Oxygen 18 fractionation during snowmelt: Implications for spring flood hydrograph separation

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[1] Isotopic hydrograph separation (IHS) to define sources of event and pre-event water during hydrological episodes has greatly improved the understanding of water, solute, and contaminant transport to streams during recent decades. However, the large variation in snowmelt isotopic composition, caused by fractionation during melting, has impeded an accurate separation of streamflow during spring flood episodes. Here we present a method that greatly improves the separation of event and pre-event water during snowmelt by accounting for both the temporal change in the snowmelt isotopic signal and the temporary storage of meltwater in the catchment. Comparison of results of this technique with previous results, using isotopic data from the 1997 spring flood on a small catchment in northern Sweden, suggests that earlier techniques significantly underestimate the pre-event contribution. This paper also explores the importance of lateral mixing across the catchment of temporally varying event inputs for the IHS results.

INDEX TERMS: 1863 Hydrology: Snow and ice (1827); 1871 Hydrology: Surface water quality; 1806 Hydrology: Chemistry of fresh water; 1860 Hydrology: Runoff and streamflow; KEYWORDS: hydrograph separation, isotopic hydrograph separation (IHS), oxygen 18, isotopic fraction, snowmelt, spring flood


1. Introduction

[2] Understanding the hydrological and geochemical response of forested watersheds to precipitation and snowmelt is important for questions related to water resource management, transport of contaminants, and biogeochemical cycling. Of special concern for high latitude and high altitude catchments with seasonal snow covers is the timing and contribution of meltwater during the spring, when a large portion of the annual runoff is discharged. One of the most important methodologies for understanding the sources of water during hydrological episodes is two-component isotopic hydrograph separation (IHS) that enables a separation of runoff water into event and pre-event water sources. Two-component hydrograph separations are based on the mass balance of water, and a tracer mass balance equation (equation (1)):

\[ Q_c C_s = Q_p C_p + Q_e C_e \]  

where \( Q \) is discharge and \( C \) is the concentration of a tracer, usually deuterium (\( \delta D \)) or oxygen-18 (\( \delta^{18}O \)) in per mil (\( \% \)) variation with respect to a standard. The subscripts \( s \), \( p \), and \( e \) refer to stream water (sampled runoff water), event water (melt or rainwater) and pre-event water (water in the catchment prior to the event), respectively. In this study the tracer is the natural stable isotope \( \delta^{18}O \).

[3] Most previous IHS work has focused on rain driven episodes, while less emphasis has been put on the special challenges of snowmelt, during which large, relatively systematic variation in the event water input signal is caused by isotopic fractionation of snowmelt \cite{Taylor2001, Unnikrishna2002}. The variation of the input signal complicates the separation of streamflow into event and pre-event components \cite{Rodhe1998}. Depth integrated snow cores have been used to define the event component \cite{Rodhe1981, Bottomley1986, Ingraham1989}. However, because this method does not account for the \( \delta^{18}O \) enrichment that occurs during melting, later studies using the snow core approach have attempted to incorporate an enrichment correction \cite{Rodhe1987, Sueker2000}. However, most recent studies using IHS during snowmelt use snow lysimeters \cite{Hooper1986, Stichler1986, Moore1989, Maulé2000, Wels1991, Mast1995, Shanley2002}, which not only account for the timing of \( \delta^{18}O \) enriched water but also include possible rain contributions during the spring flood.

[4] Although the use of snow lysimeters has greatly improved IHS during spring flood episodes, there remain methodological uncertainties associated with the variation in \( \delta^{18}O \) of snowmelt water. These include the problem of how to integrate snowmelt inputs over time, and how to account for lateral variation of the event reservoir across the catchment.

[5] In the use of snow lysimeters to follow variations in event water \( \delta^{18}O \), two approaches have previously been
used. The first is to use a volume weighted average value (VWA) from the snowmelt [Mast et al., 1995] that corresponds to Equation (2) when N samples are collected to yield one constant isotopic input value. The second approach is to use the current meltwater $\delta^{18}O$ (CMW) from the snow lysimeter at each time step of sampling during the episode [Hooper and Shoemaker, 1986; Maulè and Stein, 1990; Wels et al., 1991; Shanley et al., 2002] (equation (3)).

$$\delta^{18}O_{c}(t) = \frac{\sum_{i=1}^{N} M(i) \delta^{18}O_{m}(i)}{\sum_{i=1}^{N} M(i)}$$ (2)

$$\delta^{18}O_{i}(t) = \delta^{18}O_{m}(t)$$ (3)

where $\delta^{18}O_{c}$ and $\delta^{18}O_{m}$ express the event and meltwater isotopic compositions, respectively. $M(i)$ is the incrementally collected meltwater depth and (t) denotes each time step of hydrograph separation.

[6] The VWA approach is analogous to most IHS work during rain-driven events, when rainfall is pooled to yield a single isotopic value. The VWA does not address the within storm/snowmelt variability of the input signal. One contradiction that arises is that during analysis of the early phase of the event the VWA includes snow which has not yet melted. However, even the CMW approach to define the variable input signal (equation (3)) to the IHS has the limitation that it assumes that a given meltwater increment is only resident in the soil until the next sampling occasion. This is an oversimplification for several reasons. Although the time lag between melting and the appearance of that meltwater in the stream might be appropriately short for an overland flow component, the lag time for event water entering the soil is likely much longer. Secondly, even if there is a balance between the total amount of snowmelt and the total runoff during the episode, the literature commonly reports that between 30% and 60% of pre-event water is discharged during spring flood [Rodhe, 1998]. This means that a large fraction of the meltwater is still stored in the catchment after the episode has concluded. Although there has been some awareness about potential problems associated with the methods previously used to account for the variation in $\delta^{18}O$ during snowmelt, efforts to assess the uncertainty introduced by these methods have been limited.

[7] This paper presents a new method that accounts for the temporal change in the snowmelt isotopic signal by explicitly incorporating both the timing of the $\delta^{18}O$ signal in meltwater and the temporary storage of meltwater in the catchment. Results using this technique are compared with the previously published methods using isotopic data from the 1997 spring flood on a small catchment in northern Sweden. The importance of lateral mixing for these temporally-varying event inputs is also explored.

2. Runoff-Corrected Event Water Approach

[8] The runoff-corrected event water approach (runCE) presented here accounts for the timing and amount of meltwater entering both soil and surface water reservoirs, as well as the runoff of previously melted and subsequently stored water at every time step during the episode. At each time step a volume weighted, runoff-corrected $\delta^{18}O$ value is calculated for the event water component. The isotopic composition of this event water is based on a comparison between cumulative snowmelt (and rainwater contributions) from snow lysimeters and the cumulative volume (depth) of meltwater that has left the snowpack but has not yet discharged to the stream during the event. This way the lag between the melting of snow and its arrival at the stream is taken into account. It is assumed that all the event water that is in storage in the catchment at any given time is well mixed, although alternative mixing assumptions for the event water are investigated later in the paper.

[9] The event water $\delta^{18}O$ in the runCE is calculated as (equation (4));

$$\delta^{18}O_{e}(t) = \frac{\sum_{i=1}^{t} M(i) \delta^{18}O_{m}(i) - \sum_{i=1}^{t} E(i) \delta^{18}O_{e}(i)}{\sum_{i=1}^{t} M(i) - \sum_{i=1}^{t} E(i)}$$ (4)

where $M(i)$ is the incrementally collected meltwater depth, and $E(i)$ is the incrementally calculated event water discharged (equation (1)). $\delta^{18}O_{d}(t)$ and $\delta^{18}O_{m}(i)$ are the event and meltwater isotopic compositions, respectively.

[10] Because both $\delta^{18}O_{d}(t)$ and $E(i)$ are dependent on the calculated runCE $\delta^{18}O_{e}(t)$, equation (4) must be solved iteratively for each time step. This can be solved by starting out with $\delta^{18}O_{e}(t)$ at time step (t) set equal to runCE $\delta^{18}O_{e}(t-1)$ to calculate a first approximation of $E(i)$ at time step (t) (equation (1)). This is then used to make a first approximation of runCE $\delta^{18}O_{e}(t)$. The optimized solution of equation (4) is attained by minimizing the difference in the sum of squared errors between the runCE $\delta^{18}O_{e}(t)$ and $\delta^{18}O_{e}(i)$ at every time step.

[11] Because equation (4) involves both the incrementally collected meltwater depths and the incrementally calculated event water, specific discharge from the catchment as well as snowmelt intensity is needed in the calculation. The time step used in the current study is one hour, corresponding to the frequency of the discharge measurements.

[12] Event water is defined as any melt (or rain) water leaving the snowpack (as collected in the snow lysimeters) during spring flood. Pre-event water is defined as any liquid water present in the catchment soils/bedrock prior to the onset of snowmelt.

3. Study Site

[13] Västрабäcken is a forested 12.1 ha, headwater catchment, typical of the boreal region in northern Sweden. The catchment is part of the Svarthäger Research Station in the county of Västerbotten (64°14′N, 10°46′E) approximately 50 km inland from the Baltic Sea coast. The elevation of the 800 m stream ranges from 235 to 310 m above sea level. The channel was straightened and deepened in the 1920s, following the common practice in northern Sweden to improve drainage and thereby forest productivity. The drainage area is mainly covered by Norway spruce (Picea abies) in the lower reaches (90% of the catchment) and pine (Pinus sylvestris) in the upper, drier areas. A locally derived glacial till with an average thickness of
10–15 m overlies gneissic bedrock. Soils are predominately well developed iron podzols, with peat deposits of more than 0.5 m in the riparian zone closest to the stream channel.

4. Methods

[14] Hourly discharge measurements were made at a thin plate, 90° V notch weir at the outlet of the catchment using a pressure transducer connected to a Campbell Scientific data logger. The weir was calibrated using the bucket method. The stream sampling program was based on weekly samples of base flow prior to the onset of the snowmelt, and then daily sampling during the spring flood until the flow receded to levels close to those of base flow.

[15] Three 1.5 m², acid washed, Teflon-coated snow lysimeters were used for measuring melting intensity and isotopic composition. Melting rate and isotopic composition were averaged for each time step. The snowmelt water was sampled daily to twice daily. Data were linearly interpolated to an hourly basis.

[16] Stream water and meltwater were analyzed for δ¹⁸O at the department of Physics and Astronomy, University of Calgary using a VG 903 with CO₂ equilibration manifold. All δ¹⁸O values are expressed relative to Vienna-standard mean ocean water (VSMOW). Water samples for isotopic analyses were collected in 25 mL, narrow mouth glass bottles. The samples were stored cold and dark until analyzed. The standard error of the δ¹⁸O analysis was 0.1‰. However, in order to include any uncertainty associated with sampling, storage and shipping a standard error of 0.2‰ was used in the uncertainty analyses.

[17] The uncertainty of the IHS was calculated using the method proposed by [Genereux, 1998]

\[
W_p(t) = \frac{1}{\left( \frac{W_{18O}(t) - W_{18O}(0)}{W_{18O}(0)} + \frac{W_{18O}(0) - W_{18O}(t)}{W_{18O}(0)} \right)^{1/2}}
\]

(5)

where \( W_p(t) \) is the uncertainty in the calculation of the preevent fraction at the time \( t \) and \( W_{18O} \) is the analytical uncertainty of δ⁸O. In the runCE approach another source of error propagation results from the event water in the runCE approach being based on a proportion of the “previously melted snow” in the catchment \( (Q_e \) previously stored/\( Q_e \)) and the “most recent meltwater” \( (Q_e \) recent melt/\( Q_e \)) in the stream at the time \( t \). The uncertainty for runCE is hence not only an analytical uncertainty (as it will be for CWA and VWA) but is an uncertainty that is propagated from the very beginning of the episode. Assuming that the measurement errors in the specific discharge and rate of melting are negligible, an approximation of the propagation of errors can be made as;

\[
W_{runCE}(t) = \sqrt{\left( \frac{Q_e \text{ previously stored}(t)}{Q_e(t)} \right)^2 \cdot W_p(t + 1) - 1)^2 + \left( \frac{Q_e \text{ recent melt}(t)}{Q_e(t)} \right)^2 \cdot W_p(t)^2}
\]

(6)

where \( W_p(t) \) is derived using the runCE approach in equation (5). The \( W_{runCE}(t-1) \) is from the equation (6) solution at the previous time step \( (t-1) \). At \( t = 1 \) the \( W_{runCE}(t-1) \) is equal to \( W_p \).

5. Results

[18] The spring snowmelt period started at the end of April 1997, following a more than five month period of permanent snow cover. The runoff peaked between May 8 and 17 with an average runoff during this period of 8 mm day⁻¹ (Figure 1). The total runoff during the spring flood (25 days) was 110 mm, of which 65% was discharged during the aforementioned peak flow period. The spring flood constituted approximately 50% of the annual runoff in the study catchment during 1997. The total preevent water in the catchment prior to snowmelt was estimated from the difference in base flow δ¹⁸O before and after the event, as suggested by [Bishop, 1991]. Using the runCE approach to estimate the event water inputs and outputs, the preevent reservoir was calculated to be approximately 290 mm. With a mean water content of 33% in the upper meter of the soil during spring flood at this site [Nyberg et al., 2001], that corresponds to a preevent water reservoir depth of ca 90 cm.

[19] The snowmelt intensity averaged 8 mm day⁻¹ during the peak flow phase, but the most intensive melt of 15 mm day⁻¹ occurred on May 6 and then declined slowly until May 26 when all snow in the catchment had melted. No rain occurred during the snowmelt period. The total melt during the spring was 204 mm. Assuming no evapotranspiration, this generated a net recharge of 94 mm to the catchment.

[20] The δ¹⁸O of the runoff was −13.45‰ (with a standard deviation (SD) of 0.08‰, \( n = 5 \)) during base flow, and declined to −15.04‰ at peak flow (Figure 2). The average δ¹⁸O for the peak flow phase was −14.72‰ (SD 0.21‰, \( n = 9 \)). The δ¹⁸O of the meltwater leaving the snow lysimeter varied from −18.81‰ at the onset of snowmelt to −14.39‰ at the end of the snowmelt period. The volume weighted average snowmelt water δ¹⁸O was −16.08‰. The variation in the runCE event water δ¹⁸O varied from −18.81‰ at the onset of melting to −15.97‰ at end of snowmelt. The daily variation between sampling occasions was considerably less in the calculated runCE event water δ¹⁸O than in the snowmelt water samples (Figure 2).

[21] The uncertainty of the IHS calculation varied between the three methods. The largest uncertainty in the calculation of the preevent fraction during the spring flood was encountered using CMW with 14% on average during the episode. For VWA the uncertainty in preevent water fraction was 11% and for runCE it averaged 8% over the entire spring flood, including the propagation of errors (equation (6)). The smaller average uncertainty in the use of runCE compared to the other methods is due to the IHS being very sensitive to small differences between δ¹⁸Oe and δ¹⁸Oc. Together with the propagation errors this generates an uncertainty for the runCE method that increases from 5% to 11% as the spring flood progressed.

[22] The preevent water fractions indicated by the three methods for calculating δ¹⁸Oe were significantly different (Figure 1 and Table 1). Using the CMW δ¹⁸Oe input to the IHS gave a preevent contribution of 58% averaged over the entire episode and 38% during peak flow. The VWA δ¹⁸Oe value gave a preevent component of 66% averaged over the
entire event and 53% at peak flow. The runCE $\delta^{18}O_e$ estimated an average preevent contribution during spring flood of 74%, and a peak flow contribution of 63%.

[23] A comparison of the actual snowmelt intensity and the runoff of event water shows that most of the snowmelt is not leaving the catchment on the day it melts (Figure 3), nor is most of the meltwater leaving during the entire course of the spring flood (Figure 4). Only occasionally did the runoff of event water exceed the melting rate (i.e. the fraction of event water/meltwater was above 1.0). The three methods estimated that only between 17% and 28% of the water that melted from the snowpack left the catchment during spring flood.

6. Discussion

[24] The choice of technique used for defining the event water component during snowmelt has important consequences for the result of the separation of event and preevent water during snowmelt episodes. While the analytical uncertainty of the preevent calculation was estimated to be approximately 8%, the choice of method for defining the event water component generated a 16% variation in the estimated preevent component for the entire spring flood, and a 25% variation during the peak flow phase (Table 1). The large underestimation of the preevent component using the CMW and VWA procedures would lead to bias in any interpretation of the transport of soluble contaminants, such as acid deposition, heavy metals or organic compounds during the spring flood.

[25] Although IHS has been applied to snowmelt episodes for almost three decades [Dincer et al., 1970], most previous applications have focused on rain driven episodes. Although based on rainfall events, the work of McDonnell et al. [1990], is relevant for comparative purposes. In this study the within-storm variability of the event water input to the Glendhu catchment in New Zealand was addressed by suggesting three different weighting techniques: (1) volume weighted average isotopic composition of the rain (similar to equation (2)), (2) incremental mean (this way rain that has not yet fallen does not contribute to the event isotopic composition), and (3) incremental intensity (similar to incremental mean but weighting rain according to the intensity of the rainfall).

[26] The incremental intensity approach suggested by McDonnell et al. [1990] is not likely to be appropriate for

Figure 1. Separation of event and preevent water during the spring flood 1997 using the three methods discussed. The “spring flood” and “peak flow” definitions of Figure 1 are used in the text.
snowmelt episodes because the intensity of event water input is typically less than what is experienced during a rain episode. The rate of snowmelt averaged 7 mm day\(^{-1}\) and never exceeded 15 mm day\(^{-1}\) in the study episode. Furthermore, overland flow does not occur during the spring flood in our study catchment despite significant soil frost during the winter [Nyberg et al., 2001; Stähli et al., 2001]. Comparing the incremental mean approach suggested for rain episodes by McDonnell et al. [1990] with the runCE method does not produce significantly different pre-event results. However, the incremental mean approach will underestimate the role of pre-event water during the rising limb of the hydrograph and overestimate it during the recession limb. That is because the incremental mean approach assumes that the isotopic value of the event water is a mixture of all meltwater that left the snowpack preceding the stream sampling, and does not take discharged event water into account. While this assumption is not seriously violated in the spring flood episode reported here, the incremental mean approach could significantly overestimate the pre-event contribution during episodes when larger fractions of the snowmelt are discharged during the spring flood.

This paper (as most other IHS studies) has considered the mixing of meltwater in the time dimension. Mixing of the inputs spatially over the catchment also needs to be considered when the meltwater inputs vary over time in their \(\delta^{18}O\) signal. In the runCE approach suggested here, it is assumed that the event water is a well-mixed reservoir (Figure 5a). This is of course a simplification, as the stream is draining the soils through the middle of the catchment. Therefore, event water at the periphery of the catchment will have a longer travel time to the stream compared with event water in the riparian soil adjacent to the stream. To test the

Table 1. Comparing the Three Methods for Hydrograph Separation and Sensitivity Analyses\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>runCE</th>
<th>VWA</th>
<th>CMW</th>
<th>Fraction of Catchment Contributing Water</th>
<th>Time Delay Between Reservoirs</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>50%</td>
<td>33%</td>
</tr>
<tr>
<td>Spring flood</td>
<td>74%</td>
<td>66%(^b)</td>
<td>58%(^b)</td>
<td>73%</td>
<td>72%</td>
</tr>
<tr>
<td>Peak flow</td>
<td>63%</td>
<td>53%(^b)</td>
<td>38%(^b)</td>
<td>62%</td>
<td>61%</td>
</tr>
</tbody>
</table>

\(^a\)Significance test (two-tailed t test) to test if the different methods and the sensitivity analyses give significantly different results.

\(^b\)Significantly different results (95% confidential interval) from the runCE approach.

Figure 2. The \(\delta^{18}O\) of stream water, snowmelt (CMW), VWA, and runCE event water.
Figure 3. Fraction of the meltwater leaving the catchment at each time step.

Figure 4. Cumulative amount of meltwater that has left the catchment at each time step.
importance of this model simplification, two alternative hypotheses about the lateral mixing of event water have been considered.

[28] The first test is to analyze the sensitivity in the model results if only a fraction of catchment is contributing event water during the course of the spring flood. Here only the riparian zone contribution of water has been used, assuming that 50%, 33%, or 25% of the catchment nearest the stream is an active event water reservoir during the spring flood (Figure 5b). This implies that the rest of the catchment does not contribute any event water, and that the event water from the riparian source area is well mixed. If, for example, 25%
of the catchment is active, only a 20 m wide riparian strip along the 800 m long stream contributes event water during the spring flood, and snowmelt from the remaining 75% of the catchment only contributes to recharging the soil. Note that it is not possible for less than 25% of the catchment to contribute water in this example, because this would not produce enough snowmelt to generate the measured runoff.

Reducing the active portion of the catchment reduces the pre-event contribution but does not create statistically different results (Table 1). This is due to a larger proportion of the snowmelt water that has left the snowpack also being discharged during the spring flood. The largest effect of a reduction in the active portion of the catchment occurs during the later part of the spring flood, probably because of exhaustion of event water (Figure 6).

The second test is to use a three reservoir approach with riparian, midslope and upslope event water reservoirs of equal size. As can be seen from the schematic figure (Figure 5c), event water is transferred from the upslope reservoir into the midslope and finally into the riparian reservoir. Lateral flow between each soil reservoir has been assigned a delay that varies from 5 to 15 days. A delay of 10 days infers that meltwater from the upslope reservoir needs 20 days to reach the riparian reservoir (which equals an average lateral flow velocity of 2.5 m day$^{-1}$).

The largest and only significant difference when applying the three reservoir method occurs when inferring a 10 day delay between adjacent reservoirs (Figure 7 and Table 1). The pre-event fraction in runoff increases in this scenario by 5% on average during the entire spring flood, and by 11% during peak runoff. Either shortening or increasing the delay between the reservoirs decreased the difference relative to the runCE technique with one catchment reservoir of event water. The reason the difference decreases when the lateral delay is greater than 10 days is that the time delay becomes too long for the water in the upslope reservoir to reach the stream before the recession limb of the spring flood.

The recent study by Kirchner et al. [2000] of the travel time distribution of water through catchments found that travel times followed a power law distribution. This implies that the responsiveness to event water inputs is initially very rapid, but with a more gradual decline generating a long-term memory of previous contributions. This suggests that the $\delta^{18}$O of the event water will primarily be a function of the riparian soil water contribution, but also of a long-term average of past snowmelt and rain inputs from upslope reservoirs. Because Kirchner et al.’s [2000] study suggests that streamflow generation is composed of a more instantaneous contribution from riparian soils in combination with a delayed upslope source, the two sensitivity tests above (using only riparian contributions, or invoking lateral delays from upslope areas) provide outer boundaries for the uncertainties of the runCE approach suggested here. Furthermore, the fact that the two sensitivity tests go in opposite

Figure 6. Results from the sensitivity analyses that only a fraction of the catchment contributes water during the spring flood.
directions (a smaller pre-event fraction in the riparian contribution scenario and a larger pre-event fraction in the lateral delay scenario) further supports the notion that the runCE approach is not highly biased by the assumption that the event reservoir is well-mixed laterally across the catchment.

[33] A potentially more critical assumption identified by a number of studies is the use of a single value for the pre-event reservoir based on the base flow runoff preceding episodes [Dewalle et al., 1988; Ogunkoya and Jenkins, 1993]. The possibility that the isotopic signal of the pre-event component was spatially variable within the catchment was not tested during the 1997 spring flood. However, in a similar study during the spring flood of 1999 in the same catchment, no variation in the unsaturated and groundwater isotopic signal was found that would seriously question the assumption of two component mixing [Cory, 1999].

[34] In summary, the results of this study showed that the commonly used IHS procedures for defining the event water component in snowmelt episodes may significantly underestimate the pre-event contribution. This underestimate can have serious consequences for the separation of event and pre-event water associated with spring melt runoff, and stands in the way of a better understanding of the travel times, as well as the behavior of solutes and toxicants reaching the stream during spring flood episodes.

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References


