IONIC TRACER MOVEMENT THROUGH A WYOMING SNOWPACK

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Abstract—A meltwater ionic pulse with initial concentrations of 5–10 or more times the average was observed in lysimeters set at the base of a 2-m snowpack in an unpolluted, alpine watershed. Both background chemical species and added tracers exhibited the initial pulse. About 10 days after the onset of meltwater release, solute concentrations collected in the lysimeters dropped to near the average snowpack level. Silica was elevated more than major ions in some initial lysimeter samples, which is evidence of a soil-water or overland-flow contribution. Lysimeter flow rates were equivalent to about 2 cm of melted snow per day, approximately equal to the daily melt estimated from a temperature-index model. Less than 10 per cent of the ionic-tracer mass applied to snow directly above the lysimeters was present in the meltwater. Snow pits dug in an area adjacent to the lysimeters showed that ice lenses played a significant role in solute movement through the pack, influencing both solute depletion and horizontal vs vertical flow. Snow pits also showed depletion of at least 25–35 per cent of the solute mass during release of the first 10 per cent of meltwater.

Key word index: Ionic tracer, snowpack, meltwater, lysimeter, silica.

1. INTRODUCTION

Snowpacks in alpine watersheds of western North America accumulate wet and dry deposited chemical species for several months each year. Spring snowmelt provides most of the annual watershed discharge and can contain elevated concentrations of ionic species, which may include strong acids (Dozier *et al.*, 1988). Typically, the first 20–30 per cent of the melt volume shows concentrations several times greater than the bulk concentration in the remaining volume. Several field snowmelt observations and laboratory experiments have demonstrated this differential elution from melting snow (Johannessen and Henriksen, 1978; Colbeck, 1981; Tsiouris *et al.*, 1985; Tranter *et al.*, 1986). Spring events in the field have been reported in Scandanavia (cf. Skartveit and Gjessing, 1979), Scotland (Morris and Thomas, 1985), Canada (cf. Jefferies *et al.*, 1979), and the U.S. (cf. Galloway *et al.*, 1980; Cadle *et al.*, 1984). The ionic pulse in the first fraction of melt can cause a rapid change in the chemical composition of lakes and streams, which can have a significant effect on biota (Melack and Stoddard, 1990).

The research reported in this paper is an experimental investigation of the movement of ionic species through a well-characterized shallow snowpack in the field. Our work involved adding chemical tracers to amplify the chemical signal in snow, then making point measurements of the magnitude and timing of the ionic pulse using snow pits and lysimeters. The water and ionic flux measurements were then related to the physical and chemical properties of the snowpack during both the accumulation and melt seasons.

2. METHODS

Work was done on a topographic bench (elevation 3300 m) above East Glacier lake in the Snowy range of the Medicine Bow National Forest, Wyoming. The field study of ionic pulse used two approaches: (1) collecting meltwater in 10 snow lysimeters to determine the physical and chemical hydrograph for the pack; and (2) measuring the changes in chemical profiles within the pack from a series of five snow pits dug during the accumulation and melt seasons. In both cases acid and salt tracers were added to the snowpack at two depths during the accumulation season to ensure that the chemical signal in later snow and meltwater samples would be distinct. Background samples of some snow events were also collected on seven snow boards for comparison with snow-pit data and to estimate spatial variability within the site.

Snowpack temperature profiles and air temperature were measured for a 12-day period immediately prior to melt, water-year days 190–202. A 2.1-m thermocouple string was placed in the snowpack near right-bank lysimeter RB-1; data were recorded on a data logger. Later in the season, air temperature was available from a station 0.5 km to the southwest at the same elevation.

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2.1. Lysimeters

The lysimeters were designed to avoid two potential problems: (1) a large impermeable barrier can significantly affect snow metamorphism, apparently by blocking vapor transport from the ground (Smith and Boyne, 1982), and (2) dry deposition before the snowpack is established can contaminate lysimeters. In contrast to more-common designs, lysimeters were made long and narrow to minimize vapor blocking (Fig. 1). One research objective was to evaluate the lysimeter design. They were constructed of 2-m lengths of 10-cm i.d. PVC pipe that was cut lengthwise to form half cylinders; the ends of the lysimeters were capped and a drain installed in one end. Each lysimeter was set inside an equal-length half-cylinder section of 15-cm PVC pipe. Shafts on the ends of the lysimeter enabled it to pivot. The outer half-cylinder housing was at or just below ground level facing up, and the actual lysimeter inverted to eliminate dry deposition. A cable arrangement was provided to open (rotate) the lysimeters after the snowpack formed, but the resistance of the snow proved too great for the system. Therefore, a pit was dug adjacent to the end of each lysimeter and each was manually rotated 180°. From 0.7 to 2.5 m of snow covered the lysimeters when they were opened. The disturbed areas filled with wind-blown snow. Ten lysimeter-housing combinations were installed in a 100×100 m area (Fig. 2), and they were connected to the central collection box with 1.2-cm PVC pipe.

Tracers were added at two depths to the right bank (RB) of lysimeters, approximately 0.5 and 1.5 m below the snow surface at maximum accumulation (Fig. 3). No tracers were added to snow on the left bank (LB). The first lysimeter dosing (at the 1.5-m depth) consisted of approximately 1.8 ℓ of 0.04 M NaBr per 2 m^2, which is an application of 36 meq m^{-2}. The tracer was applied to a sub-zero snowpack using a hand-held spray bottle that produced approximately millimeter-sized drops. The second dosings (at the 0.5-m depth) used the same volumes of solution, containing 0.04 M HNO_3, 0.01 M KCl and 0.04 M K_2SO_4, and resulting in applications of 36 meq m^{-2} of NO_3^- and H^+, 9 meq m^{-2} of Cl^-, 73 meq m^{-2} of SO_4^{2-}, and
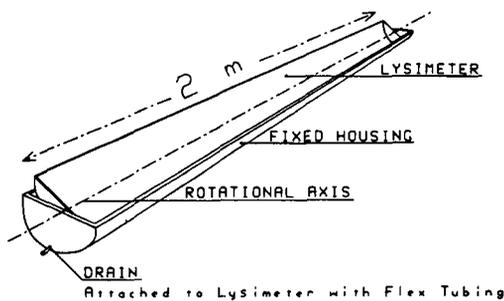

Fig. 1. Lysimeter sketch. Lysimeter was made from 10-cm PVC pipe, and outer housing from 15-cm PVC pipe.
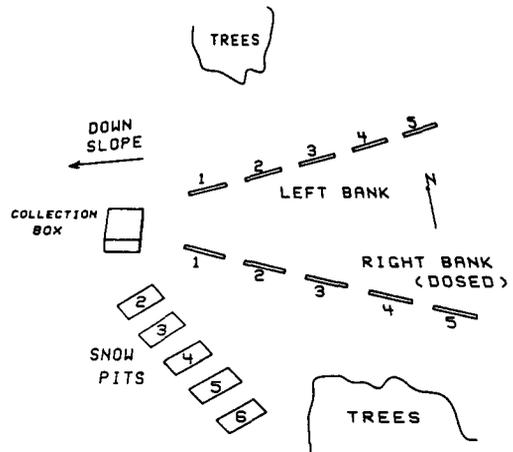

Fig. 2. Layout of field site. Two banks of five lysimeters each were laid on relatively flat ground, pointed approximately down the slope; water from each lysimeter drained to the collection box. Snow pits 2–3 were dug prior to dosing; pits 4–6 were dug into a 1 m^2 dosed area and adjacent undosed areas.
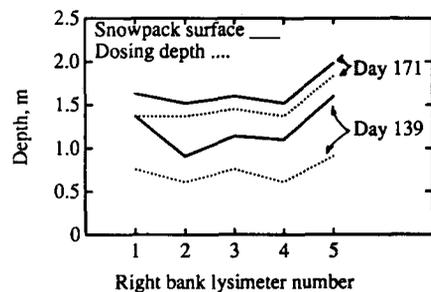

Fig. 3. Profile of snow over right-bank lysimeters at times of first (water-year day 139) and second (day 171) dosing. The surface snow was removed immediately prior to dosing. Tracer applications were approximately 36 meq m^{-2} of Na^+ and Br^- at the lower depth and 36 meq m^{-2} of H^+ and NO_3^-, 9 meq m^2 of Cl^-, 73 meq m^{-2} of SO_4^{2-} and 82 meq m^{-2} of K^+ at the upper depth.

82 meq m^{-2} of K^+. Average snowpack concentrations over the lysimeters with the tracers were 6–10 fold above background.

The 2×2 m square by 1.1-m tall central collection box had sample containers for all 10 lysimeter outlets and had a propane heater to prevent freezing. One outlet from each bank had a 24-bottle fraction collector. Lysimeters, piping, connectors and sample containers were acid washed and rinsed with distilled, deionized water (both prior to and after installation) until the conductivity of the used rinse water was the same as the distilled water.

2.2. Snow pits

Three 1 m^2 areas were dosed on water-year days 137–139 and 171, with 0.9 ℓ of the same tracers and in the same manner as for the lysimeters, giving the same

loadings. Two snow pits were dug in undosed areas prior to spring melt, on water-year days 149 and 171 (26 February and 19 March 1988). Three pits were dug during melt, on days 205, 230 and 245 (22 April, 17 May and 1 June 1988). Each snow pit was about 5-m long, 1-m wide and up to 2.2-m deep. Density was measured and samples for chemical analysis taken from individual strata along a vertical profile in one pit wall. A single profile was taken in each of the first two pits; in the later pits, one profile was taken in the dosed and two in the adjacent undosed areas. Densities were taken using a 1-ℓ triangular-wedge steel cutter fabricated by K. Elder at the University of California, Santa Barbara. Chemical samples were taken using a 30-cm sections of 8-cm PVC pipe that had been acid washed and rinsed with distilled, deionized water. Samples were put into unrinsed polyethylene bags and kept frozen until filtered and/or analyzed.

2.3. Analyses

Samples were kept in a freezer at $-6°$C for up to 2 weeks, then melted and passed through a 0.45-μm membrane filter. The filtrate was separated into two aliquots, for anion and cation analyses, and stored in polyethylene bottles at $4°$C until analyzed. Most anion analyses were done within 2 weeks; cations were acidified and analyzed 2 months later.

Anions were analyzed on a Dionex 2010i ion chromatograph equipped with an auto-sampler. Standards were run about every 10 samples, and typically showed less than 2 per cent change from one set to the next. Detection limits were less than 0.1 μeq ℓ^{-1} for most species. Na^+ and K^+ were analyzed by atomic absorption spectrophotometry (detection 0.5 μeq ℓ^{-1}) and Mg^{2+}, Ca^{2+} (detection 0.08 μeq ℓ^{-1}) and silica (detection 0.2 μeq ℓ^{-1}) by inductively coupled plasma at Colorado State University. Samples were well above detection limits. Conductivity and pH were measured

Fig. 4. Cumulative melt and water collected from two lysimeters. Average flow rates are 3.6 and 6.4 ℓ dy^{-1} for LB-2 and RB-3, respectively, based on a linear fit to the data. The day 203–204 flow in LB-2 was less than 1ℓ and is not shown. Cumulative melt calculated using degree-day method: (degree dy) $\times$ (1.1 $\times$ 10^{-3} (cm m^3/$°$C dy kg) $\times \rho_s$, where ρ_s is the bulk snow density (435 kg m^{-3}), and degree day is $°$C above 0.0 times time, based on hourly temperatures.

in the laboratory immediately following sample melting.

3. RESULTS

3.1. Snowpack temperature and melt rates

There was a general warming during the 12-day period of temperature monitoring. The 1800-h ground-level temperature increased from $-1.2°$C on water-year day 191 to $0.0°$C on day 199, when the pack became isothermal. The first meltwater was collected in one lysimeter (LB-2) on day 203. Because of subzero temperatures, the flow stopped and meltwater release did not resume until day 224.

Prior to melt, daily warming occurred in the snowpack, with peak and minimum daily temperatures at about 1800 and 0600 h, respectively. Surface air temperatures were above $0°$C for about 12 h each day from day 194 to 201. Using a degree-day method of estimating snowmelt (Martinec and Rango, 1986)[*] gave 0.1 m snow-water equivalent (SWE) of melting for that period, representing about 12 per cent by mass of the SWE over LB-2 and exceeds the irreducible-water content of the snow.

One left-bank and two right-bank lysimeters had significant water flows during the snowmelt period beginning on day 223. Flow rates for LB-2 and RB-3 averaged 3.6 and 6.4 ℓ dy^{-1}, respectively (Fig. 4). The average daily melt for days 223–232 is 2.0 cm (Fig. 4); at this rate, snow directly over a lysimeter area of 0.2 m^2 would contribute 4 ℓ dy^{-1}. Lysimeters LB-3–LB-5 experienced episodes of very high flow rates on occasion. Peak spot measurements ranged between 86 ℓ dy^{-1} (LB-4, 10:30 a.m. on day 239) and 3240 ℓ dy^{-1} (LB-5, 10:40 a.m. on day 237). Some lysimeters yielded very little water; upon digging them out in June, several were observed to be plugged with ice and filled to the rim with slush.

3.2. Snow boards

Only one set of snow-board samples (day 171) was chemically analyzed; concentrations of SO_4^{2-}, NO_3^- and Cl^- were 8.3 ± 1.6, 8.0 ± 1.0 and 2.2 ± 0.8 μeq ℓ^{-1}, respectively. Snow depths (not water equivalent) were 0.58 ± 0.24 m on day 171. Despite three-fold differences in snow depth on that day (0.30–0.94 m), there was little spatial variability in chemical composition. Only Cl^- exhibited the same high variability as did snow depth. The average standard deviation for each set of snow-board depth measurements over the season was 26 per cent of the mean.

3.3. Lysimeters

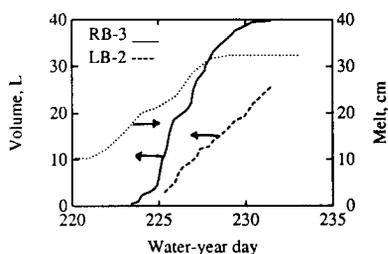Both the left (background) and right (dosed) lysimeters showed initial ionic pulses that lasted on the

order of 1 week (Fig. 5). Some samples were collected until day 246 (June 2), by which time concentrations had dropped off to near average snowpack values. Meltwater collection was terminated because of flooding of the collection box on day 247, and the lysimeters were dug out. Depth-integrated snow samples taken over the right-bank (dosed) lysimeters on day 247 also had bulk concentrations of major ions that were the same as those of the left-bank lysimeters. Less than 1 per cent of the Br^- tracer remained over the right-bank lysimeters, with the most over deeper ones.

There was a Br^- peak in RB-3 (but not in LB-2) from the NaBr applied as the lower tracer; there is no clear signal of the upper tracer in the lysimeter data. The highest Br^- concentration in RB-3 meltwater is about equal to the average snowpack concentration, based on application of $36\ meq\,m^{-2}$ and a SWE of 0.7 m.

Based on the average background snowpack concentrations, peak-to-average meltwater concentrations for major ions and conductivity in LB-2 and RB-3 were calculated to range from 5 to 20, with two values, silica in LB-2 and K^+ in RB-3 being noticeably higher (Table 2). Silica was also high in RB-3 and Na^+ was high in LB-2. In RB-3, K^+ and Cl^- were both upper-level tracers, but other species in that layer had much lower peaks. Extremely high initial K^+ and Cl^- peaks occurred in only one sample. The silica peaks in RB-3 coincide with the high K^+ and Cl^- peaks. After day 223, silica was very low in all but one sample from LB-2.

3.4. *Snow pits*

The days 139 and 171 pits (2 and 3, respectively) showed 8–12 stratigraphically and chemically distinct snow layers (Fig. 6). There was evidence of temperature-gradient metamorphism up to 0.5 m; above that, snow was generally fine grained on day 139 and medium grained on day 171. There was 30 per cent more SWE in pit 3; differences in chemical loadings (SWE × concentrations) are ambiguous. SO_4^{2-} and NO_3^- were similar in both pits 2 and 3, but Cl^- was higher near the top of the pack in pit 3, possibly due to either locally dry-deposited material or contamination of two samples. These samples were taken prior to dosing adjacent areas with the Cl^- salt. Dosing with the Br^- salt was done prior to snow pit 3, and the absence of Br^- in the samples indicates that the tracer application method did not contaminate background samples.

There was about 0.1 m more SWE by the time of the day 205 pit (profiles 4L, 4T and 4R). There were five distinct ice lenses between 0.8 and 1.8 m and an icy layer at 1.85 m in profile 4L (Fig. 6). There were also ice lenses in profile 4T at the tracer depths, and several ice lenses above 1.7 m. Limited melt-freeze metamorphism had occurred down about 0.6 m, below which there was well-advanced depth hoar. Stratigraphy in profile 4R was similar. Average anion concentrations

in profiles 4L and 4R were about the same as values in pits 2 and 3. In profile 4T the tracer layers are still quite chemically distinct; however tracers have migrated downward to the base of the pack (Fig. 7). For example, the Br^- concentration at the base of the pack was about 4 per cent of that at 1.4 m. In addition, Br^- migrated horizontally along an ice lens to profile 4R, which was 1 m downslope from the dosed area. Compared to the amounts dosed, 80–90 per cent of the anion and 70 per cent of the cation tracers were present in profile 4T.

The day-230 background profiles (e.g. 5L, Fig. 6) show no tracer contamination; nor is there clear evidence for solute removal from the pack. The pack had settled about 0.2 m, but SWE was about 0.1 m greater than on day 205. Snow was medium to coarse and very coarse grained, with multiple ice lenses above 0.79 m. Average concentrations of anion tracers were about two-fold lower in profile 5T vs 4T(Table 1), and tracer layers are still quite distinct (i.e. NaBr on Fig. 7b).

By day 245, the pack had receded about 0.2 m and lost 0.1 m of SWE (10 per cent of pit 4 accumulation). Snow was medium to coarse grained, with multiple ice lenses above 0.96 m in the tracer profile (6T). Profile 6R was similar, with the bottom 0.2 m being very wet. Profile 6L was medium to coarse grained, with fewer ice lenses. Average tracer concentrations in 6T were lower than in 5T, and show depletion near the base of the pack. About 75 per cent of the masses of the upper tracers (SO_4^{2-}, NO_3^- and Cl^-) and 90 per cent of the lower tracer (Br^-) present in profile 4T were removed by day 245. Some of the tracer was retained in the pack, however, possibly because of some snow not drained by flow channels and immobile liquid at grain boundaries. Snowpit profiles 6L and 6R showed evidence of solute depletion, with about 25 per cent lower concentrations in the total pack (Fig. 6). Excluding the surface layers, which are subject to the influence of dry deposition, average concentrations in 6L and 6R were about 35 per cent lower than those in profiles 5L and 5R.

4. DISCUSSION

The initial flow in LB-2 and other lysimeters that had a high initial silica concentration apparently had a contribution from soil water. The left-bank lysimeters were in a relatively flat area that remained wet even after snow melted, showing the emergence of sub-surface flow from higher up in the watershed. The lysimeter that gushed at an instantaneous rate of $86\ \ell\,dy^{-1}$ (LB-4, 10:30 a.m. on day 239) would have required a contributing area of about $4.3\ m^2$ based on the calculated melt rates. Vertical piping of snowmelt (Wakahama, 1968) occurs on a scale of the order $1\ m^2$ so that a flow rate of $86\ \ell\,dy^{-1}$ could be in the upper range for piped flow from the overlying snowpack. Marsh and Woo (1985) observed maximum rates of $106\ \ell\,dy^{-1}$. A flow rate of $3240\ \ell\,dy^{-1}$ (LB-5,

a. Left bank

b. Right bank
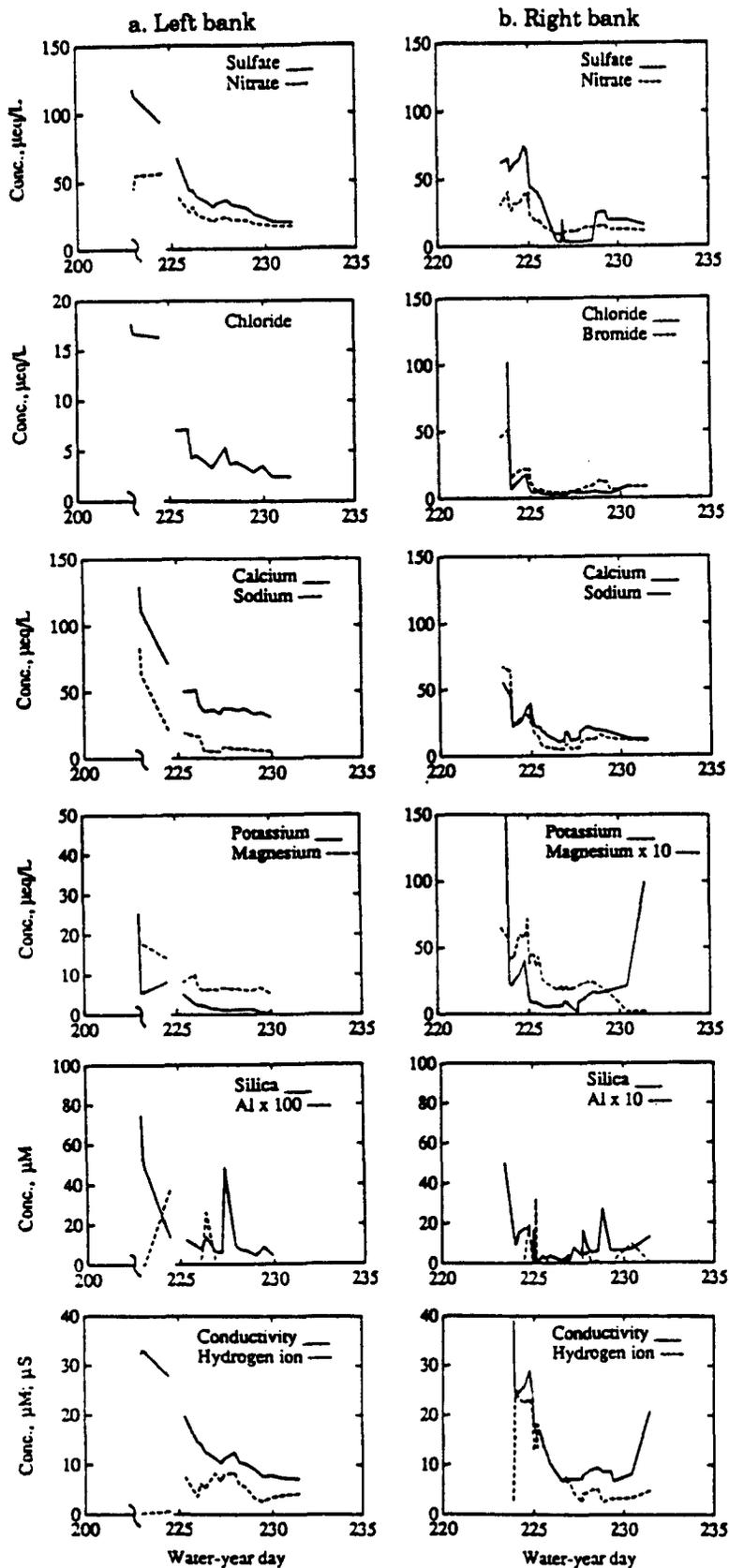

Fig. 5. Meltwater concentrations: (a) 18 samples for lysimeter LB-2 (no tracer) for days 203–204 and for days 225–232. The time axis is broken between these periods (no flow on days 205–224), but there is no discontinuity in the chemical hydrograph; (b) 36 samples for lysimeter RB-3 (with tracer) for days 224–232. Concentrations of all species except Br⁻ are at background levels, as in LB-2.

Table 1. Average snow pit concentrations

Pit	SWE (m)	Cond. (μS)	SO$_4^{2-}$	NO$_3^-$	Cl$^-$	Br$^-$	Ca^{2+}	Na$^+$	Mg^{2+}	K$^+$	Al(III)	μM Silica	H$^+$
						Concentration (μeq ℓ$^{-1}$)						
2	0.58	—	10.9	6.9	1.7	0.0	—	—	—	—	—	—	—
3	0.75	—	8.2	8.2	4.5	0.0	—	—	—	—	—	—	—
4L*	0.87	—	11.1	8.2	1.6	0.1	6.2	2.7	1.6	0.4	0.3	1.2	—
4T	0.87	—	55.1	30.7	7.8	27.7	8.7	29.1	3.3	34.2	0.6	2.3	—
4R	0.85	—	12.2†	8.6	1.5	0.7	12.5	11.1	13.4	9.3	1.6	1.5	—
5L	0.93	5.0	8.1	7.7	2.1	0.0	7.3	2.6	1.9	3.0	0.4	1.0	5.3
5T	0.92	12.8	20.2	13.6	4.5	18.8	5.2	38.5	1.7	51.2	0.7	2.0	11.4
5R	0.90	5.2	8.7	8.7	2.2	0.0	7.9	2.8	1.9	1.8	0.9	2.1	5.4
6L	0.83	4.7	6.0	7.7	1.4	0.0	6.3	0.5	1.7	1.5	0.6	0.7	6.8
6T	0.82	9.4	17.7	11.4	2.6	3.5	2.4	2.9	1.1	21.0	0.0	0.4	9.1
6R	0.88	4.7	7.1	7.8	2.1	0.0	7.1	1.8	1.9	0.8	0.7	0.7	6.1

* Bottom layer not included for cations and silica; evidence of soil contamination in sample; see Fig. 5.
† Top layer not included for SO$_4^{2-}$; data missing.

Table 2. Peak-to-average concentration ratios for initial meltwater pulse

Cond.	SO$_4^{2-}$	NO$_3^-$	Cl$^-$	Ca^{2+}	Na$^+$	Mg^{2+}	K$^+$	Silica
Average snow concentration* (standard deviation below)(μeq ℓ$^{-1}$)								
5.1	8.8	7.9	2.4	7.1	2.6	1.8	1.7	1.4
0.1	2.2	0.7	1.2	0.9	0.1	0.2	1.3	0.6
LB-2†, C/C_{av}								
6.3	12.3	6.6	7.0	14.6	21.5	9.6	13.1	44.8
RB-3‡, C/C_{av}								
5.4	6.8	3.9	13.0	4.8	15.4	2.8	123.2	20.2

* Based on Pits 2, 3, 4L, 5L, 5R for anions and 4L, 5L and 5R for cations.
† Based on average of first three samples (first day).
‡ Based on average of first five samples (first day).

10:40 a.m. on day 237) is far too great to have originated directly from the snow. It must represent either overland flow or flow originating from the soil. The chemistry of the samples favors groundwater flow.

The silica peaks in RB-3 are also evidence of soil or surface flow entering a lysimeter, as silica in the snowpack was on the order of 1–2 μM (Table 1). It is unlikely that concentrations over 10–20 μM would come from the snowpack. The low concentrations after day 223 suggest that surface-flow contributions were small.

While mitigating vapor blocking, the lysimeter design exacerbates edge problems. The most serious question is whether horizontal pressure gradients exist across the upper lip of the lysimeter, which would divert flow and cause the effective collection area of the lysimeter to differ from the physical area. This is possible if the lysimeter edge is within the pressure-gradient zone, the thickness of which is not well established. For example, Wankiewicz (1978) estimates the thickness of the pressure-gradient zone depending on the vertical flux through the collection area of the lysimeter. Assuming that the effective area of the lysimeter equals the physical area, and that flow into the lysimeters in physically homogeneous,

the average flux through the (assumed) collection area at lower flows (LB-2, Fig. 4) was 2×10^{-6} m s^{-1}. This translates to a scaled flux (flux divided by hydraulic conductivity) of 40×10^{-5} and a pressure-gradient thickness of less than 0.06 m (Wankiewicz, 1978). Thus at the lower, the edge of the lysimeters may have been within the pressure-gradient zone and the effective collection area of the lysimeters smaller than their physical area.

Three circumstances argue against the pressure-gradient-zone problem, however. First, it is unlikely that the flow is horizontally homogeneous, but rather is confined to conduits of limited area during the early melt when flow rates are low. Thus the flux was probably larger through the part of the lysimeter that actually received flow. Second, because the lysimeters were inset a few cm into the ground, a similar pressure-gradient zone—generated by the ground-snow interface—existed outside the lysimeter's perimeter. This would tend to minimize the horizontal gradients across the lysimeter edge, which are the important gradients in causing the flow to diverge from the vertical. Third, the height of the pressure-gradient zone decreases with increasing flux, so that the problem decreases for the high-flow times, which contribute most of the volume. A greater limit on the accuracy
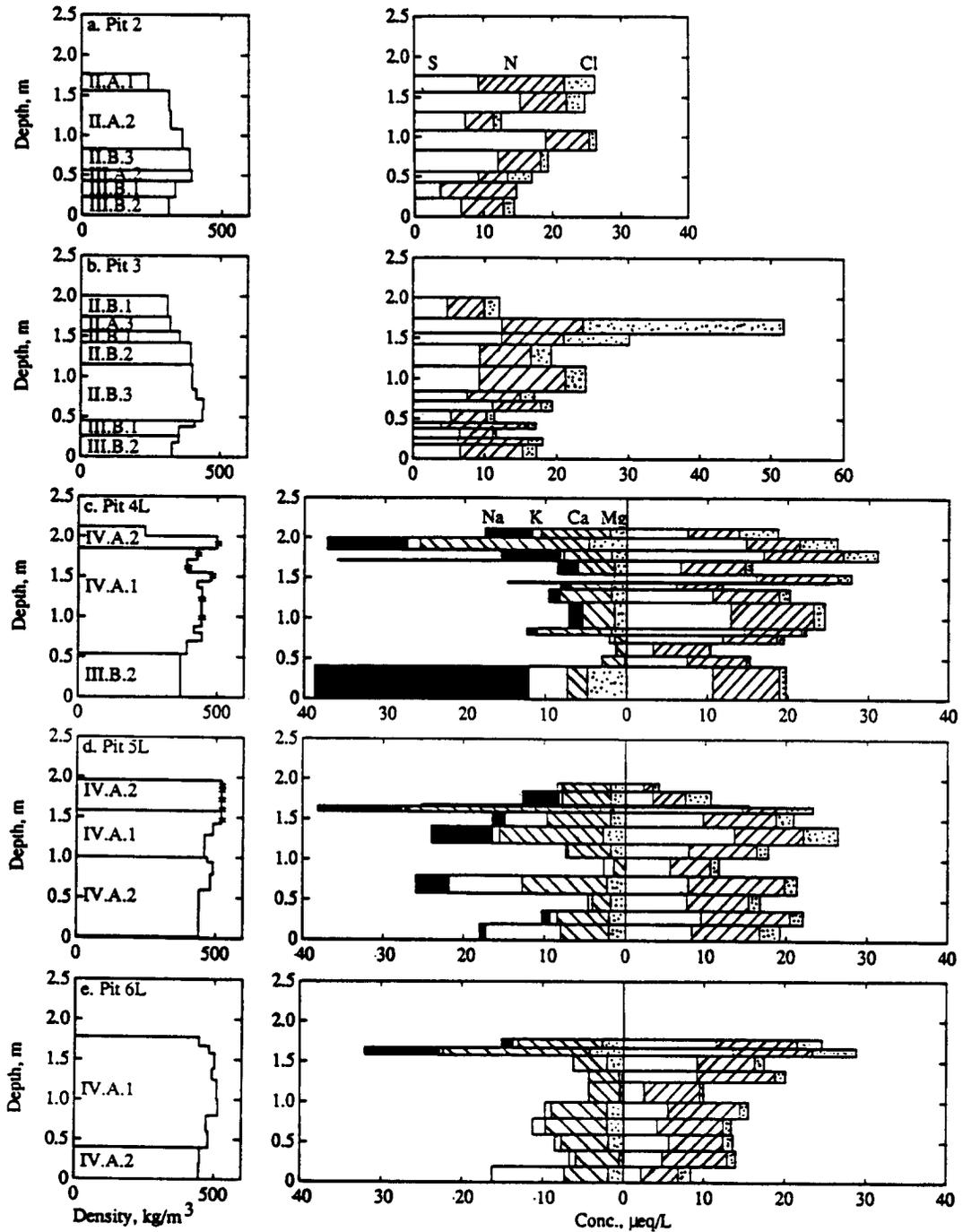
Fig. 6. Density, stratigraphy, anion and cation data for background snow pits upslope of the tracer samples. Concentrations are reported for each stratigraphically distinct layer. * indicates major ice lenses; type IV.A.2 in these profiles also contained many smaller ice lenses. The high cation concentration in the base of profile 4L (values presented are actual divided by 10) is attributed to soil contamination of the sample during collection.

of fluxes determined by lysimeter flow is the inhomogeneity of the pack.

So the lysimeter observations may underestimate meltwater fluxes at very low flow rates, but should have little effect at higher flows. The major results, concerning chemical concentrations, should be independent of this low-flow, pressure-gradient issue.

Vertical piping and downslope flow of meltwater along ice lenses significantly affected the catch of tracers by lysimeters. The relatively low Br⁻ concentrations suggest that most of the tracer mass did not enter the lysimeter and that peaks for other tracers would not be distinct from the background. An ice lens was observed in snow pits where the tracer was
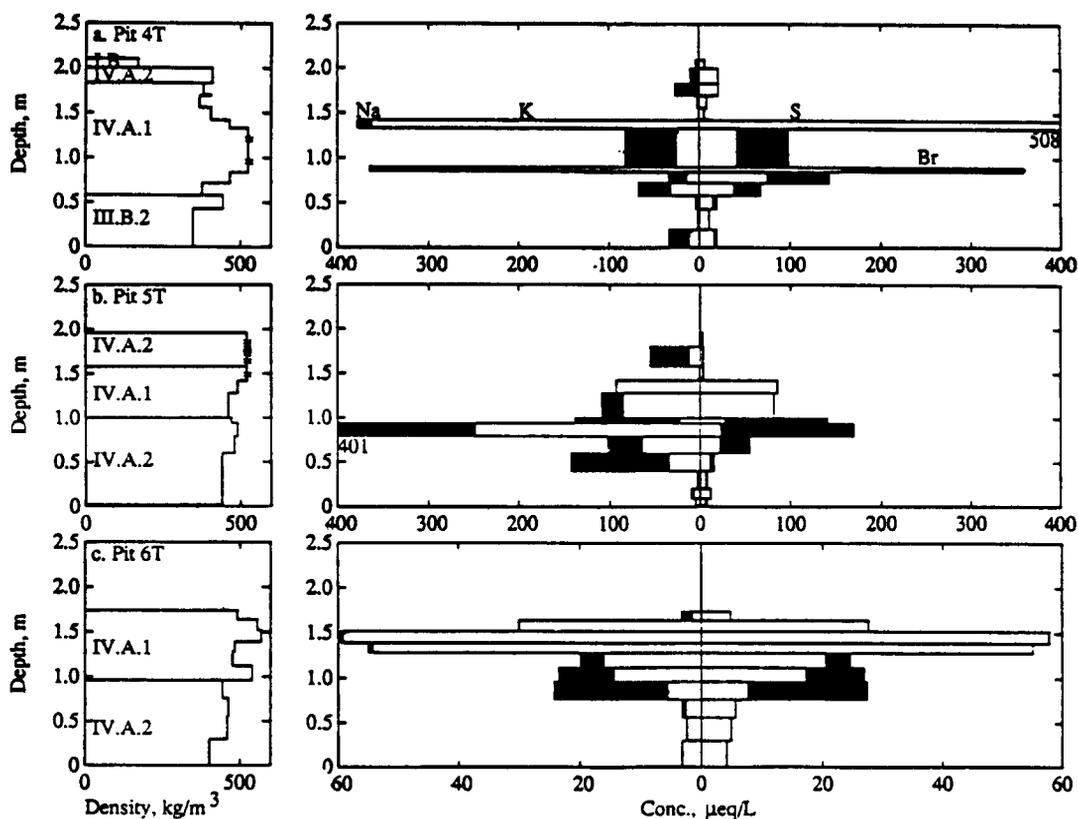
Fig. 7. Density, stratigraphy, anion and cation data for tracer snow pit samples; ions for only one upper tracer (K_2SO_4) and the lower tracer (NaBr) are given for comparison. Concentrations are reported for each stratigraphically distinct layer. * indicates major ice lenses; type IV.A.2 in these profiles also contained many smaller ice lenses.

applied. Digging out the five right-bank and two of the left-bank lysimeters on 3 June confirmed that ice build-up affected flow there as well. Narrow pipes that pierce an ice lens would result in lysimeters receiving meltwater originating above the ice lens. This piping would result in meltwater picking up only a fraction of the tracer, which was observed (e.g. Br^- in RB-3). The major part of the tracer could then flow along the ice layer to a different pipe that missed the lysimeter. Such a routing of meltwater would be consistent with observations of others (Wakahama, 1968; Kattelmann, 1985).

Thus the ionic peaks are thought to be from the snowpack both immediately above and upslope from the lysimeter. The magnitude of the peaks is quite plausible based on previous observations in the field (Davies *et al.*, 1987). The solute-concentration vs time curves for the lysimeters are also similar in shape and peak height to those observed in laboratory melt experiments (Bales *et al.*, 1989). The pulse occurred in clean snow, with no dry deposition or other pollution on either the snowpack or lysimeters.

Solute ionic (equivalents) ratios in meltwater from LB-2 show a small preferential release of SO_4^{2-}, Mg^{2+} and Cl^- relative to Ca^{2+}, NO_3^- and K^+; and a larger preferential release of Na^+. That is, the SO_4^{2-}/Ca^{2+}, SO_4^{2-}/NO_3^- and Mg^{2+}/Ca^{2+} ratios decreased from

about 1.3 to 0.7, 2.5 to 1.3 and 0.1 to 0.01, respectively, over the period sampled. The Cl^-/SO_4^{2-} and K^+/Ca^{2+} ratios were relatively constant; Na^+/Ca^{2+} ratio dropped from 0.6 to 0.2. There are no similar patterns in RB-3. Initial inhomogeneous snowpack-scale and snow-grain-scale solute distributions over the lysimeters probably contributed to the apparent preferential release (Bales *et al.*, 1989); as initial conditions were not well known, no definite explanation can be offered.

In the undosed snow profiles, there is a decrease in the depth-integrated SO_4^{2-}/NO_3^- ratio (equivalents basis from 1.3 (profiles 2 and 3 average and profile 4L) to 1.0 (profile 5L and 5R average) to 0.8 (profile 6L and 6R average), consistent with the preferential release of SO_4^{2-} observed in the lysimeter LB-2. Ratios at individual depths vary from 0.3 to 1.5 in each profile; for example, one layer with a low NO_3^-/SO_4^{2-} ratio is present in profiles 2, 3, 4L and 4R (Fig. 6) at about 0.5 m. The Cl^-/SO_4^{2-} ratio averages 0.2–0.3 in most profiles.

In the four background profiles with the most complete chemical analyses (5L, 5R, 6L, 6R), ion balances showed a 15–25 per cent excess of cation over anions. Much of this deficiency could be organic anions.

The ionic pulse was limited to about the first 10 per

cent of the meltwater flux, and results in a small, but detectable depletion of ions from the pack. The applied tracers are depleted from the pack in preference to the background solutes, as evidenced by the 4–10-fold drop in concentration in the dosed pits, vs about a 25–35 per cent drop in concentrations in the background pits. This greater drop in the tracer profiles in apparently due to both flow along ice lenses where the tracers were applied and greater contact of applied tracers with percolating meltwater. The multiple ice lenses in pit 4 indicate that melt–freeze occurred at the top of the pack, accompanied by meltwater flux from the upper to lower layers. Profile 4T indicates that there was significant meltwater redistribution as early as day 205, just after the first meltwater was collected in LB-2. Profile 5T shows further solute depletion from meltwater movement. The concentrating of solutes in ice lenses, together with higher actual concentrations in the tracer area, apparently result in the solutes being readily removed. It could be expected that ice lenses could also concentrate background solutes and contribute to preferential elution.

Even during the period up to day 205, when there was only a small amount of meltwater fulx observed in the lysimeters, there was solute depletion and significant redistribution (Fig. 7). By day 230, little meltwater had reached the base of the pack at the snow pits, but about half of the tracer mass was depleted. The depletion in the background pits is on the order of 25–35 per cent of the solute mass in the first 10 per cent of the meltwater. This is on the same order as the 70–80 per cent removal of tracer mass from a 0.4-m laboratory snowpack (no ice lenses) with the first 20 per cent of the meltwater (Bales et al., 1989). Comparing profiles 5L and 6L on Fig. 6 suggests that there were solute additions to the top of the snowpack (probably due to dry deposition), which would mean that depletion of the original solutes was near or above the 35 per cent value. Sampling later in the season could better characterize solute depletion from the snowpack.

5. CONCLUSIONS

The ionic pulse observed in samples from lysimeters set at the base of a 1.6–2.1 m snowpack was due to the differential release of ions from melting snow, with a smaller contribution from soil water or overland flow. Peak-to-average concentration ratios (initial day vs average snowpack) were 5–10 or more. The ionic pulse came from unpolluted snow, and there was no difference in its magnitude from dosed vs undosed snow. Data suggest that SO_4^{2-}, Cl^- and Mg^{2+} were depleted from the pack before NO_3^-, K^+ and Ca^{2+}, but the observations are quite variable.

The solute pulse is relatively short; about 10 days after the onset of meltwater release, 10 per cent of the SWE was depleted and concentrations dropped to

near the average snowpack level. Curves such as those shown on Fig. 5 provide point estimates of solute fluxes, and can be fit with a two- or three-parameter exponential function (Bales et al., 1989). Together with point snowmelt, they provide the distributed estimates of solute flux from snowpacks needed for detailed hydrochemical modeling of alpine watersheds (Wolford et al., 1988).

The measured daily meltwater fluxes averaged 4–6 ℓ dy^{-1} (2 cm dy^{-1} of melt) consistent with a contributing snow area on the same order as the area of the lysimeters. Other than noting that lysimeter flows were consistent with calculated melt rates, no quantitative significance should be attached to the average flows. The small lysimeter collection area, horizontal inhomogeneities, the pressure-gradient-zone effect, and spatial variability in snow depths make averaging flows between lysimeters of limited significance. Measured instantaneous flow rates up to 500-fold higher than the average suggest that there was a soil–water contribution (from melting upslope) at some times during the day. Setting lysimeters higher above the ground or on small mounds would avoid this problem, but could exacerbate the pressure-gradient-zone problem. The lack of flow in some should not be interpreted as spatial variability, but problems with the site layout. The similarity of chemical hydrographs between lysimeters and compared to previous lab and field results supports the use of this lysimeter design for chemical samples.

Well-developed ice lenses at the depths tracers were applied and other locations diverted meltwater downslope, as evidenced by the small capture of tracer mass in the lysimeters and the migration observed in snow pits. The snowpack structure was disrupted by having to dig out the lysimeters, masking spatial variability or any possible changes in stratigraphy due to altered vapor flux.

Snow-pit observations showed that tracers remained concentrated at ice lenses, but the first percolating meltwater did carry a significant amount to the base of the pack. Most tracer mass (75–90 per cent) had been removed when SWE had decreased by 10 per cent. The pits showed significant depletion of background chemical species from the pack; apparent additions to the top of the pack during the early melt period masked maximum changes in average (depth-integrated) solute concentrations.

There was well-developed depth hoar and several ice lenses by the time melt began. Although there were several distinct snow layers in each pit, the data did not show a correlation between stratigraphy and background-snow chemical composition.

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