

Temporal Variations in the Minor and Trace Element Chemistry of Meltwaters Draining Haut Glacier d'Arolla, Switzerland: Implications for Downstream Water Quality

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ABSTRACT

Concentrations of dissolved major ions in meltwaters draining glacial environments have been widely reported. However, minor and trace elements in outflow waters from glaciers have rarely been determined. Dissolved Al, Ti, Cr, Mn, Ni, Cd and U are present in meltwaters draining Haut Glacier d'Arolla at concentrations greater than the median composition of world stream waters. This suggests that river systems fed by glacierised headwaters may derive much of their dissolved minor and trace element load in the headwater region. Temporal variability in the concentrations of many dissolved minor and trace elements are inversely related to bulk discharge. However, instantaneous dissolved fluxes are positively correlated with discharge. Early meltseason waters are most concentrated in dissolved minor and trace elements. However, their contribution to the annual dissolved flux of minor and trace elements to downstream environments is small, since discharge is low. Conversely, maximum instantaneous dissolved fluxes occur in early August when annual discharges are at a maximum. Estimates of dissolved minor and trace element fluxes from Haut Glacier d'Arolla suggest that ~ 90% of the annual total is transported between mid-May and late-September. The enrichment of many of these elements in glacial meltwaters compared to world streamwaters, coupled with the timing of their delivery to downstream areas during the summer months, may have significant environmental implications.

Keywords: trace/minor elements, glacier, water quality, annual fluxes, headwater

INTRODUCTION

Minor and trace element concentrations in rivers are a consequence of catchment bedrock geochemistry, within-channel particulate-dissolved interaction (*e.g.* adsorption of metal ions onto particles, particle deposition), atmospheric deposition and anthropogenic activity (Chester, 1990; Langmuir, 1997; Leckie and James, 1974). Typically remote from urban and/or industrial centers, Alpine environments provide an ideal opportunity to study minor and trace element variations resulting from water-rock interaction (Brown and Fuge, 1998a,b), since meltwater chemistry is controlled primarily by chemical weathering processes (*e.g.* Raiswell, 1984; Tranter *et al.*, 1993; Brown *et al.*, 1996). Chemical weathering rates in glacierised catchments have been reported to be up to 2.6 times world averages (Sharp *et al.*, 1995; Anderson *et al.*, 1997). This results from (i) rapid physical weathering processes which supply an abundance of freshly ground, geochemically reactive rock flour, (ii) high suspended sediment concentrations and rock-water ratios, (iii) poorly buffered solutions, and (iv) large snow- and ice-melt-derived meltwater fluxes (Sharp, 1991). In Alpine glacierised catchments these water fluxes exhibit strong seasonal variations. These are

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driven by changes in energy receipts at the glacier surface (Röthlisberger and Lang, 1987), resulting in high runoff during the summer months. This results in an annual hydrograph which is generally inverse to that observed in temperate fluvial catchments, where most runoff occurs during the winter months (Petts and Foster, 1985; Ward and Robinson, 1990).

The *concentrations* of dissolved major ions in outflow waters from glacial environments are generally inversely related to discharge, while their *fluxes* are positively related to discharge (*e.g.* Sharp *et al.*, 1995; Brown *et al.*, 1996). While dissolved major ions are now routinely measured in bulk outflow draining Alpine glaciers, data for minor and trace elements, including potentially toxic-metals or bio-limiting nutrients (Manahan, 1991), are rarely presented, despite an increasing interest in temporal river water quality variations (*e.g.* Sherrell and Ross, 1999; Shiller, 1997), water resource exploitation (*e.g.* Agrawal, 1999), the potential influence of such dissolved ions on biota in river ecosystems (*e.g.* Malea and Haritonidis, 1999; Watras *et al.*, 1998; Johns and Timmerman, 1998; Chapman *et al.*, 1996), and the utility of dissolved ions in determining solute provenance (*e.g.* Sharp *et al.*, 1995; Brown *et al.*, 1996; Brown and Fuge, 1998 a,b).

This study presents seasonal minor and trace element concentration and flux data for bulk meltwaters draining Haut Glacier d'Arolla, Switzerland, in order to (i) evaluate minor and trace element concentrations in an area remote from urban and industrial centres, and (ii) to assess the timing and magnitude of environmentally important minor and trace element delivery from a pristine glacierised headwater catchment to a major continental river system.

STUDY AREA

Fieldwork was undertaken at Haut Glacier d'Arolla, Valais, Switzerland. The glacier is located at the head of the Val d'Herens, and meltwater ultimately enters the Rhône River system. The glacier is ~ 4.2 km long, occupies ~6.3 km² of a ~12 km² catchment, and extends between ~2560 to 3500 m a.s.l. The bedrock geology consists of igneous and metamorphic rocks of the Arolla series of the Dente Blanche Nappe (Dal Piaz *et al.*, 1977; Mazurek, 1986). Trace amounts of geochemically reactive trace minerals such as calcite (up to 0.58%) and pyrite (up to 0.71%), have been identified by microscopy (Tranter, *et al.*, 1997). Brown *et al.* (1996) recorded carbonate concentrations of up to 12% and pyrite up to 5% in fine (< 5 mm ϕ) morainic material.

METHODS

Bulk meltwater samples were collected twice daily ~ 200 m from the glacier snout at 10:00 and 17:00 h local time (approximating to minimum and maximum discharge respectively) between 16 June (Julian Day [JD] 167) and 20 August (JD 232) 1999. In addition, supraglacial meltwaters were sampled periodically throughout the study period. Meltwater samples were collected by hand in a 1 l Nalgene LDPE plastic bottle and immediately vacuum filtered through Whatman 0.45 μ m cellulose nitrate membranes using a Nalgene polysulphone filter unit and hand pump (Gurnell *et al.*, 1994). Each sample was split between two pre-cleaned Nalgene polyethylene bottles. One was acidified with 10% PRIMAR HNO₃ for cation, minor and trace element analysis while the other was left un-acidified for anion analysis. pH was determined in the field using an Orion 250A portable pH/ISE meter with an Orion Ross combination electrode and automatic temperature compensator.

Major ion composition was determined by ion chromatography (Dionex DX-100). Accuracy was \pm 3% and precision \pm 5%. Minor and trace element analysis was undertaken by inductively-coupled plasma mass spectrometry on a VG Elemental Plasmaquad in semi-quantitative mode using 100 ppb of Ru as an internal standard in each sample. Accuracy was typically \pm 15% and precision \pm 10%. Bulk discharge was monitored from a rectangular weir located in a hydroelectric power intake structure operated by Grande Dixence SA, located ~ 2 km from the glacier snout. No significant extra-glacial inputs of water are evident between the glacier terminus and the weir. Precipitation was measured by a tipping-bucket rain gauge at a Campbell Scientific meteorological station, located near the hydroelectric power intake structure.

RESULTS AND DISCUSSION

The concentration of major, minor and trace elements in supraglacial and bulk meltwaters

The concentration of major ions and selected minor and trace elements present in the samples of supraglacial meltwater and bulk meltwater are summarized in Table 1. These data indicate significant solute acquisition as dilute supraglacial waters are routed through the subglacial hydrological system. Calcium is the dominant metal in bulk outflow, with lesser quantities of Mg^{2+} , Na^+ and K^+ and Fe (Table 1). The other dominant metals are Al, Mn, Sr, Ti, Zn, Cu, and Rb, which are present at maximum concentrations of between 10 and 200 $\mu g\ l^{-1}$ (Table 1). Cadmium, Hg, Pb, As, Ni, Ba, Ga and U are present at maximum concentrations between 1 and 10 $\mu g\ l^{-1}$, while Co and Cs are present below 1 $\mu g\ l^{-1}$.

Table 1. Major ions and minor and trace elements in supraglacial and bulk meltwaters, from the 1999 ablation season, from 16 June (JD 167) to 20 August (JD 232). *At of near detection limits. ** lowest median value cited in Riemann and de Caritat (1998) or Langmuir (1997).

ELEMENT / ION	INPUT WATERS			OUTPUT WATER			World Stream Water**	
	Supraglacial			Bulk				
	Minimum	Maximum	Median	Minimum	Maximum	Median		
MAJOR IONS ($\mu g\ l^{-1}$)	Na^+	22	88	34	240	1400	370	6100
	K^+	21	77	36	260	1500	370	2300
	Mg^{2+}	9.8	18	14	230	670	400	4100
	Ca^{2+}	280	440	320	4400	10000	6600	18000
	Cl ⁻	0	67	19	31	640	88	-
	NO_3^-	0	90	25	0	1100	400	-
	SO_4^{2-}	0	110	75	2800	8900	5200	-
	HCO_3^-	900	1300	1100	7700	26000	17000	-
MINOR & TRACE ELEMENTS ($\mu g\ l^{-1}$)	Al	2.8	9.0	6.6	24	200	35	10
	Ti	0.5	1.0	0.7	1.1	46	3.7	3
	Cr	0.5	1.0	0.9	0.4	7.3	0.9	0.7
	Mn	4.4	9.7	8.8	5.0	30	9.5	4
	Fe	42	93	83	44	1500	390	40
	Co	0.0	0.1	0.0	0.1	0.7	0.1	0.1
	Ni	0.0 *	0.2 *	0.1 *	0.3	4.0	0.6	0.3
	Cu	0.1	0.3	0.2	0.3	12	0.8	3
	Zn	0.3 *	3.7	1.1	0	26	5.0	15
	Ga	0.0	0.1	0.0	0.1	2.5	0.2	0.0001
	As	0.1 *	0.4 *	0.3 *	0.4 *	4.6	0.9	4
	Rb	0.1	0.2	0.1	0.3	10.8	0.5	1
	Sr	0.5	1.2	0.9	9.4	28	16	70
	Cd	0.1	0.3	0.2	0.1	9.4	0.2	0.02
	Cs	0.0	0.0	0.0	0.0	0.4	0.0	0.03
	Ba	0.1	0.7	0.3	0.3	2.7	0.8	20.0
	Hg	0.1	0.3	0.2	0.0	5.6	0.3	0.1
Pb	0.1 *	0.3	0.2	0.0 *	4.7	0.2	3.0	
U	0.1	0.2	0.1	0.2	1.5	0.7	0.04	

The dominance of calcium suggests that carbonate dissolution is a major source of solute in the hydrological system beneath Haut Glacier d'Arolla, reflecting the geochemical reactivity of this ubiquitous, trace mineral (Tranter *et al.*, 1993). Mass balance calculations suggest that carbonate-derived Ca^{2+} is the dominant cation in other high altitude catchments that are also dominated by igneous and metamorphic bedrock (*e.g.* Raiswell, 1984; Drever and Hurcomb, 1986; Mast *et al.*, 1990; Finley and Drever, 1997). Brown and Fuge (1998a,b) explained the distribution of minor and trace elements in meltwaters draining Haut Glacier d'Arolla on the basis of lithogenic provenance. They attributed much of the Sr and Ba, along with Ca and Mg, to carbonate weathering. Iron, Ni, and Co are thought to derive primarily from the breakdown of pyrite, which is also widespread. Other calcophile elements, including Cu, Pb and Zn, were hypothesized to

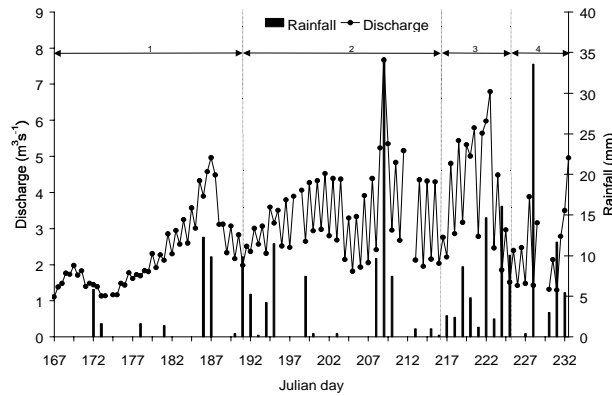
derive from other sulphides in the catchment, including chalcopyrite, galena, sphalerite and silicate minerals. Of the other minor and trace metals, Al, Ti, Mn and Rb were attributed to silicate minerals, and U from the breakdown of trace minerals such as allanite and apatite (Brown and Fuge, 1998a,b).

Many of the minor and trace elements in meltwaters draining Haut Glacier d'Arolla are present at concentrations significantly higher than the median concentration of world stream waters (Table 1). However, Sr and Ba, which being alkaline earth metals, would be expected to have relatively high concentrations in calcite, are considerably lower in bulk meltwaters than in world stream waters. In view of the dominance of calcite weathering, it seems likely that Sr and Ba concentrations in the calcite are relatively low.

Discharge characteristics for the 1999 ablation season

Figure 1 shows the discharge and rainfall events for the study period, from JD 167-232. Maximum daily discharge and discharge amplitude generally increased during the meltseason, reflecting variations in radiation receipts at the glacier surface, the up-glacier retreat of the transient snowline, and the development of an efficient channelised subglacial drainage system. Precipitation-driven discharge peaks are superimposed on these ablation-driven variations (*e.g.* JD 187 and JD 209)(Figure 1). Four hydro-meteorological periods (P1 to P4) have been defined during the 1999 study period based on a qualitative analysis of bulk discharge and meteorological records (Figure 1).

Figure 1. Seasonal variations of twice daily discharge (at 10:00 and 17:00) and daily rainfall during the 1999 ablation season, for the period 16 June (JD 167) to 20 August (JD 232). The 4 hydro-meteorological periods are identified (see text).



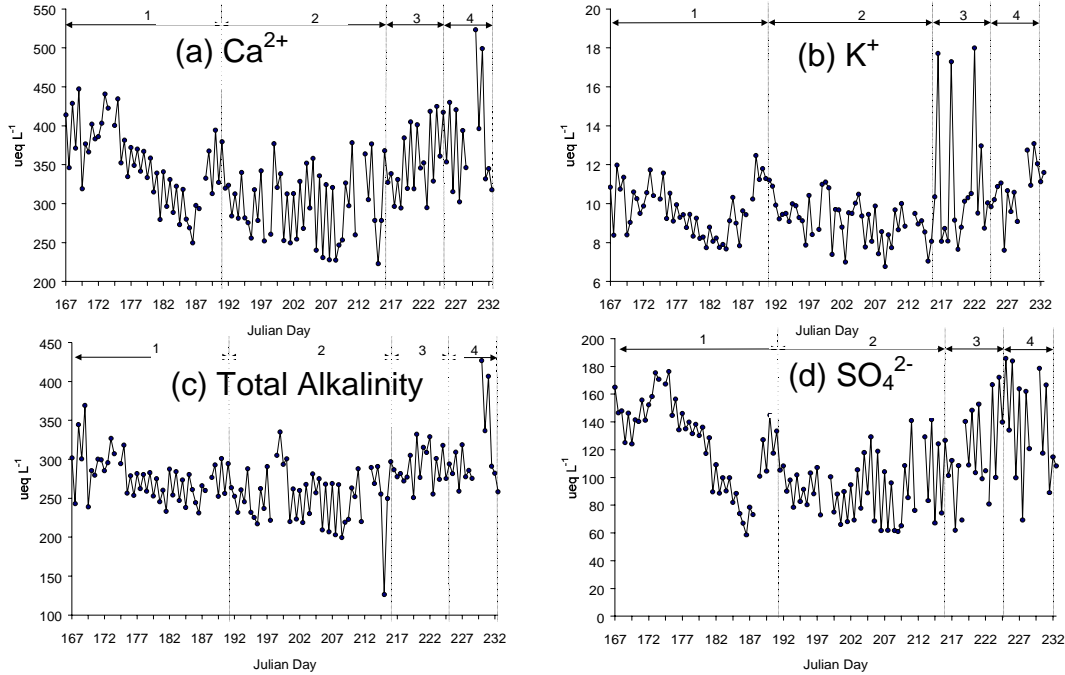
Seasonal variations in the concentration of major, minor and trace elements in bulk meltwaters

Seasonal variations in the bulk meltwater concentration of selected major ions, minor and trace elements are shown in Figures 2 and 3 and summary statistics are presented in Table 2. Concentrations of major, minor and trace elements are generally inversely related to bulk discharge during the ablation season, with the highest concentrations during periods of low discharge (P1 and P4). Aluminium deviates significantly from this general pattern, with maximum concentrations during P3. Conversely, the least concentrated waters with respect to all major, minor and trace elements occur when discharge is highest (P2 and P3).

Figures 2 and 3 suggest that Ca^{2+} , SO_4^{2-} , Al, Ti, Rb, Sr, Ba and Cu exhibit similar seasonal variations, with the lowest concentrations occurring during P2. Conversely, Ni and U appear more

concentrated in P2 than in P1 and P4. These data suggest that downstream environments will experience the most concentrated waters with respect to most minor and trace elements when discharge is lowest (*ie.* during the winter months).

Figure 2. Seasonal variations in the concentration of selected major ions in bulk meltwaters from twice-daily sampling (daily at 10:00 and 17:00) from 16 June (JD 167) to 20 August (JD 232).



Seasonal variations in the flux of major, minor and trace elements in bulk meltwaters

In contrast to dissolved ion concentrations, the instantaneous dissolved flux (or load, determined from the product of concentration multiplied by discharge) of major, minor and trace elements increases with meltwater discharge (Table 2; Figure 4). Thus, the largest dissolved fluxes are transported by the most dilute meltwaters.

Table 2. pH, discharge, major ion concentrations ($\mu\text{eq l}^{-1}$), minor and trace element concentrations ($\mu\text{g l}^{-1}$) and instantaneous fluxes (mg s^{-1}) for the 4 hydroclimatological periods. Total fluxes (kg) for sampling period, ablation season, winter, and annually.

Period		Q	pH	K ⁺	Ca ²⁺	SO ₄ ²⁻	HCO ₃ ⁻	Al	Ti	Ni	Cu	Zn	Rb	Sr	Cd	Ba	U
1	Conc	1.95	8.1	9.4	350	130	280	39	8	0.6	0.7	6.9	0.7	18	0.3	0.9	0.7
	Flux	-	-	730	14000	12000	32000	75	15	1.2	1.3	12	1.3	36	0.6	1.7	1.3
2	Conc	3.06	8.1	9.3	300	89	260	33	6.9	0.6	0.6	3.2	0.4	13	0.2	0.6	0.7
	Flux	-	-	1100	19000	13000	47000	96	22	1.9	1.5	11	1.2	40	0.8	2.2	2.1
3	Conc	3.83	8.3	9.9	340	110	280	48	7.5	0.5	0.9	5.2	0.5	16	0.2	0.8	0.4
	Flux	-	-	1600	26000	20000	67000	160	27	2.2	3.5	21	1.7	61	0.7	3	1.6
4	Conc	2.39	8.3	11	350	120	290	35	7.6	0.7	1.1	8	0.6	18	0.2	0.9	0.8
	Flux	-	-	920	17000	12000	41000	71	18	1.2	2.4	19	1.4	39	0.3	1.5	1.4
SAMPLING PERIOD (kg)		-	-	6200	100000	72000	260000	810	120	9.9	-	-	9.6	230	-	14	10
ABLATION SEASON (kg)		-	-	10000	160000	120000	420000	1300	200	16	-	-	16	380	-	22	16
WINTER (kg)		-	-	1300	21000	15000	55000	170	26	2.1	-	-	2.1	50	-	2.9	2.2
ANNUAL (kg)		-	-	11000	180000	130000	480000	1500	220	18	-	-	18	430	-	25	19

Figure 3. Seasonal variations in the concentration of selected minor and trace elements in bulk meltwaters from twice-daily sampling (daily at 10:00 and 17:00) from 16 June (JD 167) to 20 August (JD 232).

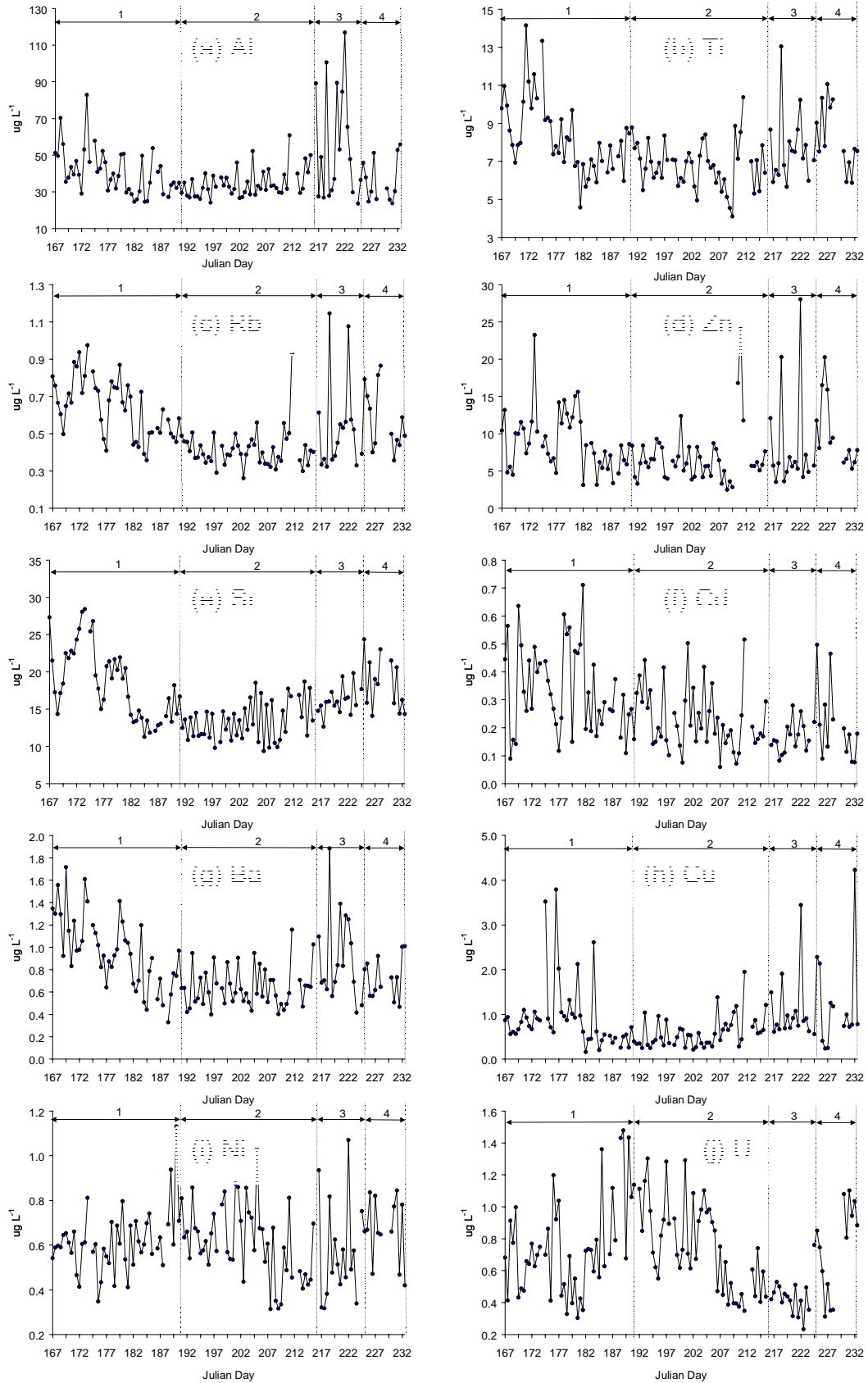
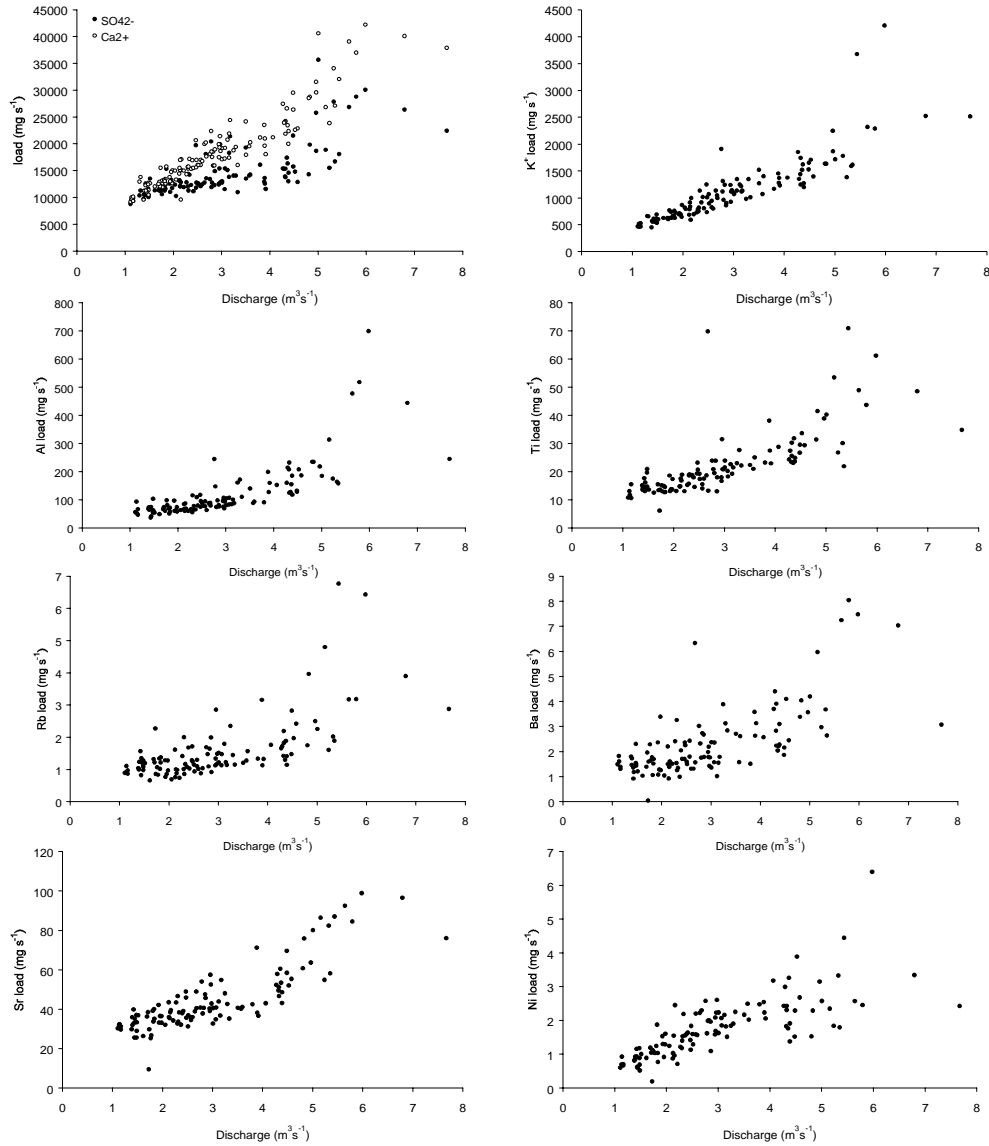


Figure 4. Instantaneous fluxes of selected major, minor and trace elements versus bulk discharge.



Dissolved Ca^{2+} , K^{+} and Sr fluxes have an approximately linear relationship with discharge over the range of discharges measured. However, the form of the relationship between bulk discharge and other dissolved ion fluxes varies. For example, SO_4^{2-} and Ni fluxes increase less rapidly for each unit increase in discharge above $\sim 3 \text{ m}^3 \text{ s}^{-1}$. Conversely, Al , Ti , Rb and Ba exhibit a greater increase in dissolved flux per unit increase in discharge $> 4 \text{ m}^3 \text{ s}^{-1}$.

While early- and late-meltseason waters exhibit maximum minor and trace element dissolved concentrations, their contribution to the annual dissolved flux (and hence export) of these elements is small. Indeed, for the nearby Gornergletscher, cation fluxes outside the May-September period only constituted between ~ 4.5 and 8.4% of the annual total (Collins, 1983; Metcalf, 1986). Least squares linear regression relationships between dissolved ion fluxes and discharge may be exploited to estimate fluxes outside the study period, and annual fluxes of individual minor and trace elements (Table 2). Discharge records are only available for Haut Glacier d’Arolla from early May until late September 1999. However, analysis of previous annual discharge hydrographs

from Haut Glacier d'Arolla suggest that the winter period is characterized by a relatively constant discharge. Assuming a winter discharge of $0.2 \text{ m}^3 \text{ s}^{-1}$, annual flux estimates suggest that ~ 88 % of dissolved Al, Ti, Ni, Sr, Ba and U are exported between mid-May and late-September. Only ~ 12 % of the annual dissolved flux is exported outside this 5 month period (Table 2). This estimate is in good agreement with that of Sharp *et al.* (1995), who suggest that winter major ion solute fluxes may contribute up to 10 % of the annual flux. Estimates of annual dissolved fluxes of individual minor and trace elements range between $\sim 20 \text{ kg yr}^{-1}$ (Ni, Rb, Ba, U) and $1,500 \text{ kg yr}^{-1}$ (Al) (Table 2). These are small by comparison with annual dissolved fluxes of major ions, which range between $11,000 \text{ kg yr}^{-1}$ (K^+) and $180,000 \text{ kg yr}^{-1}$ (Ca^{2+}). If annual dissolved ion fluxes from the glaciers in the Rhône valley exhibit a similar pattern, this suggests that this major continental river will receive a disproportionately large flux of environmentally important minor and trace elements during the summer months.

These data have important implications for the timing and quantity of minor and trace element delivery to all river systems fed by glacierised headwater catchments. The relatively large fluxes of environmentally significant minor and trace elements during the summer months may result in the downstream accumulation of these elements in biota (e.g. Malea and Haritonidis, 1999; Watras *et al.*, 1998; Johns and Timmerman, 1998; Chapman *et al.*, 1996) and on sediments (e.g. Tessier and Campbell, 1987; Santiago *et al.*, 1994). Seasonal variations in the accumulation of metals in aquatic organisms resulting partly from changes in the flux and concentration of metals in waters have been reported elsewhere (e.g. Malea and Haritonidis, 1999). Additionally, water resource exploitation in downstream environments may be influenced by the large flux of major, minor and trace elements from glacierised catchments in the summer months. For example, irrigated agriculture is widespread in the Rhône valley (Grove and Grove, 1990), and the large flux of minor and trace elements to irrigated crops at these times may lead to the accumulation of these species in crops. This may be common in many Alpine and mountainous environments where water is derived from glacierised headwater regions.

Finally, it is important to acknowledge that minor and trace element transport in fluvial systems is complex, as the dissolved concentration of elements are affected by factors such as the nature of the weathering solution (e.g. pH, the presence of organic acids) and interactions with solid material carried in suspension (Chester, 1990; Leckie and James, 1974; Langmuir, 1997). Therefore, the total trace element export from a glacierised basin comprises transport in solution and in association with abundant glacial flour (e.g. Santiago, 1994; Ramesh *et al.*, 2000). The minor and trace element concentrations and fluxes presented here are therefore minimum estimates, since only the solute load is considered (*cf.* Mitchell *et al.*, submitted).

CONCLUSIONS

Alpine glacial meltwaters acquire significant quantities of solute during transit through the subglacial hydrological system. While major ions are more concentrated in bulk meltwaters than minor and trace elements, many minor and trace elements associated with the breakdown of silicates are present at concentrations higher than world stream-water averages. This suggests that river systems fed by glacierised headwaters may derive much of their minor and trace element load in the headwater region.

Temporal variations in dissolved ion concentrations indicate that the most concentrated waters are exported outside the summer meltseason. However the greatest flux of major, minor and trace elements occurs during the summer ablation season (mid May – late September). This may have significant implications for (i) the temporal variation of water quality in rivers fed by glaciated headwater catchments, such as the Rhône, and (ii) the biological and non-biological accumulation of potentially toxic or bio-limiting minor and trace elements in downstream environments.

Acknowledgements

This work was supported by a University of Wales Aberystwyth studentship (AM), and University of Wales College Research Fund (GHB and RF). A.M. acknowledges Grande Dixence S.A for the provision of discharge data, and Ian Willis and Doug Mair for meteorological data. Field assistance was provided by Becky Goodsell, Sam Clemens and Kaspar Arn. Thanks must also go to Lorraine Hill for assistance and guidance in the laboratory, and Bill Perkins for help with the ICP-MS determinations. Two anonymous referees are thanked for their helpful comments on an earlier version of this manuscript.

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