The Impact of Heterogeneous Flow Paths on Snowmelt Runoff Chemistry

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ABSTRACT

The role of heterogeneous flow paths in determining the chemical composition of meltwater was examined in a field experiment north of Inuvik, NWT. The concentrations of major anions were determined for the pre-melt snowcover and for the daily flow in 16 separate compartments within a 0.25 m^2 lysimeter. Daily melt water samples were retained for chemical analysis from four compartments representative of the total range in flows. Early in the melt period the daily flow volume varied from 0.2 to 2.5 times the daily mean flow for the entire lysimeter, while the solute concentrations were typically 2 to 5 times higher in the compartments with low flow than in those with the highest flows. The concentration factors (CF) [ratio of the solute concentration in the flow to the initial snowpack solute concentration] early in the melt varied from 1.5 to 10, and then decreased to between 0.1 and 0.5 and after 50% of the melt there was no relationship between flow and concentration.

INTRODUCTION

During the last 15 years, numerous studies have considered the chemistry of meltwater from snowpacks (eg. as included in Davies et al., 1991; Jones and Orville-Thomas, 1987). This work has clearly described the basic features, including: (1) fractionation and (2) preferential elution. Fractionation refers to the release of inorganic ions at variable rates over time, while preferential elution describes the release of some ions before others. Although there have been a variety of explanations for these observations, recent studies have suggested that they are explained by the micro-scale variations in ion location on and within snow particles. These variations occur due to chemical exclusion during ice crystal growth (Hewitt et al., 1991). Previous studies (eg. Tranter, 1991) have noted considerable variations in the timing, magnitude, and sequence of ion release. For example, the magnitude of fractionation, expressed as a concentration factor (CF) [ratio of the solute concentration in the flow to the initial snowpack solute concentration], typically varies from 2 to 10. Some of the factors used to explain these variations include: melt rate (Tranter, 1991), location of the solute in the snowpack (Bales et al., 1989), heterogenous flow paths (Marsh and Webb, 1979 as referenced in Tranter, 1991), and selective ion retention by ice (Tranter et al., 1986). Field and laboratory experiments have been used to show the relative importance of most of these, but there have been no published studies of the role that flow paths play in controlling the CF.

Heterogeneous flow paths are initiated when meltwater first enters a snowcover and the wetting front develops flow fingers at its leading edge (Marsh, 1991). These flow fingers develop due to instabilities at the leading edge of the wetting front (eg. Parlange, 1974) and structural variations in the snow. The permeability of the snow in the flow finger increases as a result of more rapid grain growth (Colbeck, 1976; Marsh, 1987) due to the higher water content in the flow path as compared to the surrounding "non-flow path" zone. These higher permeability pathways may remain for much of the snowmelt period. These pathways, in combination with horizontal ice layers which decrease flow in certain areas and increase it in others, result in variations in vertical meltwater flux across a horizontal plane. Few measurements have been made of this flow variability, but it has been suggested that the surface area required to average the spatial variations in flow is of the order z^2, where z is the snow depth (Male and Gray, 1981). Field measurements of the variability in vertical flow in shallow Arctic snowpacks (z from 1 to 1.5 m), has shown that flow is relatively uniform over areas of

approximately 1 m², while within 0.02 m² areas flow varies from 0.2 to 3 times the mean flow over a larger area (Marsh and Woo, 1985). In deeper snow of the Sierra Nevada Mountains (z up to 2.4 m), Kattelmann (1989) found that flow could be non-uniform over areas of several square metres.

The objective of this paper is to provide field observations of the spatial and temporal variations in meltwater flow volume and chemistry.

METHODS AND STUDY AREA

Field work was carried out during May and June 1992 near Trail Valley Creek located approximately 50 km north-northeast of Inuvik, NWT and 80 km south of the Beaufort Sea. Snowcover typically begins to develop in this area in late September or early October, melt begins in mid to late-May and the snowcover is completely removed by mid-June. The mean daily January temperature at Inuvik is -30°C, and the mean annual precipitation is 266 mm, of which 57% falls as snow. Trail Valley Creek is within the zone of continuous permafrost, and consists of an upland tundra plateau incised by a broad river valley. Elevations range from 70 to 140 m above sea level. Low-bush tundra vegetation dominates, with short (0.3 m high) willows, moss, and grass. In addition, there are occasional patches of black-spruce forest (up to 10 m high) and high-bush willows and alders (up to 2 m in height) on valley sides and bottoms. In the low-bush tundra, late winter snowcover is typically 0.2 to 0.5 m in depth, while in the high-bush areas the snow is often between 1 and 2 m in depth.

In order to document the transport of water and solutes through this arctic snowpack, a site within a stand of high bush vegetation on the upland plateau was selected (68° 44' 41" N, 133° 27' 49" W). This site has a nearly circular ring of willows (approximately 2 m in height) and is approximately 10 m in diameter. Within this ring, the vegetation is dominated by short grasses. The snowpack within this natural snow trap was between 1 and 2 m deep at the end of the 1991/92 winter.

A 0.25 m² lysimeter, divided into 16 separate compartments each 0.0156 m² in area, was installed at the base of this snowpack. Each compartment was lined with a clean, plastic liner. The lysimeter was installed into a snowpit wall as the pack approached isothermal conditions, using the methodology described by Marsh and Woo

(1987). Melt water from each compartment was collected in individual containers and the cumulative flow volume was measured daily at the time of minimum flow. This typically occurred in the early morning. This sampling scheme ensured that each sample contained flow originating over a single melt day. Melt water from four compartments was saved each day for subsequent chemical analysis. These samples included the compartments with the lowest and highest flows, while two other samples were saved to represent compartments with flows between these extremes. Since the compartments with the highest and lowest flow varied from day to day, the chemistry samples were obtained from different compartments on each day. In addition, snow physical properties and premelt snow chemistry was often obtained from a snowpit located approximately 2 m away from the lysimeter pit.

All snow and meltwater samples were collected, prepared and analyzed as follows. Snow pits were dug with teflon coated shovels and scraped clean with scoops that had been washed in hydrochloric acid and rinsed with deionised water. Snow was sampled from distinct snow strata and snow density was measured from each layer. Snow samples were collected in clean polyethylene resealable bags, while lysimeter samples were collected in HDPE bottles that had been acid washed then rinsed several times with deionised water. Melted snow samples and lysimeter meltwater samples were filtered through 0.25 μm nucleopore filters. pH was measured with a Hach-one meter and low-ionic-strength research probe before and after filtering. All samples were then stored in HDPE bottles which had been pre-washed as noted above, and then shipped from Inuvik to Saskatoon for analysis.

Anion analyses (Cl^-, NO_3^-, SO_4^{2-}) were conducted on a Dionex 2010i ion chromatograph with a 100 μl injection loop, 0.75 m $NaHCO_3$/ 1.5 m Na_2CO_3 eluent and suppressed conductivity detection. Samples were introduced by Technicon sampler into the loop after mixing 9 parts sample to 1 part concentrated eluent (10x the working eluent concentration). A Dionex 4270 Integrator measured peak area and a Linear 100 recorder measured peak height of Dionex concentration traces. Numerous blanks on scoops, bottles, filters and analytical equipment were consistently below detection limits, indicating that no measurable contamination of samples occurred. The level of precision and limits of detection of the Dionex is normally at least an order of magnitude less than the levels measured.

Although the cations were also measured, this paper will only report chloride (Cl⁻), nitrate (NO₃⁻), and sulphate (SO₄²⁻) values since they represent the complete anion elution order $SO_4^{2-} > NO_3^- > Cl^-$ (Davis, 1991).

RESULTS

The premelt snowpack, sampled on May 19, 1992, near the lysimeter site was 125 cm in depth, had a mean density of 352 kg/m³, and a total snow water equivalent (SWE) of 440 mm. The thickness, grain type, SWE, and Cl⁻, NO₃⁻, and SO₄²⁻ concentrations of each layer are given in Table 1. Although there were large variations in Cl⁻ and SO₄²⁻ concentrations between layers, there were no trends from top to bottom of the pack, or layers with concentrations much larger than the rest of the pack. NO₃⁻, however, was considerably different. The top layers of the pack had NO₃⁻ concentrations which were 1 to 2 orders of magnitude larger than the bottom layers of the pack. Pomeroy et al.

(1993) suggest that low concentration of NO₃⁻ in the bottom of the pack is due to depletion during temperature-gradient metamorphism over the winter.

Because of the variations in SWE between layers, a weighted mean concentration was calculated for each anion. These values will be used when calculating a concentration factor for the outflow chemistry. The concentration factor (CF) is found as: CF = (concentration in the meltwater outflow/ weighted mean concentration in the premelt snowcover).

Figure 1 shows the total daily flow from each of the 16 compartments in the lysimeter, with flow expressed as a fraction of the mean daily flow from all compartments, for the period day 149 to 164. From day 149 to 155, daily maximum air temperature ranged from 5.9 to 9.6°C, and daily minimum temperature from 0.5 to -3.1°C. Between day 156 to 160 temperatures remained below zero and lysimeter flow ceased. Flow resumed again by day 162, and temperatures remained above zero for the remainder of the study period, with a maximum temperature of 23.9°C.

Table 1 - Premelt snowpit data at the multicompartment lysimeter site, May 19/92 (day 140). The SWE for the ice layer is estimated assuming a density of 700 kg/m³. Grain shape follows the classification of Colbeck et al. (1990). Grain shape descriptions are as follows: 1 - precipitation particle, 3b - large rounded particles > 0.5mm, 8a - horizontal ice layer, 5a - cup-shaped depth hoar crystal.

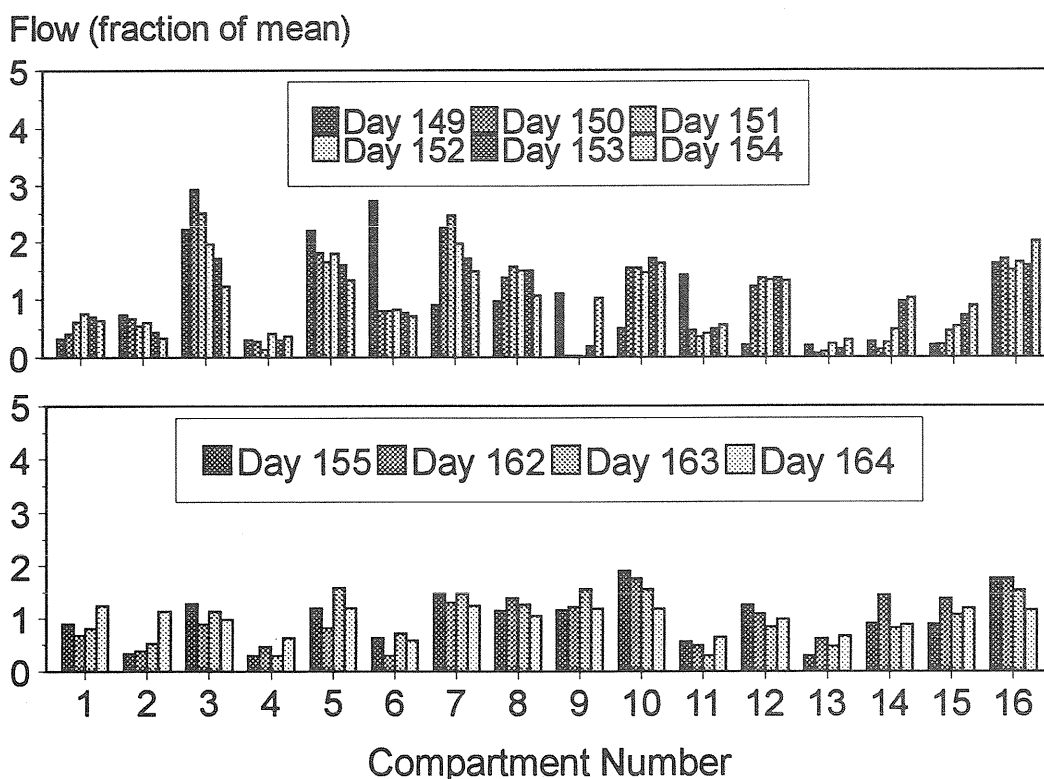| Description	Layer #	Thickness (mm)	Grain shape	SWE (mm)	Cl⁻ (μeq/l)	NO₃⁻ (μeq/l)	SO₄²⁻ (μeq/l)
Top Layer	9	40	1	14	33.3	5.2	10.4
wind crust	8	--		0	--	--	--
	7	140	3b	60	14.8	3.3	5.6
	6	140	3b	51	8.4	3.1	4.7
ice layer	5	10	8a	7	--	--	--
	4	50	5a	17	26.7	6.2	7.5
	3	390	5a	138	49.9	0.049	9.2
	2	200	5a	54	22.9	0.049	8.1
Bottom Layer	1	280	5a	99	24.9	0.82	6.9
total		1250		440			
mean					25.8	2.7	7.5
weighted mean					29.2	1.4	7.4

Flow (fraction of mean)

Figure 1. Daily flow in each of 16 compartments within a 0.25 m² lysimeter installed near the base of the snowpack. The flow for each compartment is expressed as a fraction of the mean daily flow for all compartments. During the period day 155 to 162, subfreezing air temperatures resulted in little melt, and no flows at the lysimeter.

Between day 149 and day 154 the flow in individual compartments varied from 0.2 to 3 times the mean flow, however, there are apparent trends in the data. Note that the compartments with high initial flow (for example, #3, 5, and 7) tend to decrease with time, while those with an initial low flow (for example, #1, 4, 13, 14, and 15) tend to increase with time. There are also cases with dramatic changes in flow from one day to the next. For example, compartment #6 had a flow of 2.5 times the mean on day 149, but it decreased to about 0.75 times the mean flow the following day. During the last 4 melt days (day 155, and days 162 to 164 on Figure 1), the variability had decreased substantially, with compartment flows varying from 0.25 to 1.5 times the mean flow. These variations in flow are similar to those reported from other Arctic sites (Marsh and Woo, 1985).

Figure 2 shows the CF for the compartments with the lowest and highest flows over the entire study period. This figure clearly shows fractionation (with CF decreasing over time), and preferential elution (some ions are enriched

more than others, as indicated by different CF values). In addition, Figure 2 demonstrates the effect of flow volume on CF. During the early portions of the melt period, the compartments with the highest flow, had the lowest solute concentration. The only exception was for NO_3^- when the CF was largest in the compartment with high flow on the first day of measurement. After which the CF in the high flow compartment decreased and that in the low flow compartment increased. During the remainder of the melt period the concentrations gradually converged in the low and high flow compartments and during the last 50% of the flow there was little difference between compartments.

The maximum CF in the low flow compartments varied from 2.8 for Cl⁻, to 10.3 for NO_3^-, to 4.1 for SO_4^{2-}, this represents concentrations of 81.2, 14.6, and 30.0 µeq/l respectively. The CFs for Cl⁻ and SO_4^{2-} are similar to those reported by other studies (Tranter, 1991), however, that for NO_3^- was significantly higher than those typically reported. This is probably due to the fact that the

pre-melt concentration of NO_3^- is much higher in the upper portions of the snow pack. As reported by Bales et al. (1989), this type of distribution results in higher CF's than if the solute is evenly spread through the pack. Using the measured meltwater concentrations and the premelt snowpack concentration in the upper portion of the pack for reference, results in a calculated CF of between 2 and 3 for NO_3^-.
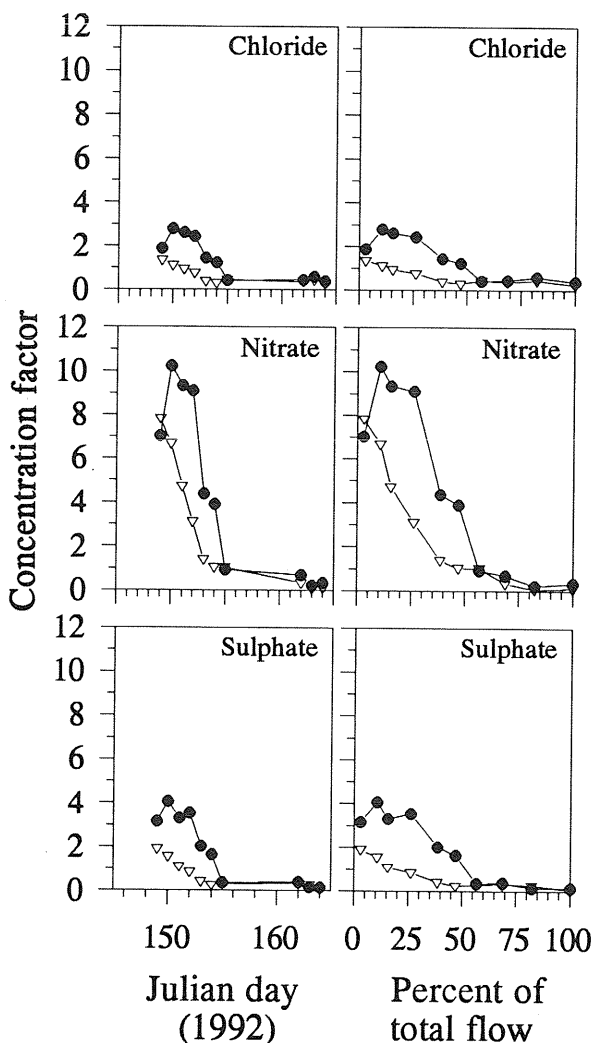
Variations in CF with flow are also shown in Figure 3 for four typical days during the early part of the melt period. Two points should be noted. First, in most cases CF is related to daily flow volume, with CF decreasing with increasing flow during the early part of the melt period. In general, this appears to be an exponential decrease, but the exponential curves fit the data only marginally better than a linear fit. However, the exponential fit is more reasonable since CF>0 over the range of flows is expected, whereas the linear best fit lines produce CF<0, which is unreasonable.
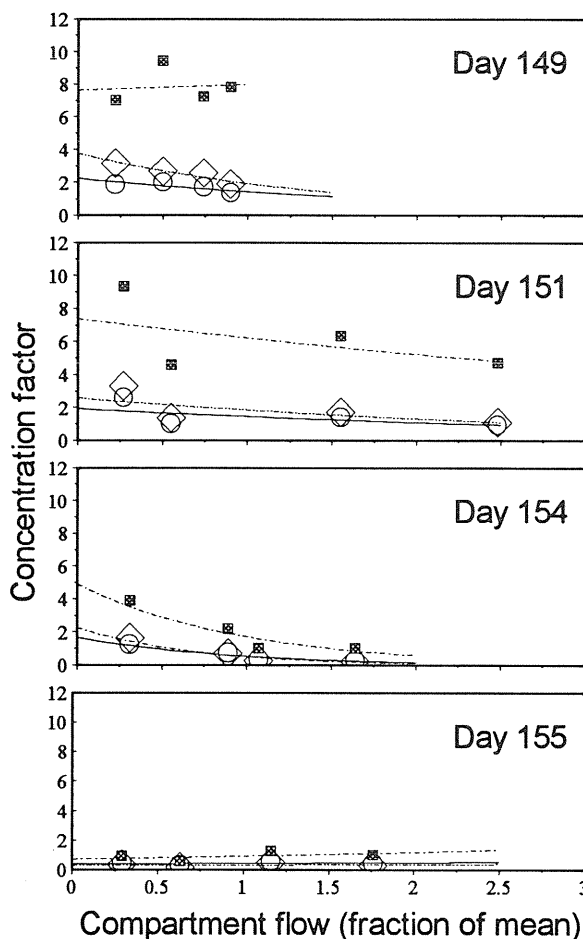

Figure 2. Concentration factors (CF) for Cl⁻, NO_3^-, and SO_4^{2-} for the compartments with the highest (▽) and lowest flows (•). The data are plotted against Julian Day and percent of total flow (this is the flow from the day the lysimeter was installed until it was removed. Over this time, approximately 80% of the snowpack was removed.).

Figure 3. Concentration factors (CF) for lysimeter compartments for Cl⁻ (O), NO_3^- (■), and SO_4^{2-} (◊) plotted against the compartment flow for Julian Days 149, 151, 154, and 155. These are the only days with 4 data points each day, and for the period up to day 155 when the curves in Figure 2 converge. An exponential curve has been fitted to each data set.

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There were occasions, however, when there was no relationship between CF and flow volume. For example, NO_3^- on day 149. Second, the CF of the low flow compartment gradually declined with time, while that of the high flow compartment remained similar in magnitude. As a result, by day 155 there was no relationship between CF and flow. This continued for the remainder of the study period.

Preferential elution is also demonstrated in Figure 4, which shows changes in ionic ratios with time. The decreasing SO_4^{2-}/Cl^- and NO_3^-/Cl^- ratios suggest that SO_4^{2-} and NO_3^- elute earlier than the Cl^-, while the nearly constant SO_4^{2-}/NO_3^- ratios imply that these ions do not elute differentially. It is interesting to note that only the NO_3^-/Cl^- ratios vary with flow volume, with the low flow compartment having higher ratios early in the melt period.

DISCUSSION

The observations reported in the previous section result from a number of complex processes occurring within the snowpack, none of which are presently well known. However, previous studies have discussed possible processes which are responsible for fractionation and preferential elution, and this work provides at least a qualitative understanding of the role of flow volume on solute concentration in meltwater. For example: Hibberd (1984) presented a simple model for predicting meltwater chemistry which assumed the following: (1) uniform heat flux at surface and no solute input from the surface, (2) solutes are evenly distributed through the snowpack, (3) solutes are held in the irreducible water content, and (4) solutes are transferred from the immobile water to the mobile water with the arrival of the first meltwater
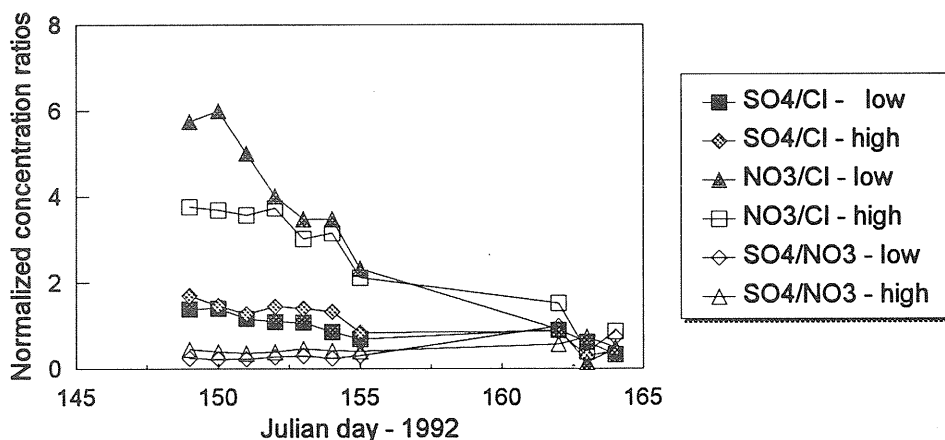

Figure 4. Normalized ion ratios for each of the low and high flow compartments in the multicompartment lysimeter. Changes in ratios with time suggest that the ions elute at differing rates.

wavefront and then dispersed within the meltwater by hydrodynamic dispersion (molecular diffusion and mechanical dispersion). Hibberd (1984) used the one-dimensional theory of water percolation through homogeneous snow developed by Colbeck (1978) to describe water flux through the pack. Bales (1991) extended the work of Hibberd (1984) to include the retention of solutes in the immobile liquid or ice phases of the snowpack.

Hibberd (1984) calculated contaminant concentrations (C) for various liquid water contents and non-dimensional dispersion coefficients (D). D is defined as $D=(1-S_i) D^*/kL^*$, where S_i is the irreducible liquid content of the snow, k is the permeability, and L^* is the non-dimensional snowpack depth. D^* is the hydrodynamic dispersion

coefficient, where $D^* \approx vd$, v is the particle speed of water molecules, and d is the grain size (Colbeck, 1975). Calculated values of C/C_i (where C_i is concentration in irreducible water) for $D > 10^{-3}$ showed that C/C_i decreased with increasing water content (Figure 5). Since flux and flow velocity are related to liquid water content, this implies that the concentration in the meltwater decreased with increasing flow, as was found in the field measurements reported in this paper. With $D < 10^{-3}$, however, Hibberd (1984) reported the inverse with C/C_i increasing with increasing water content. Given the results from the field studies reported in this paper, it would appear that $D > 10^{-3}$ is a reasonable value. However, there have been no studies demonstrating whether a value of $D > 10^{-3}$ is

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appropriate for natural snowpacks, and as a result, D is largely a fitting parameter.

It appears from this work, therefore, that the relationship between flow volume and concentration can be explained by the variations in flow velocity, the transfer of solutes from areas of irreducible water with a high solute concentration, to lower concentration melt water flux, and the hydrodynamic dispersion of solutes within the meltwater flux.
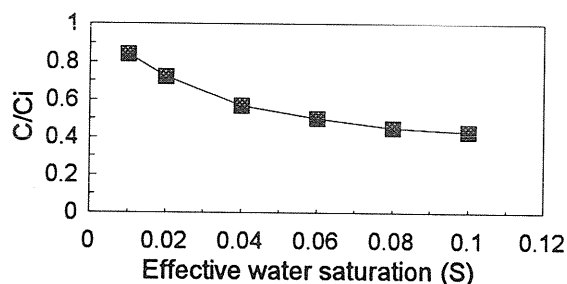

Figure 5. Relationship between effective water saturation (S) and the initial relative concentration (C/C$_i$, where C is the concentration in the meltwater and C$_i$ is the concentration in the irreducible water content). These data are for a dispersion parameter (D = 10^{-2}). Data in this figure is from Figure 6 in Hibberd (1984).

CONCLUSIONS

The field observations reported in this paper provide the first direct measurements of the spatial and temporal variations in meltwater chemistry over a small horizontal plane. These observations show that in a typical shallow (1.25 m) snowpack, flow varies from 0.25 to 3 times the mean over small areas and the variability decreases over the melt period to between 0.5 and 1.5 times the mean flow. In conjunction with these observed variations in flow volume, it was found that the concentration of solutes within the meltwater also varied greatly. In zones of low flow, the concentration factor (CF) was higher than in zones of high flow. Over time, the differences in solute concentration between high and low flow areas decreased, and after approximately 50% of the observed snow melt, the high and low flow zones had similar CF's. These observations demonstrate that the CF measured over "large" areas in snowpacks is a result of the mixing of water with a wide range of CF's. From a practical point of view,

these observations clearly demonstrate that the CF measured in lysimeter flow is dependent on the scale of measurements. This suggests that at least some of the variability in CF's reported in the literature may be due to differences in lysimeter size in relation to the representative scale of variability for any given snowpack. For example, in a shallow snowpack, a small lysimeter might provide a representative sample, whereas the same size lysimeter in a deep snowpack will not.

REFERENCES

Bales, R.C., R.E. Davis, and D.A. Stanley. 1989. Ion elution through shallow homogeneous snow. Water Resources Research, 25, 1869-1877.

Bales, R.C. 1991. Modeling in-pack chemical transformations. in: Davies, T.D., M. Tranter, and H.G. Jones (editors). 1991. Seasonal Snowpacks: Processes of Compositional Change. NATO ASI Series. Series G, Ecological Sciences, Vol. 28, Springer Verlag, Berlin, 139-163.

Colbeck, S.C. 1975. Tracer movement through snow. Isotopes and Impurities in Snow, IAHS Publication 118, 255-262.

Colbeck, S.C. 1976. An analysis of water flow in dry snow. Water Resources Research, 12, 523-527.

Colbeck, S.C. 1978. The physical aspects of water flow through snow. Advances in Hydroscience, 11, 165-206.

Colbeck, S.C., E. Akitaya, R. Armstrong, H. Gubler, J. Lafeuille, K. Lied, D. McClung, and E. Morris. 1990. The International Classification for Seasonal Snow on the Ground. Issued by: The International Commission on Snow and Ice of the International Association of Scientific Hydrology and Co-Issued by: International Glaciological Society, 23pp.

Davies, T.D., M. Tranter, and H.G. Jones (editors). 1991. Seasonal Snowpacks: Processes of Compositional Change. NATO ASI Series. Series G, Ecological Sciences, Vol. 28, Springer Verlag, Berlin, 471 pp.

Davis, R.E. 1991. Links between snowpack physics and snowpack chemistry. in: Davies, T.D., M. Tranter, and H.G. Jones (editors). 1991. Seasonal Snowpacks: Processes of Compositional Change. NATO ASI Series. Series G, Ecological Sciences, Vol. 28, Springer Verlag, Berlin, 115-138.

Hewitt, A.D., J.H. Cragin, and S.C. Colbeck. 1991. Effects of crystal metamorphosis on the elution of chemical species from snow. 48th Eastern Snow Conference, Guelph, Ontario, 1-10.

Hibberd, S. 1984. A model for pollutant concentrations during snowmelt. Journal of Glaciology, 30, 58-65.

Jones, H.G. and W.J. Orville-Thomas. 1987. Seasonal Snowcovers: Physics, Chemistry, Hydrology. NATO ASI Series. Series C: Mathematical and Physical Sciences, Vol. 211. D. Reidel Publishing Company, Holland, 746 pp.

Kattelmann, R. 1989. Spatial variability of snow-pack outflow at a site in Sierra Nevada, U.S.A. Annals of Glaciology, 13, 124-128.

Male, D.H. and D.M. Gray. 1981. Snowcover ablation and runoff. in D.M. Gray and D.H. Male (Editors), Handbook of Snow: Principles, Processes, Management and Use. Pergamon Press Canada, Willowdale, Ontario, 360-436.

Marsh, A.R.W. and A.H. Webb. 1979. Physico-chemical aspects of snow-melt. CEGB Reports, RD/L/N, 60/79, 12pp.

Marsh, P. 1991. Water flux in melting snow covers. Chapter 2 in: M.Y. Corapcioglu (Editor). Advances in Porous Media, Vol. 1, Elsevier, Amsterdam, 61-124.

Marsh, P. 1987. Grain growth in a wet Arctic snow cover. Cold Regions Science and Technology, 14, 23-31.

Marsh, P. and M-k. Woo. 1985. Meltwater movement in natural heterogeneous snow covers. Water Resources Research, 21, 1710-1716.

Marsh, P. and M-k. Woo. 1987. Soil heat flux, wetting front advance and ice layer growth in cold, dry snow covers. in: Snow Property Measurement Workshop, P.R. Kry (Compiler), National Research Council Canada, Technical Memorandum 140, 498-524.

Parlange, J.-Y. 1974. Water movement in soils, Geophys. Surv., 1, 357-387.

Pomeroy, J.W., P. Marsh, and L. Lesack. 1993. Relocation of major ions in snow along the tundra-taiga ecotone. Nordic Hydrology, 24, 151-168.

Tranter, M. 1991. Controls on the composition of snowmelt. in: Davies, T.D., M. Tranter, and H.G. Jones (editors). 1991. Seasonal Snowpacks: Processes of Compositional Change. NATO ASI Series. Series G, Ecological Sciences, Vol. 28, Springer Verlag, Berlin, 241-272.

Tranter, M., P. Brimblecombe, T.D. Davies, C.E. Vincent, P.W. Abrahams, and I. Blackwood. 1986. The chemical composition of snowpack, snowfall, and meltwater in the Scottish Highlands - evidence for preferential elution. Atmospheric Environment, 20, 517-525.