

How Isotopic Fractionation of Snowmelt Affects Hydrograph Separation

SUSAN TAYLOR^{1,2}, XIAHONG FENG², MARK WILLIAMS³, AND JAMES MCNAMARA⁴

ABSTRACT

We present the isotopic composition of meltwater samples from four seasonal snowpacks: a warm, maritime snowpack in California, a temperate continental snowpack in Vermont, a cold continental snowpack in Colorado, and an Arctic snowpack in Alaska. Despite the very different climate conditions, the $\delta^{18}\text{O}$ of meltwater from all four snowpacks increased as melting progressed. This trend is consistent with theoretical results that model isotopic exchange between water and ice as meltwater percolates through a snowpack.

We have estimated the systematic error in the hydrograph separation if the isotopic composition of a snow core were used in place of that of meltwater. Assuming no error in the old water or stream water values, the error in the new water fraction depends on 1) the isotopic difference between the snow core and the old water, 2) the isotopic difference between the snow core and the meltwater, and 3) the new water fraction contributing to the stream flow during a spring melt event. The error is large when snowmelt contributes a dominant fraction of the stream flow, which may be expected where infiltration of snowmelt is limited (e.g., permafrost, urban areas). A particular challenge will be how to incorporate the changes in isotopic composition of meltwater measured at a point into hydrograph separation models conducted at the watershed scale.

Key Words. Snowmelt, ^{18}O , new water component, hydrograph separation, error analysis

INTRODUCTION

Isotope hydrograph separation is a technique that partitions the contributions of new water (event water like rain or snowmelt) and old water (pre-event water such as groundwater, soil water, and pore water) to a stream hydrograph. Dinçer et al. (1970) pioneered the use of isotopes for hydrograph separation. They measured oxygen and tritium isotope compositions of groundwater, rain, and snow in a 2.7-km² Czechoslovakian watershed and determined that 63% of the river flow during spring melt was contributed by old water. The technique has been extensively

¹ U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH 03755
Phone: 603-646-4239 Fax: 603-646-4785 E-mail: staylor@crrel.usace.army.mil

² Department of Earth Sciences, Dartmouth College, Hanover, NH 03755
Phone: 603-646-1712 Fax: 603-646-3922

³ Department of Geography and Institute of Arctic and Alpine Research, University of Colorado,
Denver, CO 80217
Phone: 303-492-4794 Fax: 303-492-6388

⁴ Department of Geosciences, Boise State University, Boise ID 83725
Phone: 208-426-1354

used by the hydrological community to track the components of runoff (Hooper and Shoemaker 1986, Wels et al. 1991, Rodhe 1998), to trace water flow in unsaturated soils (Buttle and Sami 1990), and to evaluate possible consequences of the new-water/old-water ratio for stream chemistry and surface water quality (Bottomley et al. 1986, Bishop et al. 1990, Kendall et al. 1995).

Isotope hydrograph separation is based on the assumption that the isotopic compositions (e.g., $\delta^{18}\text{O}$) of both new water and old water (water existing in the watershed prior to the event) at a given instant in time are known and that the stream water is a mixture of the two (Sklash and Farvolden 1979). The simplest form is a two-component system, where the $\delta^{18}\text{O}$ of the pre-event base flow is used as the composition of the old water ($\delta^{18}\text{O}_{\text{Old}}$) and the $\delta^{18}\text{O}$ of the bulk precipitation (or snowmelt) is used as the composition of new water ($\delta^{18}\text{O}_{\text{New}}$). Then the stream water $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{Str}}$) can be expressed as

$$\delta^{18}\text{O}_{\text{Str}} = x \delta^{18}\text{O}_{\text{New}} + (1-x) \delta^{18}\text{O}_{\text{Old}} \quad (1)$$

where x is the fraction of new water at a given instant in time during the event. Therefore,

$$x = \frac{\delta^{18}\text{O}_{\text{Str}} - \delta^{18}\text{O}_{\text{Old}}}{\delta^{18}\text{O}_{\text{New}} - \delta^{18}\text{O}_{\text{Old}}} \quad (2)$$

For (1) and (2) to be valid along an event hydrograph, it is necessary that both $\delta^{18}\text{O}_{\text{Old}}$ and $\delta^{18}\text{O}_{\text{New}}$ are temporally invariant, and so a change in $\delta^{18}\text{O}_{\text{Str}}$ can be attributed only to a change in x .

Isotope hydrograph separation of snowmelt events in temperate and cold regions has been done by many investigators (Table 1 and Buttle 1994). The composition of the new water end member has been estimated in different ways, including using a snow core to obtain an average isotopic value for the snowpack, taking a series of snow cores to account for changes in the snowpack, or measuring the meltwater directly (Table 1). Past studies have shown that during snowmelt the first meltwaters draining from the snowpack are isotopically depleted in ^{18}O relative to the average snowpack composition (Rodhe 1981, Stichler et al. 1981, Shanley et al. 1995a, Taylor et al. 2001), and that subsequent meltwaters show a progressive isotopic enrichment. Using a physically based 1-D model where water-ice isotopic exchange is simulated, Taylor et al. (2001) were able to model the isotopic trend seen in snowmelt.

We have two objectives for this contribution. First, we show that the isotopic enrichment in ^{18}O seen in meltwater over the course of the melting period is a widely occurring phenomenon. We demonstrate this by presenting isotopic time series of meltwater from four locations having different climates. Second, we estimate the uncertainty of isotopic hydrograph separation if this temporal trend is ignored.

OBSERVED ISOTOPIC VARIATIONS IN SNOWMELT

Figure 1 presents the isotopic compositions of meltwater samples from four U.S. snowpacks: 1) a warm, maritime snowpack in California, 2) a temperate continental snowpack in Vermont, 3) a cold continental snowpack in Colorado, and 4) an Arctic snowpack in Alaska. Detailed descriptions of the field sites are given in Taylor et al. (1998 2001), Williams et al. (1996), and McNamara et al. (1997). We provide only brief information below and in Table 2.

The California site is located at the Central Sierra Snow Laboratory (CSSL) on the southwest crest of the Sierra Nevada near Soda Springs, California (Taylor et al. 2001). Meltwater samples were collected from a pipe draining a 6-m \times 3-m meltpan and the isotopic values are shown in Figure 1a. An average isotopic composition for the pack of -14.1‰ was obtained from data from a snow pit collected at peak accumulation. The $\delta^{18}\text{O}$ of the meltwater followed an increasing trend until the pack was completely melted. The overall $\delta^{18}\text{O}$ change in the meltwater was 4‰. The first 50% of the meltwater was isotopically lighter than the average of the snowpack and the remaining 50% heavier.

Table 1. Hydrograph separation studies where snowmelt is the new water component. Only values obtained using ^{18}O or D for the separation are listed in the % New column. The last column tabulates information on how samples were collected to determine a value for the new water component.

Reference	Location	Basin area (km ²)	Tracers	% New	New water
Dinçer et al. (1970)	Czechoslovakia	2.7	^{18}O , ^3H	1/3	snowpack
Martinec et al. (1977)	Switzerland	43.3	^{18}O , ^3H	<50	snow cores
Herrmann et al. (1978)	Germany	18.7	D	20 to 30 (total runoff)	meltpan
Rodhe (1981)	Sweden	6.6 and 4	^{18}O	10 and 30	snow cores
Bottomley et al. (1984)	Ontario, Canada	1.2, 1.8, and 10.5	^{18}O	10 to 60	snow cores
Obradovic and Sklash (1986)	Baffin Island, Canada	60	^8O , chemical	40 (total runoff)	ave. snow cores
Bottomley et al. (1986)	Ontario, Canada	10.5	^{18}O	40 to 50 (peak flow)	snow cores
Hooper and Shoemaker (1986)	NH, USA	0.42	D, chemical	<25	melt
Lawrence (1987)	NY, USA	13 sites	D	<26	snow
Rodhe (1987)	Sweden	0.03 to 7	^{18}O	<50	snow core
Ingraham and Taylor (1989)	CA, USA	1600	^{18}O , D	<50	snow
Moore (1989)	Quebec, Canada	0.053	^{18}O , D	15	meltpan
Maule and Stein (1990)	Quebec, Canada	0.62	^{18}O , Si	72	3 meltpans
Wels et al. (1990)	Canada	0.03 to 2	D, pH	40 to 51	meltpan
Cooper et al. (1991)	AK, USA	2.2	^{18}O	>86	snow cores
Buttle and Sami (1992)	Ontario, Canada	0.031	D	40	snow cores
Buttle et al. (1995)	Ontario, Canada	1.066	^{18}O	48 to 58 (total runoff)	meltpan
Mast et al. (1995)	CO, USA	4.50	^{18}O , Si	90 (peak flow)	average meltpan
Lepisto (1995)	Finland	1.65	^{18}O	53 (1992) and 63 (1998)	meltpan
McNamara et al. (1997)	AK, USA	145	^{18}O	93	melt

The Vermont site is at Sleepers River Research Watershed (SRRW) located in Danville, Vermont (Taylor et al. 1998). Meltwater was collected from a pipe draining a 3 m-diameter meltpan. The isotopic compositions of hourly meltwater samples are shown in Figure 1b. The data also show a general increasing trend, with daily variations superimposed on the trend during the early stages of melting. The total isotopic change in the meltwater was slightly over 5%.

The Colorado site is at Niwot Ridge, a mountain saddle located in the Colorado Front Range of the Rocky Mountains (Williams et al. 1996). Meltwater samples were collected from a pipe draining a 1-m² meltpan. The data (Fig. 1c) show an increase in the $\delta^{18}\text{O}$ of meltwater of 4.5%.

The Alaska site is located at Imnavait Creek, which drains 2.2 km² in a north–northwest trending glacial valley in the headwaters of the Kuparuk River in the northern Brooks Range, Alaska (McNamara et al. 1997). A snow core and a meltwater sample were collected each morning. To collect meltwater, a 2-cm × 10-cm × 30-cm plastic tray was inserted into the snowpack at the base of a snow pit. The meltwater sample represents the melt of the previous day and night. The $\delta^{18}\text{O}$ of the core and meltwater samples are shown in Figure 1d. The $\delta^{18}\text{O}$ of both the meltwater and the snowpack increased through the melt period. The $\delta^{18}\text{O}$ change of meltwater was about 3.5%.

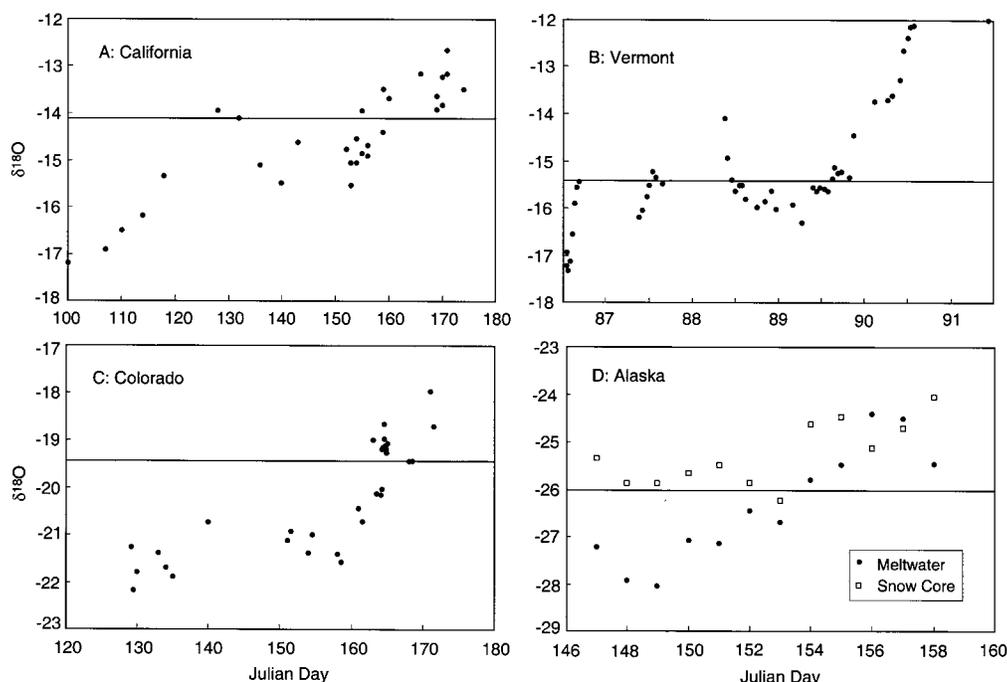


Figure 1. Isotopic composition of meltwater from A) Central Sierra Snow Laboratory, California, B) Sleeper River Research Watershed, Vermont, C) Niwot Ridge, Colorado, and D) Innvait Creek, Alaska. The average pack value is shown as a line.

Table 2. General information on the field sites discussed in this paper.				
Field site	CSSL	SRRW	Niwot	Innavait
Year of study	1997–98	1997–98	1995–96	2000–01
Maximum snow depth (m)	3.3	0.93	2.7	0.94
Maximum SWE (m)	1.37	0.36	1.14	0.16
Average winter temperature (°C)	-3*	-10**	-4***	-25
Duration of melt (days)	68	5	42	23
Minimum $\delta^{18}\text{O}$ of melt (‰)	-17.3	-17.3	-22.2	-28.0
Maximum $\delta^{18}\text{O}$ of melt (‰)	-13.2	-11.7	-18.0	-24.4
Average pack $\delta^{18}\text{O}$ (‰)	-14.1	-15.4	-20.2	-26.0
* Osterhuber (1999)				
** Shanley et al. (1995b)				
*** Williams et al. (1996)				

Despite the very different climate conditions, the meltwater from all four snowpacks had low $\delta^{18}\text{O}$ values at the beginning of the melt event followed by increasingly higher values throughout the event. The magnitudes of the increases in $\delta^{18}\text{O}$ for all sites were similar (3.5 to 5.6‰). Both field observations reported here and the theoretical calculations in Taylor et al. (2001) suggest that the increasing trend of $\delta^{18}\text{O}$ in meltwater from a snowpack occurs in most seasonal snowpacks, although the specific shape of the trend and local fluctuations (e.g., daily variations) may differ.

ACCURACY OF HYDROGRAPH SEPARATION

Usually, snowmelt is more depleted in ^{18}O than groundwater, the typical old water end member. If the average $\delta^{18}\text{O}$ of a pre-melt snowpack is used as the new water end member, the $\delta^{18}\text{O}$ of snowmelt or the actual new water is lower than this average value early in the melt season

and higher later in the season. From Equation 2, one can see that a hydrograph separation using the average snowpack value would overestimate the fraction of the new water component near the beginning of the melting event but underestimate it towards the end.

More quantitatively, the estimated error in x , due only to an error in $\delta^{18}\text{O}_{\text{New}}$, can be expressed as

$$\Delta x = \frac{\partial x}{\partial \delta^{18}\text{O}_{\text{New}}} \Delta \delta^{18}\text{O}_{\text{New}} = -\frac{x}{\delta^{18}\text{O}_{\text{New}} - \delta^{18}\text{O}_{\text{Old}}} \Delta \delta^{18}\text{O}_{\text{New}} \quad (3)$$

where Δx is the estimated error of x and $\Delta \delta^{18}\text{O}_{\text{New}}$ is the error in $\delta^{18}\text{O}_{\text{New}}$, which is the difference between the average pack and the meltwater samples. Therefore, the error of x is proportional to the value of x itself and to the error in $\delta^{18}\text{O}_{\text{New}}$, and inversely proportional to the isotopic difference between new and old water. Figure 2 graphically illustrates the error of x (contour lines) as a function of these three variables. Negative values indicate overestimates (the correction is a negative value) and positive ones underestimates. For example, suppose that early in the melt season the meltwater is 3‰ more depleted than the average of the pack ($\delta^{18}\text{O}_{\text{Melt}} - \delta^{18}\text{O}_{\text{Ave}} = -3$), and that the average pack is 6‰ more depleted than the groundwater (Fig. 2b). If the stream flow is 50% new water, x would be overestimated by 0.25 (or 25%).

The above calculation estimates the systematic error introduced when ignoring the temporal variation in the $\delta^{18}\text{O}$ values of snowmelt. It is important to note that on top of the overall trend of $\delta^{18}\text{O}$ enrichment in meltwater shown in Figure 1, there are significant local (e.g., daily) variations. These variations may be caused by a number of factors, including rainfall input, changing melt rates, and different flow mechanisms (e.g., finger flow versus homogenous flow). These variations contribute to the random uncertainties (e.g., Genereux 1998) of the new water end member and add to the systematic errors shown in Figure 2.

DISCUSSION

Equation 3 and Figure 2 indicate that the error in the estimate of the new water fraction (x) is dependent upon the value of x , and that the error increases proportionally with x . Fortunately, in most investigations, the new water fraction is relatively low. Table 1 shows that, out of 20 hydrograph separations, 14 of them predicted a new water fraction lower than 0.5 and only four predicted new water fraction greater than 0.7. However, if meltwater dominates the hydrograph, large errors in the predicted new water fraction may result if the temporal isotopic change in the meltwater were ignored. For example, in areas of continuous permafrost, little infiltration occurs and meltwater may directly control the isotopic composition of the stream water (McNamara et al. 1997, Cooper et al. 1991, Cooper et al. 1993). If the progressive isotopic enrichment of the meltwater is not considered, hydrograph separation may significantly underestimate the new water component by mistaking the increasingly ^{18}O -rich stream water as a mixture of new water with heavier old water (Cooper et al. 1993).

The error calculated in Figure 2 is the maximum possible error at a given instant of time during a melting event. If one is interested in the total new water contribution for the entire event, the error is much smaller. There are two reasons for the smaller error. First, during the middle part of the melt season, the isotopic composition of melt is not considerably different from the $\delta^{18}\text{O}$ value of average snowpack (e.g., Fig. 1). Second, the largest isotopic difference between $\delta^{18}\text{O}_{\text{Ave}}$ and $\delta^{18}\text{O}_{\text{Melt}}$ occurs at the beginning and end of the melting event. During these times, the errors run in opposite directions and may largely cancel out.

In this error analysis, we do not consider new water storage in the catchment. In temperate areas, melting process may last weeks (e.g., the Vermont site) to months (e.g., the California site). Meltwater released from the bottom of the snowpack on one day may not reach the stream on the same day or even in the same week. As a result, the new water component reaching a stream may be a mixture of meltwaters released from the pack at different times. A comprehensive

mathematical treatment should consider the travel time distribution of new water in the catchment (Kirchner et al. 2000, 2001) but is beyond the scope of this paper.

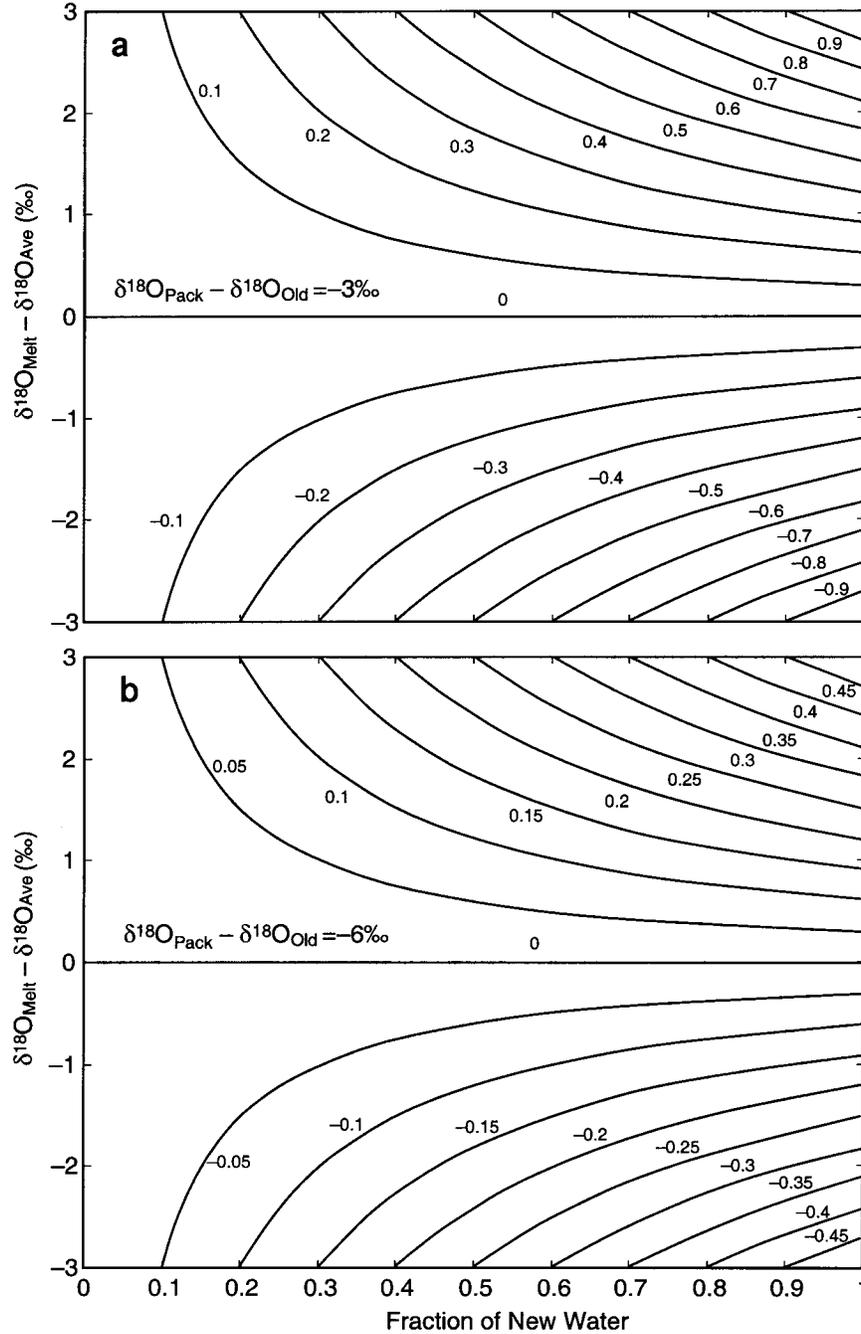


Figure 2. A plot of the error in the predicted new water fraction as a function of the isotopic difference between the meltwater value and the average snowpack value and the fraction of new water. These analyses were done for two different conditions: a) for a 3‰ difference between the old water isotopic composition and the average value of the snowpack and b) for a 6‰ difference.

CONCLUSIONS

We presented isotopic compositions of meltwater from four field sites having significantly different winter regimes. All the data sets show that the initial meltwater is depleted in ^{18}O but that the melt becomes progressively enriched in ^{18}O as the pack melts. The isotopic change during a melting event is typically 3 to 5‰.

Systematic errors in hydrograph separation may be introduced if the temporal isotopic variation of meltwater is ignored and the average $\delta^{18}\text{O}$ of the snowpack is used as the new water composition. Because of this error, the new water fraction contributing to the stream flow is overestimated in early stages of melting and underestimated in later stages. The magnitude of the error is proportional to the new water fraction and the isotopic difference between the average snowpack and the meltwater, and inversely proportional to the isotopic difference between the old water and the average snowpack value.

The error is particularly large when new water dominates the stream flow, a situation that may occur in areas of low infiltration, such as permafrost and urban areas. In addition to this systematic error, other systematic or random errors may also be significant if the uncertainties in the new water $\delta^{18}\text{O}$ values are greater than the analytical precision. This situation may occur as a result of a number of processes or factors such as rain events, isotopic change in meltwater due to varying melt rates, mixing of meltwater released at different times, and spatial isotopic heterogeneity in snowmelt. How to incorporate changes in the isotopic composition of meltwater measured at one point into distributed snowmelt models may be particularly challenging.

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