper and Middle Cambrian carbonates, and the Bow River catchment contains all three groups (Figure 1). The Miette Group is exposed on the valley floor (41% of the catchment area), the Gog Group on either side of the valley (42%), and the Upper and Middle Cambrian carbonates (17%) at higher elevations and on steep slopes (Figure 1).

METHODS

Sample collection and analysis

Samples were collected from the Bow River and glacial streams (sites BR and GL, Figure 1) approximately every 3–5 days throughout the melt seasons of 1998, 1999 and 2000. Samples were filtered on site through

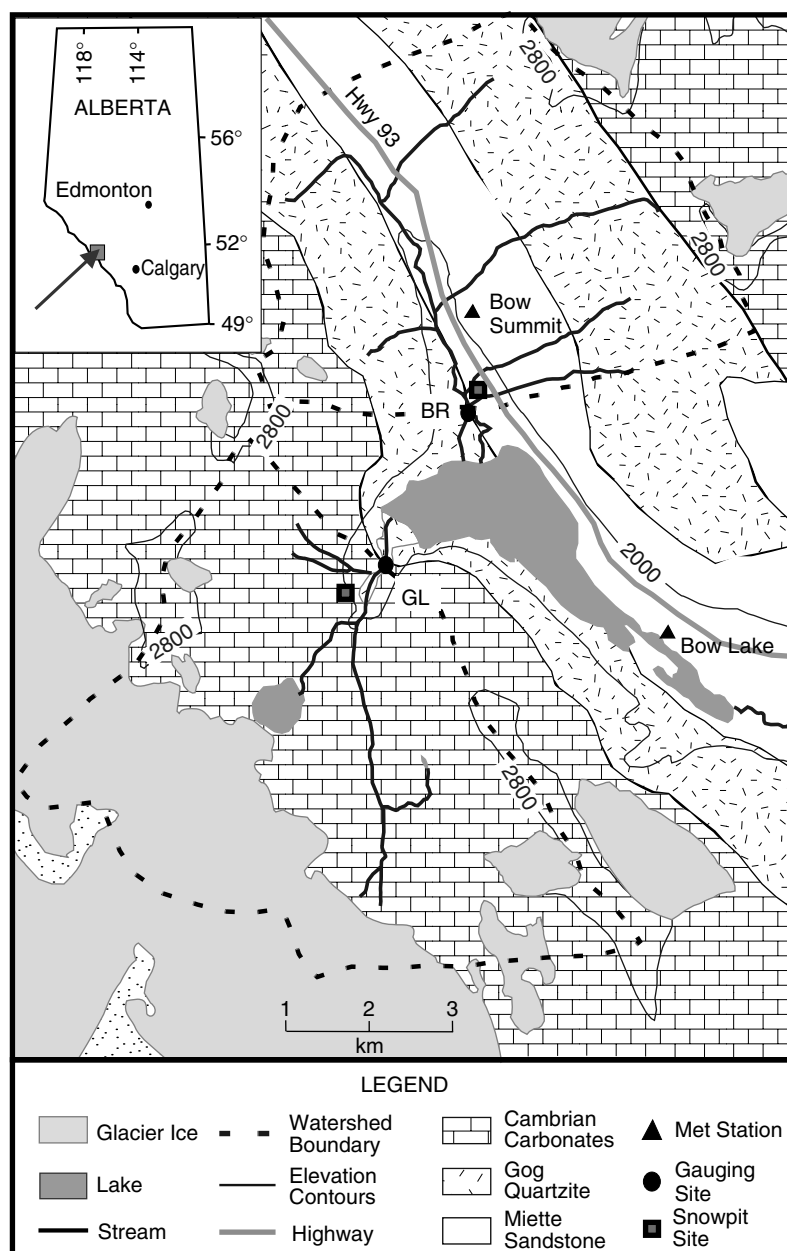


Figure 1. Map of the bedrock geology and boundaries of the Bow River (BR) and glacial stream (GL) catchments. Locations of the gauging/sampling sites for BR and GL, and the weather stations are shown

0.45 μm cellulose nitrate membranes immediately after collection. Two 20 ml aliquots of sample were collected in polyethylene scintillation vials, pre-rinsed with filtered sample, for anion and cation analysis. Alkalinity and pH were measured on site immediately following filtration. pH was measured using an Orion 290 digital meter, with automatic temperature compensation. The error on pH measurements is approximately ± 0.1 pH units. Alkalinity (as HCO_3^-) was determined colorimetrically by titration with sulphuric acid, using

a Hach digital titrator and brom-cresol green–methyl red indicator. Snow samples were collected from snow pits dug at sites in both the GL and BR catchments (Figure 1) in February 1999, and in January and March 2000. Snow samples from each visible layer were collected in double-layered clean plastic bags, stored frozen, and then slowly melted in the sealed plastic bags in the laboratory prior to analysis. The resulting meltwaters were filtered in the laboratory, bottled, and analysed for pH and alkalinity as described above.

Ion concentrations were determined by liquid ion chromatography on a Dionex DX500 ion chromatograph. The uncertainty in ion concentrations was estimated from analyses of duplicate samples run on separate days (Kretz, 1985). The uncertainties (standard error ($\mu\text{eq l}^{-1}$), coefficient of variation (%) in parentheses, $p < 0.05$), based on 16 duplicates, were: $\text{Na}^+ \pm 0.5$ (3%), $\text{K}^+ \pm 0.4$ (5%), $\text{Mg}^{2+} \pm 19$ (2%), $\text{Ca}^{2+} \pm 25$ (2%), $\text{Sr}^{2+} \pm 0.7$ (9%), $\text{Cl}^- \pm 0.3$ (2%), $\text{NO}_3^- \pm 0.5$ (8%) and $\text{SO}_4^{2-} \pm 4.9$ (1%). Accuracies based on measurement of standards were better than 1% for Ca^{2+} , Mg^{2+} , SO_4^{2-} , better than 5% for Na^+ , K^+ , and NO_3^- , and better than 10% for Cl^- and Sr^{2+} .

The charge balance errors (CBEs) were calculated as

$$\text{CBE} = \frac{\Sigma^+ - \Sigma^-}{\Sigma^+ + \Sigma^-} \times 100 \quad (1)$$

where Σ^+ is the sum of cations and Σ^- is the sum of anions. The mean CBE for stream meltwater was +6%, and the CBE for the majority of the samples was between 0 and 10%. Since the total errors on the results from ion chromatography were relatively small, a systematic error in the alkalinity titration was thought to be the most likely cause of the consistently positive charge balance. Where samples produced large CBEs (>10% or <0%), it was evident, from the concentrations and ratios of the other major ions, that there was a large error in the alkalinity measurement. As a result of the apparent lack of precision and accuracy of the titration, the alkalinity concentration calculated from the charge deficit was considered to be a better measure of the true alkalinity than the titration results. Five samples that had large negative charge balances were excluded from the analysis on the basis of very low cation concentrations.

To assess the provenance of sulphate in runoff, samples for the analysis of its isotopic composition ($\delta^{34}\text{S}-\text{SO}_4^{2-}$ and $\delta^{18}\text{O}-\text{SO}_4^{2-}$) were collected from the two streams in March 2000 and July 2000 (four samples total). The SO_4^{2-} isotope samples were collected in four 1 l polyethylene bottles (pre-rinsed with deionized (DI) water, and with sample). The samples were kept refrigerated and then passed through anion exchange resins in the laboratory to concentrate the SO_4^{2-} . The resin columns were shipped to the Environmental Isotope Laboratory, University of Waterloo, where the SO_4^{2-} was extracted and the isotopes were analysed on a VG Micromass 602 Dual collector mass spectrometer (for details of methods, see Hemskerk (1993a, b)).

In 1998, aliquots (250 ml) of filtered sample were collected for the measurement of the isotopic composition and dissolved concentration of strontium by isotope dilution thermal ionization mass spectrometry (ID-TIMS). Procedures for sample collection, chemical separation by column chromatography and mass spectrometric analysis followed those described by Sharp *et al.* (2002: 597). Samples for dissolved organic carbon (DOC) analysis were filtered on-site using a glass filtration apparatus and Whatman GF/F glass-fibre filters. Filtered sample 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. Between uses, the filtration apparatus was soaked and rinsed with 30% hydrogen peroxide, DI water, and sample. DOC was measured as non-purgeable organic carbon (NPOC) by high-temperature combustion (680 °C) with a Shimadzu TOC 5000A analyser equipped with high-sensitivity platinum catalyst.

Procedures for measurement of stream discharges are described by Lafrenière and Sharp (2003). The hourly discharge records ($\text{m}^3 \text{s}^{-1}$) for the two streams are presented in Figure 2. Table I presents the mean snowpack conditions at Bow Summit, and the mean monthly air temperature and precipitation recorded at the Bow Lake meteorological station in the 1997–98, 1998–99, and 1999–2000 seasons (Figure 1).

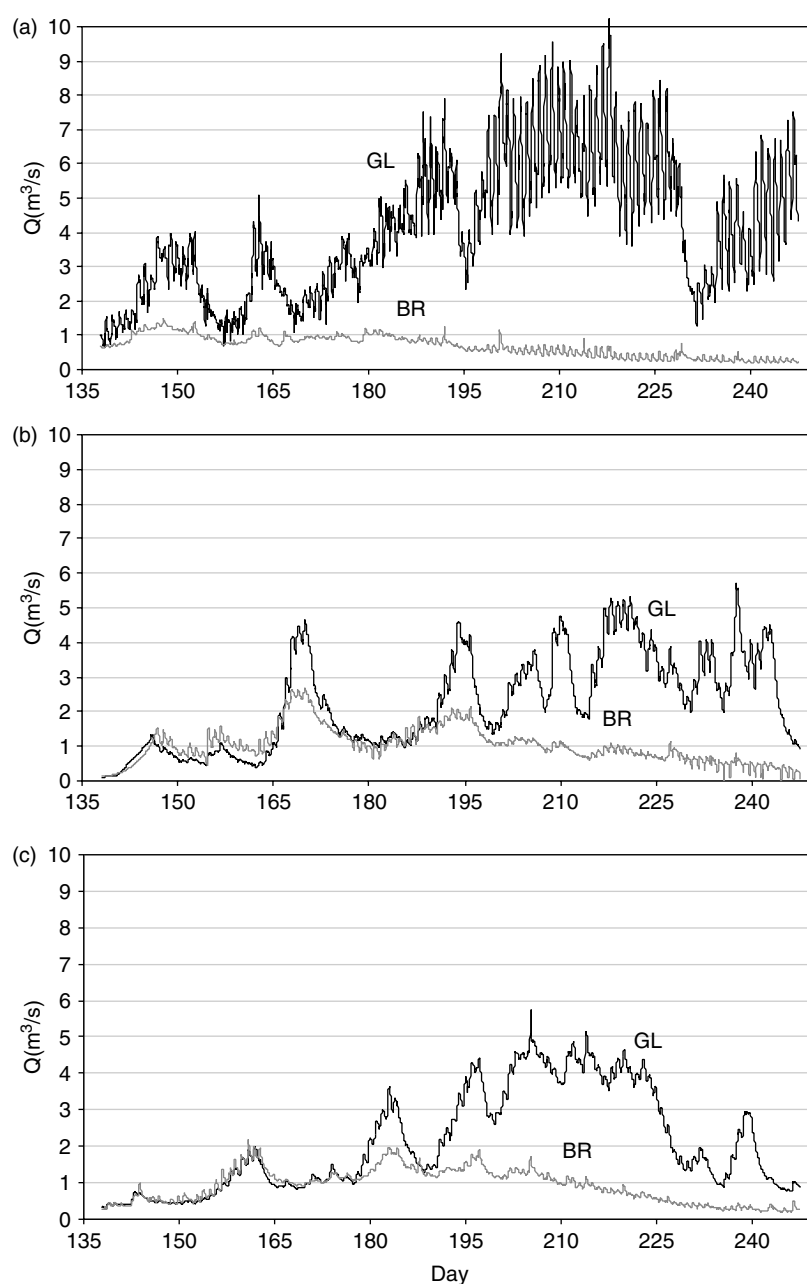


Figure 2. Hourly stream discharge Q for BR and GL for days 137–247 (17 May to 4 September) in (a) 1998, (b) 1999 and (c) 2000

Flux calculations

The relationship between the concentration ($\mu\text{eq l}^{-1}$) of each dissolved ion and meltwater discharge ($\text{m}^3 \text{s}^{-1}$) in each year was determined by least-squares regression. A total of 61 regressions were determined. The relationships were generally very strong (all $R^2 > 0.40$; 60% of the relationships had $R^2 > 0.80$). Only seven regressions (11%) yielded $R^2 < 0.60$. The regression equations and discharge records were used to calculate

Table I. Snowpack depth (mm of snow water equivalent (SWE)), mean monthly air temperature and rainfall recorded at the Bow Lake meteorological station for 1997–98, 1998–99, and 1999–2000

Snowpack (mm SWE) at Bow Summit (2080 m a.s.l.)	1997–98	1998–99	1999–2000
30 March	257	460	434
30 May	0	329	239
Exhaustion of snowpack at Bow Lake Met Station (1940 m a.s.l.)	2 May	30 May	23 May
Mean air temperature (°C)	1998	1999	2000
May	5.5	0.9	1.3
June	6.8	5.3	6.0
July	12.6	7.8	9.6
August	11.1	10.5	8.6
Total rain (mm) May–August	266	263	155

hourly records of ion concentrations for the periods 17 May to 4 September (or days 137–247) of 1998, 1999 and 2000. The hourly ion fluxes (meq h^{-1}) were calculated from the predicted hourly ion concentration ($\mu\text{eq l}^{-1}$) and discharge ($\text{m}^3 \text{h}^{-1}$), and summed to determine the summer ion flux (milliequivalents). The error on the summer flux was estimated as the quadratic sum of the uncertainties of the discharge estimates (errors in the discharge measurements and errors in the stage–discharge regression) and concentration estimates (the error in the ion concentration measurements (listed in the previous section), and the error of the ion–discharge regression) (Taylor, 1997). The uncertainties in the summer solute fluxes were between 11 and 21%, except for nitrate in the Bow River in 1998, for which the uncertainty was 32%.

The average ‘winter’ fluxes in each stream were estimated using the average ion concentrations of samples collected between October and April and an estimate of daily mean discharge. As only a limited number of samples were taken during fall and winter, the discharge and solute fluxes were estimated using the means of samples taken during all three years ($n = 4$ for both GL and BR). The stream gauging stations had to be removed in the fall of each year in order to avoid damage from ice. The daily mean winter discharge was therefore taken to be the lower of the values recorded on the last full day of record in the fall and the first day of record the following spring. It is recognized that this approach likely overestimates the winter solute flux from each catchment.

RESULTS

Table II lists the summer (May–September), winter (October–April) and annual solute fluxes in BR and GL for 1998, 1999 and 2000. The solute fluxes and discharges in both streams were similar in 1999 and 2000, but significantly different in 1998. In 1998, the discharge and fluxes of most solutes in GL were higher than in the other years, whereas in BR they were lower in 1998 than in subsequent years (Table II). The estimated winter solute fluxes and discharges were very similar in the two streams. The most significant interstream differences in winter fluxes were that Na^+ and HCO_3^- fluxes were higher in BR, whereas Sr^{2+} and SO_4^{2-} fluxes were higher in GL (Table II). The winter solute flux constituted 12–17% of the annual flux in GL and 24–31% in BR (Table II).

The rest of the paper focuses on the summer fluxes, which are well constrained and most strongly affected by climate-driven changes in runoff and flow routing.

Interannual variability of solute fluxes

To facilitate the interpretation of interannual changes in solute fluxes relative to changes in discharge, the ratio of the solute fluxes in different years divided by the ratio of the discharges in the same years (i.e.

Table II. Calculated solute fluxes for GL and BR for summer (May–September) and estimated average winter (October–April) fluxes, annual solute fluxes, and winter flux as a fraction of annual flux 1998–2000

	Q (10^7 m ³)	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Total	Mg ²⁺ : Ca ²⁺	(Ca ²⁺ +Mg ²⁺)/ HCO ₃ ⁻
Summer and winter fluxes (units: flux, 10^4 eq/season; Q , 10^7 m ³)													
GL 1998	3.93	30.1	14.5	1610	3250	31.3	6.25	14.5	869	4000	9830	0.50	1.22
GL 1999	2.13	22.1	10.5	1440	2230	21.8	7.43	14.3	728	3120	7600	0.65	1.18
GL 2000	1.99	22.1	9.30	1340	2000	22.3	6.05	14.6	739	2660	6820	0.67	1.25
GL winter	0.241	4.78	1.72	301	384	5.24	2.09	1.96	255	438	1390	0.78	1.56
BR 1998	0.647	17.9	5.15	652	813	1.60	4.46	0.536	191	1290	2970	0.80	1.14
BR 1999	0.964	30.8	7.59	954	1190	1.97	9.05	2.39	271	1930	4400	0.80	1.11
BR 2000	0.866	25.8	6.54	816	1040	1.62	8.53	2.29	240	1740	3880	0.79	1.07
BR winter	0.212	9.01	1.97	311	351	0.363	1.94	1.37	134	535	1340	0.89	1.24
Annual fluxes (units: flux, 10^4 eq year ⁻¹ ; Q , 10^7 m ³)													
GL 1998	4.17	35.4	16.3	1920	3640	36.7	8.47	16.5	1130	4430	11 200		
GL 1999	2.37	27.4	12.2	1750	2610	27.2	9.65	16.2	994	3560	8990		
GL 2000	2.23	27.4	11.1	1640	2390	27.7	8.27	16.5	1000	3100	8220		
BR 1998	0.859	26.9	7.12	963	1160	1.97	6.40	1.91	325	1820	4330		
BR 1999	1.18	30.8	9.56	1260	1540	2.34	9.05	3.76	404	2460	5780		
BR 2000	1.08	34.8	8.51	1130	1390	1.99	10.5	3.66	374	2270	5140		
Winter flux as a fraction of annual flux (units: Q , m ³)													
Glacial													
1998	0.06	0.14	0.11	0.16	0.11	0.14	0.25	0.12	0.23	0.10	0.12		
1999	0.10	0.18	0.14	0.17	0.15	0.19	0.22	0.12	0.26	0.12	0.16		
2000	0.11	0.18	0.16	0.18	0.16	0.19	0.26	0.12	0.26	0.14	0.17		
Bow River													
1998	0.25	0.33	0.28	0.32	0.30	0.18	0.30	0.72	0.41	0.29	0.31		
1999	0.18	0.23	0.21	0.25	0.23	0.16	0.18	0.36	0.33	0.22	0.23		
2000	0.20	0.26	0.23	0.28	0.25	0.18	0.19	0.37	0.36	0.24	0.26		

$(F_{1998}/F_{1999})/(Q_{1998}/Q_{1999})$ was calculated (Table III). This parameter is referred to as the 'flux change relative to discharge' (FCRD). For consistency, values are calculated by taking the ratio of the year with the higher discharge to the year with lower discharge (Table III). For $\text{FCRD} < 1$, the proportional increase in the solute flux between years was less than the proportional increase in discharge, so the additional water led to a dilution of solute concentrations in runoff. For $\text{FCRD} \approx 1$, then the change in solute flux was proportional to the change in discharge. Thus, the additional water was accompanied by a proportional addition of solute (either because there was an increase in weathering rates, or because the water source was as concentrated as the stream runoff). For $\text{FCRD} > 1$, the proportional increase in the solute flux exceeded the proportional increase in discharge. This suggests that the additional discharge introduced/accessed a new source of the solute, caused a disproportionate increase in weathering rates, or that there was a decrease in a sink for the solute.

The summer discharge in GL in 1998 was 1.8 and 2.0 times higher than in 1999 and 2000 respectively (Table III). For most ion species, the FCRDs in GL for 1998:1999 and 1998:2000 were only 0.7–0.8 (or 70–80%, Table III). There was little difference in either discharge or solute fluxes between 1999 and 2000, for either stream (Table III). In GL, Cl⁻ and NO₃⁻ showed the smallest FCRDs for both 1998:1999 and 1998:2000 (0.46–0.55, Table III). Over the 3 years, the fluxes of these two ions in GL were virtually independent of variations in discharge (Table II), so the added runoff in 1998 probably diluted the sources of these solutes in the stream relative to 1999 and 2000. Compared with other major ion species in GL, FCRDs

Table III. FCRD (F_{1998}/F_{1999})/(Q_{1998}/Q_{1999}) for GL and BR. The discharge column Q shows the ratio of the discharges for the years specified (e.g. Q_{1998}/Q_{1999}). The solute columns show the FCRD

	$Q(\text{m}^3)$	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Total
GL											
1998:1999	1.8	0.74	0.75	0.61	0.79	0.78	0.46	0.55	0.65	0.70	0.70
1998:2000	2.0	0.69	0.79	0.61	0.82	0.71	0.52	0.50	0.60	0.76	0.73
1999:2000	1.1	1.00	1.13	1.08	1.11	0.98	1.23	0.98	0.99	1.17	1.11
BR											
1999:1998	1.5	1.15	0.99	0.98	0.98	0.82	1.36	3.00	0.95	1.01	0.99
2000:1998	1.3	1.08	0.95	0.93	0.95	0.76	1.43	3.19	0.94	1.01	0.97
1999:2000	1.1	1.07	1.04	1.05	1.03	1.09	0.95	0.94	1.01	1.00	1.02

for Mg^{2+} and SO_4^{2-} were also low (0.60–0.65) for 1998:1999 and 1998:2000 (Table III). This suggests either that these solutes are derived from more resistant lithologies than other solutes (i.e. weathering was rate limited), or that the routing of the additional snow and ice melt in 1998 gave runoff more limited access to sources of these solute species than to those of other solutes.

The Bow River discharges in 1999 and 2000 were respectively 1.5 and 1.3 times higher than in 1998 (Table III). In contrast to GL, fluxes of K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} and HCO_3^- in BR increased approximately in proportion to discharge (Table III). The increases in the flux of Sr^{2+} in BR in 1999 and 2000 relative to 1998 were, however, much less than the increases in runoff (i.e. fluxes were diluted by the additional snowmelt input in 1999 and 2000). For NO_3^- and Cl^- , flux increases for 1999:1998 and 2000:1998 were much greater than the corresponding increases in discharge (Table III). This suggests that the increases in BR discharge in 1999 and 2000 either introduced a new source of these solutes, or reduced the removal or retention of these solutes in the BR catchment.

Intercatchment comparison

Since the glacial catchment is larger than the Bow River catchment, specific solute fluxes (meq m^{-2}) and discharges ($\text{m}^3 \text{m}^{-2}$) were used to compare solute generation in the two catchments (Table IV). The specific flux is the quantity of solute generated per square metre of the catchment, and is often referred to as the denudation rate of a catchment (Anderson *et al.*, 1997). The specific flux of total solute from the GL catchment was more than double that from the BR catchment in 1998, but only marginally higher in 1999 and 2000 (Table IV). The higher specific solute flux in GL relative to BR in 1998 was apparently largely due to the additional discharge, since the specific discharge for GL was much higher than for BR in that year (Table IV). GL also had higher specific discharge than BR in 1999 and 2000, but the two streams had similar specific solute fluxes in these years (Table IV).

Table IV lists the ratios for the specific solute fluxes and specific discharges between the two streams ($F_s^{\text{GL}}/F_s^{\text{BR}}$ and $Q_s^{\text{GL}}/Q_s^{\text{BR}}$) in each of the 3 years. For Mg^{2+} , Ca^{2+} , and HCO_3^- the ratios of the specific fluxes were usually approximately equal to or greater than one, but less than the ratios of the specific discharges between the streams (Table IV). This indicates that the equal, or higher, denudation rates in the GL catchment are due to the higher discharges from this catchment. The only solutes for which the specific flux ratios between the two catchments exceeded the specific discharge ratios were Sr^{2+} , NO_3^- , and SO_4^{2-} (Table IV). Thus, GL usually generates more Sr^{2+} , SO_4^{2-} and NO_3^- per unit area and unit volume of runoff than BR (i.e. the solute is more concentrated in GL). The ratios of the specific fluxes for Na^+ and K^+ (in 1999 and 2000) and Cl^- (in all years) were less than one (Table IV), which suggests that the BR catchment generated much more of these solutes per unit area despite the lower specific discharge. These species were, therefore, more concentrated in the BR than in GL (Table IV and Table VI).

In terms of bulk solute composition, the two streams were very similar. Most of the total solute flux (99%) from both catchments was composed of HCO_3^- , Ca^{2+} , and Mg^{2+} , indicating that carbonate weathering was

Table IV. Seasonal discharge, specific discharge, Q_s specific ion fluxes F_s for GL and BR, and the ratios of specific water and solute fluxes between GL and BR (Q_s^{GL}/Q_s^{BR} and F_s^{GL}/F_s^{BR}) for 1998, 1999 and 2000

	$Q(m^3)$	$Q_s(m^3m^{-2})$	$F_s(meq m^{-2})$									
			Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Total
GL 1998	3.93×10^7	1.45	11	5.4	597	1204	12	2.3	5.4	322	1482	3641
GL 1999	2.13×10^7	0.79	8.2	3.9	534	825	8.1	2.8	5.3	270	1156	2814
GL 2000	1.99×10^7	0.74	8.2	3.4	496	740	8.3	2.2	5.4	274	987	2524
GL winter	2.41×10^6	0.09	1.8	0.6	112	142	1.9	0.8	0.7	94	162	516
BR 1998	6.47×10^6	0.38	11	3.0	384	478	0.9	2.6	0.3	112	757	1749
BR 1999	9.64×10^6	0.57	18	4.5	561	701	1.2	5.3	1.4	159	1135	2587
BR 2000	8.66×10^6	0.51	15	3.8	480	611	1.0	5.0	1.3	141	1023	2281
BR winter	2.12×10^6	0.12	5.3	1.2	183	207	0.2	1.1	0.8	79	315	791
GL/BR 1998	6.07	3.82	1.06	1.78	1.56	2.52	12.30	0.88	17.08	2.86	1.96	2.08
GL/BR 1999	2.21	1.39	0.45	0.87	0.95	1.18	6.97	0.52	3.75	1.69	1.02	1.09
GL/BR 2000	2.30	1.45	0.54	0.90	1.03	1.21	8.66	0.45	4.02	1.94	0.96	1.11

the dominant weathering reaction in both catchments, despite significant differences in the distribution of carbonate lithologies. However, the relationships between the fluxes of the dominant ions were very different in the two streams. The $Mg^{2+}:Ca^{2+}$ ratios were much lower, and the $(Ca^{2+} + Mg^{2+}):HCO_3^-$ ratios higher in GL than in BR (Table II). As illustrated in the preceding analysis, there were also substantial interannual and intercatchment differences in the relative abundance of many of the less-abundant ion species, specifically Na^+ , Cl^- , Sr^{2+} , NO_3^- , and SO_4^{2-} .

The influences of solute sources and biogeochemical processes on the behaviour of these species are considered in the next section. Table V lists the principal weathering reactions anticipated, based on the geology of the catchments.

DISCUSSION

Solute sources

Sulphate. Sulphate may be derived from both atmospheric and crustal sources. Atmospheric sources of SO_4^{2-} include sea salt and sulphuric acid (H_2SO_4) aerosols. The average concentration of SO_4^{2-} in the stream

Table V. Principal weathering reactions expected in the Bow Lake area based on catchment geology

1	Carbonation of carbonate: $(Ca, Mg)CO_3(s) + CO_2(aq) + H_2O \rightarrow (Ca, Mg)^2 + 2HCO_3^-$
2	Pyrite oxidation: $2FeS_2(s) + 4H_2O + 6O_2 \rightarrow Fe_2O_3(s) + 4SO_4^{2-} + 8H^+$
3	Pyrite oxidation couple with carbonate dissolution: $4FeS_2(s) + 16(Ca_{1-x}, Mg_x)CO_3(s) + 15O_2(aq) + 14H_2O \rightarrow$ $16(1-x)Ca^{2+} + 16xMg^{2+} + 16HCO_3^- + 8SO_4^{2-} + 4Fe(OH)_3(s)$
4	Dissolution of anhydrite: $CaSO_4(s) \rightarrow Ca^{2+} + SO_4^{2-}$
5	Carbonation of an alkali feldspar: $Na_{1-x}K_xAlSi_3O_8(s) + 9H_2O + 2H_2CO_3 \rightarrow AlSi_2O_5(OH)_4 + 2(1-x)Na^+ + 2xK^+ + 2HCO_3^- + 4H_4SiO_4$
6	Carbonation of a calcium feldspar: $CaAl_2Si_2O_8(s) + 2H_2O + 2CO_2 \rightarrow Ca^{2+} + 2HCO_3^{2-} + H_2Si_2O_8(s)$
7	Dissolution of halite: $NaCl \rightarrow Na^+ + Cl^-$

Table VI. Mean summer solute concentrations C in runoff GL and BR for 1998–2000, calculated from specific discharge and specific ion fluxes
 $(C_{1998} = F_S 1998 / Q_S 1998)$

	Q (m ³)	Q_s (m ³ m ⁻²)	C (meq l ⁻¹)										$Na^+ : Cl^-$			$NO_3^- : Cl^-$			$SO_4^{2-} : Cl^-$		
			Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Total									
GL 1998	3.93×10^7	1.45	7.7	3.7	411	828	8.0	1.6	3.7	221	1019	2504	4.8		2.3				139		
GL 1999	2.13×10^7	0.79	10.4	4.9	678	1046	10.3	3.5	6.7	342	1466	3568	3.0		1.9				98		
GL 2000	1.99×10^7	0.74	11.1	4.7	672	1005	11.2	3.0	7.3	371	1339	3425	3.7		2.4				122		
GL winter	2.41×10^6	0.09	19.8	7.1	1247	1590	21.7	8.7	8.1	1056	1815	5774	2.3		0.94				122		
BR 1998	6.47×10^6	0.38	27.7	8.0	1008	1258	2.5	6.9	0.8	296	1991	4598	4.0		0.12				43		
BR 1999	9.64×10^6	0.57	32.0	7.9	989	1236	2.0	9.4	2.5	281	2001	4561	3.4		0.26				30		
BR 2000	8.66×10^6	0.51	29.8	7.5	942	1198	1.9	9.8	2.6	277	2008	4477	3.0		0.27				28		
BR winter	2.12×10^6	0.12	42.5	9.3	1465	1655	1.7	9.1	6.5	629	2521	6340	4.6		0.71				69		

runoff (Table VI) was, however, very high relative to snowpack concentrations (Table VII), indicating that atmospheric sources of sulphate could not have represented more than a small fraction of the total summer SO_4^{2-} flux in these streams.

The potential crustal sources of SO_4^{2-} are pyrite oxidation (Table V, Equation (2)) and the dissolution of evaporites such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and/or anhydrite (CaSO_4 , Table V, Equation (4)). Pyrite is known to exist throughout many of the formations within the Middle Cambrian carbonates (Atkinson, 1983), whereas evaporites appear to be uncommon within these rocks (Aitken, 1997: 78). Although it is unlikely that there are any significant deposits of evaporites in this area, dolostones formed from seawater-derived fluids are often associated with considerable amounts of gypsum and/or anhydrite (Machel and Anderson, 1989). Therefore, it is likely that there are sulphate-bearing evaporites within the Upper and Middle Cambrian dolomites.

Since, in the presence of bicarbonate, both pyrite oxidation (coupled with carbonate dissolution) and gypsum dissolution require that $(\text{Ca}^{2+} + \text{Mg}^{2+})$ be balanced by $(\text{HCO}_3^- + \text{SO}_4^{2-})$, the relative importance of the two sets of reactions cannot readily be determined from the ratios between these ions. The stable isotopes of SO_4^{2-} can, however, usually distinguish between evaporite and sulphide sources because the isotopes of oxygen and sulphur in SO_4^{2-} are highly fractionated between compounds during geochemical and/or biological reactions. The results of $\delta^{34}\text{S}$ – SO_4^{2-} and $\delta^{18}\text{O}$ – SO_4^{2-} isotope analysis of SO_4^{2-} from the stream samples are presented in Table VIII. The $\delta^{34}\text{S}$ – SO_4^{2-} in GL is very near the mean for Cambrian marine sulphate, while the $\delta^{18}\text{O}$ – SO_4^{2-} is depleted by $\sim 10\%$ relative to the average $\delta^{18}\text{O}$ of Cambrian marine sulphate (Table VIII) (Claypool *et al.*, 1980). In BR, $\delta^{34}\text{S}$ – SO_4^{2-} is depleted by $\sim 11\%$ and $\delta^{18}\text{O}$ – SO_4^{2-} is depleted by $\sim 24\%$ relative to Cambrian marine sulphate (Table VIII).

In GL, $\delta^{34}\text{S}$ is too enriched for much of the SO_4^{2-} to have been derived from oxidized sulphide minerals ($\delta^{34}\text{S}$ -20 to $+15\%$ CDT; Clark and Fritz, 1997: Figure 6-1). $\delta^{18}\text{O}$ – SO_4^{2-} is, however, too depleted for the SO_4^{2-} to have originated directly from the dissolution of marine evaporites of Cambrian age. The only process that can explain the large reduction in $\delta^{18}\text{O}$ with minimal reduction in $\delta^{34}\text{S}$ is the biological reduction of SO_4^{2-} to HS^- , followed by re-oxidation to SO_4^{2-} in a nearly closed system (van Everdingen *et al.*, 1982; Grasby *et al.*, 2000). If there is minimal loss of HS^- , then the $\delta^{34}\text{S}$ – SO_4 should not be altered by the biological cycling. Much of the oxygen used during the oxidation of HS^- is, however, derived from water (van Stempvoort and Krouse, 1994). Since the $\delta^{18}\text{O}$ of surface water in these catchments in 2000 was, on average, $-20.7 \pm 0.4\%$ VSMOW (Lafrenière, unpublished data), the re-oxidized SO_4^{2-} will be depleted in ^{18}O relative to the original SO_4^{2-} ($\delta^{18}\text{O}$ of marine SO_4^{2-} is approximately $+14\%$). It is possible, however, that a small fraction of the sulphate in GL is derived from sulphide oxidation under anoxic conditions (Table VIII). Under anoxic conditions where three of the four oxygen atoms in the sulphate are derived from water, the maximum $\delta^{34}\text{S}$ – SO_4 and $\delta^{18}\text{O}$ – SO_4 values would be 15% and -12% respectively (Bottrell and Tranter, 2002; Wadham *et al.*, 2004). In this case, the SO_4^{2-} in GL samples could be explained by mixing 80% sulphate from Cambrian evaporites with 20% sulphate from sulphide oxidation. This mixture would yield sulphate with isotope values of $\delta^{34}\text{S}$ – $\text{SO}_4 = 27\%$ and $\delta^{18}\text{O}$ – $\text{SO}_4 = 7\%$. Biological cycling of this mixed

Table VII. Average solute concentrations C in winter snowpack at Bow Lake

Site	Date	SWE (mm)	C (meq l^{-1})									$\text{NO}_3^- : \text{Cl}$
			Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	
GL	15 Feb 1999	233	2.2	1.2	3.0	8.8	0.0	1.2	3.2	2.3	11.0	2.7
BR	16 Feb 1999	364	1.5	0.4	1.4	3.4	0.0	0.7	2.8	1.2	3.2	4.0
BR	29 Jan 2000	180	6.0	1.0	2.6	10.7	0.0	2.9	4.8	2.3	12.5	1.7
BR	18 Mar 2000	268	2.8	2.1	4.3	13.6	0.0	2.3	4.9	2.1	13.5	2.1
GL	18 Mar 2000	266	3.9	4.1	4.3	12.0	0.0	2.0	5.1	2.5	16.2	2.6
Mean		262	3.3	1.8	3.1	9.7	0.0	1.8	4.2	2.1	11.3	2.6
SD		67	1.7	1.5	1.2	3.9	0.0	0.9	1.1	0.5	4.9	0.9

Table VIII. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of SO_4^{2-} from stream and snow samples, from cambrian evaporites, and the potential values for SO_4^{2-} derived from both oxic and anoxic sulphide oxidation

Sample	Date	$\delta^{34}\text{S}(\text{‰ CDT})$	$\delta^{18}\text{O} (\text{‰ VSMOW})$	$[\text{SO}_4^{2-}] \text{ (meq l}^{-1}\text{)}$
GL	18 Mar 2000	28.9	4.1	1213
GL	26 Jul 2000	27.0	1.6	271
BR	18 Mar 2000	18.9	-9.9	689
BR	26 Jul 2000	18.1	-9.8	338
Cambrian evaporites ^a		30 ± 4	13.9 ± 0.5	
Oxic sulphide oxidation ^b		-20 to +15	6 to 15	
Anoxic sulphide oxidation ^b		-20 to +15	-12 to -21	

^a Mean values from Claypool *et al.* (1980).

^b The upper limit for $\delta^{18}\text{O}$ for SO_4^{2-} under oxic conditions ($\delta^{18}\text{O}-\text{SO}_4^{2-} = 15\text{‰}$) represents the $\delta^{18}\text{O}$ value of atmospheric O_2 ($\delta^{18}\text{O}-\text{O}_2 = +23.7\text{‰}$, references) after the -8.7‰ fractionation on incorporation of oxygen atoms from O_2 into SO_4^{2-} . The lower limit for $\delta^{18}\text{O}$ for SO_4^{2-} under oxic conditions ($\delta^{18}\text{O}-\text{SO}_4^{2-} = 6\text{‰}$) was calculated assuming three of the four oxygen molecules in the product SO_4^{2-} were derived from atmospheric O_2 and one oxygen was derived from water ($\delta^{18}\text{O}-\text{H}_2\text{O} = -21\text{‰}$). The upper limit for $\delta^{18}\text{O}$ for SO_4^{2-} derived from sulphide under anoxic conditions ($\delta^{18}\text{O}-\text{SO}_4^{2-} = -12\text{‰}$) was determined assuming three of the four oxygen atoms in the SO_4^{2-} were derived from water and only one from atmospheric O_2 . The lower limit for SO_4^{2-} under anoxic conditions ($\delta^{18}\text{O}-\text{SO}_4^{2-} = -21\text{‰}$) assumes all four molecules of oxygen in the resulting SO_4^{2-} were derived from water. See Bottrell and Tranter (2002) for further examples and explanation of calculations.

pool of sulphate under closed-system conditions would also be required to deplete the $\delta^{18}\text{O}-\text{SO}_4$ further to the observed value ($\sim 3\text{‰}$, Table VIII). Thus, at least 80% of the sulphate in the glacial stream was likely derived from Cambrian evaporite minerals. This conclusion differs from other studies of glacial meltwater draining the same Cambrian carbonate formations at other sites in the Rockies, where the dominant source of sulphate was determined to be pyrite oxidation (Atkinson, 1983; Fairchild *et al.*, 1994). However, these conclusions were not based on the analysis of sulphur isotopes.

For Bow River SO_4^{2-} , both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ are too light for the sulphate to be derived from simple dissolution of Cambrian marine evaporites, but they are slightly heavier than would be expected for sulphate derived from sulphide oxidation under anoxic conditions (Table VIII). These results suggest three possible explanations for the source of SO_4^{2-} in BR: (1) the SO_4^{2-} is primarily from pyrite that was enriched in $\delta^{34}\text{S}$ ($\delta^{34}\text{S} > 15\text{‰}$) and oxidized under anoxic conditions ($\delta^{18}\text{O} \approx -12\text{‰}$); (2) there is a mix of evaporite- and sulphide-derived SO_4^{2-} ; (3) there was a mixing of evaporite- and sulphide-derived SO_4^{2-} as well as some biological cycling of sulphur. The simplest explanation is that the SO_4^{2-} is primarily from the oxidation of pyrite. Although the $\delta^{34}\text{S}$ values are somewhat higher than normally expected for sulphide minerals, the $\delta^{34}\text{S}$ of pyrite has been shown to vary by as much as 50‰ within a limited region of a single formation (Machel *et al.*, 1995). Without knowing the $\delta^{34}\text{S}$ composition of pyrite in the catchment, it is difficult to rule out the possibility that the SO_4^{2-} is derived from oxidized pyrite, especially since $\delta^{18}\text{O}-\text{SO}_4$ values for the BR samples (-10‰ , Table VIII) are within a few per mill of the values associated with anoxic sulphide oxidation (-12‰ , Table VIII). It is also possible that the SO_4^{2-} in Bow River is derived from a mixture of evaporite and sulphide sources. However, the fraction of SO_4^{2-} derived from the dissolution of Cambrian evaporites would have to be very small (less than 10%).

Strontium. As with sulphate, the relative concentrations and patterns of variability of strontium in the two streams are very different from those of most other solutes. Strontium is widely dispersed; it replaces calcium in many minerals, and ^{87}Sr is the daughter nuclide in the radioactive decay of rubidium, which substitutes for potassium in potassium-bearing minerals such as biotite and potassium feldspars. Strontium, therefore, occurs in a variety of silicate, carbonate and evaporite minerals. Strontium is more than twice as abundant in carbonates as in shales, and generally 10 times more abundant in shales than in sandstones (Turekian

and Wedepohl, 1961). Strontium abundance in evaporites is difficult to assess because it depends on the environment of formation (Hanor, 2000), but it is similar to that in carbonates and shales, since Sr^{2+} is a minor component of seawater and can replace Ca^{2+} in anhydrite (Hanor, 2000).

As with sulphate, the flux of Sr^{2+} was always greater in GL (Table II), and the ratios of the specific fluxes of Sr^{2+} between the two streams were many times greater than the ratios of the specific discharges (Table IV). However, unlike SO_4^{2-} , Sr^{2+} concentrations in GL were always many times higher than in BR (Table VI). This suggests that strontium is derived from different sources in the two catchments. If the Sr^{2+} in both streams was derived primarily from carbonates, then we would expect the Sr^{2+} concentrations in GL and BR to be similar, and possibly higher in BR than in GL, since Ca^{2+} , Mg^{2+} and HCO_3^- concentrations are higher in BR than in GL (Table VI). A correlation analysis of the concentrations of the major cations and anions shows that, in GL, Sr^{2+} is most strongly correlated with SO_4^{2-} , and then with Mg^{2+} and Ca^{2+} (Table IX). This suggests either that Sr^{2+} and SO_4^{2-} in GL were derived from the same source (evaporite minerals), or that Sr^{2+} was derived from the same host rocks as the evaporite minerals, i.e. the Cambrian carbonates. In BR, the only ions that have statistically significant ($p < 0.05$) correlations with Sr^{2+} are SO_4^{2-} and K^+ (Table IX). The correlation between Sr^{2+} and SO_4^{2-} suggests that some Sr^{2+} may be derived from rocks containing pyrite (the dominant source of sulphate in BR), or that the acidity from pyrite oxidation is driving weathering of minerals from which Sr^{2+} is derived. The weak, but significant ($p < 0.05$), correlation with K^+ suggests that some of the Sr^{2+} in this stream may be derived from potassium-bearing silicate minerals. The higher K^+ concentrations in BR relative to GL (Table VI) also suggest that potassium-bearing minerals may be a more important source of Sr^{2+} in the BR. Since both pyrite and potassium-bearing clay minerals such as micas (biotite and muscovite) are normally abundant in shales, it is likely that shales are the dominant source of Sr^{2+} in BR.

This suggestion is supported by the isotopic composition of Sr^{2+} in the two streams. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Sr^{2+} in the streams are clearly distinct, with BR having higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.71622 ± 0.00025) than GL (0.71008 ± 0.00008 ; Table X). Carbonates and evaporites contain high concentrations of strontium with low $^{87}\text{Sr}/^{86}\text{Sr}$. Silicate rocks typically have lower strontium concentrations but higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The $^{87}\text{Sr}/^{86}\text{Sr}$ of GL is higher than is typical ($0.7089\text{--}0.7094$) for Cambrian seawater (Burke *et al.*, 1982; Montañez *et al.*, 2000). However, $^{87}\text{Sr}/^{86}\text{Sr}$ of dolomite and calcite within the Cathedral Formation of the Cambrian

Table IX. Correlation matrices for the concentrations of cations, SO_4^{2-} and bicarbonate in stream water samples from Bow River and the glacial stream

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	SO_4^{2-}	HCO_3^-
<i>Bow River</i>							
Na^+	1.00	0.86	0.78	0.75	0.70	0.72	0.70
K^+		1.00	0.71	0.68	0.57	0.58	0.69
Mg^{2+}			1.00	0.98	0.81	0.86	0.95
Ca^{2+}				1.00	0.78	0.87	0.94
Sr^{2+}					1.00	0.92	0.63
SO_4^{2-}						1.00	0.67
HCO_3^-							1.00
<i>Glacial Stream</i>							
Na^+	1.00	0.68	0.84	0.87	-0.04	0.43	0.85
K^+		1.00	0.77	0.76	0.26	0.51	0.73
Mg^{2+}			1.00	0.97	0.17	0.70	0.92
Ca^{2+}				1.00	0.13	0.59	0.96
Sr^{2+}					1.00	0.44	0.02
SO_4^{2-}						1.00	0.38
HCO_3^-							1.00

carbonate units in the region range from 0.709 to 0.712 (Koffyberg, 1994; Nesbitt and Muehlenbachs, 1994). Values for host rocks within the Upper Proterozoic Miette Group averaged 0.7345 ± 0.0014 for limestones ($n = 2$), 0.767 ± 0.016 for slate ($n = 2$), and 0.752 ± 0.014 ($n = 9$) for calcite from vein carbonates.

These $^{87}\text{Sr}/^{86}\text{Sr}$ values and the correlations between Sr^{2+} and other ions suggest that the Cambrian carbonates (or evaporites within these units), which have high strontium abundance but low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, are likely the primary source of Sr^{2+} in GL, whereas BR derives strontium primarily from rocks containing more radiogenic strontium at lower strontium abundances. The $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr^{2+} in BR is slightly higher than that of strontium from Cambrian carbonates, and substantially lower than values derived from rocks and minerals within the Miette Group. The low concentrations of Sr^{2+} in BR suggest that although the Cambrian carbonates may contribute Sr^{2+} to this stream, it is likely a very small fraction of Sr^{2+} , and that there is some mixing with strontium from a more radiogenic source (probably from the Miette or Gog groups). However, it is likely that although the source of strontium in BR is silicate minerals, the $^{87}\text{Sr}/^{86}\text{Sr}$ released during silicate weathering in BR does not match that of strontium in the source mineral(s). Several laboratory studies of potassium-silicate weathering have shown that the $^{87}\text{Sr}/^{86}\text{Sr}$ of weathering solutions can be either higher or lower than that of the minerals being weathered, and that the $^{87}\text{Sr}/^{86}\text{Sr}$ can change over time (Brantley *et al.*, 1998; Taylor *et al.*, 2000).

Sodium and chloride. In catchments lacking halite in bedrock, it is usually assumed that chloride is derived entirely from atmospheric sources (mainly sea-salt aerosol). Since chloride does not participate in biogeochemical, weathering, or ion exchange reactions, it is generally regarded as a conservative solute. Conversely, sodium may be derived from both atmospheric and crustal sources, and it is involved in weathering and ion-exchange reactions. The principal crustal source of Na^+ is the weathering of aluminosilicate minerals (Table V, Equation (5)), but Na^+ may also be derived from carbonate sources (aragonite and magnesium calcite bear significant sodium; Fairchild *et al.*, 1994). Sodium is, however, generally much less abundant in waters draining carbonate catchments (1–5% of total cations) than in streams from sandstone and shale catchments (13–45% of total cations; Meybeck, 1987). Sodium and chloride may also be derived from the dissolution of halite (Table V, Equation (7)). There are, however, no known deposits of halite in the geological formations in the study area, and $\text{Na}^+ : \text{Cl}^-$ ratios are much greater than unity in these streams (Table VI). Hence, it seems unlikely that dissolution of bedrock halite is a major source of solute.

The concentrations of Cl^- in the winter runoff from the two catchments were very similar, but the average winter Na^+ concentration in BR was more than double that in GL (Table VI). The higher $\text{Na}^+ : \text{Cl}^-$ in winter

Table X. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and Sr^{2+} concentrations measured by ID-TIMS for BR and GL. The R^2 values for the linear regressions of Sr^{2+} concentrations as a function of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are indicated

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{sm}$	Sr^{2+} ($\mu\text{eq l}^{-1}$)	Mg^{2+}	Ca^{2+}
BR 051 495 10:00	0.716 453	0.000 019	1.39	932	1207
BR 052 698 17:45	0.715 933	0.000 015	1.52	884	1137
BR 061 298 18:30	0.716 059	0.000 016	1.79	961	1186
BR 072 098 10:40	0.716 577	0.000 018	1.95	1071	1324
BR 072 798 13:00	0.716 136	0.000 013	1.43	896	1229
BR 081 998 17:00	0.716 132	0.000 016	2.42	1178	1414
GL 051 298 13:00	0.709 972	0.000 016	8.48	726	1068
GL 052 698 13:30	0.710 045	0.000 016	7.80	566	891
GL 061 398 13:10	0.710 046	0.000 014	9.23	537	896
GL 072 898 10:00	0.710 129	0.000 019	6.37	415	879
GL 072 898 15:00	0.710 218	0.000 017	4.61	427	1065
GL 081 998 15:20	0.710 072	0.000 019	7.62	480	871

runoff in BR suggests that groundwater in this catchment derives much more sodium from rock weathering than does groundwater in the GL catchment. This might be the result of (a) a longer residence time of groundwater in the Bow River catchment, as indicated by the higher concentrations and specific fluxes of Ca^{2+} , Mg^{2+} and HCO_3^- (Tables III and VI), and/or (b) more Na^+ derived from the weathering of silicate minerals (such as alkali feldspars). This is expected, given the relative abundance of non-carbonate rock in the BR catchment (Figure 1).

Although it is not surprising that BR had higher Na^+ concentrations than GL, it is curious that, unlike most other solutes, the summer fluxes of Na^+ and Cl^- in 1999 and 2000 were higher in BR than in GL (Tables II and IV). The high FCRD for Na^+ and Cl^- in BR for 1999:1998 and 2000:1998 suggests that a source of Na^+ and Cl^- was introduced or accessed as a result of the additional runoff in 1999 and 2000 (Table III). In contrast, the FCRD values for Na^+ and Cl^- in GL for 1998:1999 and 1998:2000 were less than unity (Table III), indicating that, in GL, Na^+ and Cl^- concentrations were diluted by the additional discharge from ice melt in 1998 (Table VI). The higher FCRDs for Na^+ and Cl^- in BR likely reflect the greater input of atmospherically derived sea salt associated with the higher snowmelt contribution to BR in 1999 and 2000. The higher FCRDs for Cl^- (1.36 and 1.43) relative to Na^+ (1.15 and 1.08) in the BR indicate that atmospheric sources account for a large proportion of the Cl^- flux, whereas atmospheric inputs likely make up only a small fraction of the total Na^+ flux.

Nitrate. Snowpack NO_3^- originates almost solely from atmospheric deposition. Both wet and dry deposition of NO_3^- and nitric acid are important sources of snowpack NO_3^- (Cress *et al.*, 1995; Rusch and Sievering, 1995). The balance of gains by atmospheric deposition to the snowpack and nitrogen mineralization (ammonification and nitrification) in soils, and losses due to NO_3^- assimilation and denitrification in soils determines the flux of NO_3^- in runoff. Several studies indicate that the delivery of NO_3^- to surface waters from the snowpack in high-elevation ecosystems is controlled primarily by the balance of soil microbial processes (mineralization versus assimilation/denitrification) beneath the snowpack prior to snowmelt (Williams *et al.*, 1996; Brooks and Williams, 1999; Brooks *et al.*, 1999; Heuer *et al.*, 1999). Brooks and Williams (1999) found that a deep consistent snowpack increased microbial activity and microbial biomass, but reduced the net NO_3^- export from the catchment relative to shallow, inconsistent snow cover. In other words, the deeper snowpack resulted in greater use (assimilation/denitrification) of NO_3^- by soil microbes relative to the release of NO_3^- from mineralization. In contrast, another study of nitrogen cycling in alpine catchments found higher stream NO_3^- concentrations and lower inorganic nitrogen retention during years with deep/late-melting snowpacks (Sickman *et al.*, 2001). This was attributed to the combination of lower NO_3^- uptake by plants due to longer snow-lie, and greater production of labile nitrogen in soils, because nitrogen mineralization and nitrification in snow-covered soils continued later into the spring.

NO_3^- fluxes were always an order of magnitude higher in GL than in BR (Table II). The seasonal average NO_3^- concentrations in the streams were approximately 2–4 $\mu\text{eq l}^{-1}$ in BR, and 4–8 $\mu\text{eq l}^{-1}$ in GL (Table VI). NO_3^- concentrations in the snow at Bow Lake were between approximately 3 and 5 $\mu\text{eq l}^{-1}$, and NO_3^- : Cl^- ratios were 2–4 (Table VII). Assuming that Cl^- behaves conservatively, then the difference in the NO_3^- : Cl^- ratio between the snow and the streams is an indication of the effect of catchment processes on NO_3^- export to the streams. The NO_3^- : Cl^- ratios in GL (1.9–2.4, Table VI) were similar to the ratios observed in snows (Table VII), whereas the NO_3^- : Cl^- ratios in BR (0.1–0.3, Table VI) were always substantially lower than in the snow (Table VII). Furthermore, the NO_3^- : Cl^- ratio for GL was higher in the summer than in the winter, whereas the opposite was true for BR (Table VI). These results suggest that there is limited removal of atmospherically derived NO_3^- in the glacial catchment during the spring and summer, whereas the Bow River catchment appears to act as a sink for NO_3^- deposited to the snow pack.

The higher flux and concentration of NO_3^- in GL (i.e. lower catchment retention of NO_3^-) relative to BR may be largely due to differences in the extent of soil and vegetation cover in the two catchments. Several recent analyses of inorganic nitrogen yield and retention in high-elevation ecosystems of the Sierra Nevada and Rocky Mountains have found that the yield of dissolved inorganic nitrogen (DIN, i.e. $\text{NH}_4^+ + \text{NO}_3^-$)

decreased with increasing soil cover, while the DIN retention increased (Sueker *et al.*, 2001; Sickman *et al.*, 2002). The seasonal variation in NO_3^- relative to DOC (which is flushed from catchment soils during snowmelt; Lafrenière and Sharp, 2004) also suggests that the flow routing of runoff through soils results in a decrease in NO_3^- concentrations (Figure 3). When DOC concentrations increased during the first stages of snowmelt, NO_3^- concentrations in BR decreased substantially in 1999 and 2000. In BR, NO_3^- also tends to vary inversely with DOC over the rest of the summer, suggesting that it is losing NO_3^- when runoff is flushing DOC from soils (Figure 3). In GL, NO_3^- generally increased with DOC during snowmelt, except occasionally during the later stages of snowmelt (Figure 3, 1998 (days 150–175) and 1999 (days 165–175)). This suggests that, at the catchment scale, NO_3^- in snowmelt is largely unaffected by contact with soils in the GL catchment.

The higher concentrations of NO_3^- in GL relative to those in the snowpack suggest that the glacial catchment may be a source of NO_3^- . This might also have to do with the lack of vegetated soils in this catchment. Williams *et al.* (1997) found that fine sediments under talus fields ‘subtalus soils’ supported microbial activity, and that in high-elevation catchments talus fields may contribute NO_3^- to stream waters. Subtalus soils contained similar amounts of extractable NH_4^+ and NO_3^- to well-developed, vegetated soils. They contained much less microbial biomass, however, suggesting that inorganic nitrogen was rapidly assimilated in vegetated soils, but inorganic nitrogen production exceeded assimilation and uptake by plants and microbes in the subtalus soils (Williams *et al.*, 1997). The role of steep slopes and unvegetated terrain in elevating NO_3^- concentrations in alpine streams has also been noted in other studies (Campbell *et al.*, 2000; Sueker *et al.*, 2001). NO_3^- concentrations in soil waters collected from tension lysimeters from four sites around Bow Lake also suggest that unvegetated and poorly developed soils represent potential sources of NO_3^- in the catchment (Table XI). NO_3^- concentrations in soil waters were much higher in the two sites where there was little vegetation and poorly developed soils (BR-S2, GL-S1) than in the two sites where there was vegetation and well-defined soil structure (BR-S1, GL-S2; Table XI). The details of the soil lysimeter locations and sampling methods are described by Lafrenière and Sharp (2004).

NO_3^- concentrations and fluxes in BR increased with runoff and snow depth (Tables II and VI). The $\text{NO}_3^-:\text{Cl}$ ratio also increased in 1999 and 2000 relative to 1998 (despite the significant increases in Cl^- fluxes), which suggests that the catchment was less of a NO_3^- sink in 1999 and 2000 than in 1998. The FCRDs for both 1999:1998 and 2000:1998 also indicate that there was a decrease in the removal (or else an added source) of NO_3^- in 1999 and 2000 compared with 1998 (Table III). In GL, nitrate fluxes were virtually unaffected by interannual changes in runoff. Even though the 1998 runoff was almost double that in 1999 and 2000,

Table XI. NO_3^- concentrations in soil solutions collected from tension lysimeters at four sites around Bow Lake in 2000

Soil lysimeter site	Depth (CM)	Mean $\text{NO}_3^- \pm \text{SD}$ ($\mu\text{eq l}^{-1}$)	N	Site description
BR-S1	12	1.0 ± 1.2	10	Small willows and plant litter underlain by soil with a thin organic horizon (2–3 cm), organic A horizon (5 cm), and oxidized (brown–orange) B horizon
	24	2.1 ± 1.8	11	
BR-S2	12	29 ± 22	10	Grassy area underlain by shallow poorly developed sandy soil (0–8 cm), sand and gravel at depth
	24	92 ± 57	10	
GL-S1	12	129 ± 53	9	Litter and humus at surface (2 cm), underlain by fines/silt
	24	166 ± 57	9	
GL-S2	12	0.9 ± 0.3	4	Forested area, with grass and small plants. Soil has a thin organic horizon (4 cm), leached A horizon (4 cm), and oxidized (brown–orange) B horizon
	24	1.0 ± 0.5	5	

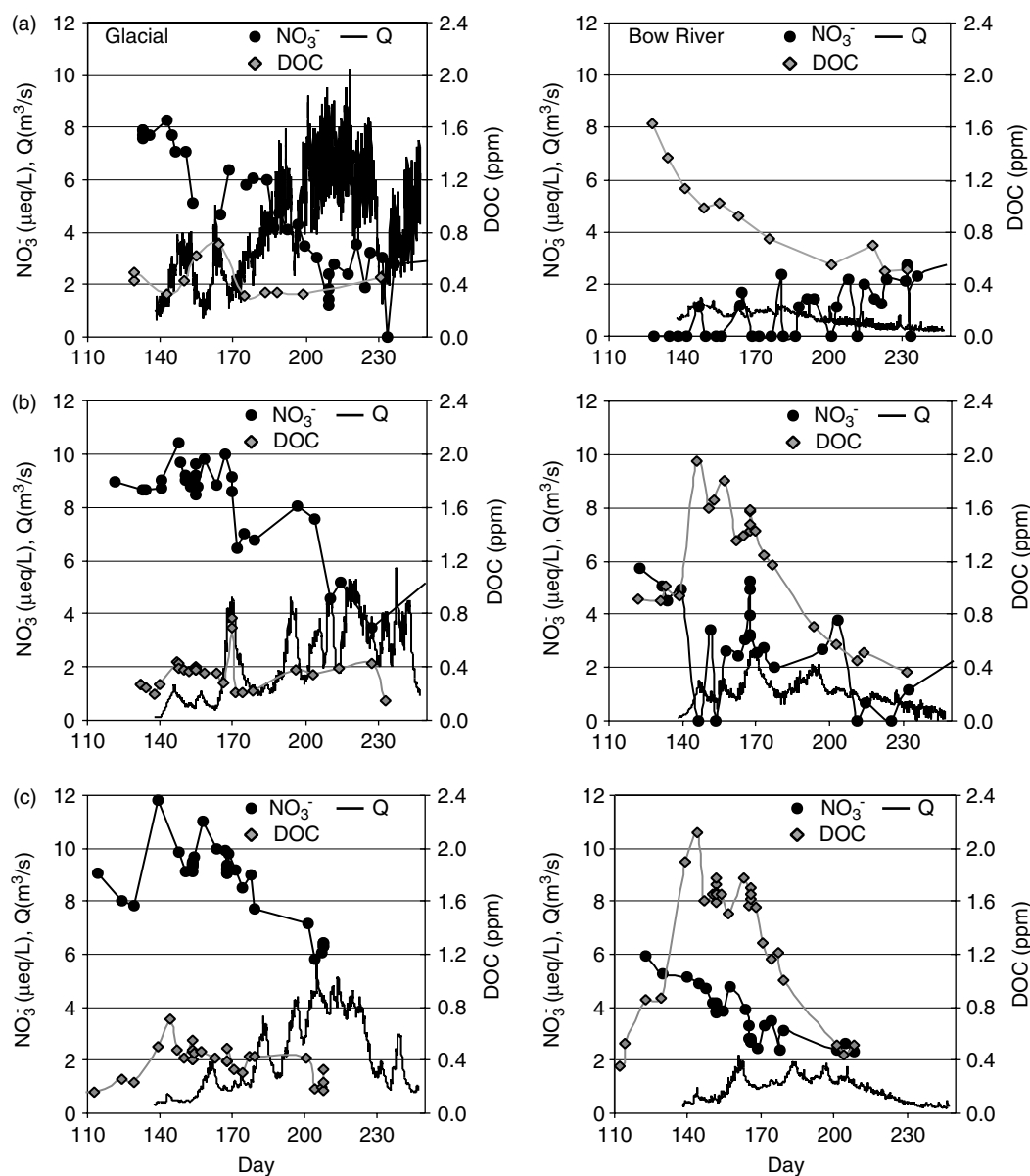


Figure 3. Seasonal DOC and NO_3^- concentrations for GL and BR in (a) 1998, (b) 1999 and (c) 2000. Discharge Q is also plotted

NO_3^- flux from the catchment was virtually unchanged (Table II). The increased discharge in 1998 resulted in lower mean seasonal NO_3^- concentrations (Table VI) than in years with lower discharges.

The lower NO_3^- concentrations observed in GL runoff in 1998 are to be expected. Increased ice ablation in the summer should result in a dilution of NO_3^- in the stream, because ice and firn are depleted of solute as a result of the leaching of NO_3^- from snow (Tranter *et al.*, 1993; Fountain, 1996). The observation that the BR catchment is a sink for NO_3^- , but that the sink is less effective in high snowfall/high runoff years, is consistent with results from other studies of nitrogen cycling in high-elevation catchments in the Sierra Nevada (Sickman *et al.*, 2001, 2002). Sickman *et al.* (2001) attribute the higher NO_3^- flux to greater mineralization,

and less uptake by plants because of the longer snow lie. However, the relative increases in NO_3^- during high snowfall years could also be hydrologically controlled. For example, the larger volume of water contained in the deeper snowpack could mean that a lower proportion of available water (and solute) is required to bring soils to saturation, resulting in a greater proportion of snowmelt runoff occurring as overland flow. If this were the case in the BR catchment, then a smaller proportion of the snowpack nitrate would infiltrate the soil zone when runoff is high, resulting in a greater export of NO_3^- , since less is available for biological uptake in the soils.

The results of this study, therefore, indicate that the lower NO_3^- concentrations and fluxes in BR are largely due to the much greater soil-covered area in this catchment. The greater water volume, and/or longer snow lie from the deeper snowpack in 1999 and 2000, resulted in an increase in the fraction of NO_3^- exported from the BR catchment. A more extensive study of NO_3^- dynamics in the area would be required to determine exactly how snow depth and duration affect the various processes controlling the export of nitrate from the BR catchment.

Interannual and intercatchment solute flux variations

Runoff volume was the dominant control on the interannual variations in total solute flux, with solute flux in both streams increasing with discharge. However, since the two streams exhibited opposite discharge responses to changes in climate, they also displayed opposite solute flux changes between years. Thus, for the 1998 El Niño year, when winter precipitation was low and summer temperatures were high, runoff and solute fluxes from BR were low, and those for GL were high relative to 1999 and 2000, when winter snowfalls were higher and spring/summer temperatures were cooler (Tables I and II).

The glacial stream had higher chemical denudation rates (specific solute flux) than BR, in any given year (Tables II and IV). The higher chemical denudation rates in the GL catchment seem to be primarily the result of higher specific discharge in GL. BR always had higher solute concentrations than GL, even though it drained a catchment containing abundant silicate minerals that are generally more resistant to weathering than carbonates. The greater solute generation per unit of water in the BR catchment is likely due to a combination of catchment processes, such as the provision of protons from pyrite oxidation or from carbonic and organic acids from the soils (Drever, 1997), longer water–rock contact times (e.g. as a result of significant routing of water through the saturated zone and soils), and possibly concentration by evapotranspiration (White and Blum, 1995). These results are consistent with the findings of Anderson *et al.* (1997), that glacier-covered catchments produced higher cation fluxes than non-glacial catchments draining similar rock types, but that the high denudation rates in glacier-covered catchments are a consequence of higher water fluxes.

In 1998, there was a substantial increase in the seasonal solute flux from GL relative to 1999 and 2000, but the increase was only 70–73% of the increase in discharge (Table III). Thus, mineral dissolution did not keep pace with the increase in discharge, and solute concentrations were reduced. This likely reflects changes in the flow routing, water–rock contact time and mineral surface area to water volume ratios resulting from the substantial glacial ablation and the development of subglacial channels in the summer of 1998 (Lafrenière and Sharp, 2003). The slow transit of waters through a distributed subglacial drainage system (which likely dominated in 1999 and 2000; Lafrenière and Sharp, 2003) promotes relatively efficient chemical weathering compared with weathering in a well-developed channelized subglacial system (Tranter *et al.*, 1993). The stronger dilution of Cl^- and NO_3^- (i.e. the low FCRD, Table III) is expected under conditions of increased glacial ablation, since these solutes are not derived from mineral weathering, and snowmelt-derived solutes would be diluted by ice melt. The crustally derived ions that experienced the lowest flux increases in 1998 relative to 1999 and 2000 were SO_4^{2-} and Mg^{2+} . The low FCRDs for SO_4^{2-} and Mg^{2+} (Table III) suggest that the dissolution of sulphate (from evaporites) and magnesium (from dolomites) in the glacial catchment is constrained by either the spatial distribution of source minerals relative to runoff, or by their dissolution kinetics. Evaporite minerals, the source of SO_4^{2-} in this catchment, are almost certainly associated with the dolomites in the Cambrian carbonate units (Machel and Anderson, 1989; Nesbitt and Muehlenbachs, 1994).

Since gypsum and anhydrite have high solubilities, the relatively low flux of SO_4^{2-} is most likely related to the distribution or rate of dissolution of the host dolomites. Dolostones are present within outcrops surrounding the Wapta Icefield and Bow Glacier (Price and Mountjoy, 1978), so there is no reason to suspect that the distribution of dolomite in the subglacial environment is restricted, although it may be isolated from the flow of water in channels. Hence, the slow dissolution kinetics of dolomite (and thus evaporites within the dolomites) likely account for the limited release of SO_4^{2-} and Mg^{2+} relative to the other major solutes in 1998, when high ablation and the development of channelized subglacial drainage likely reduced the average rock–water contact time in this catchment.

In BR, the total solute flux increases in 1999 and 2000 relative to 1998 were approximately proportional (97–99%) to the increases in discharge (Table III). Analysis of the runoff regime of BR between 1998 and 2000 indicates that the flow routing of meltwater was faster/more efficient in 1998 than in 1999–2000 (Lafrenière and Sharp, 2003). This suggests that slower flow routing in the catchment in 1999 and 2000 enabled weathering rates to keep pace with the increases in the volume of runoff. The additional snowmelt may also have increased weathering rates by providing more protons from carbonic and organic acids from the soils.

CONCLUSIONS

This study shows that adjacent glacial and non-glacial catchments experience opposite solute flux responses to climate perturbations such as ENSO. Relative to La Niña conditions, El Niño conditions (low winter snowfall and warm summer and spring air temperatures) led to increases in the flux of solutes from the glacial catchment and decreases in the solute flux from the snowmelt-fed catchment. In all years, intercatchment differences in solute composition were primarily controlled by differences in catchment geology (e.g. SO_4^{2-} , Na^+ , and Sr^{2+}) and the presence of soils (e.g. NO_3^- , Ca^{2+} and Mg^{2+}), whereas differences in total solute fluxes were largely dependent on specific discharge. The higher overall concentration of solutes in the non-glacial Bow River is likely the result of both longer average water–rock contact times in this catchment (i.e. more contact between water and both mineral and organic soils, reflecting larger contributions of groundwater and soil water to runoff) and a greater supply of protons from organic soils and/or pyrite oxidation. The higher chemical denudation rates in the glacial catchment under El Niño conditions seem to be primarily due to the high rates of catchment flushing (high specific discharge), since the two catchments had similar chemical denudation rates when the specific discharges were similar (Table IV).

The results of this study suggest that weathering rates in alpine areas of the Canadian Rocky Mountains may be sensitive to changes in the frequency and duration of El Niño events. Such changes are a feature of the climate record of the last 53 years. Prior to 1976, the mean monthly value of the southern oscillation index (SOI) was 0.116, whereas since 1976 it has been -0.604 (negative values indicate El Niño conditions). Between 1951 and 1975, 46% of months had negative SOI values, compared with 62% between 1976 and April 2004 (NOAA, 2004). This post-1975 shift in the regime of atmospheric teleconnection patterns such as the SOI and the Pacific decadal oscillation (PDO) is well known (Moore and Demuth, 2001). The effects of these changes are immediately apparent in the mass balance records from Peyto Glacier, located 4 km to the north of the Bow Lake catchment. Between 1966 and 1975, the mean winter balance of the glacier was 1432 mm water equivalent and the mean annual balance was -362 mm water equivalent. Between 1976 and 1995, these figures changed to 1062 mm and -647 mm water equivalent, respectively (Dyurgerov, 2002). Clearly, reduced winter snowfall after 1975 resulted in an increased rate of mass loss from the glacier.

The results presented here suggest that it is likely that runoff and denudation rates in highly glacierized alpine catchments in this region of the Canadian Rocky Mountains will have increased since 1975, whereas those in unglaciated catchments may well have decreased as a result of the more pervasive El Niño conditions. The greatest increases in glacially derived solute yields are likely to have involved the products of carbonate weathering (Ca^{2+} and HCO_3^-), with lesser increases in the flux of solutes derived from more resistant

lithologies. The flux of atmospherically derived solutes such as Cl^- and NO_3^- from glacial catchments may have shown little to no change, but our results suggest that the total flux of these solutes in alpine streams (glacial and non-glacial combined) would have decreased as a result of lower snowfall conditions. If the high frequency of El Niño conditions persists into the future, then it is likely that continued high summer ablation conditions will lead to a point where declining ice cover and low winter snowfalls result in a reduction in runoff and solute flux from both glacial and non-glacial catchments. If, on the other hand, El Niño-type conditions become less common, then higher winter snowfalls and limited exposure of glacial ice would lead to decreases in the total flux of solute from glaciated catchments, but likely moderate increases in the flux of atmospherically derived solutes from both glaciated and unglaciated catchments. ENSO-related variations in NO_3^- flux from alpine catchments might have significant impacts on productivity in downstream aquatic ecosystems.

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