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Solute yield from a glacierized high mountain basin

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ABSTRACT Electrical conductivity and discharge of meltwaters in the Gornera, which drains from the basin of Gornergletscher, Pennine Alps, Switzerland, were monitored for extended periods during the 1978-1979 hydrological year. Samples of meltwater were analysed for the cations Na^+ , K^+ , Mg^{2+} and Ca^{2+} by atomic absorption spectrophotometry. Relationships between individual and sums of cations with electrical conductivity were ascertained. Rhythmic diurnal inverse variations of solute transport occurred roughly in phase with those of discharge. The relationship between load and discharge is nonlinear, and middle-range flows account for the highest transport of solute load. The annual gross cationic denudation rate was estimated as $478.1 \text{ meq m}^{-2} \text{year}^{-1}$ (net of precipitation input 454.0 meq $m^{-2}year^{-1}$), which is significantly higher than continental averages. Almost all the dissolved load was transported during the summer ablation season.

La perte de solides dissous d'un bassin glaciaire de haute montagne

La conductivité électrique et le débit de l'eau RESUME de fusion de la Gornera, émissaire du bassin du Glacier du Gorner, Alpes valaisannes, Suisse, furent observés durant des périodes prolongées de l'année hydrologique 1978-1979. Des échantillons de l'eau furent analysés pour les cations Na⁺, K^+ , Mg^{2+} , et Ca²⁺ par absorption atomique. Des relations entre la conductivité et les concentrations individuelles ou la somme des cations ont été mises en évidence. La charge dissoute variait journellement en raison inverse des débits. La relation entre charge et débit n'est pas linéaire, et les débits moyens transportent les charges les plus grandes. Le taux brut de l'érosion cationique annuelle est évalué à 478.1 meq m^{-2} anne e^{-1} (454.0 net), valeur considérablement plus élevée que la moyenne mondiale. Presque tous les solides dissous sont exportés pendant la saison estivale d'ablation.

INTRODUCTION

High precipitation and high specific discharge, coupled with delivery to runoff of large quantities of suspended sediment produced by subglacial erosional processes, suggest that geochemical activity will also be considerable in glacierized high mountain areas. Although glaciers outside polar regions occupy only 0.2% of the world land area (Flint, 1971), the formation of runoff and the transport of dissolved load from the thousands of small glacier basins in high mountains are of disproportionate importance since flows in the headwater tributaries of many great continental rivers originate in the alpine zone. In summer, alpine glaciers supply meltwaters and solutes to the major rivers of North America, South America, Europe and Asia. Almost all studies of rates of chemical denudation in small basins relate to ice-free and vegetated areas, and few to those mountain environments in which hydrological response is modified by the presence of snow and ice. Estimates of dissolved solids transport at regional and continental levels from measurements in major rivers subsume alpine contributions with those arising from downstream areas of lower elevation (e.g. Durum et al., 1960; Meybeck, 1976). However, significant concentrations of dissolved solids have been determined in meltwaters draining from the snouts of alpine glaciers (Collins, 1979; Lemmens & Roger, 1978). Subglacial chemical weathering processes have been inferred from the chemical composition of meltwaters flowing at the interface between glacier sole and bed (Vivian & Zumstein, 1973), and from the presence of thin discontinuous layers of precipitates on former beds where ice has recently retreated (e.g. Hallet et al., 1978). In Baffin Island, higher concentrations of dissolved solids were reported in meltwater rivers draining basins with larger percentage glacierization (Church, 1974). A coarse estimate of the role of chemical denudation in the South Cascade Glacier basin, Northern Cascade Mountains, USA, which is 43.5% glacier covered, was distinctly greater than regional, continental and global levels (Reynolds & Johnson, 1972). Individual ionic and total dissolved solids concentrations in alpine meltwater streams are inversely related to discharge during the summer ablation season (Collins, 1979), and are generally also lower than winter values. During the ablation period, such overall decreases in concentration are far more than offset by the increase in runoff volume, as indicated by an index of instantaneous dissolved load transport (Collins, 1981).

The aim of this paper is to provide detailed cationic load data for a meltwater river draining from an alpine glacierized basin, using field measurements of discharge and electrical conductivity (EC) and laboratory determinations of major cations in water samples. In addition to intrinsic interest in rates of chemical denudation in high mountains, the objective of this study was to achieve an accurate and reliable assessment of solute yield throughout an annual discharge cycle, which may be compared with data collected in areas having other climatic, relief and geological conditions. Short term, diurnal variations of dissolved load are also examined in an attempt to assess the role of glaciers in the relationship between solute transport and discharge in alpine regions. Field measurements were made in the basin containing Gornergletscher, Pennine Alps, Kanton Wallis, Switzerland (45°57'N, 07°46'E) as part of an intensive series of investigations of the total environment of proglacial streams. The Gornera drains an area of 82 km^2 , which is currently 83% glacierized and extends over 2629 m above a gauge at 2005 m a.s.l. to the highest peak, Dufourspitz, at 4634 m. The bedrock underlying the basin, of igneous and metamorphic origins, is considered to be watertight.

MEASUREMENTS

Strategy

Ideally, continuous hydrograph and chemograph records are desirable since the sum over a hydrological year of the products of instantaneous discharge and solute concentration provides an accurate representation of total solute load evacuated from a drainage basin (Walling, 1978). Results of hydrochemical investigations of meltwaters in the Gornera during the ablation season of 1975 suggested the need for continuous measurements of EC in determinations of solute loads. Discharge-EC and discharge-individual cation concentration relationships in summer are so variable at diurnal and daily levels that the derivation of accurate rating relationships is prevented. Intensive sampling throughout the repeating diurnal fluctuations of flow produced by ablation is necessary (Collins, 1979). Since the seasonal pattern of variation of solute concentration outside the months June to September was unknown, it was decided to monitor EC continuously throughout the study period from November 1978 to October 1979, which also removed the logistical difficulty of frequently obtaining water samples during winter. Samples of meltwaters were collected for laboratory analysis in 1975, 1976 and 1979 in order to determine empirically relationships between EC and cationic concentrations. The period November to October was selected for the study since flow in October is derived from meltwater stored within the glacier, and stable winter minimal discharge is not reached until November.

Measurement records

Hourly mean flows were calculated using continuous discharge records from 14 May to 30 September 1979. Winter flows were lower than the operational minimum for the flume. EC was monitored in the periods 28 December 1978-29 January 1979, 17 February-4 April, 5-14 May, 26 May-4 June, 26 June-6 September and 16 September-17 October 1979. EC was not standardized to a reference temperature since the temperature of meltwaters ranged only between $0.1^{\circ}-1.2^{\circ}C$.

Chemical analyses

Samples of meltwater were collected and stored in polyethylene bottles. Immediately after collection, samples were filtered through a rinsed Oxoid 0.45 μ m membrane and refrigerated until analysis between 2 days and 3 months after collection. Concentrations of Na⁺, K⁺, Mg²⁺, and Ca²⁺ were determined with a Perkin-Elmer 403 atomic absorption spectrophotometer operating under standard conditions.

EC-IONIC CONCENTRATION RELATIONSHIPS

Steele (1976) has suggested that EC offers a measure of individual ionic concentration, given by:

$$C_i = a + b EC$$

where C_i is the concentration of each ionic species i (mg 1⁻¹), and a and b are constants. This model was applied to the determined individual cations and to the sum of these cations expressed in both mg 1⁻¹ and as equivalents (μ eq 1⁻¹), with EC as measured at the time of sampling. The relationships obtained were poor for Na⁺ and K⁺, better for Ca²⁺ and Mg²⁺, and considerably improved for total cations, particularly for the sum of equivalents where the correlation coefficient was 0.94 (Table 1). In all cases, the intercept a was appreciably larger than the theoretical value of zero. Low explanation of variance for the individual ions may result from ion-exchange processes between sediment and water during filtration rather than from errors in chemical analysis of the samples. Varying proportions

TABLE 1 EC-ionic concentration relationships for meltwaters from the Gornera estimated by linear regression (equation (1))

Ci	a	b	r^2	п
$Na^+ (mg l^{-1})$	0.73	0.00	0.00	119
K^+ (mg l^{-1})	0.51	0.01	0.05	120
Ca^{2+} (mg l^{-1})	1.68	0.14	0.31	122
Mg^{2+} (mg 1^{-1})	0.49	0.02	0.33	121
$\Sigma C_{j} (mg l^{-1})$	2.28	0.20	0.74	115
$\Sigma C_{j} \ (\mu eq \ l^{-1})$	94.83	11.27	0.88	115

n = Number of samples.

 r^2 = Coefficient of determination.

of individual ionic species in meltwaters of the Gornera at different times will also contribute (Collins, 1979). Ca²⁺ is the dominant ion in these meltwaters followed by Mg²⁺, and these ions account for 45.0-90.9% and 5.2-23.3% respectively of the total determined cations. An improved fit for the sums of cations probably results from the net effect of displacement and release of cations absorbed on the surfaces of sedimentary particles by exchange with ions previously in solution, a process envisaged by Lorrain & Souchez (1972). Despite a relatively good fit, estimation of the sum of cationic equivalents from EC results in errors of up to $\pm 25\%$ at low concentrations and of up to $\pm 10\%$ for higher values.

DISCHARGE-LOAD RELATIONSHIPS

Rhythmic diurnal discharge variations of the Gornera concurrent with daily ablation of the glacier surface consist of steep rising and more gradual falling limbs, which are roughly in phase with sharp decreases and less rapid recoveries in EC values (Fig.1). An index (S) of solute load, calculated by:

$$S = EC \times Q$$

where S is instantaneous load in arbitary units and Q is discharge, has a pattern of diurnal variation similar to and in phase with that of EC, although daily maximum load usually follows minimum discharge and minimum load precedes maximum flow, both by 1-3 h. This repeating characteristic shows that initially as discharge is augmented with the onset of ablation, the supply of solutes also increases, but



FIG.1 Discharge hydrograph (upper), measured electrical conductivity (centre), and solute load as index S (lower) for meltwaters in the Gornera, 27 July-1 August 1975.

then decreases rapidly, before commencing recovery which is continued throughout falling flows. As meltwater discharge increases, some water is forced under pressure away from major conduits to enter cavities at the ice-bedrock interface, where chemical enrichment ensues. This water is returned when pressures become equalized and continues as discharge and pressures decline (Collins, 1979).

Figure 2 presents a plot of hourly mean values of S against Q for a period of 43 days in 1975. Individual diurnal inverse relationships between S and Q are agglomerated in the scatter of points in the range from about 8 to $22 \text{ m}^3 \text{s}^{-1}$, and a tendency towards reduction of load at larger flows is indicated. Lower flows in the Gornera occurred when periods of snow cover reduced ablation during two events each persisting for several days. The relationship between S and Q at low flows reflects differing solute concentration characteristics between the two recession events, but also indicates rising solute load with discharge. Throughout the range of observations of discharge a considerable spread of load values is associated with a



FIG.2 Relationship between hourly mean values of the index S and discharge of the Gornera for the period 20 July-31 August 1975.

given level of flow. This suggests that estimates of solute loads from a rating curve with discharge are inappropriate in the case of glacial meltwater rivers.

ESTIMATE OF ANNUAL CATIONIC YIELD

The sum of cationic equivalents was estimated from EC (Table 1), and it was intended to obtain cationic load from the sum of the products of cationic equivalents and discharge, using hourly mean data. However, because of instrument malfunction resulting from icing in winter and sedimentation in summer, some records were lost. An attempt was therefore made to assess the relative accuracy of load calculation using daily mean values of the concentration of total cations and daily mean discharge. In a 45-day period of unbroken records, daily



FIG.3 Seasonal variations of daily mean values of electrical conductivity and discharge of meltwaters in the Gornera for the hydrological year November 1978-October 1979. Broken lines indicate interpolated values of electrical conductivity.

load estimates using the product of daily means ranged from -4.9 to +8.4% of the values obtained from the sum of products of hourly means. The estimate of cumulative load throughout this period derived using daily mean values was 99.75% of that obtained from the more detailed data. Since daily mean EC could be linearly interpolated where records were missing (Fig.3), daily cationic loads were therefore estimated from mean daily data for the entire period of the hydrolog-ical year. Discharge data were estimated for the winter months as $0.1 \text{ m}^3 \text{s}^{-1}$ in October to December and $0.05 \text{ m}^3 \text{s}^{-1}$ in January to April.

Seasonal variations of the transport of cationic load from Gornergletscher are given in Table 2, together with those of discharge during summer. Estimated winter discharge was $1.29 \times 10^6 m^3$, giving a total annual flow of 110.86 $\times 10^6 m^3$, the months May-September contributing 98.8%. Transport of cationic load occurred predominantly

Month	Cationic load: (10 ⁶ eq)	(%)	Discharge: (10 ⁶ m ³)	(%)
November	0.27	0.7		_
December	0.31	0.8	_	-
January	0.16	0.4	-	-
February	0.15	0.4	-	
March	0.16	0.4	-	
April	0.15	0.4	-	
Мау	1.73	4.4	3.28	3.0
June	7.13	18.2	21.81	19.9
July	12.18	31.1	38.63	35.3
August	10.37	26.5	30.79	28.1
September	6.05	15.4	15.05	13.7
October	0.53	1.4	-	-
Total	39.21		109.56	

TABLE 2Seasonal variations of the transport of cationicload and discharge from the Gornergletscher basin

from June to September, the months also with highest discharges. Only 4.5% of the total solute load was removed in the period outside the months May-September. The gross annual cationic denudation rate was 478.1 meq m⁻²year⁻¹. This rate includes an atmospheric component, which can be estimated from the cation content of meltwaters on the glacier surface. Between 9.7 and 38.5 meq m⁻²year⁻¹ of cations are contributed by the atmosphere. Taking a mid-range value of 24.1 meq m⁻²year⁻¹, the net annual removal of cations is 454.0 meq m⁻² year⁻¹.

DISCUSSION

Error in the estimated cationic denudation associated with the application of this method in the glacial environment is probably of

the order of $\pm 20\%$. Error results from: (a) unexplained variance in the relationship between EC and sum of cation concentration modelled by equation (1); (b) errors in the determinations of cation concentration, both instrumental and because of changes during storage and by ion-exchange reactions in filtration; and (c) error in gauging the flow of turbulent meltwater streams. No attempt has been made to include in the cationic load those ions partitioned from the solution in the adsorbed phase on sediments, which would probably increase cationic yield by about 10\%. Error from data interpolation is unlikely to change the estimate of denudation significantly since the records are complete for almost all the summer when over 95% of solute transport occurred.

Estimates of rates of cationic denudation for other glacierized basins have been based on less detailed chemical and hydrological information. In assessing a gross rate of 960 meq $m^{-2}year^{-1}$ (930 net) for South Cascade Glacier, Reynolds & Johnson (1972) estimated the total cation concentration for any day of the year by assuming sinusoidal annual variation. The curve was fitted using 12 sample determinations. This annual variation pattern is not applicable to the data for Gornergletscher as indicated by Fig.3. Eyles et al. (1982) averaged eight analyses of meltwater samples in order to obtain a rate of denudation of 947 meq m^{-2} year⁻¹ (gross) for Berendon Glacier. northern Coastal Mountains, British Columbia, Canada. While comparability of these results with those obtained in this study is uncertain because of the variety of methods used in the calculations, it is apparent that cationic yield from glacierized basins is significantly higher than the overall world average of 390 meq $m^{-2}year^{-1}$ (Livingstone, 1963). Individual glacial basins differ in the percentage of the area covered by ice and alpine environments differ in total annual amounts of precipitation and runoff. Both South Cascade and Berendon basins receive considerably more precipitation (3840 and 5200 mm year⁻¹ respectively) than Gornergletscher (1023 mm year⁻¹), are less intensively glacierized (43.5 and 62.3%) and are located at lower elevations.

CONCLUSIONS

Although the data presented relate to only one year, the estimated rate of cationic denudation provides evidence of considerable chemical activity in the alpine glacial environment. Further measurements are required in the Gornergletscher basin in order to investigate the role of annual hydrological variations in controlling solute transport and to confirm the level of denudation indicated by this study. The importance of glaciers in the processes of chemical denudation remains enigmatic because of the nonlinear relationship between solute load and discharge. Middle range flows are the most effective in solute transport because of the hydro-glaciological control of meltwater enrichment in subglacial sites. Decrease in the rate of solute transport at higher flows suggests that suspended sediment provides only a small supply of ionic material to meltwaters after initial reaction at the glacier bed. Detailed studies of solute yield from glacierized basins in maritime precipitation regimes remain outstanding, together with investigations of the spatial

distribution of solute sources both within alpine basins and in those larger basins in which there is a mountain component.

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