

Controls on the major-ion chemistry of the Dokriani glacier meltwaters, Ganga basin, Garhwal Himalaya, India

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ABSTRACT. A detailed study of the major-ion chemistry of the Dokriani glacier meltwaters, feeding the Bhagirathi river, Ganga basin, Garhwal Himalaya, India, has been carried out to assess the role of active glaciers in the higher chemical-denudation rate (CDR) in this area. The CDR of the Dokriani glacier catchment is $321.6 \text{ t km}^{-2} \text{ a}^{-1}$, higher than in other glacierized catchments of the world, indicating intense chemical erosion in the glacierized catchments of the Himalaya. The dominance of Ca^{2+} , HCO_3^- and SO_4^{2-} in meltwaters throughout the 6 month (May–October) ablation period suggests that the chemical weathering is dominated by coupled reactions involving sulphide oxidation and carbonate dissolution. Good positive correlation between SO_4^{2-} and suspended-sediment concentration during July and August ($r^2 = 0.72$ and 0.67 , respectively) suggests that the southwest monsoonal rainfall enhances the weathering of supraglacial moraine and contributes significant amounts of sulphate to the high meltwater discharges. The sulphate flux, as a proportion of combined ($\text{SO}_4^{2-} + \text{HCO}_3^-$) flux, also increased from 45% at $2 \text{ m}^3 \text{ s}^{-1}$ to 63% at $10 \text{ m}^3 \text{ s}^{-1}$.

INTRODUCTION

The Ganga river basin, Garhwal Himalaya, India, has an area of $30\,000 \text{ km}^2$. It contains more than 1020 large and small glaciers (Vohra, 1993). It is estimated that 3.4% of the Ganga basin is presently covered by active glaciers (Vohra, 1981). Earlier studies of the major-ion chemistry of waters in the basin were focused on identifying the source water (Sarin and others, 1989, 1992). It was estimated that the chemical-denudation rate (CDR) of the Bhagirathi and Alaknanda river basins was 110 and $137 \text{ t km}^{-2} \text{ a}^{-1}$, respectively, suggesting intense chemical weathering in the Ganga headwater catchments. The two rivers join together at Devprayag to form the river Ganga.

In this work, we studied the major-ion chemistry of Dokriani glacier meltwater, with a view to assessing the contribution of active glaciers to the higher CDRs derived for the Ganga headwater rivers. Of particular importance is the monsoon which bursts over the eastern part of the Himalaya in the first week of June and contributes a large proportion of the annual runoff in a few months (Sharma, 1993). The monsoon is deflected by mountains and moves westward, extending throughout the region by the end of July, where it persists till mid-September (Mani, 1981).

The runoff from the glacierized valleys of the Ganga river basin is first fed by snowmelt as the transient snowline recedes, and this results in discharge peaks by the end of June. However, the dense cloud cover of the southwest monsoon between July and August over the Garhwal Himalaya cuts off the radiation, and melt from the glacier ice is subdued (Collins and Hasnain, 1995). The potential of solute acquisition by meltwaters in the subglacial environment is several times higher than in other glacial environments, due to (i) the slow transit time of water within the subglacial system (Tranter and Raiswell, 1991; Tranter and others, 1993;

Brown and others, 1994, 1996; Collins, 1995), (ii) the availability of large amounts of freshly comminuted rock flour, (iii) the availability of reactive minerals, such as carbonates and sulphide in the rock flour, and (iv) the relatively rapid oxidation of sulphide in the fresh rock flour, providing additional protons for chemical weathering (Tranter and others, 1993; Brown and others, 1996).

In this paper, we present detailed chemical results from daily meltwater samples collected during May–October 1994 from the Dokriani glacier in the Ganga basin. The results are analyzed with a view to evaluating the role of monsoonal rainfall and supraglacial weathering of moraine in controlling runoff chemistry.

STUDY AREA

The Dokriani glacier is a small glacier, located in the Uttarakashi district of Uttar Pradesh. The glacier lies 25 km east of Bhukki. It extends from latitude $31^\circ 49'$ to $35^\circ 20'$ N and from longitude $78^\circ 47'$ to $78^\circ 05'$ E (Fig. 1). The total length of the glacier is 5 km. The stream emerging at the glacial portal is Din Gad, which joins with the Bhagirathi at Bhukki. The total area of the glacier catchment is 9.58 km^2 , of which 5.76 km^2 is glacierized. Three-quarters of the glacier ablation area is covered by thick debris. The accumulation area of the glacier is about 2.5 km^2 , consisting of two cirque glaciers, one originating on Draupadi ka Danda and the other on Janoli. The equilibrium line is at $\sim 4960 \text{ m}$.

METHODOLOGY

Field studies were carried out for a period of 6 months from 8 May to 31 October 1994, covering the entire ablation period. Samples were collected at a gauging station estab-

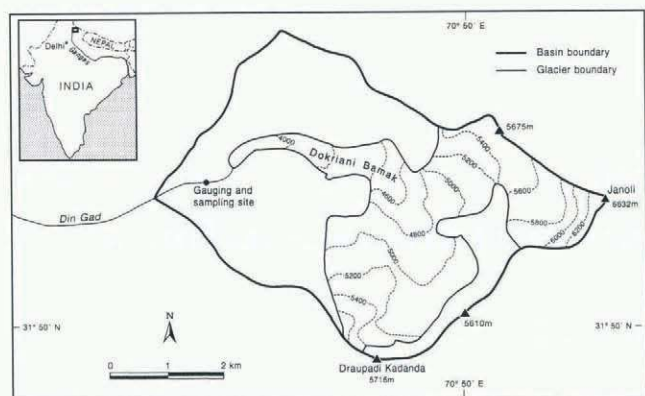


Fig. 1. Map of the Dokriani glacier catchment.

lished 600 m downstream from the glacier snout. Two samples were collected each day, corresponding with diurnal low flow (0800 h) and high flow (1700 h). Samples were immediately filtered through a Millipore 0.45 µm membrane filter paper by using a pneumatic pump and filtration apparatus. Bicarbonate was determined in the field by using an Orion 201 auto-titrator. Fifty millilitres of the sample was titrated against 0.004N HCl until an end-point of pH 4.5 was reached (APHA, 1985). Filtered samples were later brought to the laboratory at Delhi and were analyzed for the major cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) and anions (SO₄²⁻ and Cl⁻). Analysis of cations was carried out by flame atomic absorption spectroscopy with a GBC (906) atomic absorption spectrophotometer. Calcium and magnesium were analyzed in absorption mode, and sodium and potassium were analyzed in emission mode. Sulphate analysis was carried out by a turbidimetric method, using a

GBC (911) UV/VIS spectrophotometer. The absorbance of BaSO₄ suspension was measured at 420 nm (APHA, 1985). The minimum detection limit by this method is 1 mg L⁻¹. Chloride was determined by the mercury (II) thiocyanate method (Florence and Farrar, 1971). The absorbance of chloromercurate ions was measured at 460 nm with a UV/VIS spectrophotometer. Three replicates were run for cation analysis, and the instrument was recalibrated after every 15 samples. An overall precision, expressed as per cent relative standard deviation (RSD) was obtained for entire samples. Analytical precisions for Ca²⁺, Mg²⁺, Na⁺ and K⁺ were 1.5, 1.1, 2.0 and 1.2, respectively. Overall data reproducibility for anions was ±5%. Discharge was calculated by establishing a rating curve for the gauging site.

RESULTS AND DISCUSSION

The chemical composition of Dokriani glacier meltwater for low flows (0800 h) and high flows (1700 h) for selected flow regimes during the 1994 ablation period is shown in Table 1, which also shows the percentage charge balance error. The charge balance between cations and anions is <10%, confirming the reliability of the analytical results. The total cations (TZ⁺) and anions (TZ⁻) are related by the equation, TZ⁺ = 0.98TZ⁻ + 27.6 with a correlation coefficient of 0.95 for 360 samples. The range of ionic concentrations during the pre-monsoon, monsoon and post-monsoon seasons of the 1994 ablation period is given in Table 2. The major anions, sulphate and bicarbonate, have ranges of 85–1140 and 128–1053 µeq L⁻¹, respectively. Ca²⁺ was the major cation, with a concentration of 234–1941 µeq L⁻¹, and accounts for 66–90% of the total cations. K⁺ and Mg²⁺

Table 1. Major-ion composition of the Dokriani glacier meltwater at selected discharges, 8 May–31 October 1994 (in µeq L⁻¹)

Date (1994)	Time h	Julian day	Discharge m ³ s ⁻¹	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	% diff
8 May	0800	128.334	0.50	525	114	58	65	366	418	3	-1.56
	1700	128.708	0.60	458	92	49	60	286	279	7	7.02
24 May	0800	144.334	1.22	405	75	44	65	262	277	9	3.61
	1700	144.708	1.43	365	68	40	65	251	250	6	2.91
20 June	0800	171.334	3.88	307	49	22	48	246	191	3	-1.68
	1700	171.708	4.26	246	37	30	53	158	244	11	-6.14
29 June	0800	180.334	6.78	420	73	24	82	294	297	5	0.25
	1700	180.708	7.47	469	58	18	77	318	279	4	1.65
30 June	0800	181.334	5.26	1384	73	24	108	803	737	7	1.36
	1700	181.708	7.95	1941	72	20	128	1053	1140	3	-0.80
1 July	0800	182.334	5.68	990	65	24	96	673	557	3	-2.41
	1700	182.708	7.71	693	56	18	82	458	426	4	-2.25
2 July	0800	183.334	5.68	619	70	22	89	455	342	2	0.06
	1700	183.708	7.95	686	60	20	89	449	424	4	-1.29
3 July	0800	184.334	4.52	421	54	20	72	234	312	3	1.59
	1700	184.708	8.15	537	51	18	72	375	301	2	-0.05
24 July	0800	205.334	5.69	418	44	16	57	362	218	2	-4.16
	1700	205.708	12.50	603	42	13	72	403	349	2	-1.65
11 August	0800	223.334	5.02	283	45	24	45	205	171	2	2.37
	1700	223.708	7.93	271	34	18	47	185	190	3	-1.27
25 August	0800	237.334	4.57	319	62	26	59	198	266	2	-0.08
	1700	237.708	9.47	278	41	18	64	130	268	2	0.17
16 September	0800	259.334	2.44	373	68	34	52	275	197	2	5.29
	1700	259.708	3.92	253	44	21	41	184	139	1	4.78
8 October	0800	281.334	0.98	467	103	48	61	349	296	2	2.46
	1700	281.708	1.31	346	71	36	62	247	201	3	6.71
31 October	0800	304.334	0.44	593	96	54	65	377	402	1	1.73
	1700	304.708	0.71	569	92	54	65	376	368	1	2.34

Table 2. Ionic concentration range of Dokriani glacier meltwaters in pre-monsoon, monsoon and post-monsoon seasons, May–October 1994

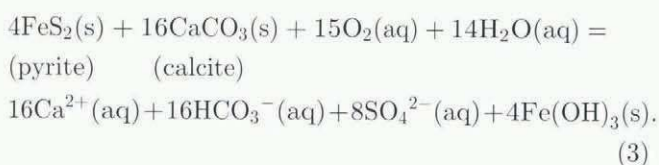
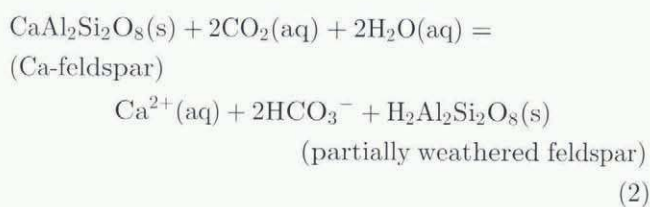
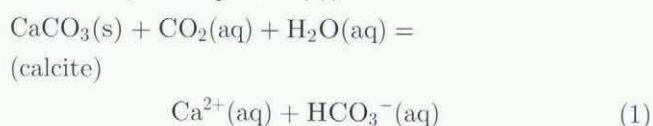
	Discharge m ³ s ⁻¹	Ca ²⁺ µeq L ⁻¹	Mg ²⁺ µeq L ⁻¹	Na ⁺ µeq L ⁻¹	K ⁺ µeq L ⁻¹	HCO ₃ ⁻ µeq L ⁻¹	SO ₄ ²⁻ µeq L ⁻¹	Cl ⁻ µeq L ⁻¹
Pre-monsoon	2.81–0.41	608–262	117–40	65–23	73–45	397–159	418–160	24–2
Monsoon	17.43–1.76	1941–236	80–31	36–12	128–41	1053–128	1140–85	12–1
Post-monsoon	3.92–0.44	593–234	107–37	57–20	68–40	384–168	431–137	7–1

comprise 6–20% and 3–15% of the total cations, respectively. Table 3 shows the cationic composition of Dokriani glacier meltwater in comparison with other glaciers.

SOURCES OF DISSOLVED IONS

The chemical composition of glacial meltwaters has demonstrated high rates of chemical weathering in subglacial environments (Reynolds and Johnson, 1972; Collins, 1979; Raiswell, 1984; Sharp and others, 1995; Brown and others, 1996). The two major anions, HCO₃⁻ and SO₄²⁻, in glacial meltwaters are mainly derived from the dissolution of atmospheric carbon dioxide and carbonates, and the oxidation of sulphides (Souchez and Lemmens, 1987). Dissociation of CO₂ and sulphide oxidation are the two main reactions that provide the bulk of the protons to weather carbonates, silicates and aluminosilicate in the drainage basin. The anionic content of glacial meltwater therefore reflects the acid sources used in the chemical weathering of bedrock minerals. The relative proportions of various ions in solution depend on their relative abundance in the bedrock and their solubility (Raiswell, 1984; Tranter and others, 1993). Sources of dissolved ions in the Dokriani glacier meltwaters can be evaluated by studying the relationship among the ions. A parametric correlation analysis for all measured ions during the 6 month observation period is given in Table 4. HCO₃⁻ and SO₄²⁻ are highly correlated with calcium (r² = 0.94 and 0.92, respectively) and with potassium (r² = 0.71 and 0.74). The proportion of HCO₃⁻ and SO₄²⁻ in the meltwaters reflects the relative dominance of the two major sources of protons during the subglacial chemical erosion. According to Brown and others (1996), the ratio of HCO₃⁻ to (HCO₃⁻ + SO₄²⁻), referred to as the C-ratio, has a value of 1.0 when carbonation reactions involving atmospheric CO₂ dominate (as in Equations (1) and (2)), and a value of 0.5 when coupled reactions involving the weathering of

carbonates by protons derived from sulphide oxidation dominate (as in Equation (3)).



The C-ratio of the Dokriani glacier meltwater during May and June is 0.5 (Fig. 2), suggesting the dominance of carbonate dissolution and the oxidation of sulphides (Brown and others, 1994). From late June to early July (Julian days 174–187), high discharges were derived largely from ice- and snowmelt, which rapidly passed through the hydro-

Table 4. Correlation matrix for ions, May–October 1994

	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻
Ca ²⁺	–					
Mg ²⁺	0.50	–				
Na ⁺	0.35	0.93	–			
K ⁺	0.76	0.30	0.10	–		
HCO ₃ ⁻	0.94	0.53	0.38	0.71	–	
SO ₄ ²⁻	0.92	0.47	0.35	0.74	0.80	–
Cl ⁻	0.15	0.28	0.39	0.14	0.13	0.18

Table 3. Summary of cationic composition of Dokriani glacier meltwater in comparison with other glaciers

Glacier	Date	Number of samples	Range of % as % (Ca ²⁺ +Mg ²⁺ +Na ⁺ +K ⁺)				Source
			Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	
Dokriani glacier	August–September 1992	180	45–70	3–28	6–18	8–18	This study
	October–November 1993	88	39–75	9–21	6–18	8–21	This study
	May–October 1994	360	66–90	3–15	9–15	7–23	This study
Gornergletscher	July–August 1974	69	45–90.9	5.2–23.3	1.3–17.4	1.8–22.0	Collins (1979)
	July–September 1975	59	57–71.3	14–18	1.9–8.8	9.6–26.5	Collins (1979)
	July–August 1976	41	52.7–76.1	13.5–17.6	3.2–8.1	3.9–25.0	Collins (1979)
Lewis Glacier	June–August 1974	14	38.1–39.7	7.5–11.0	44.6–47.0	4.7–12.4	Church (1974)

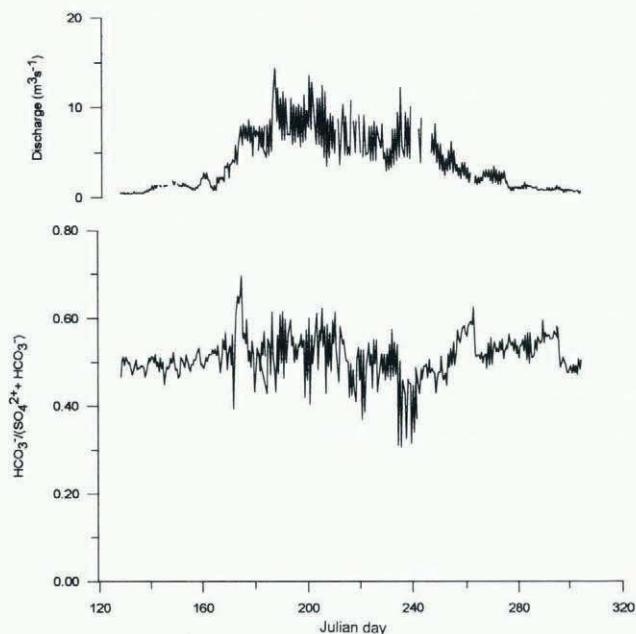


Fig. 2. Ratio of HCO_3^- to $(\text{HCO}_3^- + \text{SO}_4^{2-})$ in bulk meltwaters draining the Dokriani glacier, May–October 1994.

logical system. The enhanced C-ratio (0.55 and 0.7) during this period indicates that protons are additionally derived from the dissolution and dissociation of atmospheric CO_2 (Brown and others, 1996). During July and August (Julian days 195–243), cloud cover over the Himalaya, linked to the onset of the southwest monsoon, cuts off radiation and causes snowfall in the accumulation zone and rainfall in the ablation region (Collins and Hasnain, 1995). Meltwater discharges during this cloudy, monsoonal period were likely to be sustained by drainage of a subglacial reservoir built over the previous months. Hence, runoff contains a very high proportion of stored subglacial water. The C-ratio during this period varies between 0.31 and 0.63, suggesting the dominance of carbonate dissolution and sulphide oxidation in controlling the meltwater composition. The cloud-burst on 24 August (Julian day 236) resulted in high discharge ($17.45 \text{ m}^3 \text{ s}^{-1}$) and the lowest C-ratio (0.31), as shown in Figure 2, suggesting that rainfall running through supraglacial moraine may also have a strong control on the chemical characteristics of meltwater.

Figure 3 shows the relationship of SO_4^{2-} and HCO_3^- to total cations for the rising limb, the crest segment and the falling limb of all hydrographs from May through October. Both sulphate and bicarbonate show good correlation with TZ^+ on the rising limb, with sulphate showing better correlation, whereas bicarbonate was better correlated to TZ^+ on the falling limb. The crest segment is characterised by comparatively low correlation of TZ^+ with bicarbonate and sulphate individually, but the relationship improves to $r^2 = 0.82$ when bicarbonate and sulphate are combined. These data show that pyrite oxidation and carbonate dissolution are dominant solute suppliers to waters on the ascending limb of the hydrograph, and that carbonation reactions became more important on the falling limb of the hydrograph.

ROLE OF MONSOONAL RAINFALL AND WEATHERING OF SUPRAGLACIAL MORaine

A total of 1269 mm of rainfall fell on the Dokriani glacier

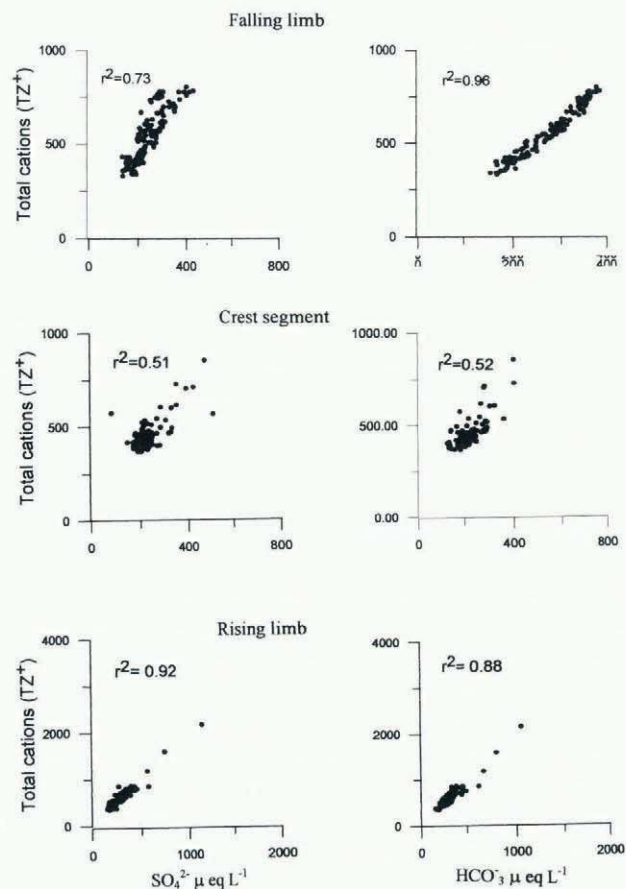


Fig. 3. Relationship of SO_4^{2-} and HCO_3^- to total cations for rising limb, crest segment and falling limb, May–October 1994.

during the May–October 1994 observation period, mostly during the months of July and August. This rainfall pushed large quantities of debris into the glacier sole through crevasses (Hasnain and Chauhan, 1993). During June, HCO_3^- and SO_4^{2-} show a good positive correlation with suspended-sediment concentrations ($r^2 = 0.84$ and 0.89 , respectively), as shown in Figure 4. This probably indicates the dominance of water from a solute-rich source, water either discharged through sediments at the glacier bed or that has been kept in storage for a long period, as a major transporter of suspended sediment. Successive diurnal melting of snow and ice rapidly leaches most of the sulphate from the snow and ice (Davies and others, 1987). Later in the ablation season, the leached snow and ice gives rise to sulphate-depleted supraglacial meltwater (Tranter and Raiswell, 1991). The release of sulphate by the oxidation of sulphides in suspended sediment is a slow process and therefore is only likely to contribute significant sulphate concentrations to waters which have spent long periods at the glacier bed in contact with sediments (Brown and others, 1994). However, contrary to these observations, Dokriani glacier meltwaters show higher sulphate concentrations during July and August and show good positive correlation between SO_4^{2-} and suspended-sediment concentration ($r^2 = 0.72$ and 0.67 , respectively), as shown in Figure 4. One possible explanation is as follows: Continuous low-intensity rainfall may have initiated pyrite oxidation within the supraglacial moraines. Thereafter, occasional high-intensity showers may leach the sulphate from the debris and cause its domination during the seasonal high-flow period of July and August, when suspended-sediment concentra-

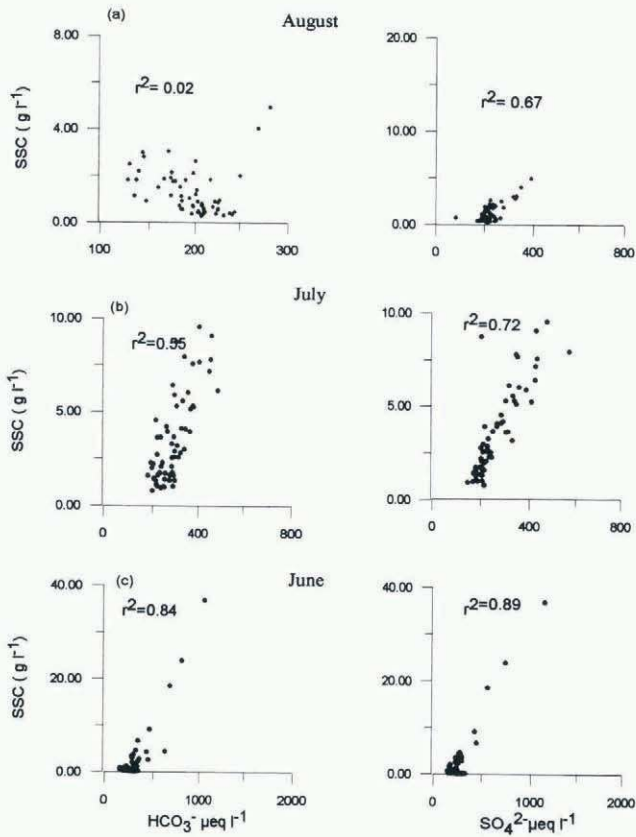


Fig. 4. Relationship between SO_4^{2-} and HCO_3^- with suspended-sediment concentration (SSC) for June–August 1994.

tions are high. The percentage contribution of suspended sediments from the supraglacial sources in the bulk flow is not known. The post-monsoon dry period of September exhibits a weak correlation between SO_4^{2-} and suspended-sediment concentration ($r^2 = 0.09$), and thus substantiates the observation of Tranter and others (1993) that reactive sulphides will be largely absent from rock flour transported from the subglacial system.

SOLUTE FLUXES AND CHEMICAL-DENUDATION RATES

Solute fluxes in glacial meltwaters usually increase with discharge. The largest solute fluxes are transported by the most dilute meltwater as solute concentration is usually inversely related to discharge (Sharp and others, 1995). Figure 5 shows the relationship between the fluxes of SO_4^{2-} and HCO_3^- with the glacial discharge. The flux of SO_4^{2-} as a proportion of the flux of $SO_4^{2-} + HCO_3^-$ increases from 40–45% at $2 m^3 s^{-1}$ to 40–63% at $10 m^3 s^{-1}$. This reinforces our contention that the weathering of supraglacial moraines initiated by monsoonal rainfall enhances the sulphate concentration at high discharges. This is contrary to the results obtained by Sharp and others (1995) in the catchment of Haut Glacier d’Arolla in Switzerland.

The cationic denudation rates from some of the important glaciers in the European Alps and North America are given in Table 5. The cationic denudation rate of Dokriani glacier is $4160 meq m^{-2} a^{-1}$, about four times higher than the highest recorded at Gornergletscher, Swiss Alps (Metcalf, 1986). The CDR of the Dokriani glacier was $321 t km^{-2} a^{-1}$. Monthly values of chemical denudation during the 1994

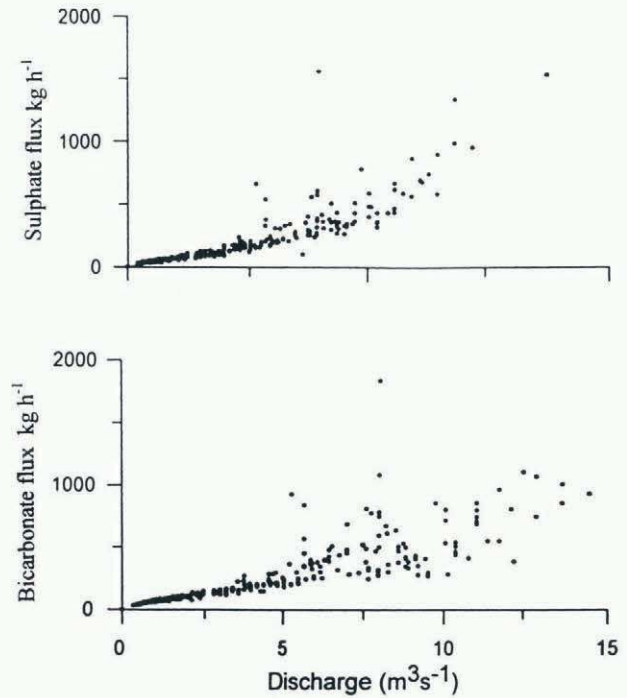


Fig. 5. Relationship between the fluxes of SO_4^{2-} and HCO_3^- with meltwater discharge during May–October 1994.

observation period are given in Table 6. The high CDR substantiates our observation that the high relief, southwest monsoonal rainfall and supraglacial moraines are very significant in controlling the chemistry of Garhwal Himalaya glacial meltwaters.

CONCLUSIONS

A detailed hydrochemical study of Dokriani glacier meltwater has been carried out with a view to evaluating the controls on the major-ion chemistry of the glacierized Himalayan basin. The important conclusions are:

1. The dominance of Ca^{2+} , HCO_3^- and SO_4^{2-} in meltwaters throughout the ablation period suggests that the meltwater chemistry is dominated by coupled reactions involving sulphide oxidation and carbonate dissolution.
2. High sulphate concentrations and the good relationship between SO_4^{2-} and suspended-sediment concentrations

Table 5. Cationic denudation rates of the Dokriani glacier in comparison with other glaciers

Glacier	Denudation rate $meq m^{-2} a^{-1}$	Source
<i>European glaciers (Swiss Alps)</i>		
Haut Glacier d’Arolla	640–685	Sharp and others (1995)
Glacier de Tsijiore Nouve	508	Souchez and Lemmens (1987)
Gornergletscher	454	Collins (1983)
Gornergletscher	1010 ± 505	Metcalf (1986)
<i>North American glaciers</i>		
South Cascade Glacier (WA)	930	Reynolds and Johnson (1972)
Berendon Glacier (B.C.)	947	Eyles and others (1982)
<i>Southern Himalaya</i>		
Dokriani glacier	4160	This study

Table 6. Monthly solute flux and chemical-denudation rates of Dokriani glacier catchment, 1994

Month	Solute flux	Solute flux	CDR t km ⁻²
	t	%	
May	86.0	3.0	9.0
June	431.0	18.0	45.0
July	970.0	40.0	101.0
August	563.0	23.0	59.0
September	279.0	11.0	29.0
October	124.0	5.0	13.0

during July and August suggests that the monsoonal rainfall enhances the supraglacial moraine weathering, providing high SO₄²⁻ content in the meltwater during periods of high discharge. This is substantiated by observed higher sulphate fluxes during high discharges.

- The CDR of the Dokriani glacier catchment is 321.6 t km⁻² a⁻¹, suggesting very high rates of chemical weathering in the southern Himalayan glaciers.

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