

**Snowpack Chemistry  
During Snow Accumulation and Melt  
in Mature Subalpine Forest and Regenerating  
Clear-Cut in the Southern Interior of B.C.**

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Chemical profiles in snowpacks were observed during snow accumulation and melt periods at subalpine sites in the southern interior of British Columbia. During accumulation periods, concentrations of nitrate, sulphate, chloride and sodium were higher than those of bulk snowfall in surface snowpack layers and lower in middle and basal layers. During melt periods, the opposite was true. This process of chemical profile reversals was found to repeat itself through successive cycles of melt and non-melt periods that typically occur at the site during the spring. This recurring cycle of chemical enrichment resulted in two distinct processes of ion elution. A "seasonal" process was observed in which there is an initial ion pulse followed by a slow exponential decline in concentration. An event based process consisting of ion pulses due to leaching of enriched surface layers was superimposed on the seasonal process. Forest cover type was found to exert an influence on snowpack chemistry during accumulation and melt. Significant differences between forest cover types were found among average chemical concentrations in enriched and depleted layers, suggesting that canopy density causes differences in chemical metamorphosis of snowpacks.

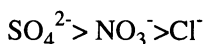
## **Introduction**

Chemical changes in snowpacks during melt have been the subject of several studies in eastern Canada, New England, the Canadian Arctic and Scandinavia. Two processes, "fractionation" and "preferential elution" have been widely reported in the literature. The process of fractionation involves the relative enrichment in impurities

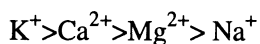
of the earliest meltwater fractions, and is well understood and widely accepted. This occurs because the impurities that are not easily incorporated into the ice crystal lattice migrate to the grain surfaces during snow metamorphism (Colbeck 1981). Semkin and Jefferies (1986), English *et al.* (1986) and Hazlett *et al.* (1992) studied the chemistry of  $H^+$ ,  $NO_3^-$  and  $SO_4^{2-}$  at Turkey Lakes watershed in northern Ontario. All studies noted that there was a rapid release of those ions early in the melt period; a laboratory simulation by Colbeck (1981) yielded similar results. Semkin and Jefferies (1986) noted that more than 50% of those ions were lost from the snowpack during the first 30% of the melt period. In a similar project conducted in Norway, Johanssen and Henriksen (1978) reported selective ion release of 50-80% of each component during the first 30% of snowmelt. They defined a concentration factor as the ratio of the concentration of a particular chemical species to that in the parent snow. Tranter (1991) reviewed several field and laboratory studies reporting fractionation, and reported that initial concentration factors typically ranged from 2 to 6, falling to 0.2 to 0.5 by the time about 50% of the snow had melted. Lab studies of ion elution through shallow snowpacks were conducted by Bales *et al.* (1989) and Davis *et al.* (1995). Melt-freeze metamorphism within the snowpack concentrates chemicals on the surface of the snow grains and makes them easily leached early in the melt process. A 24-hour melt-freeze cycle was more efficient at ion leaching than short cycles or continuous melt. Also, a concentration of tracer near the surface of the snowpack was more readily leached than a uniform distribution throughout the snowpack.

There are models currently under development to predict elution of chemicals from snowpacks. One such model, SNOQUAL (*e.g.*, Jones *et al.* 1991) models the concentration of a chemical in meltwater as an exponential function of the concentration of that chemical in the snow, using a leaching coefficient and the incremental volume melted as exponents.

The process of preferential elution is less well understood, and less well accepted because there is lack of agreement among studies documenting the sequence of ion release. Semkin and Jefferies (1986) observed that  $H^+$ ,  $NO_3^-$  and  $SO_4^{2-}$  all behaved similarly, however Hazlett *et al.* (1992) documented selective release of ions from the snowpack during early melt. Brimblecombe *et al.* (1985) and Davies *et al.* (1987) report somewhat conflicting elution sequences. There is general agreement that  $Na^+$  and  $Cl^-$  are the least mobile in melt, possibly because they are more soluble in ice than other ions. Tranter *et al.* (1986) have suggested the anion elution sequence



and Brimblecombe *et al.* (1987) have proposed the cation elution sequence



Rascher *et al.* (1987) examined  $H^+$ ,  $NO_3^-$  and  $SO_4^{2-}$  as well as base cations and

Cl<sup>-</sup> in snowpacks and forest floor leachates in New England. Ions were selectively released from the snowpack over a period of about eight days during early melt resulting in a series of pulses of concentrated ions. The pulses of acidic ions were enhanced by processes that occurred in the forest floor, whereas the Ca<sup>2+</sup> pulse was absorbed by the forest floor. Chemical stratification within the snowpack was also observed; concentrations in the lower snowpack strata were lower than the concentrations in bulk precipitation, whereas the surface stratum was enriched in ions relative to bulk precipitation. A reason for this was not suggested.

The above studies all document a pulse of chemicals leaving the snowpack during early melt, with implications for the chemical behaviour of surface water bodies. Those studies do not stipulate how many melt events there were during the spring season; thus, in subalpine areas where the snowmelt season consists of several melt events interspersed with cold periods, the pattern of ion release from the snowpack might be different. Furthermore, those studies did not attempt to document the effects of different forest cover types on snowpack chemistry, and have not as yet resulted in a snowpack chemistry model.

In the winter and spring seasons of 1989 and 1990, snowpack chemistry was studied at Upper Penticton Creek as part of a water chemistry modeling project. The study was not specifically designed to investigate fractionation or preferential elution. Rather, the purpose of this research was to monitor chemical evolution of subalpine snowpacks during snowmelt, to investigate the stratification of individual chemical species during snow accumulation and melt, and to provide some insight that could be used to model direct runoff due to snowmelt in a component based water chemistry simulator. The water chemistry simulation effort is described by Hudson (1995).

## **The Study Area**

Upper Penticton Creek (UPC) is located in the southern interior of British Columbia on the Okanagan Highlands, northeast of Penticton. The study area occupies the dry, cold subvariant of the Engelmann Spruce-Subalpine Fir (ESSFdc) Biogeoclimatic Zone that was originally described by Krajina (1969). UPC is the site of a watershed experiment, the purpose of which is to study the effect of rate of cut on streamflow, water chemistry and suspended sediment production in different subalpine forest cover types. The study area contains four watersheds, 240, 241, Dennis and Edelweiss Creeks with drainage areas of 520, 464 and 390 and 43 hectares respectively (Fig. 1). The first two creeks are dominated by lodgepole pine (*Pinus contorta*) stands 80-140 years of age, with elevation 1,605-2,005 m and generally south aspect, while Dennis Creek is dominated by mature Engelmann spruce – subalpine fir (*Picea engelmannii*, *Abies lasiocarpa*), with elevation 1,780-2,140 m and a westerly aspect. Edelweiss Creek ranges in elevation 1,730-1,890 m with a southwesterly aspect, and is dominated by mature Engelmann spruce – subalpine fir in the upper

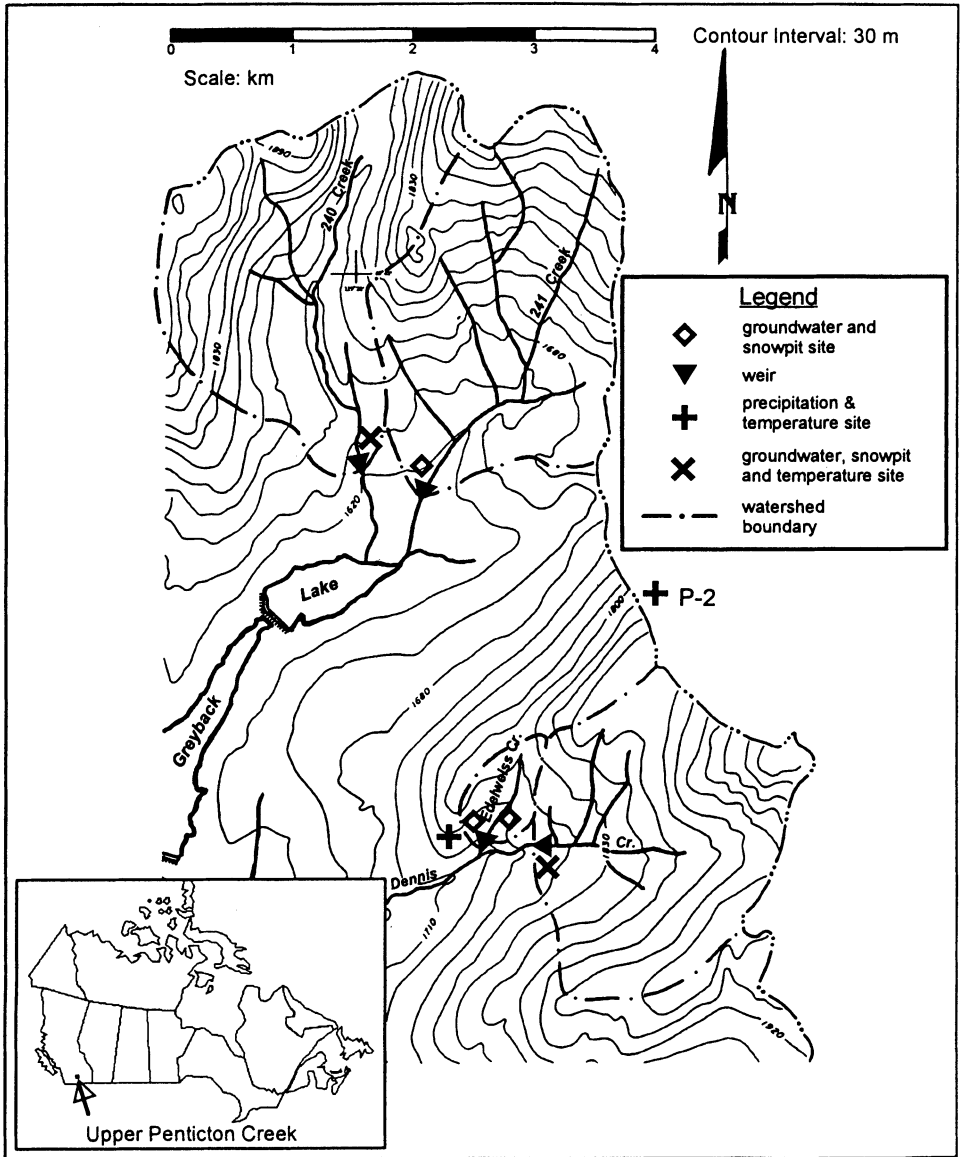


Fig. 1. Upper Pentiction Creek experimental watersheds.

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75% of the catchment. The lower 25% of the catchment is within a clear-cut that was harvested in the mid 1970's, and at the time of the study contained mixed pine, spruce and fir regeneration of 3-6 m height.

The creeks are gauged for streamflow and nearby instrumentation measures air temperature and precipitation (Fig. 1). Streamflow was measured using sharp crested rectangular notch weirs with V-notch inserts for improved measurement precision at low flow. Stage was monitored continuously using Stephens A35 float actuated chart recorders. Precipitation was monitored using Belfort weighing precipitation gauges with chart recorders at three sites, although only the site "P-2" (Fig. 1) was used in this study. Air temperature was monitored with Lambrecht chart driven thermographs at sites below the forest canopy in 240 and Dennis Creeks, and in the clear-cut at Edelweiss Creek. Temperatures in the mineral soil were measured at the same sites at depths of 5, 20 and 50 cm below the organic horizon using thermistors that were measured with a multi-meter during field trips.

The mean annual precipitation was 737 mm for the period between September 1987 and August 1990, with more than 50% falling as snow. Snowpacks generally start to develop between mid-October and mid-December, and melt usually starts in early April at the clear-cut and continues through until mid-June under the spruce-fir canopy. Snowpack depths were 0.6m, 0.65m and 0.68m at the sampling sites at 240, Edelweiss and Dennis Creeks respectively, on 3 April 1990. Timing and duration of snowmelt varies from site to site, depending on forest cover, aspect and elevation. Peak streamflow typically occurs in late spring to early summer due to radiation snowmelt and/or rain on snow. Maximum mean daily streamflow during the study period was 1.000 m<sup>3</sup>/s (1.92 litres/sec/ha) on 240 Creek, 0.901 m<sup>3</sup>/s (2.307 litres/sec/ha) on Dennis Creek, and 0.18 m<sup>3</sup>/s (2.8 litres/sec/ha) on Edelweiss Creek. Streamflow is perennial in the study creeks, receding to less than 0.001 m<sup>3</sup>/s at low flow. Soils at all sites freeze in late fall. During active snowmelt, soil temperatures rise to just below the freezing point, but soils do not thaw until after the snowpack has disappeared.

## **Methods**

Snow sampling was carried out under the lodgepole pine and spruce-fir canopies at 240 and Dennis Creeks, and in the regenerating clear-cut at Edelweiss Creek. Measurements were made once per month during the winter and more frequently during snowmelt. Two types of samples were collected; "fresh" surface grab samples and snowpack samples. The surface grab samples were assumed fresh (un-metamorphosed) if collected within 24 hours of falling, and were used to determine the chemistry of bulk snowfall, as opposed to that of snowpacks that had been subject to chemical and physical metamorphosis. Surface or near-surface snow was assumed to be part of the snowpack (as opposed to fresh snow) if its density was greater than

150 kg/m<sup>3</sup>. Snowpack samples were collected at snow pits in 240, Edelweiss and Dennis Creeks. Snow pits were dug so that the exposed face of the pit faced north to avoid melting of the profile during sampling. The depth of the profile was measured and up to five (usually four) samples were collected from the pit wall such that a profile of evenly spaced measurements was obtained from just below the snow surface to the base of the snow pack. Ice lenses in the snowpack were generally not observed in the snow pits, although on occasions when they were observed, sampling intervals were adjusted so as to sample directly above the ice layers. The samples were collected using a soup can with a sharpened rim which was weighed after collection to determine the snow density, and then transferred to a wide mouthed jar and allowed to melt. Thus, each sample represented a layer of snow 6.5 cm thick. All samples were filtered in the field and then transferred to clean 150 ml Nalgene containers such that only a small air bubble was trapped inside the container, tightly sealed and packed in ice in a cooler for the duration of each field trip. Average grain size was estimated using a grid and magnifying glass for each layer that was sampled.

Chemical analyses were performed on all samples to determine concentrations of the anions bicarbonate (HCO<sub>3</sub><sup>-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>), chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), ortho-phosphate (HPO<sub>4</sub><sup>2-</sup> or H<sub>2</sub>PO<sub>4</sub><sup>-</sup>), the cations hydrogen (H<sup>+</sup>), calcium (Ca<sup>2+</sup>), sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), magnesium (Mg<sup>2+</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>), and dissolved silica (SiO<sub>2</sub>). Hydrogen ion was measured as pH with a low ionic strength probe. HCO<sub>3</sub><sup>-</sup> was measured as alkalinity by potentiometric titration. SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and SiO<sub>2</sub> were measured with a Technicon Autoanalyser and cations by atomic absorption spectrophotometry in Faculty of Forestry, U.B.C. labs.

Charge balance error was calculated as +0.65% for 202 samples where all ions were measured. The standard deviation overall was 15%. This low precision overall occurs because in leached snowpack samples, the concentrations of most of the chemical species tend to be close to the detection limits of the methods used. In snowfall samples, the charge balance error is +6.9% with a standard deviation of 6.8%.

Daily snowmelt and direct runoff due to snowmelt were not measured directly, but calculated using the UBC Watershed Modeling System (Quick *et al.* 1995). The UBC model is a conceptual model, using a spatially distributed temperature-based energy balance approach to model snowmelt. There are four lumped runoff components, in which the storage and runoff/recession rates of each component are specified by calibration parameters. The fastest component is interpreted as direct runoff. Thus, total basin daily melt and direct runoff were determined by calibrating the model to observed streamflow and groundwater levels using daily precipitation and air temperature data (Hudson 1995) for each study basin individually.

## Results and Discussion

### Snowpack Profiles

Profiles of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  concentration in the snowpack showed very distinctive patterns that were different for melt and non-melt periods. For those chemical species, the concentrations are higher in the surface snowpack layers than for bulk snowfall, and lower than for bulk snowfall in the middle and basal layers prior to the onset of snowmelt (Figs. 3a-b, 4a-b). Similar results were reported by Rascher *et al.* (1987). This will be referred to as a positive profile because the chemical concentration increases with height above the ground surface. Rapid melt at 240 and Edelweiss Creeks caused reversals of those chemical concentration to form negative profiles, presumably due to leaching of those chemicals down through the snowpack (Figs. 3d-e, 4c). In the typical negative profile, the chemical concentrations of those same ions at the base of the snowpack were greater than average and at the middle and surface layers, less than average. Because  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  all exhibited the same behaviour in the snowpack, these chemicals were lumped together (Group 1) and the sum of their concentrations was used to plot vertical profiles of snowpack chemistry. In contrast,  $\text{HCO}_3^-$ , ortho-P,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{H}^+$  and  $\text{SiO}_2$  did not show the same pronounced concentration patterns within the snowpack at any site, and concentrations of all except  $\text{K}^+$  in snowpacks were usually depleted relative to the average concentration in bulk snowfall at all three sites. These chemicals were therefore lumped together and their combined chemical behaviour is represented by the sum of their concentrations (Group 2).

The 1990 water year (Sept 1989 – August 1990) was a wetter than average year (859 mm) with several cycles of accumulation and melt in the spring. As an example, early afternoon snowpack profiles during a melt sequence in mid-April at 240 Creek (Fig. 2) and Edelweiss Creek (Fig. 3) are given. On April 3, prior to the onset of melt, there was a positive profile at both sites (Figs. 2a, 3a). At that point there had been very little melt, as indicated by the mean daily temperatures, and probably only enough to prime the snowpack; the initial rise in streamflow on 240 Creek and Edelweiss Creek due to the spring freshet began about that time (Fig. 4). The positive snowpack profile still existed on the April 13 at 240 Creek (Fig. 2b), and on April 14 at Edelweiss Creek (Fig. 3b); this may have been partially affected by 7 mm water equivalent of snow that fell between April 9-13. Snowpack profiles during the initial melt event in mid-April show that chemicals move rapidly through the snowpack in response to only moderate snowmelt (Figs. 2 and 3). By the April 15, the snowpack profile was negative at both sites. The snowpack profile seems to go from positive to negative at Edelweiss Creek in the course of about 1 day, whereas this process seems to take about 2 days at 240 Creek. The melt rate at Edelweiss Creek in the regenerating clear-cut is more than twice that at 240 Creek under mature forest for the same period (Fig. 4). On April 16, the concentrations at the base of the snowpack decreased at both sites in response to increasing melt rates. At Edel-

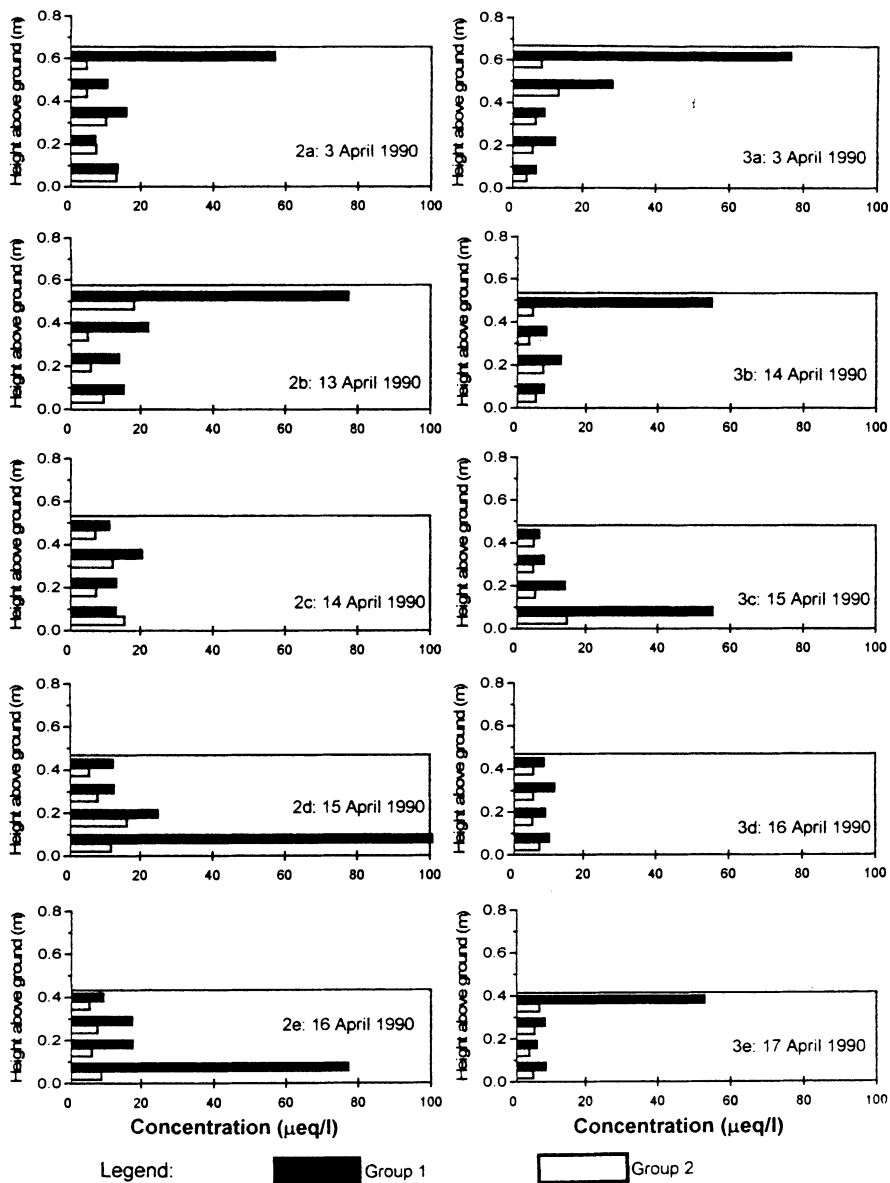


Fig. 2-3. Snowpack chemistry at the 240 and Edelweiss Creek sites respectively, April 1990. Group 1 represents the sum of concentrations of nitrate, sulphate, chloride, calcium and sodium. Group 2 represents the sum of concentrations of bicarbonate, magnesium, potassium and silica. For each graph, the top of the box containing the bars represents the depth of snowpack on each sample date.



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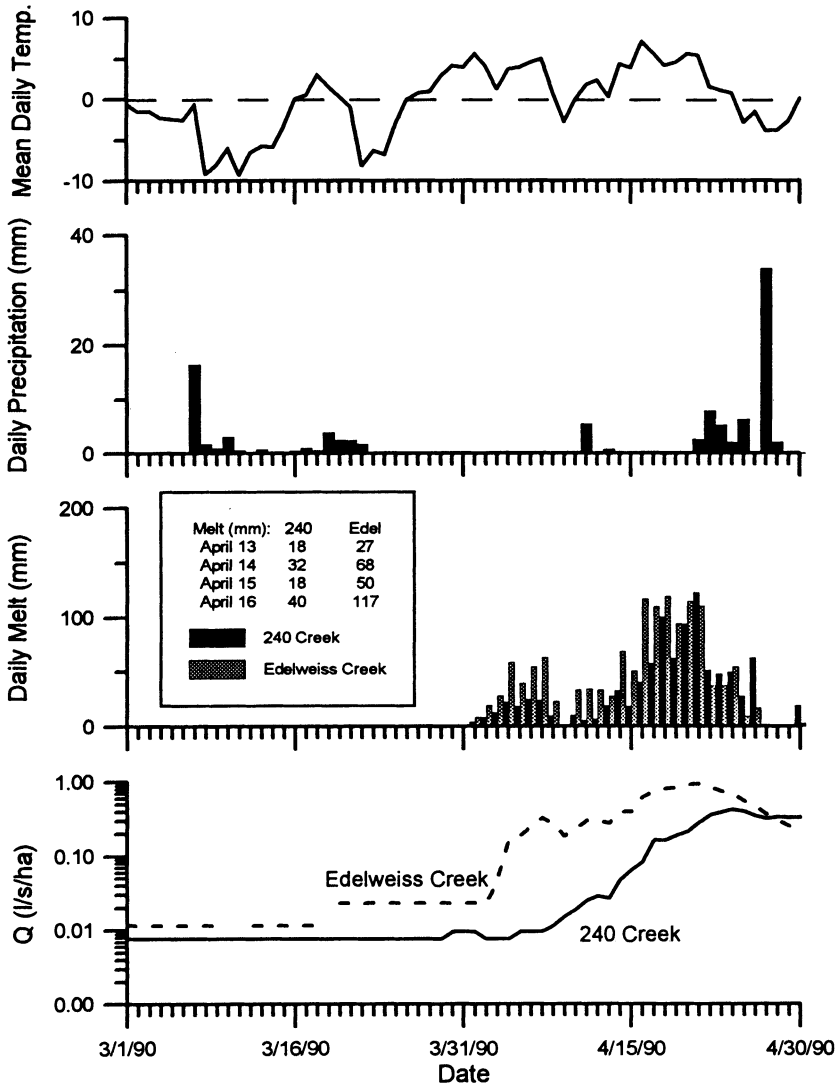


Fig. 4. Mean daily temperature (°C, averaged for UPC sites), total daily precipitation at P-2 site (mm), snowmelt (mm) and mean daily streamflow (litres/sec/ha) at 240 and Edelweiss Creeks for March and April 1990. This period includes conditions prior to and during initial snowmelt and relates to Figures 2 & 3.

weiss Creek the snowpack appears to be depleted of chemicals (Fig. 3d) while at 240 Creek, the chemical load at the base of the snowpack was depleted by about 30% (Fig. 2e). This suggests that during active melt, chemicals are rapidly leached to the base of the snowpack, and then to groundwater or direct runoff at a rate proportional to the melt rate.

Interestingly, the snowpack observed at Edelweiss Creek on April 17 had a positive profile. Whereas most snow profile data were collected in the early afternoon at an open site, the April 17 data were collected at 09:00 am at a site in a stand of 5-7 metre trees. The surface snow layer was frozen at the time of sampling. Because the conditions of sampling were unusual in more than one sense it is difficult to speculate why the positive profile was observed. On April 14 at 240 Creek, the snowpack appeared to pass through a neutral phase. This may suggest that the base of the snowpack received chemicals from a source other than the snowpack itself. However, Marsh and Pomeroy (1993) showed that chemical elution is heterogeneous particularly during the early phases of snowmelt, due to the development of preferential flow paths through the snowpack. Therefore, small changes in the location of the snow pit from day to day may have a significant influence on the observed profile.

Snowpack observations during subsequent melt and non-melt periods in 1990, and in other years (1988-89) show similar sequences in the development of chemical profiles. On April 27, a non-melt period, snowpacks at all sites had reverted to positive chemical profiles. This observation was made prior to a snowfall of 33 mm water equivalent later the same day. Snowpack profiles observed at 240 and Edelweiss Creeks during snowmelt on May 9-11 showed a sequence of profile reversals similar to that described above for mid-April. Thus, unlike other studies where ion elution gave rise to single ion pulses in the early phases of snowmelt, at UPC this is a recurring process. Typically, snowmelt occurs as a series of short (3-5 day) melt events interspersed with non-melt periods during which positive chemical profiles are restored by dry deposition and/or new snowfall. Therefore, each short melt event could potentially be accompanied by an ion pulse.

Rascher *et al.* (1987) attributed the depletion of ions from lower snow layers prior to snowmelt to periodic partial melts during the winter. According to this suggested mechanism, chemicals are slowly leached from the lower layers throughout the winter while chemical enrichment occurs at the surface due to either sublimation or by dry deposition. In fact, there was a positive profile at 240 Creek on February 7, at a time when air temperatures had remained below freezing since the beginning of November. While it seems likely that dry deposition is occurring to enrich the snowpack surface, the partial melting mechanism could not explain the positive profile on February 7, since both air and soil temperatures had been below 0°C since early November. Therefore, the depletion of chemicals from lower layers of the snowpack is likely due at least in part, to snow metamorphosis. Steeper positive profiles that occurred on later dates are probably attributable to gradual leaching from ripe lower snowpack layers.

It has been suggested that biotic factors within the snowpack could modify the chemistry of the pack. In particular, several recent studies have documented the presence and influence of algae in the snowpack. Green algae (*Chloromonas spp.*) is found in shaded snowpacks, whereas red algae (*Chlamydomonas nivalis*) is found in

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open exposures in large openings and above the timberline. Hoham (1989) observed that snow containing green algae had lower concentrations of nutrients than snow from a control site lacking the algae. In particular, results suggested that the algae had metabolized roughly 50% of the  $K^+$  and  $NO_3^-$  in the snowpack. Thomas (1994) studied red snow algae in the Sierra Nevada, where patches of red snow are clearly visible and widespread. Patches of red snow contained about two orders of magnitude more algal production than adjacent white snow. The red snow was confined to the upper 10 cm of the snowpack. Bacteria were also 3-8 times more abundant in red snow than white snow according to Thomas (1994), suggesting that the bacteria subsist off  $CO_2$  excreted by the algae. Brooks *et al.* (1993) found bacteria to be confined to the lower 20 cm of the snowpack, and found no significant correlation between microbial biomass and snow chemistry data. All snowpacks at UPC were white, *i.e.*, there was no visual evidence of snow staining due to algae. Arboreal lichens (*Alectoria sarmentosa*) were found in the snowpacks at forested sites, but not at the Edelweiss Creek site. These lichens are known to be nitrogen fixers, yet there was no significant difference between  $NO_3^-$  levels from site to site. Thus, there is no evidence to suggest that snowpack chemistry at UPC is subject to any significant biotic modification from external factors.

### **The Effect of Forest Cover on Chemical Metamorphosis of Snowpacks**

Following the above discussion, snow at UPC can be divided into three types: fresh snow, enriched snowpack and depleted snowpack (Table 1). When the snowpack chemistry data are examined, there is a clear distinction between enriched and depleted snow. Enriched snow is almost always found at the top or bottom layer of the snowpack. Depleted snow can be found at any level in the pack, but generally the middle layers were almost always depleted. When the average chemical concentrations of each type of snow at each site are examined, it is reasonable to pose several questions; is there a significant difference between fresh and "enriched" snow, and does forest cover type influence the process of chemical metamorphosis of snow? To answer these questions, two statistical methods were used: ANOVA, and two sample t-tests.

Snowfall was sampled at random locations throughout the study area, either under a forest canopy (mature lodgepole pine; no samples of snowfall were collected under mature spruce-fir) or in open areas (*i.e.*, from the regenerating clear-cut site, or from roads). Therefore, it is appropriate to use a 2-sample t-test to look for differences among snowfall samples attributable to forest cover (Table 1). A marginally significant difference was detected in  $NO_3^-$  concentrations between mature forest and open areas, whereas for all other chemicals, forest cover did not have a significant effect on chemical concentrations in snowfall. This was probably because fresh snow that was sampled at forested sites did not come in contact with the trees as it fell.

Table 1 - Average Concentrations of chemicals (meq/l) in snowfall, depleted and enriched snowpack layers. Results of ANOVA and *t*-tests. Statistically significant effects are denoted by bold text in the body of the table.

		NO <sub>3</sub>	H <sub>2</sub> PO <sub>4</sub>	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	NH <sub>4</sub>	Ca	Mg	K	Na	H	SiO <sub>2</sub>
average conc.													
Snow Forest	n = 11	6.20	0.21	9.59	9.09	5.19	3.23	15.47	2.31	2.84	6.11	4.26	13.31
Snow Clear-cut	n = 11	9.02	0.20	12.00	8.07	6.85	4.78	15.61	2.27	2.37	11.65	3.86	12.70
Forest vs. c/c	<i>t</i>	2.13	0.10	0.81	0.24	0.55	0.79	0.03	0.04	0.41	1.17	0.25	0.17
Forest vs. c/c	<i>p</i>	0.05	0.92	0.43	0.81	0.59	0.44	0.97	0.97	0.69	0.26	0.81	0.87
average conc.													
leached 240	n = 45	5.06	0.28	5.91	3.82	2.15	2.44	4.52	0.91	2.80	3.09	5.08	1.00
leached Dennis	n = 34	3.85	0.53	5.21	3.66	1.13	2.56	3.94	0.66	3.13	2.36	4.34	2.03
leached Edel.	n = 42	4.51	0.12	2.18	2.45	0.25	1.86	2.70	0.36	0.65	1.35	4.12	1.54
ANOVA	F (site)	2.11	2.37	4.54	1.04	1.06	1.00	3.99	2.30	4.91	0.72	1.49	2.76
	<i>p</i>	0.154	0.126	0.027	0.376	0.370	0.391	0.039	0.132	0.022	0.504	0.255	0.093
	F (time)	2.25	1.35	2.46	0.360	1.34	0.53	1.64	2.76	1.27	1.66	1.93	21.35
	<i>p</i>	0.080	0.287	0.060	0.926	0.293	0.815	0.191	0.040	0.326	0.184	0.125	<0.001
Contrasts between sites	240 vs Ed	0.980	1.024	4.011	1.399	2.024	0.986	3.207	2.485	3.490	2.617	1.574	-0.759
	Den vs Ed	-1.120	2.466	3.013	1.147	0.869	1.104	2.024	1.270	3.718	1.403	0.342	0.647
	240 vs Den	2.051	-1.536	0.708	0.150	1.016	-0.193	0.956	1.042	-0.493	1.031	1.128	-1.365
average conc.													
enriched 240	n = 22	11.46	0.52	18.68	14.10	8.07	2.35	17.44	2.47	4.01	26.84	3.87	2.63
enriched Dennis	n = 16	13.04	0.59	29.86	25.73	4.28	3.52	18.64	3.03	5.65	44.99	3.24	0.38
enriched Edel.	n = 12	11.91	0.13	13.80	10.06	2.43	2.49	3.99	0.45	2.07	23.36	2.77	2.84
ANOVA	F (site)	1.99	2.10	5.48	16.30	2.53	1.75	10.72	11.10	7.14	4.87	0.62	1.12
	<i>p</i>	0.179	0.165	0.020	<0.001	0.121	0.215	0.002	0.002	0.009	0.028	0.557	0.357
	F (time)	2.80	0.35	1.61	0.850	2.75	1.98	10.22	10.83	4.29	1.03	1.69	5.05
	<i>p</i>	0.061	0.899	0.226	0.559	0.064	0.148	<0.001	<0.001	0.015	0.452	0.208	0.008
Contrasts between sites	240 vs Ed	-0.394	1.518	1.085	1.477	1.931	-0.285	8.718	4.065	2.248	0.438	1.030	-0.112
	Den vs Ed	0.895	1.593	3.219	5.171	0.573	1.875	8.568	4.675	3.736	2.462	0.397	-1.177
	240 vs Den	-1.385	-0.247	-2.482	-4.253	1.296	-2.363	-0.777	-1.116	-1.892	-2.290	0.590	1.193

Table 2 – Assignment of blocks according to sampling date.

Blocks: Depleted snowpack						Blocks: Enriched snowpack						
site:	240	Edelweiss	Dennis	site:	240	Edelweiss	Dennis					
Block Number	sampling dates	n	sampling dates	n	Block Number	sampling dates	n	sampling dates	n			
N/A	4/27/88	2	3/19/88	5	1	4/5/89	3	3/3/89	2	5/5/89	2	
1	4/5/89	3	3/3/89	2	3/3/89	2	3/3/89	2	4/22/89	1	5/12/89	5
2	4/14/89	7	4/22/89	4	4/28/89	4	4/3/89	3				
2	4/21/89											
3	4/28/89	2	4/29/89	5	5/5/89	3						
	5/6/89	1										
N/A	1/3/90	2	1/3/90	2	1/3/90	2	1/3/90	2	1/3/90	2	1/3/90	2
	2/7/90	1	2/7/90	3	2/7/90	3						
4	3/10/90	4	3/10/90	3	4/3/90	3	4/3/90	3	4/3/90	3	4/3/90	3
5	4/3/90	4	4/3/90	4	4/14/90	4	4/14/90	4	4/14/90	4	4/14/90	4
	4/13/90		4/14/90									
6	4/14/90	12	4/15/90	12	4/27/90	3	4/27/90	3	4/27/90	3	4/27/90	3
	4/15/90		4/16/90									
	4/16/90		4/17/90									
7	4/27/90	3	4/27/90	1	5/10/90	3						
8	5/9/90	2	5/9/90	3	5/28/90	3						
9	5/11/90	2	5/10/90	3	6/18/90	3						

Since the chemistry of fresh snow was not significantly affected by forest cover type, any chemical differences between snowpacks at each site can be attributed to the effect of the forest canopy on the chemical metamorphosis of snow. This can be treated as an analysis of variance (ANOVA) problem in which the forest cover types are the treatments, and the individual snow pits are the blocks within those treatment units. This design differs from a standard biometrics experiment in two ways; first, the blocks represent a temporal rather than spatial distribution within treatment units; and second, the processes that results in enriched and depleted layers and the leaching of enriched layers through the snowpack cannot be controlled in the experiment. However as mentioned above, there is an obvious and marked difference in chemical concentrations between enriched and depleted snow, therefore there is no need to devise a statistical test to demonstrate those differences. Therefore the two types of snowpack layers were separated and analyzed separately.

Any differences due to block effects detected by the ANOVA represent changes in the chemistry of enriched or depleted snow over time. Snowpacks were not always sampled at the same time at each site. In particular, at the Dennis Creek site, snowmelt tended to lag behind the other sites by as much as one month. Consequently, intensive snowpack sampling to detect chemical changes during snowmelt was conducted later at Dennis Creek than at 240 or Edelweiss Creeks. Thus, the blocks were assigned at each site to compare samples collected at roughly the same stage in the snowmelt process (Table 2). Within each block, there was duplication according to multiple snowpack layers with similar chemical characteristics, or to consecutive sampling dates.

ANOVA was conducted on each chemical species for enriched and leached snow separately. The analysis will detect whether or not there is a significant difference between at least one site in the response variable (*i.e.* chemical species). Because there are potential differences in both site and block effects, the predictor variables are site, block and the interaction variable site\*block. The statistic to test for differences in either site or block effects is calculated as

$$F = \frac{MS_{\text{site,block}}}{MSE} \quad (1)$$

where *MSE* is the mean squares due to the interaction term site\*block. If the ANOVA reveals a significant difference between treatments, a comparison t-test can be used to determine where the difference lies. There are several comparison methods; selection of the appropriate method depends on the nature of the "experiment" and of the data. In this case, means are based on different numbers of observations, but the comparisons are planned in that the study was set up to determine if there were differences in snow chemistry between sites that could be attributed to forest cover type. Milliken and Johnson (1992) recommend that the Least Significant Difference (LSD) method should be used for planned comparisons with unequal number of observations. The *t* statistic is formulated as follows

$$t = \frac{\bar{C}_1 - \bar{C}_2}{\sqrt{MSE(1/n_1 + 1/n_2)}} \quad (2)$$

with  $((n_1 + n_2 + n_3) - 3)$  degrees of freedom.  $\bar{C}_1$  and  $\bar{C}_2$  are the mean concentrations of chemical species  $C$  and  $n_1$  and  $n_2$  are the number of observations at sites 1 and 2 respectively. Because there are more than two treatments, the comparison test can be done even if the ANOVA F-test is non-significant. Sit (1995) recommends using the Bonferroni correction, which involves using a two-sided critical  $t$  value at an error rate of  $\alpha/k$ , where  $k$  is the number of comparisons to be made.

For the statistical analysis, a confidence level of  $\alpha=0.1$  was used. This significance level is used to compensate for the low precision in some of the chemical analyses (e.g.  $\text{SO}_4^{2-}$ ). For depleted snow, a significant difference due to site was discovered in the concentrations of  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{SiO}_2$ . However, the comparison tests detected a difference between the 240 and Edelweiss Creek sites in  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ , and also between Dennis and Edelweiss Creeks in  $\text{Cl}^-$  and  $\text{K}^+$  (Table 1). The ANOVA also detected a significant block effect in  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and  $\text{SiO}_2$  indicating that there may be significant changes in those chemicals in depleted snow with time, although the effect is generally of marginal significance.

For enriched snow the pattern was similar although the effects were stronger. There was a significant effect due to site in concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ . For  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , there were significant differences between Dennis and Edelweiss Creeks, and between 240 and Dennis Creeks. For  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , there are significant differences between 240 and Edelweiss Creeks, and between Dennis and Edelweiss Creeks. Concentrations of  $\text{K}^+$  and  $\text{Na}^+$  were significantly different between Dennis and Edelweiss Creeks. A significant block effect was also found in  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{SiO}_2$ . This effect was much stronger than in depleted snow, suggesting significant changes in the chemistry of enriched snow over time.

In the enriched snow, where significant between-site differences among ion concentrations were found, concentrations of those ions were highest at Dennis Creek, lowest at Edelweiss Creek, and at 240 Creek, were between concentrations at Dennis and Edelweiss Creeks. In some cases the spread in the means is not sufficient to detect a significant difference between 240 Creek and other sites. For example, this occurs with  $\text{K}^+$  and  $\text{Na}^+$ . However, there is sufficient evidence to suggest that canopy density may be controlling the chemical concentrations of enriched snow; canopy density was measured using a spherical densiometer at the Dennis, 240 and Edelweiss Creek sites at about 75%, 45% and 5% respectively. It seems likely that snow that is trapped in the canopy picks up chemicals from contact with foliage, resulting in chemical enrichment of surface snowpack layers when snow sloughs off the canopy.

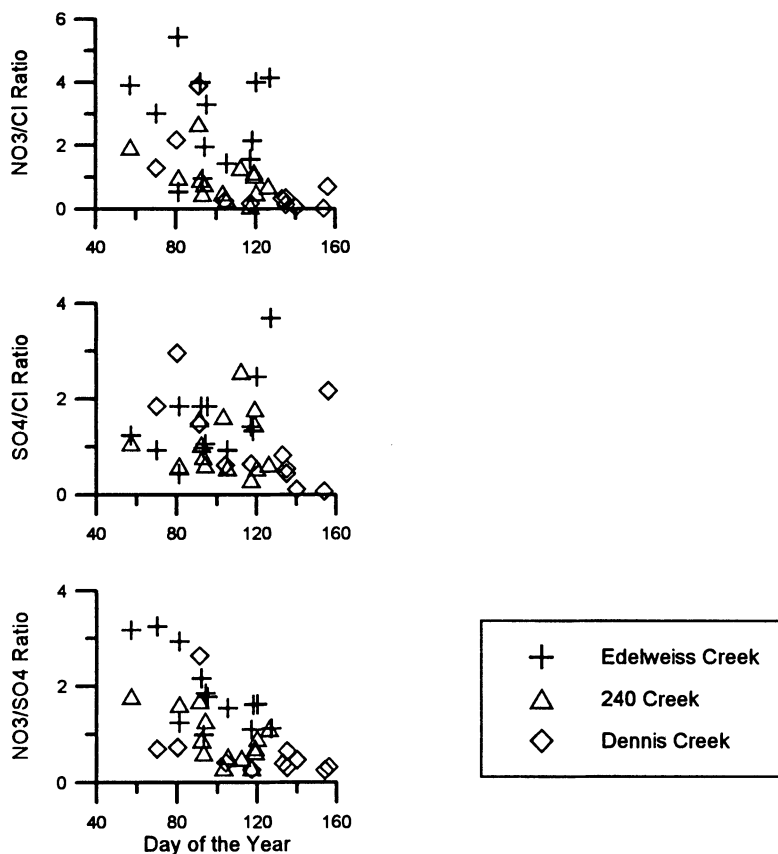


Fig. 5. Evidence for preferential elution of anions.

### Evidence of Preferential Elution

Studies that focus specifically on fractionation and preferential elution of solutes from melting snowpacks generally involve collection and analysis of snowmelt collected in lysimeters on a daily or hourly basis (*e.g.* Colbeck 1981; Johanessen and Henriksen 1978; Marsh and Pomeroy 1993). At UPC soil freezing reduces infiltration and therefore meltwater that percolates down through the snowpack will accumulate at the base of the snowpack. The middle snowpack layers were generally depleted of chemicals prior to and during snowmelt as discussed above. However, chemical concentrations at the base of the snowpack showed very distinct temporal patterns. Therefore, evidence of fractionation and preferential elution can be found by examining the chemical concentrations at the base of the snowpack.

To examine the data for evidence of preferential elution, a method similar to that of Marsh and Pomeroy (1993) was used. If ionic ratios are found to change over



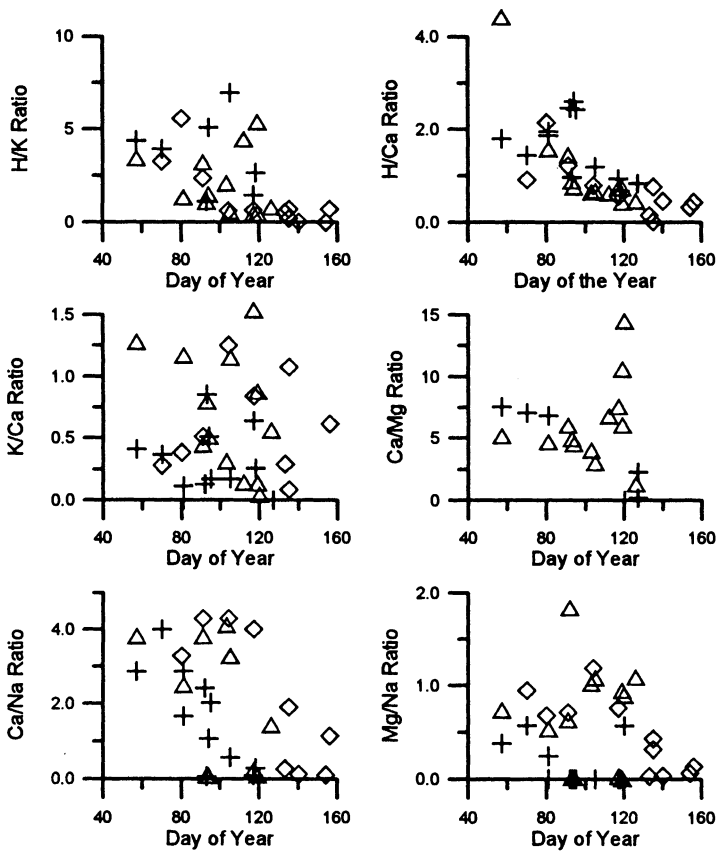


Fig. 6. Evidence for preferential elution of cations.

time, this demonstrates that one ion has eluted in preference to the other. Therefore, plots of ion ratios over time can be used to determine the elution sequences for anions (Fig. 5) and cations (Fig. 6). Marsh and Pomeroy (1993) used meltwater collected daily in lysimeters to demonstrate an anion elution sequence. At UPC, the data collection was more sporadic, and sampling was carried out in three separate seasons. Therefore the results are less conclusive. To account for differences in year-to-year timing of melt, the day of the year was adjusted to make the date of peak runoff the same for each year. Ionic ratios were then plotted against the adjusted day of the year for each site to look for general patterns of ion elution.

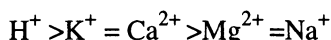
For each ion pair examined, preferential elution is suggested in Figs. 5 and 6 for at least one site (Table 2). However, in many cases the evidence is either inconclusive (*e.g.*,  $\text{Ca}^{2+}$  vs.  $\text{Na}^+$  at 240 Creek, Fig. 6) or suggests no difference in elution between a pair of ions (*e.g.*,  $\text{Mg}^{2+}$  vs.  $\text{Na}^+$ , Fig. 5). Based on this evidence, the following elution sequences are proposed

Table 3 – Preferential elution of anions and cations in snowmelt.

Site:	Ion:	K	Ca	Mg	Na	
Edelweiss 240 Dennis		H>K H>K H>K	H>Ca H>Ca H>Ca	H>Mg H>Mg H>Mg	inconclusive H>Na H>Na	<b>H</b>
Edelweiss 240 Dennis			K=Ca K>Ca K=Ca	K>Mg K>Mg K=Mg	K>Na K>Na K=Na	<b>K</b>
Edelweiss 240 Dennis	SO <sub>4</sub>	inconclusive inconclusive inconclusive		Ca>Mg Ca>Mg Ca=Mg	Ca>Na inconclusive Ca>Na	<b>Ca</b>
Edelweiss 240 Dennis	NO <sub>3</sub>	inconclusive NO <sub>3</sub> >Cl inconclusive	NO <sub>3</sub> >SO <sub>4</sub> NO <sub>3</sub> >SO <sub>4</sub> NO <sub>3</sub> >SO <sub>4</sub>		Mg=Na Mg=Na Mg>Na	<b>Mg</b>
		Cl	SO <sub>4</sub>			



for anions, and



for cations. The anion elution sequence differs from that proposed by Tranter *et al.* (1986) in that at UPC, NO<sub>3</sub><sup>-</sup> elutes in preference to SO<sub>4</sub><sup>2-</sup> (Fig. 5). This may occur because a relatively high dry deposition rate of SO<sub>4</sub><sup>2-</sup> is suggested. In the case of cation elution, the evidence is not inconsistent with the sequence suggested by Brimblecombe (1987). It is quite clear that H<sup>+</sup> elutes from the snowpack before base cations (*e.g.*, H<sup>+</sup> vs. Ca<sup>2+</sup>, Fig. 6. The pattern is similar for H<sup>+</sup> vs. Mg<sup>2+</sup> and Na<sup>+</sup>). The pattern in the data suggests an exponential decay function of H<sup>+</sup> with respect to base cations over time. In the case of K<sup>+</sup> vs. Ca<sup>2+</sup> and Mg<sup>2+</sup> vs. Na<sup>+</sup> there is no overall pattern in the ion ratios over time. In the case of Ca<sup>2+</sup> versus Mg<sup>2+</sup>, there is a temporal pattern in the ratios, but the graph also suggests that there may be an external source of Ca<sup>2+</sup> that causes an increase in the Ca<sup>2+</sup>/Mg<sup>2+</sup> ratio at the base of the snowpack at specific times.

### Evidence of Chemical Fractionation

At UPC, there is evidence to suggest that chemical fractionation occurs, giving rise to ion pulses in response to individual snowmelt events. Using ion concentrations at the base of the snowpack at 240 Creek for the 1990 melt season, it appears that there are two distinct fractionation processes that affect individual ion concentrations differently (Fig. 7). The concentration factor is the ratio of the concentration in bulk

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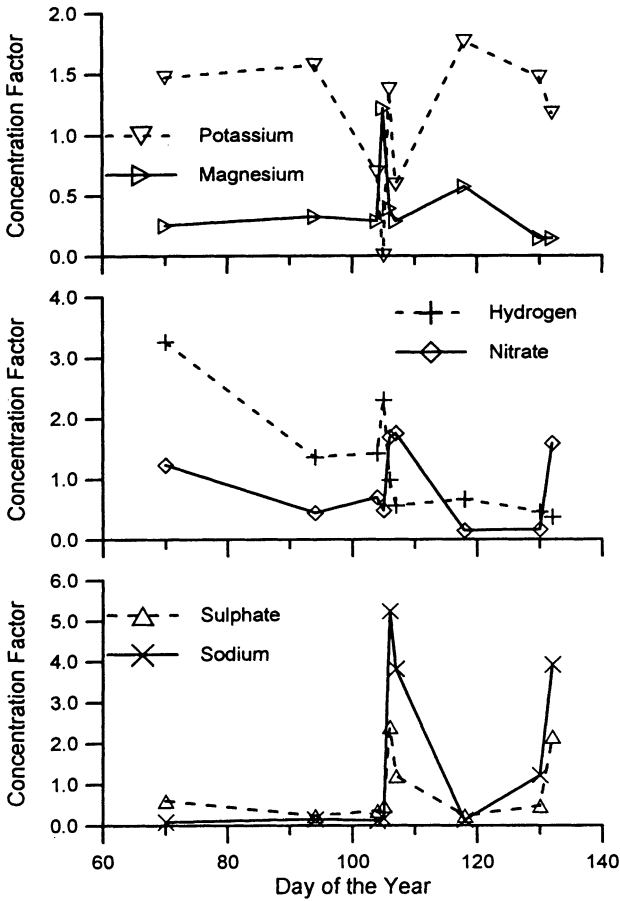


Fig. 7. Concentrations of ions at the base of the snowpack at 240 Creek, 1990.

snowfall to the concentration at the base of the snowpack. For hydrogen and  $\text{NO}_3^-$ , and to a lesser extent  $\text{SO}_4^{2-}$ , the exponential decline in concentration factor over time suggests that over the melt season, ions are leached fairly slowly from the body of the snowpack. Initially the concentration factor is slightly greater than 1 for  $\text{NO}_3^-$ , and slightly greater than 3 for hydrogen, followed by an exponential decline approaching residual concentration in about 50 days, similar to the observations of Johannessen and Henriksen (1978) and Colbeck (1981). However, superimposed on this seasonal elution pattern are ionic pulses associated with elution of enriched surface snow layers during individual melt events. These pulses were observed in 14-16 April and again on 9-11 May at 240 and Edelweiss Creeks, and were of 1-3 days' duration depending on the site and the ion (Fig. 7). As noted by Bales *et al.* (1989) the concentration of ions at the surface of the snowpack is more readily leached than a

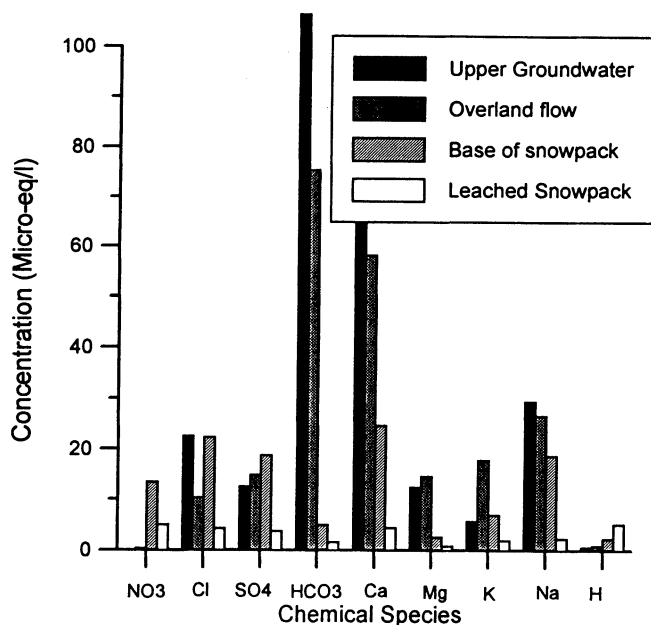


Fig. 8. Chemical concentrations of ions in upper groundwater, overland flow, and at the base of the snowpack under high flow conditions and in leached snow suggest that elevated concentrations at the base of the snowpack could be derived in part from groundwater outflow or overland flow for all ions except nitrate and hydrogen.

uniform distribution in the snowpack, hence the time duration of the individual event driven pulses is much shorter than the seasonal ion elution. In the case of  $\text{NO}_3^-$  and hydrogen, the event pulses have concentration factors of 2 to 2.5.

For  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ , there was no evidence of gradual ion leaching over the season (Fig. 7). The concentrations of  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  at the base of the snowpack were dominated by ion pulses associated with the melt events.  $\text{Ca}^{2+}$  and  $\text{K}^+$  concentrations demonstrated more complex behaviour. The pattern of  $\text{Ca}^{2+}$  concentrations at the base of the snowpack was similar to that of  $\text{K}^+$  in Fig. 7, although the variability in concentrations was less. During the melt sequence of 13-16 April 1990,  $\text{Mg}^{2+}$  and  $\text{H}^+$  concentrations peaked on 14 April. At this time,  $\text{Ca}^{2+}$  and  $\text{K}^+$  concentrations had declined to below the detection limit, presumably having been leached out of the snowpack.  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations peaked on the April 15, and  $\text{NO}_3^-$  on April 16. The peak in  $\text{Ca}^{2+}$  and  $\text{K}^+$  concentrations on April 15 following the decline to zero on the previous day suggests that groundwater or overland flow had discharged into the base of the snowpack at that time. This may also partially explain the very large event based peaks in  $\text{Na}^+$ . A comparison of chemical concentrations of ions in upper groundwater, overland flow, and at the base of the snowpack under high flow conditions and in leached snow suggest that elevated

concentrations at the base of the snowpack could be derived in part from groundwater outflow or overland flow (Fig. 8). The influence of groundwater or overland flow is suggested for  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  because concentrations at the base of the snowpack are roughly mid-way between overland flow and leached snow. The same is true of  $\text{H}^+$  although the pattern is reversed. For  $\text{Mg}^{2+}$ , there is little difference between concentrations at the base of the snowpack and leached snow relative to the concentration in overland flow, suggesting that  $\text{Mg}^{2+}$  at the base of the snowpack may be derived entirely from bulk snow. The fact that  $\text{NO}_3^-$  concentrations are higher at the base of the snowpack than in overland flow and  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations are comparable suggest that these ions are derived entirely from the snowpack.

Similar patterns of event based ion pulses at the base of the snowpack were observed at Edelweiss Creek. However at Dennis Creek, ion pulses were not observed because rapid snowmelt did not occur there concurrent with the other sites.

## **Conclusions**

The results presented in this paper have led to the following conclusions:

- 1) Chemical species were divided into two groups. Group 1 chemicals consisted of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^+$  and exhibited positive profiles (concentrations greater than for bulk snowfall at the surface layer, and lower than for bulk snowfall in the middle and lower snowpack layers) during non-melt periods, switching to negative profiles under melt conditions. Group 2 chemicals, consisting of  $\text{HCO}_3^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{SiO}_2$  did not demonstrate these patterns, and all except  $\text{K}^+$  had concentrations in snowpacks that were consistently lower than bulk snowfall. These results are in agreement with other studies that document preferential elution. Group 1 chemicals have potential atmospheric sources and are thus most likely to be added to the snow surface by dry deposition. Rascher *et al.* (1987) also found that some of these chemicals are subject to enhancement by the forest floor.
- 2) Rapid leaching of chemicals to the base layer of the snowpack during early phases of snowmelt has been documented, in agreement with results of other studies. However, at UPC, this is a recurring process. During non-melt periods in the spring, group 1 chemicals revert to positive profiles, by increased chemical loading from snowfall or rain on snow. Subsequent melt periods cause leaching of chemicals to the base of the snowpack again. This process appears to occur several times during spring snowmelt at UPC. Chemical elution models that currently assume a single pulse of ions early in the melt period should be modified to account for multiple ion pulses due to discontinuous melt.

- 3) It has been shown that high chemical concentrations at the base of the snowpack must be at least partly derived from the forest floor. Prior to melt, positive group 1 chemical profiles always exist. Results show that during rapid melt, leaching results in neutral chemical profiles, followed by negative profiles as melt proceeds. In the absence of precipitation, the most likely source of increased chemical loading is the forest floor. This is also consistent with results of other studies, in which the forest floor was a demonstrated source of acidic ions.
- 4) It has been shown that forest cover type influences the chemical composition and metamorphosis of snowpacks during accumulation and melt periods. Using ANOVA, significant differences attributable to forest cover type were found in average chemical concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and base cations, in leached and enriched snow. It is suggested that the cause of these differences is canopy density.

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