How isotopic fractionation of snowmelt affects hydrograph separation

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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 $\delta^{18}O$ 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. Published in 2002 by John Wiley & Sons, Ltd.

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 km^2 Czechoslovakian watershed, and determined that 63% of the river flow during spring melt was contributed by old water. The technique has been used extensively 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. $\delta^{18}O$) 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 $\delta^{18}O$ of the pre-event base flow is used as the composition of the old water ($\delta^{18}O_{Old}$) and the $\delta^{18}O$ of the bulk precipitation (or snowmelt) is used as the composition of new water

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($\delta^{18}O_{New}$). Then the stream water $\delta^{18}O$ ($\delta^{18}O_{Str}$) can be expressed as

$$\delta^{18}O_{Str} = x\delta^{18}O_{New} + (1 - x)\delta^{18}O_{Old} \qquad (1)$$

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

$$x = \frac{\delta^{18}O_{Str} - \delta^{18}O_{Old}}{\delta^{18}O_{New} - \delta^{18}O_{Old}} \qquad (2)$$

For Equations (1) and (2) to be valid along an event hydrograph, it is necessary that both $\delta^{18}O_{Old}$ and $\delta^{18}O_{New}$ are temporally invariant, and so a change in $\delta^{18}O_{Str}$ 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 I 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 I). 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 one-dimensional 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 US 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 only provide brief information below and in Table II.

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 $-14 \cdot 1‰$ was obtained from data from a snow pit collected at peak accumulation. The $\delta^{18}O$ of the meltwater follows an increasing trend until the pack has completely melted. The overall $\delta^{18}O$ 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% was heavier.

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 m^2 meltpan. The data (Figure 1C) show an increase in the $\delta^{18}O$ of meltwater of 4·5‰.

The Alaska site is located at Imnavait Creek, which drains 2·2 km^2 in a north–northwest-trending glacial valley in the headwaters of the Kuparuk River in the northern Brooks Range, Alaska (McNamara

Table I. 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, ^{3}H	1/3	Snowpack
Martinec et al. (1977)	Switzerland	43·3	^{18}O, ^{3}H	<50	Snow cores
Herrmann et al. (1978)	Germany	18·7	D	20 to 30 (total runoff)	Meltpan
Rodhe (1981)	Sweden	6·6, 4	^{18}O	10 and 30	Snow cores
Bottomley et al. (1984)	Ontario, Canada	1·2, 1·8, 10·5	^{18}O	10 to 60	Snow cores
Obradovic and Sklash (1986)	Baffin Isl., Canada	60	^{18}O, chemical	40 (total runoff)	Average 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

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 δ^{18}O of the core and meltwater samples are shown in Figure 1D. The δ^{18}O of both the meltwater and the snowpack increased through the melt period. The δ^{18}O change of meltwater was about 3·5‰.

Despite the very different climate conditions, the meltwater from all four snowpacks had low δ^{18}O values at the beginning of the melt event followed by increasingly higher values throughout the event. The magnitudes of the increases in δ^{18}O for all sites were similar (3·5 to 5·6‰). Both the field observations reported here and the theoretical calculations in Taylor et al. (2001) suggest that the increasing trend of δ^{18}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.
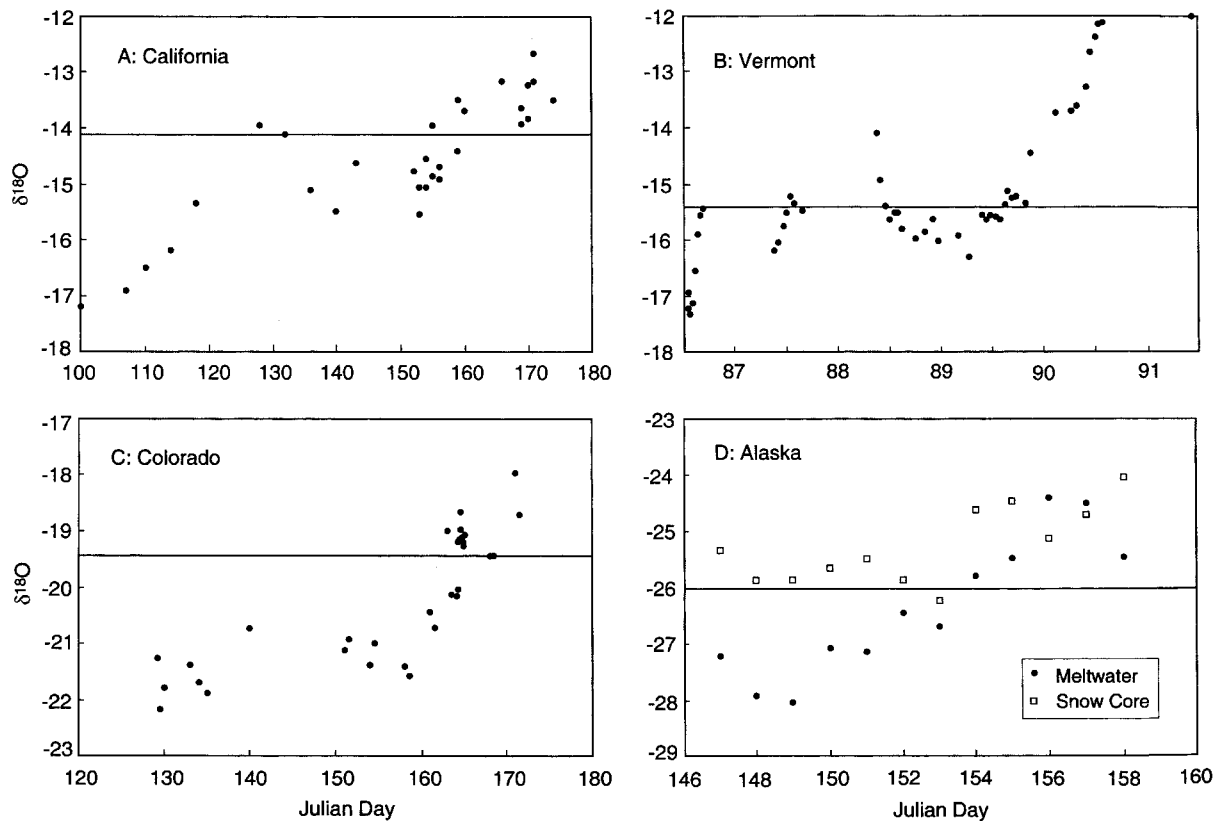
Figure 1. Isotopic composition of meltwater from (A) Central Sierra Snow Laboratory, California, (B) Sleeper River Research Watershed, Vermont, (C) Niwot Ridge, Colorado and (D) Imnavait Creek, Alaska. The average pack value is shown as a line

Table II. General information on the field sites discussed in this paper

Field site	CSSL	SRRW	Niwot	Imnavait
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^a	-10^b	-4^c	-25
Duration of melt (days)	68	5	42	23
Minimum $\delta^{18}O$ of melt (‰)	$-17\cdot3$	$-17\cdot3$	$-22\cdot2$	$-28\cdot0$
Maximum $\delta^{18}O$ of melt (‰)	$-13\cdot2$	$-11\cdot7$	$-18\cdot0$	$-24\cdot4$
Average pack $\delta^{18}O$ (‰)	$-14\cdot1$	$-15\cdot4$	$-20\cdot2$	$-26\cdot0$

[a] Osterhuber (1999).
[b] Shanley *et al.* (1995b).
[c] Williams *et al.* (1996).

ACCURACY OF HYDROGRAPH SEPARATION

Usually, snowmelt is more depleted in ^{18}O than groundwater, the typical old-water end member. If the average $\delta^{18}O$ of a pre-melt snowpack is used as the new-water end member, the $\delta^{18}O$ 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 $\delta^{18}O_{New}$, can be expressed as

$$\Delta x = \frac{\partial x}{\partial \delta^{18}O_{New}} \Delta \delta^{18}O_{New} = -\frac{x}{\delta^{18}O_{New} - \delta^{18}O_{Old}} \Delta \delta^{18}O_{New} \tag{3}$$

where Δx is the estimated error of x and $\Delta \delta^{18}O_{New}$ is the error in $\delta^{18}O_{New}$, 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 $\delta^{18}O_{New}$, 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 are underestimates. For example, suppose that early in the melt season the meltwater is 3‰ more depleted than the average of the pack ($\delta^{18}O_{Melt} - \delta^{18}O_{Ave} = -3$), and that the average pack is 6‰ more depleted than the groundwater (Figure 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 $\delta^{18}O$ values of snowmelt. It is important to note that, on top of the overall trend of $\delta^{18}O$ 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 homogeneous 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 I 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 then large errors in the predicted new water fraction may result if the temporal isotopic change in the meltwater is ignored. For example, in areas of continuous permafrost, little infiltration occurs and meltwater may directly control the isotopic composition of the stream water (Cooper et al., 1991, 1993; McNamara et al., 1997). 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 $\delta^{18}O$ value of average snowpack (e.g. Figure 1). Second, the largest isotopic difference between $\delta^{18}O_{Ave}$ and $\delta^{18}O_{Melt}$ 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, the 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.
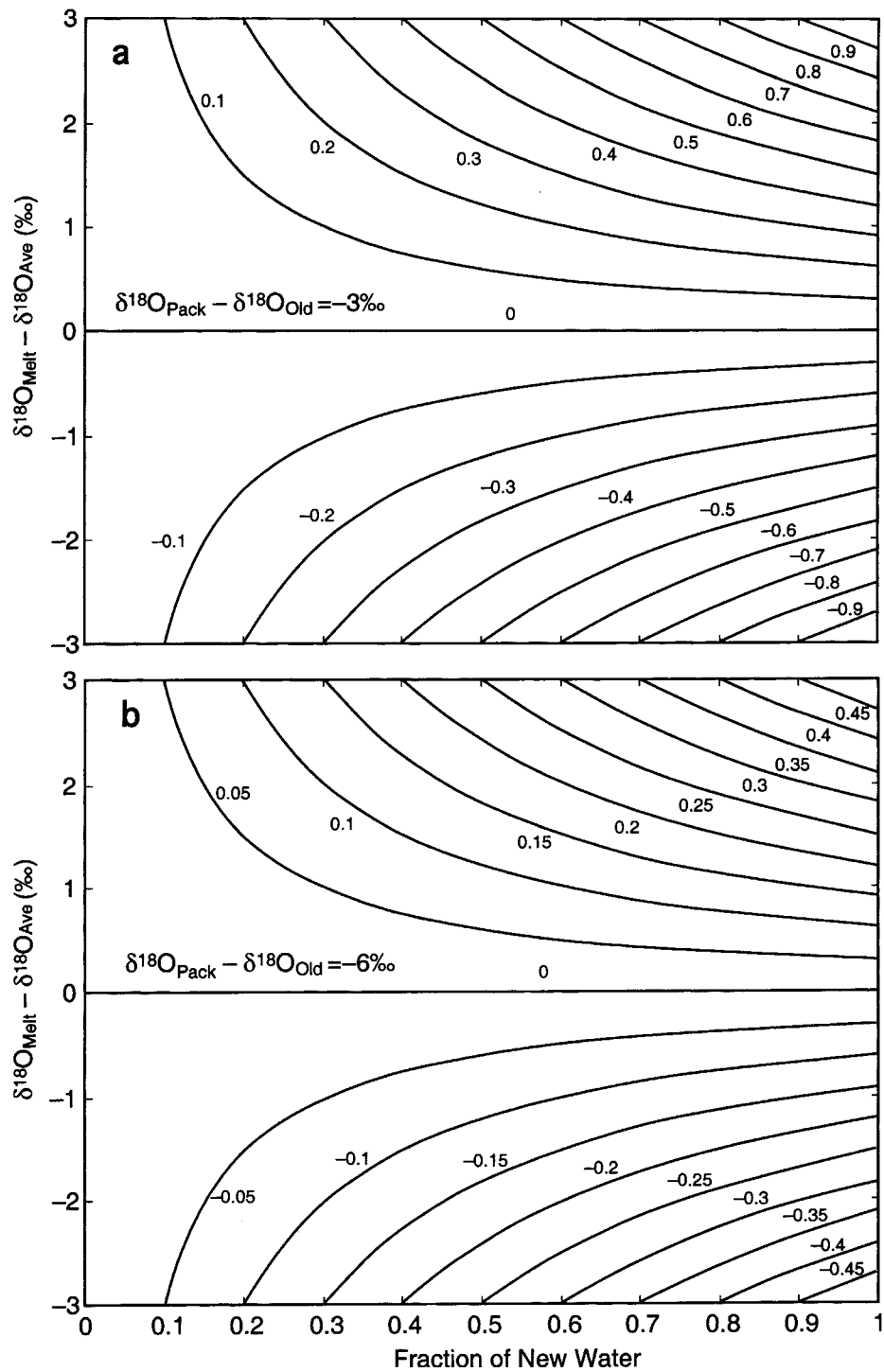
Figure 2. A plot of the error in the predicted new water fraction as a function of the isotopic difference between the meltwater value and the average snowpack value and the fraction of new water. These analyses were done for two different conditions: (a) for a 3‰ difference between the old water isotopic composition and the average value of the snowpack and (b) for a 6‰ difference

CONCLUSIONS

We have 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 δ^{18}O of the snowpack is used as the new water composition. Owing to 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 it is 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 δ^{18}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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