A study of solute redistribution and transport in seasonal snowpack using natural and artificial tracers

Jeonghoon Lee [a,*], Valisa E. Nez [a], Xiahong Feng [a], James W. Kirchner [b,c], Randall Osterhuber [c], Carl E. Renshaw [a]

[a] *Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, United States*
[b] *Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, United States*
[c] *Central Sierra Snow Laboratory, Box 810, Soda Springs, CA 95728, United States*

Summary Solute releases from a seasonal snowpack are important features of spring - runoff in temperate climate zones because meltwater accounts for a significant proportion of contaminant loading to catchments. Here we report a study that traces the movement of natural and artificial solutes in snow through the processes of snow deposition, snowpack metamorphism, and snowmelt at the Central Sierra Snow Laboratory (CSSL), Soda Springs, California, USA. Rare earth elements (REEs) were added to the snowpack to mark individual snow layers. New snow, snowpack profiles and snowmelt were sampled and analyzed for REE and anion (SO_4^{2-}, Cl^- and NO_3^-) concentrations.

Correlations between NO_3^- and SO_4^{2-} concentrations increased from new snow to snowpack profiles and to snow melt, suggesting significant redistributions of natural solutes in the snowpack. The maximum concentrations of NO_3^- and SO_4^{2-} were both five times greater in the snow melt than in the new snow. Solute release by the snowpack was strongly controlled by weather conditions; high concentrations of natural tracers were observed at the onset of intensive melting episodes separated by relatively cold days of little melting. This weather pattern resulted in three ionic pulses rather than one. Natural solutes also showed a diurnal variation that was negatively correlated with the diurnal melting cycle. This pattern can be simulated by the standard water percolation equation linked with a mobile—immobile solute transport model (MIM). The diurnal variations of REE tracers showed positive association with the discharge, and cannot be satisfactorily simulated by the same model, suggesting that additional physical processes, such as dual or multiple flow regimes, may be needed to accurately describe solute transport in snow.
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* Corresponding author. Tel.: +1 603 646 3318; fax: +1 603 646 3922.
E-mail address: jeonghoon.lee@dartmouth.edu (J. Lee).

Introduction

Seasonal snowmelt often delivers significant amounts of pollutants to catchments in temperate regions because atmospherically derived contaminants accumulate in snowpacks during winter via wet and dry deposition. Intensive release of pollutants to catchments from snowpacks at the onset of snowmelt — often referred to as the ionic pulse (Bales et al., 1990) — may result in rapid and significant changes in the chemistry of lakes and streams (Wolford et al., 1996), and may influence surface water acidification and forest response to nitrogen inputs (e.g., Meixner et al., 2004; Williams et al., 1995; Brooks and Williams, 1999; Sickman et al., 2002). With increasing atmospheric loading of pollutants (Wilkening et al., 2000), understanding the processes of solute transport in, and release from, snowpacks is important for predicting surface water quality and the long-term health of temperate forests.

The magnitude and timing of ionic pulses depend on the history of snow metamorphism through the winter, and on the mechanisms by which solutes are eluted from the snowpack (Harrington and Bales, 1998; Feng et al., 2001). Johannessen and Henriksen (1978) reported an exponential decrease in solute concentrations through the melting process (ionic pulse). Other investigators found additional fluctuations in solute concentrations due to changes in the melting rate (Tsiouris et al., 1985; Williams and Melack, 1991; Bales et al. 1993), with high solute concentrations being associated with low melting rates. These studies suggested that dilution of solutes by relatively clean melt of snow grains was responsible for the observed decrease in concentrations with flow. By contrast, Feng et al. (2001) showed that rare earth element tracers, experimentally introduced into a snowpack, exhibited increasing meltwater concentrations as a function of flow during artificial rain-on-snow events. The results of Feng et al. (2001) suggest that both hydrological and chemical conditions are important for solute transport in and delivery from the snowpack.

Our present work was designed to investigate how meteorological and hydrological conditions control solute redistribution and transport in the snowpack throughout an entire winter season. We applied rare earth element (REE) tracers to mark individual snow layers, and monitored both natural and artificial tracers in the seasonal snowpack. The artificial tracers (rare earth elements, REEs) were applied to the snow surface and their redistribution was observed later in the snow profile. Concentrations of natural tracers (SO_4^{2-} and NO_3^-) were measured in new snow, snowpack profiles and snowmelt. Meteorological and hydrological controls on tracer redistribution by snowpack metamorphism, and on their elution by snowmelt, are discussed.

Study area

The study was carried out at the Central Sierra Snow Laboratory (CSSL), located at 39 22′19.5″N and 122 22′15″W, at an altitude of 2100 m, just west of the crest of the Sierra Nevada near Soda Springs, California, USA. Average annual precipitation, annual snowfall, and maximum snow depth at CSSL are 1.3, 10.4, and 2.4 m, respectively. The mean annual maximum and minimum air temperatures are 26 and −10 °C. On average, the site receives ∼80% of its precipita-

tion in the form of snow, and the peak annual accumulation in the snowpack at CSSL averages about 90 cm of water equivalent.

The snow laboratory is constructed in a 0.5 hectare pine forest clearing. It is instrumented to measure meteorological variables, such as air temperature, precipitation, snow accumulation, snow depth, snow water equivalent, wind speed, humidity, and shortwave incident and reflected radiation. There are two $6 \times 3 \, m^2$ melt pans (north pan and south pan) that are sloped gently to a corner drain. The discharge from each melt pan is measured by a 4-L tipping bucket attached to a data logger in a hut to which the snowmelt flows underground through 8 m of PVC pipe. An auto-sampling system for collecting melt water samples was installed. It intercepted the PVC pipe upstream of the tipping bucket and pumped ∼125 mL of water into precleaned plastic bottles sitting on a rotating carousel.

Our experiments were conducted in the winter of 2001, during which the total precipitation, from November 1, 2000 to May 31, 2001, was 832 mm; 88% (∼73.7 cm) was snow with 67.0 cm of the maximum water equivalent.

Methodology

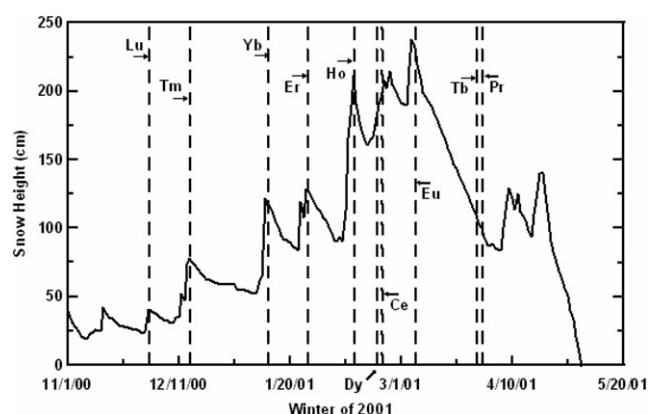### Rare earth element tracers

We added REE tracers to the snowpack after each major storm. The usefulness of the REE tracers has been discussed earlier by Taylor et al. (2001). In brief, because REEs have very low natural abundance, applying these elements in very low concentrations can provide a large signal-to-noise ratio without significantly altering the melting point of the snow (Taylor et al., 2001). Each tracer solution contained approximately 25 ppm of La (a common tracer in every solution), and approximately 25 ppm of another REE, both prepared from ultrapure REE chloride solutions (Table 1). We will not discuss the variations of chloride concentration in the snowpack and snowmelt because the chloride was introduced both in the REE chloride applications and through natural snowfall. Each tracer solution was applied to two $6 \times 3 \, m$ areas using a compressed air sprayer (∼3000 mL of solution applied to each plot). One of the plots where tracers were applied was located directly above the north melt pan, whose outflow was monitored and sampled by the instrumented tipping facilities. The second plot was similar and located nearby, and was used for destructive sampling (by digging a snow pit) shortly before the melt season started. Snow accumulations above ground (cm) over time for the winter 2001 are plotted in Fig. 1. Each tracer application is marked by a vertical dashed line. Snow accumulation was dominated by several major storms. Lu, Tm, Yb, Er, Ho, and Eu were applied directly following storms. Dy and Ce were applied during an individual storm, and Tb and Pr were applied during snowmelt.

Sampling

Three types of samples were collected: fresh snow, snow profiles and snowmelt. New snow was collected for each of the major storms depositing more than ∼15 cm of snow. Following each storm, samples were collected with a plastic or Plexiglas corer, melted in precleaned (with Citronox®)

Table 1 Application of rare earth element (REE) tracers (ppm)

REE tracers	Date of application	Time (PST)	Tracer concentration (ppm)	La concentration (ppm)
Lu	11/30/2000	1135	18.03	28.78
Tm	12/15/2000	1015	29.99	28.18
Yb	1/12/2001	1215	22.34	29.49
Er	1/26/2001	1100	24.63	30.80
Ho	2/12/2001	1430	26.28	28.63
Dy	2/20/2001	830	26.53	31.35
Ce	2/22/2001	845	29.93	30.06
Eu	3/6/2001	1400	21.72	29.80
Tb	3/28/2001	0630 −0710	24.07	31.95
Pr	3/30/2001	0645 −0700	34.34	32.24

Figure 1 Changes in snow depth and dates of rare earth element (REE) applications (marked by dashed lines).

plastic bags, then transferred into precleaned (with Citronox®) plastic bottles. The concentrations of the major anions and REEs in new snow provide the background initial conditions for detection of later changes.

On April 1, samples were collected from snow profiles in the second tracer-sprayed area, and in a 'clean' area where no tracers were applied. The snow depth was 1 m at the time of sampling. The clean snow profile was from a single snow column measuring $1\,m \times 20\,cm \times 14\,cm$. Individual samples were collected at 5 cm intervals in depth, so each snow sample is a $20 \times 14 \times 5\,cm^3$ block. The tracer snow profile was about a 1 m deep and 1 m wide. This volume was partitioned into 7 columns and 20 rows, so that each sample had the same dimensions as the samples from the clean pit. Samples were sectioned with flat stainless steel tools that were rinsed with deionized water between each use to avoid cross-contamination. Snow blocks were melted in plastic bags at room temperature and then transferred to 125 mL plastic bottles. Both the bags and bottles were pre-cleaned with Citronox®. The physical properties of the snowpack (e.g. position of ice lenses and changes in grain sizes) were noted during the sampling process. Coarse layers were noted at 65, 50 and below 28 cm above ground. Within the bottom 6 cm, ice grains were particularly coarse and granular. The bulk snow density was measured at 5 cm intervals of snowpack height for three trials of samples taken from the east, west, and middle profiles of the tracer sprayed area. The average bulk density was 0.415 g/cm³, which was implied an average snowpack porosity of 0.58.

Meltwater was collected with an autosampler throughout the entire winter season (with a few breaks due to equipment issues). Since the melt rate was very slow in the winter, the autosampler was programmed to sample every 2 h or with every bucket tip, whichever was less frequent. Thus the autosampling frequency varied throughout the sampling period.

Chemical analysis

Each snow sample was split into three fractions, $\sim$15 mL for anion (Cl^-, SO_4^{2-}, and NO_3^-) analysis, $\sim$30 mL for isotopic analysis (not discussed in this paper) and $\sim$60 mL for REE analysis. Anion samples were stored in a freezer until analysis. The REE samples were acidified to a 1% HNO_3 solution with ultrapure nitric acid (Seastar). REE element concentrations were measured with a High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS, Element1, Finnigan). The precision of HR-ICP-MS analyses was within ±5%. Anion concentrations were determined using an Ion Chromatograph (IC, Dionex, DX-500). Standards were run for about every 10 samples, and the relative standard deviation was within 2%.

Results

Tracers in new snow

Natural abundances of REEs in new snow were below 50 ppt for all REE tracers except Ce and La, and most concentrations were below 5 ppt. Statistics from the REE analyses of new snow are given in Table 2. Sulfate, nitrate and chloride concentrations of new snow samples are plotted as functions of time in Fig. 2. Concentrations are less than 1 ppm for all anions, with an exception of nitrate concentrations in the sample from November 19, 2000, 2.87 ppm. There is some degree of co-variation among the anion tracers. For example, the sample of 11/19/00 has the highest concentrations of all three tracers.

Tracers in snow profiles

The concentrations of REE tracers in the clean snow profile are generally low (Table 2). In four cases (Lu, Er, Ce, and La), there are statistically significant differences between the mean concentrations in the new snow samples and the

Table 2 Concentrations of REEs (ppt) and anions (ppm) in new snow and the clean snow profile

Tracers	Average (new snow)	Standard deviation ($n = 21$)	Average (clean snow pit)	Standard deviation ($n = 20$)
Lu	4.25	7.10	0.08	0.16
Tm	0.23	0.21	0.36	0.31
Yb	2.04	4.35	1.93	1.72
Er	0.67	1.06	2.41	2.11
Ho	0.80	0.94	0.90	0.73
Dy	5.90	10.55	4.35	3.60
Ce	34.80	40.04	89.26	67.00
Eu	1.07	1.41	0.63	0.77
Tb	0.43	0.57	0.41	0.55
Pr	5.15	5.48	8.14	6.46
La	19.28	19.65	37.94	30.35
SO_4^{2-}	0.15	0.15	0.30	0.26
Cl^-	0.12	0.11	0.21	0.23
NO_3^-	0.37	0.61	0.11	0.08
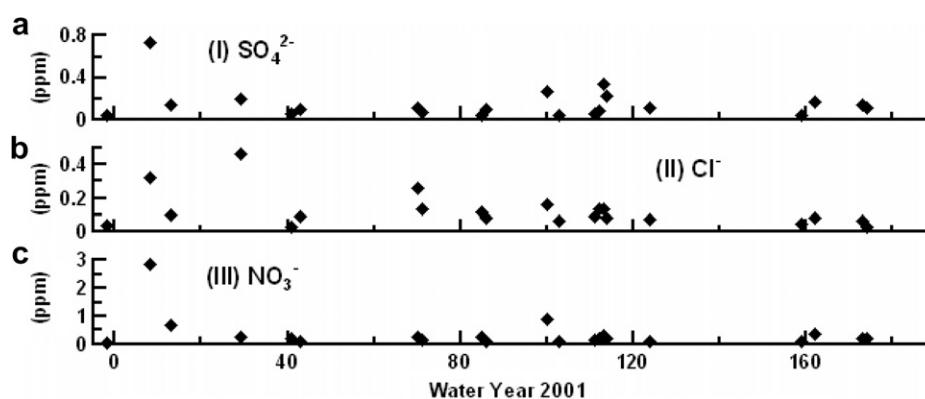
Figure 2 Concentrations in new snow of (a) sulfate, (b) chloride, and (c) nitrate.

clean snowpack ($p < 0.05$ by two-tailed t-test). Fig. 3 contains surface contour maps representing the spatial distributions of REEs and anion tracers within the sampled snowpack profile beneath the sprayed plot. Lu is highly concentrated in the lowest 20 cm of the profile. Tm is more diffused, occurring mostly between 5 cm and 40 cm above ground with the highest concentration around 23 cm above the ground. Yb is mostly concentrated at 50—55 cm above the ground, and there are other less concentrated patches at 10—20 cm and 35—40 cm. The highest concentration of Er is found from 65 to 75 cm. The positions of these four tracers correspond to the sequence in which they were applied. Ho, Dy, Ce, and Eu show puzzling patterns, being concentrated only at the west corner of the section (only Ho is shown as an example). One possible explanation for these patterns could be that by the date the snowpit was excavated, the layers containing these four tracers had already melted at the snowpack surface, and thus the tracers had already been lost from most of the snowpack. The fact that they are found together at the upper west corner of the sampled section could indicate either lateral redistribution between the snowpack, or greater retention of REE's by surface sediment in that area. Unfortunately this cannot be confirmed because we did not measure dust concentrations in the samples, and high dust concentrations were not visi-

bly obvious in the sampled section. Nonetheless, this conjecture is consistent with the fact that Tb and Pr, which were applied during the period of active snowmelt, are also concentrated in the top 5—10 cm of the section, with their highest concentrations also occurring at the upper west corner (only Tb is shown as an example). Compaction affected the relative elevation of the REE tracers. For example, the interval between Lu and Tm decreased from 36.5 at the time of application to 20 cm when the snow profile was sampled; likewise the interval between Tm and Yb decreased from 39.5 to 30 cm.

Distributions of NO_3^- and SO_42- in the snow profile were more uniform than the REE tracers, as expected. Since some Cl^- was introduced as REE salts, its distribution is more similar to REE tracers than to the other anions. For all three naturally occurring tracers, relatively high concentrations occurred around 55 cm above ground. This level does not correspond to a snow layer that was particularly dirty; instead it seems more closely associated with the ice layer at 50 cm (see ''Discussion'').

Tracers in meltwater

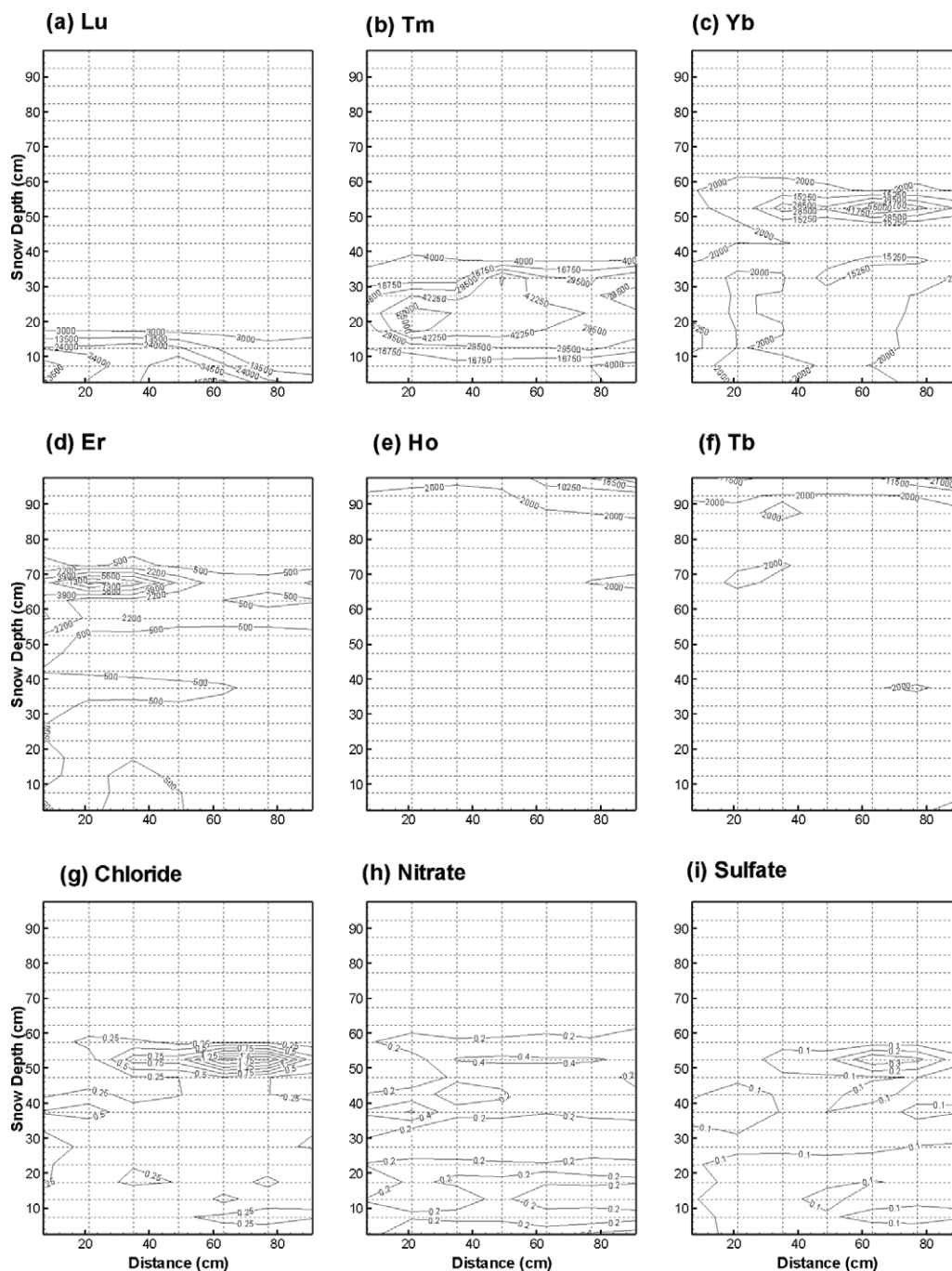In Fig. 4, meltwater concentrations and meltwater flow (mm/h) are plotted as functions of time. Meltwater dis-

Figure 3 Contour maps of tracer distributions across the face of a snowpit in the destructive sampling plot (see ''Methods''). Numbers in contour lines are concentration of REEs (panels a—f) in ppt, and of anions (panels g—i) in ppm.

charge is low throughout the winter season except for episodic melting events. During spring, meltwater discharge increased and there were three distinctive melting episodes with intermittent cold periods when little meltwater was generated.

Lu, Tm, Yb, and Er appeared in the discharge shortly (0.6—10 days) after they were applied to the snowpack. When the tracers reached the base of the pan, their concentrations increased abruptly and sharply, and then decreased exponentially (in Fig. 4, concentrations are plotted on logarithmic axes to accommodate their large dynamic range).

However, Ho, Dy, Ce, and Eu did not appear in the discharge right after they were applied. In fact, after Ho was applied on 2/12/01, no tracers were eluted from the snowpack until 03/29/01. On March 29, it was found that sediment had built up in the pipe draining the melt pan. When the sediment was cleaned out, all tracers appeared in the discharge as a spike (Fig. 4). It was possible that REE tracers had been adsorbed onto the sediment, resulting in their delayed release to the meltwater. Unfortunately, the sediment was not sampled and thus cannot be analyzed for its tracer concentrations.
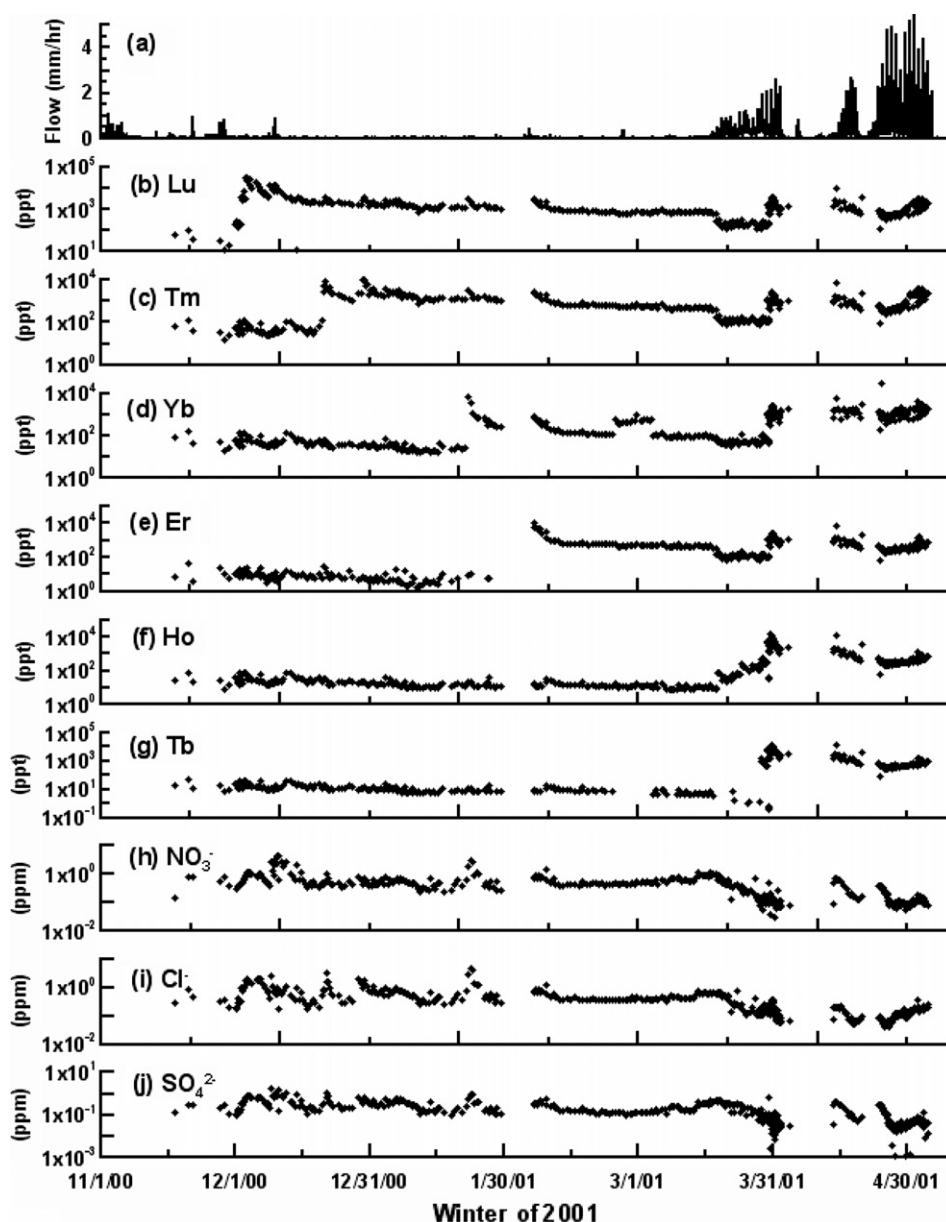
Figure 4 Discharge throughout the study period (a); and meltwater concentrations of REEs (b–g) and anions (h–j).

Fig. 4h–j shows how anions were released from the snow-pack. Variations in anion tracer concentrations are greater in snowmelt than in new snow or the snowpack profile. In particular, the maximum concentrations in meltwater were much higher than those in new snow or the snowpack profiles. For example, the maximum SO_4^{2-}, concentration in the snowmelt was 1.8 ppm, compared to 0.3 ppm in new snow and 0.4 ppm in the snowpack profiles. The concentrations of different anions show similar variations that are associated with water flow. During the early winter (days 40–85), the anion concentrations also appear to increase when the flow rate slightly increased. This is most distinctively shown on 12/11/00, while the correspondence of concentration peaks (around 1/23/01) with other discharge events was not so clear due to low resolution of the discharge measurement with the tipping bucket. From 2/9/

01 to 3/16/01, anions concentrations were relatively stable. Throughout the first major melting event in April (around 4/1/01), anion concentrations show continuous decreases (following gradual increases). However, high concentrations occurred again at the onset of the second melting episode (starting on 4/13/01), and were again followed by exponential decreases (shown as linear decreases on the logarithmic concentration scales shown in Fig. 4h and j). A similar trend occurred again during the third melting episode (starting on 4/23/01).

It is interesting to observe that REE tracer concentrations do not always exhibit the same patterns as those of the anions. Particularly noticeable is around 3/31/01 (Fig. 4) when the discharge reached the highest levels within the first melting episode. All REE tracer concentrations increased while NO_3^- and SO_4^{2-} concentrations decreased; Cl^-, which
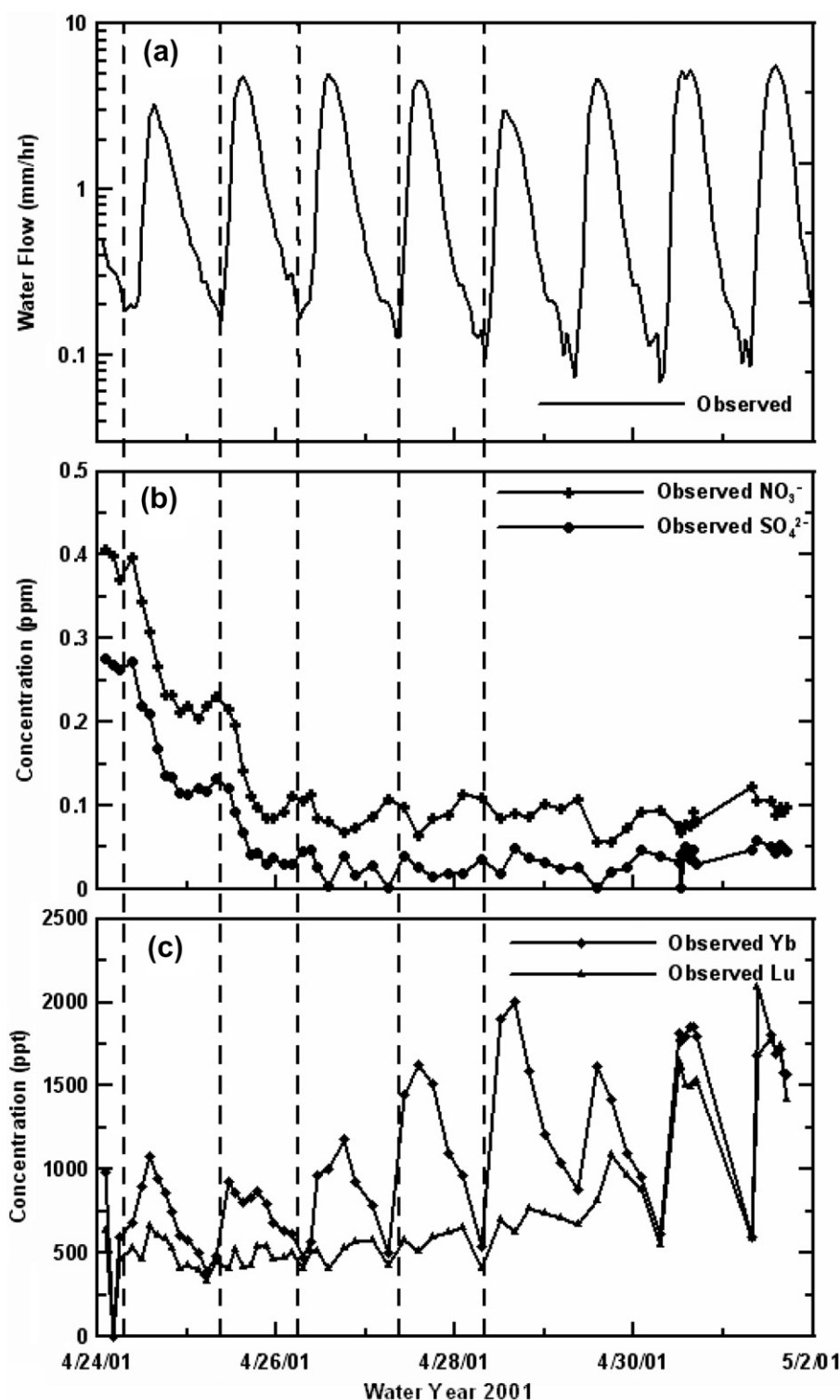
Figure 5 Diurnal variations of selected REEs and natural anions in discharge. (a) Water flow, (b) concentrations of nitrate and sulfate, and (c) concentrations of Yb and Lu. Lu concentration increased drastically on the second last day of the melting period because the snow layer containing Lu was being melted.

was introduced by both natural deposition and artificial applications, showed a pattern that combined the behavior of the REE tracers and anions.

Diurnal melting cycles were most dramatic during the last spring melting episode. Both REE tracers and natural an-

ion tracers showed systematic variations accompanying diurnal changes in meltwater discharge (Fig. 5). REE concentrations in the meltwater corresponded positively with daily cycles: high concentrations occurring with high melting rates (Fig. 5c). REE concentrations increased in the

morning, reached a peak concentration in the afternoon, then decreased, and reached the lowest values at night when meltwater flow was low. In addition, the daily maximum concentration seemed to increase with time. On the contrary, sulfate and nitrate responded negatively to meltwater daily cycles (Fig. 5b). From 4/23/01 to 4/25/01, anion concentrations were low during the day, and rose at night. There were three recognizable rises in anion concentrations during the daily low flows, each becoming less distinct than the previous one. Then the diurnal signal disappeared for sulfate, but continued for nitrate for two more days until 5/1/01.

Mass balance of REE tracers

Mass balance calculations for REE tracer recovery are summarized in Table 3. The mass balance considers the amount of tracer present in the snow profile sampled on April 1, 2001 and that found in the discharge until March 31. The to-tal tracer recovery varied from 2% for Eu to 76% for Tm. The mass balance estimates may have significant errors mainly because the melt water samples did not include every bucket of the snowmelt. In addition, we do not know how much tracer was adsorbed onto the sediment. However, one can see that first a few tracers had relatively better recoveries than the tracers applied later in the experiment. This result is qualitatively consistent with the observation that later tracers were not found in the snow profile; neither were they found in the melt.

Discussion

Our research objective was to study how meteorological and hydrological conditions control solute redistribution and transport in the snowpack throughout an entire winter season. In this section, we first discuss solute redistribution and transport in snowpack. We then discuss how meteorological and hydrological conditions are related to solute transport.

REEs as marker of snow layers

Taylor et al. (2001) found REE tracers to be effective markers for snowpack layers. In this study, the REE tracers were useful markers in some cases. As an example of how REE tracers can be used, consider the high concentrations of anions at 50—55 cm above ground, which also correspond to high concentrations of Yb (Fig. 3). The high concentration of Yb indicates that the snow layer near 50 cm fell on January 12, when Yb was applied. Checking the new snow sampled for that storm (concentration was below the detection limit), we found that anion concentrations during this storm were not unusually high. The maximum concentration in the new snow before the spray was 3.2 ppt on November 9. Therefore, the high anion concentration must have resulted from post-deposition snow metamorphism. We could not have been able to draw such an inference without REE trac-

Table 3 Mass balance of REE tracers

REE element	% in snowpack	% in meltwater to 3/31/01	% Recovered
Lu	43	12	55
Tm	73	3	76
Yb	38	2	40
Er	5	3	8
Ho	10	5	15
Dy	1	3	4
Ce	1	2	3
Eu	1	1	2
Tb	14	8	22
Pr	27	10	37
La	16	4	20

Table A1 Snowpack properties and symbols used in this study

Symbol	Meaning (values used in the simulations if not otherwise specified)	Units	Dimension
C_i	Tracer concentration in immobile phase	g/cm^{-3}	g of solute mass/cm^3 of immobile water
C_m	Tracer concentration in mobile phase	g/cm^{-3}	g of solute mass/cm^3 of mobile water
D	Dispersion coefficient	cm^2/h	
K	Hydraulic conductivity	cm h^{-1}	
n	Exponent		Dimensionless constant = 3
S	Effective water saturation $(S_w - S_i)/(1 - S_i)$		cm^3 of (total water-immobile) volume/cm^3 of (pore-immobile) volume
S_i	Irreducible water content: irreducible volume of water over pore volume		cm^3 of immobile water volume/cm^3 of pore volume
S_w	Total water content: total water volume over the pore volume		cm^3 of total water volume/cm^3 of pore volume
t	Time	h	
u	Water velocity	cm h^{-1}	cm snow/s
z	Depth	cm	
β	$S_i/(1 - S_i)$		
θ	Volumetric water content		cm^{-3} of water volume/cm^3 of pore volume
φ	Porosity		cm^{-3} of pore volume/cm^3 of total volume
ω	Exchange rate coefficient	h^{-1}	

ers. In this case, the Yb successfully provided a marker for the layer of snow deposited during the January 12 storm.

REE tracer solutions were prepared at similar concentrations (25.8 ± 4.8 ppm among 10 tracers, see Table A1), but the concentrations in the snow profile varied greatly among tracers (e.g., peak concentrations varied from ∼3000 ppt for Ce to ∼1,00,000 ppt for Pr), and also varied greatly both vertically and horizontally for individual tracers. Furthermore, the mass balance calculations show that only a few tracers remained in the snowpack, while most tracers exhibited significant mobility. In the report of a previous similar experiment, Taylor et al. (2001) suggested that tracers should be applied when the air temperatures were below freezing and prior to a snowstorm to prevent melting from solar radiation. In our experiment, the low recovery rates of Dy, Ce, Eu in the snow profile were probably caused by warm daytime temperatures following the days that they were applied. It is not clear, however, why Er and Ho also had low concentrations in the profile because daytime temperatures were quite low after they were applied. Compared to the previous experiment reported by Taylor et al. (2001), tracers in this experiment seemed to show more mobility within the snowpack, as indicated by the diffused distribution of tracers in the profile. For example, Tm was distributed from ∼40 cm down to the ground, whereas tracers in the previous experiment were mostly concentrated within snow layers 10–20 cm thick. The snowpack studied in this work had more coarse-grained layers, compared to the previous experiment, which is consistent with the relatively high mobility of the REE tracers in the present experiment.

Redistribution of solutes in snow

Solutes are redistributed in the snowpack due to snow metamorphism, which can be observed in several ways. First, ionic concentrations vary more widely in snowmelt than in either fresh snow or the snow profile. The maximum concentrations of naturally occurring solutes are much higher in meltwater than in either new snow or snowpack as described earlier. This is because snow metamorphism and the resulting purification of snow grains leave the pore water with high solute concentrations. Such pore water

caused some concentrations in the discharge to be many times higher than concentrations in the new snow.

Second, distributions of REE tracers in the snow profile do not correspond to the time series of concentrations in new snow. An example was given earlier that anions were mostly concentrated near the ice layer at 50 cm, which does not correspond to a particularly anion-rich snowstorm. Ice layers are relatively impermeable such that they may trap melt water above them. Slow flowing snowmelt during the cold winter carried pore fluids that might be concentrated in solutes due to snow metamorphism, and thus solute concentrations above the ice layers could be high as a result.

Third, nitrate and sulfate concentrations show increasingly strong correlations (r) from fresh snow ($n = 20$, $r = 0.61$) to the snowpack profile ($n = 140$, $r = 0.76$) and to the melt water ($n = 452$, $r = 0.87$) (Fig. 6). This observation suggests that anion distributions in snow were modified by snow metamorphism and elution of snowmelt, with both processes moving redistributing SO_4^{2-} and NO_3^- similarly to one another. For example, recrystallization would remove both SO_4 and NO_3 from the ice, and both SO_4 and NO_3 could become concentrated during cold periods and mobilized during melting events.

Meteorological and hydrological control of solute transport

Variations in tracer concentrations are related to flow conditions on different time scales (Figs. 4 and 5). The naturally deposited anions, NO_3^- and SO_4^{2-} showed measurable concentration increases when snowmelt discharge increased after a period of relatively low flows. The concentration peaks around 12/11/00 and 1/25/01 are two examples from the early winter (although near 1/25/01 the discharge only increased very slightly and is hardly visible in the figure). More obvious fluctuations of NO_3^- and SO_4^{2-} concentrations are associated with the three melting episodes near the end of the season. This suggests that during the cold period between two melting episodes, snow metamorphism continued to occur by diurnal melting and freezing cycles. These cycles resulted in further snow grain purification, leaving impurities in the pore fluids and causing the ionic concentrations to in-
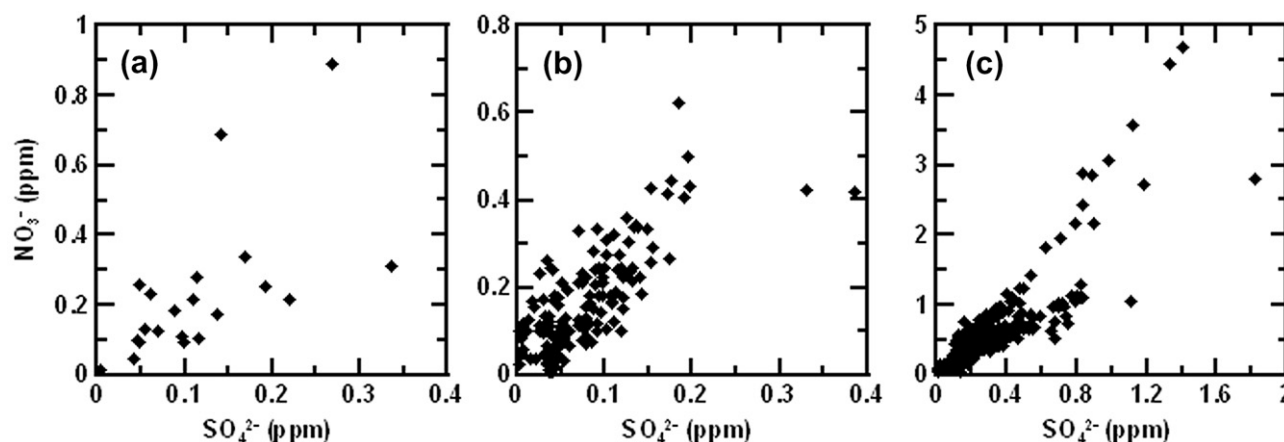

Figure 6 Correlation between nitrate and sulfate from (a) new snow ($n = 20$, $r = 0.61$), (b) snow profile ($n = 140$, $r = 0.76$), and (c) snowmelt ($n = 452$, $r = 0.87$).

crease with the onset of the next melting event. These observations indicate that the ionic pulse does not necessarily occur as one big peak. Waldner et al. (2004) pointed out that solute transport and delivery to the soil surface are strongly dependent upon meteorological conditions and their effects on snow metamorphism, melting and water flow.

As described earlier REE tracer concentrations exhibit different patterns than those of the natural anions. Particularly during the first major melting episode near 3/31/01, all REE tracer concentrations increased at the highest discharge levels while NO_3^- and SO_4^{2-} concentrations decreased. The fact that all REE tracers behaved the same way rules out the possibility that the concentration increases were caused by melting a specific layer of snow containing the tracers. Fig. 3 shows that Lu was only present in the bottom 20 cm of the snowpack; this layer could not be mobilized by melting on March 31 when the snowpack was 94 cm deep, but nonetheless the concentration of Lu peaked similarly to other REE's. This suggests that some of the REE tracers, including Lu, were eluted by percolating snowmelt, with the high-flow conditions activating channels or accessing pores that are infrequently flushed at lower flow rates. These channels and pores would thus still contain relatively high levels of REE tracers, leading to higher REE concentrations at higher discharges. The question is why these infrequently flushed pores and channels would not also contain high levels of natural anion tracers. One possible explanation is that these areas of snow had experienced less significant recrystallization by wet metamorphism compared to areas that are frequently wetted by percolating water. In this conceptual picture, the artificial tracers may have initially been evenly distributed among the pores in the layer where they were applied, with differences in concentrations among the pores developing due to differences in the frequency of flushing. Because the natural tracers were suffused throughout the grains of newly fallen snow (in contrast to the artificial tracers, which were introduced directly into the pore fluids), their concentration differences in the pore fluid would presumably result from spatial variations in the conditions controlling snow metamorphism This example demonstrates how solute transport in snow can be affected by many factors including weather conditions, water transport pathways, and snow texture and its evolution with time.

Both REE and natural tracers showed clear diurnal variations as shown in Fig. 5 in the last melting episode. In this case, the two types of tracers again showed opposite patterns. Anion concentrations are negatively associated with discharge (Fig. 5b), whereas REE concentrations are positively associated with discharge (Fig. 5c). The same mechanism discussed above should also apply here. During high flow, infrequently flushed pathways should become hydraulically connected, permitting water with high levels of REE tracers to mix into the bulk water flow, and causing the concentrations in the discharge to increase. For example, at the onset of the last melting episode, the snowpack depth was 91 cm, which was well above the layers containing the Lu tracer. Thus meltwater generated at the surface should have had only background concentrations of Lu. The concentrations observed in the meltwater, however, reflect the mixing of this clean meltwater with concentrated pore water flushed out under high flow conditions. Fig. 5 shows that Lu concentrations significantly increased

on the last three days of the melting season, indicating that the snow layers containing the Lu tracer was finally melted.

The concentration—discharge relationship for the natural anion tracers was the opposite of that for the REEs: concentrations were inversely correlated with flow. In this case, we infer that the tracer concentrations in the infrequently flushed pores were not much higher than in the bulk meltwater, so that hydraulically connecting these pores at high flow would not offset the effect of dilution by the input of clean snowmelt at the surface.

Solute transport simulations

The conceptual discussion above is difficult to simulate by one-dimensional models. The most frequently used model for solute transport in percolating snow is the mobile—immobile water model (MIM), in which solutes in the mobile water are transported by advection and dispersion, and those in the immobile water are transported only by exchange between immobile and mobile water (Harrington and Bales, 1998). This model may not be adequate for describing transport of the REE tracers because it does not have a mechanism to develop chemical heterogeneity in the immobile water through time. It may also not be adequate for describing the natural anion tracers because it does not allow initial chemical heterogeneity in the immobile pore water at the spatial scale of the flow channels.

We used the MIM described by Lee et al. (2008, see the Appendix) to simulate the diurnal concentration variations of NO_3^- and Yb, with the objective of testing how well the physical processes of tracer transport are represented by the MIM conceptualization. Fig. 7 shows the results of our simulations. For NO_3^- we assumed that the ice phase has a concentration of zero. With a uniform initial solute distribution in both mobile and immobile waters (0.4 ppm, see more information in figure caption), the basic feature of NO_3^- concentration variations can be reproduced. This suggests that the heterogeneity of NO_3^- concentration in the pore water may not have been significant.

The tracer Yb was concentrated in the snow layer between 50 cm and 60 cm above ground (Fig. 3), and when the third melting episode started, the snowpack was about 100 cm high. We assumed that the mobile water had a concentration of zero because the discharged meltwater was relatively clean when the simulation started. The immobile water was assumed to be clean above the Yb layer (60 cm of depth) and had a concentration of 3000 ppt below it. The Yb concentration in ice was assumed to be zero above 60 cm, and 1500 ppt below it. The concentration levels assumed here are somewhat arbitrary; we will come back to these assumptions later. When the snowmelt was clean (4/24/01 to 4/26/01), the simulated concentrations had diurnal variations but with the opposite phase as the observed tracer variations (Fig. 7c). In addition, the simulated concentration decreased in its peak value significantly from day to day, while the observed diurnal fluctuations are similar in magnitude. On the 4th day (4/27/01), the simulated Yb concentration increased significantly because the snow layer containing Yb was melted. During the subsequent days, the Yb concentration oscillated diurnally and in phase with the flow, although the magnitude of the oscillation was much smaller. The actual values for the initial concentra-
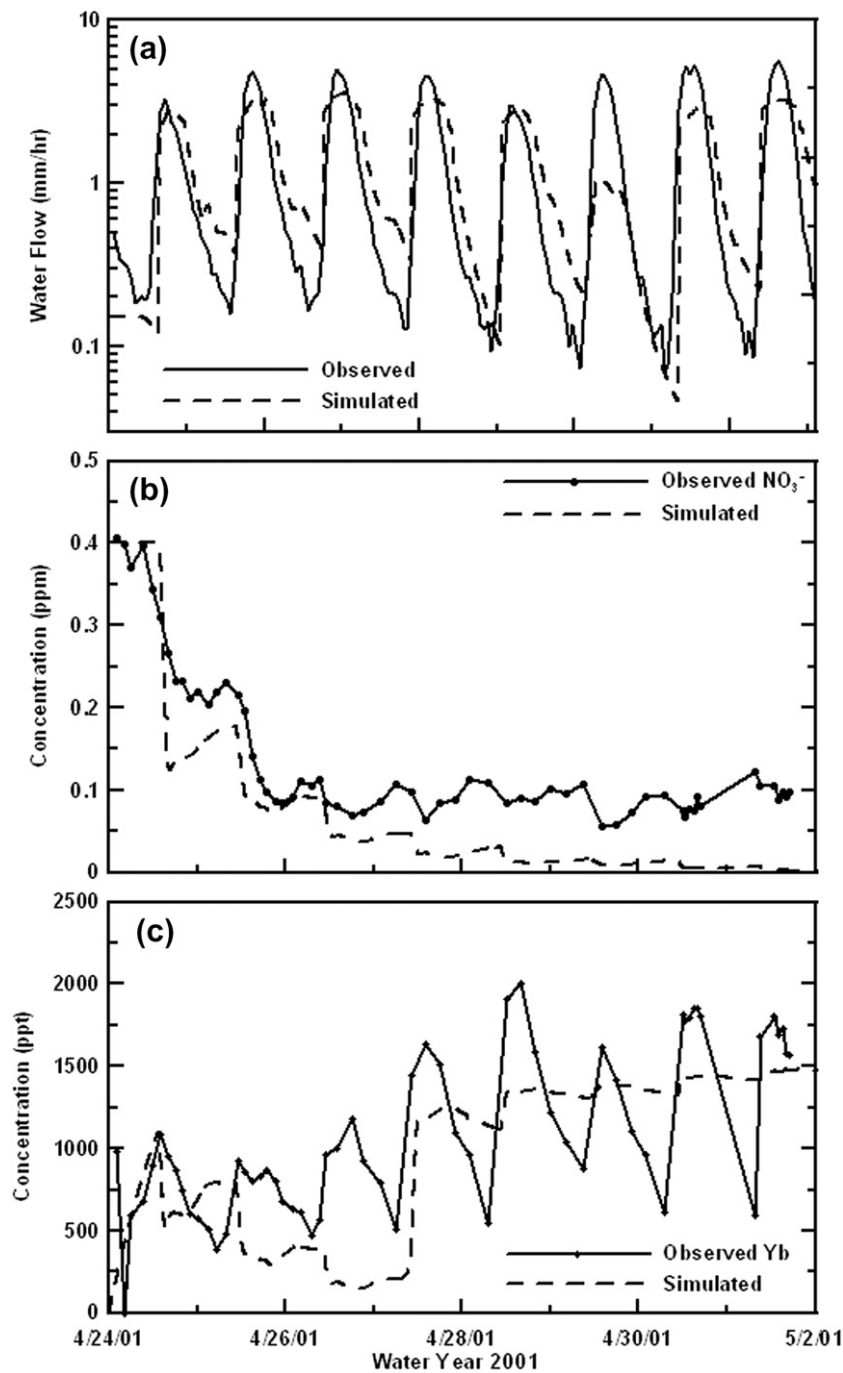
Figure 7 Measured (solid lines) and simulated (dashed lines) water flow and tracer concentrations in diurnal melting cycles. For simulations, we used measured porosity of 0.58, measured bulk density of 0.415 g/cm³, 3 for n, and 0.05 for S_i. The exchange rate between mobile and immobile was a function of the effective saturation ($\omega = 2 \times S^2$). The initial conditions for the nitrate simulation were that concentrations of mobile (C_m) and immobile (C_i) waters were both 0.4 ppm, and the concentration in ice (C_{ice}) was zero; the initial conditions for the Yb simulation were that $C_m = \begin{cases} 0 & \text{when } z \leqslant 60 \\ 0 & \text{when } z > 60 \end{cases}$, $C_i = \begin{cases} 0 & \text{when } z \leqslant 60 \\ 3000 & \text{when } z > 60 \end{cases}$, and $C_{ice} = \begin{cases} 0 & \text{when } z \leqslant 60 \\ 1500 & \text{when } z > 60 \end{cases}$.

tions of the mobile and immobile water do not change the general pattern of the output. The important point here is that some Yb had to be released by melting ice to create the concentration increase on 4/27/01. This means that either Yb was incorporated into the solid phase or some

immobile water with high Yb concentration did not effectively exchange with mobile water. We consider the latter to be more likely the case. We suggest that the important physics missing in the model is probably the assumption that the immobile water always has a zero advection velocity.

The observed concentration pattern seems to imply that some fraction of water in the snowpack that is significantly concentrated in Yb is being ''turned on and off'', such that it flows and delivers Yb during high flow but shuts down during low flow, causing much greater diurnal concentration fluctuations than the simulated result. The homogeneous flow equation (single-porosity flow system) has been demonstrated to be adequate to describe water percolation in snow (Colbeck, 1972; Colbeck, 1974), and has been widely used. However, certain the solute transport patterns observed in this and in some previous work (Feng et al., 2001; Lee et al., 2008) call for a dual- or double-porosity model, as has been widely used for solute transport in fractured rocks and soils (e.g., Gerke and van Genuchten, 1993).

Conclusion

We traced the deposition, redistribution and elution of both natural and artificial tracers in snow through the processes of snow accumulation, metamorphism and melting of the snowpack. REEs tracers were used as chemical markers of snow layers, and indicated redistribution of natural as well as REE species in snow. In particular, an ice layer caused local accumulation of solutes probably due to its low permeability. Redistributions of natural solutes were also suggested by increasing covariation of NO_3^- and SO_4^{2-} from the new snow to snow profile, and to snowmelt.

Solute transport and discharge is strongly controlled by both meteorological and hydrological conditions on different time scales. Throughout the melting season, high concentrations of natural solutes were associated with the onset of each of the three major melting episodes separated by cold days in between, and as each melting episode proceeded, the solute concentrations decreased exponentially. In other words, the natural solutes were released in three seasonal ionic pulses rather than a single one. Diurnal variations of water flow also caused concentrations of natural solutes to fluctuate, with relatively low concentrations being associated with high, daytime melting rate. This diurnal variation resulted from dilution of solutes by clean snowmelt under high flow conditions.

The patterns of variation of the REE tracer concentrations are substantially different from those of the natural tracers. Most obviously, the diurnal variations in REE concentrations were positively correlated with discharge. This concentration pattern suggests that channels containing concentrated REE tracer were activated during high flow conditions, causing the bulk concentrations to increase significantly during the day and decrease at night. This positive concentration—discharge relationship and the large oscillations observed in REE concentrations cannot be simulated by the standard homogeneous flow with MIM transport regime, suggesting that a more sophisticated flow model, e.g., a dual- or double-porosity model, is needed.

Acknowledgements

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