

ACCOUNTING FOR TIME AND SPACE VARIATIONS OF  $\delta^{18}\text{O}$  IN A  
SNOWMELT ISOTOPIC HYDROGRAPH SEPARATION IN THE BOISE FRONT.

by

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The thesis presented by Patrick R. Kormos entitled Accounting for Time and Space Variations of  $\delta^{18}\text{O}$  in a Snowmelt Isotopic Hydrograph Separation in the Boise Front is hereby approved:

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## ABSTRACT

A reliable isotopic hydrograph separation is possible for a snow melt event if spatial and temporal variability in  $\delta^{18}\text{O}$ , and travel time to the stream can be taken into account. Spatial variability of melt  $\delta^{18}\text{O}$  cannot be accounted for with elevation, slope, or aspect. Standard deviations of  $\delta^{18}\text{O}$  on the meter scale range between 1.29‰ and 0.40‰. Results of hydrograph separations of the 2003 melt in the Bogus Experimental Catchment using various methods to account for the new water  $\delta^{18}\text{O}$  range from 44.8% to 99.4% old water. The proposed method of constructing a new water isotopic signal by distributing a daily averaged isotopic time series across the basin yields an old water fraction of 68.1%. A hydrograph separation using silica yields similar results.

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## 1. INTRODUCTION

The majority of hydrograph separation studies since 1969 (Pinder and Jones, 1969) have concluded that nonevent water (old water) dominates runoff events (Buttle, 1994). Prior to this time, event water (new water) was thought to travel quickly overland to a stream and cause an increase in discharge. Many hydrologic models currently in use are based on the overland flow runoff generation mechanism. Dunne and Black (1970a; 1970b) proposed a mechanism of subsurface flow runoff generation based on hydrometric studies. The introduction of the conservative tracer-based hydrograph separation technique has confirmed the results of Dunne and Black and lead to the current conception of how water moves through a catchment. Improving tracer methods to explain hydrologic pathways and incorporating those methods into hydrologic models continue to be topics at the forefront of hydrologic research. This thesis attempts to improve hydrograph separations during snowmelt events.

A two-component hydrograph separation study separates an event hydrograph into contributions from the new and old water reservoirs. The new water is defined as any water that is introduced into the basin during the hydrograph event, and the old water is defined as any water that exists in the basin prior to the event. The majority of hydrologic events have chemically different old and new water reservoirs. Tracking the chemistry of the stream and the two contributing reservoirs allows the stream to be separated into new and old water contributions. Based on equations for conservation of mass, the quantity of old water contributing to a storm hydrograph is:

$$Q_o = Q_s \frac{(C_o - C_n)}{(C_s - C_n)}, \quad (1)$$

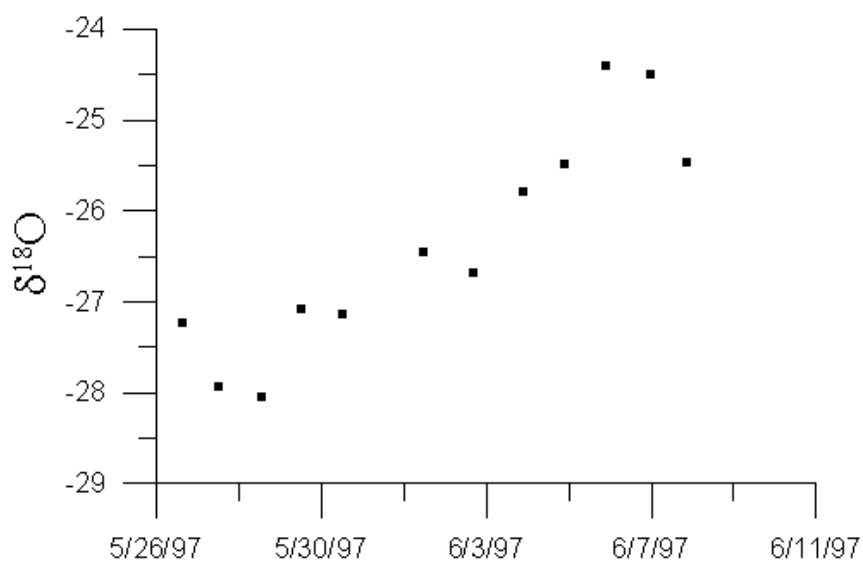
where  $Q$  is the discharge,  $C$  is the tracer concentration, and the subscripts  $s$ ,  $n$ , and  $o$  refer to the total streamflow, the new component of flow, and the old component of flow respectively (McNamara, Kane, and Hinzman, 1997). This hydrograph separation equation is explained in more detail in Section 1.2. Reliable results from the hydrograph separation equation are contingent upon well-defined conservative tracer concentrations for new, old, and stream waters.

A conservative tracer is one that does not change in concentration as water moves through a catchment during a hydrologic event. A commonly used tracer is the stable isotope  $^{18}\text{O}$ , an isotope of oxygen that occurs naturally in water. Since  $^{18}\text{O}$  is a part of the water molecule and not an ion dissolved in the water, chemical reactions of the tracer while in the hill slope are minimized.

The isotopic hydrograph separation works well on rain events (Sklash and Farvolden, 1979), as they are commonly of short duration and have relatively persistent isotopic chemistries compared to snowmelt events. Because changes in isotopic concentration arise from phase changes common in a snowpack, the isotopic chemistry of snowmelt is observed to be significantly variable in time (Figure 1.1) (Taylor, Feng, Kirchner, Osterhuber, Klaue, and Renshaw, 2001). Large errors in a hydrograph separation result from the wide range of values that can be used for the new water concentration in Equation 1. Recent studies have addressed temporal variations (enrichment) in snow melt  $\delta^{18}\text{O}$  throughout the melt event (Taylor, Feng, Williams, and McNamara, 2002), but implementation of methods to account for observed spatial variability are limited.

Spatial variability in snowmelt isotopic chemistry is observed on the catchment scale in response to elevation, distance from the ocean, and latitude (Dansgaard, 1964; Ingraham, 1998; Ingraham and Taylor, 1986; Siegenthaler and Oeschger, 1980). Spatial variability in isotopic melt chemistry is also expected to vary on the meter-scale similar to melt volumes as observed by Williams, Sommerfeld, Massman, and Ridders (1999). Small-scale controls on variability may include, snow redistribution in response to abrupt changes in vegetation and complicated pathways of melt through the snowpack.

This thesis contributes to methods that define a new water input for Equation 1 during snowmelt events. Specific objectives of this thesis include 1) evaluating the spatial and temporal variation of snow melt  $\delta^{18}\text{O}$  in the snowpack in the Bogus Experimental Catchment (BEC), 2) demonstrating the wide range of possible outcomes for Equation 1 depending on the new water chemistry used, 3) developing a method of combining measured melt chemistry into a new water isotopic input for Equation 1 that



**Figure 1.1. Typical  $\delta^{18}\text{O}$  enrichment of melt from an Alaska snowpack on the North Slope of the Brooks Range (Modified from Taylor et al., 2002).**

takes into account spatial and temporal variation, and 4) estimating new and old water contributions using the developed hydrograph separation technique.

### **1.1 Project Scope**

The evaluation of isotopic variability in snowmelt and new methods of accounting for that variability in the BEC contributes to hydrograph separation research dating to 1967 (La Sala, 1967). Although steady improvements have been made in hydrograph separation techniques, there is a need to improve methods of obtaining a reasonable new water isotopic concentration for snow melt events. As snow melts, phase changes in the snowpack enrich melt. Factors such as elevation and aspect should affect large-scale spatial variability, while preferred pathways through the snowpack and vegetation should affect small-scale spatial variability. A very significant, but often overlooked source of error in new water chemistry is the time it takes melt in the upper portion of the catchment to travel to the stream. Only by accounting for all of these factors can one be confident in a new water melt chemistry.

The completion of a hydrograph separation study in the BEC during the 2003 melt season supports a large-scale investigation of cold season hydrologic pathways in the semiarid Dry Creek Experimental Watershed composed of rangelands and forests north of Boise, Idaho. Ongoing studies in the Dry Creek Experimental Watershed examine hill slope processes and their relations to watershed functions. Results from such studies will be incorporated into watershed models, which predict and evaluate water resources and flood hazards (Weiler and McDonnell, 2004).

The Dry Creek Experimental Watershed is a 28 km<sup>2</sup> basin that sustains flow throughout the summer in the absence of any significant precipitation. It is composed of

numerous valleys with intermittent and perennial streams. A better understanding of how mesoscale watersheds function relies on studies of different subcatchments in which various hydrologic conditions prevail.

Yenko, McNamara, and Chandler (2001) conducted hydrologic investigations in the 0.01 km<sup>2</sup> Treeline Site of the Dry Creek Experimental Watershed, which contains an intermittent stream that flows from November through May most years. Sixty percent of the snowmelt event hydrograph is contributed by new water according to a hydrograph separation during the melt of 2001 using silica as a conservative tracer. The melt event hydrograph is dominated by new water because the shallow sandy soils limit the amount of soil water that can be stored in the catchment. New water from snowmelt overwhelms the soil water that is left from the previous year.

The Bogus Experimental Catchment (BEC) is a 0.6 km<sup>2</sup> headwater basin with a perennial stream that receives the majority of its annual precipitation as snow. It is bigger than the Treeline Site and it is made of many subcatchments that contain either an intermittent stream or perennial stream. An isotopic hydrograph separation in the BEC separates the 2003 snowmelt event into a new water contributing reservoir and an old water contributing reservoir. Associated inferences about cold season processes that govern contributing reservoirs to streamflow may lead to more dependable watershed models, which facilitate better land management policies for rangelands and forests, as well as more accurate flood predictions and contaminant response tactics for all semiarid watersheds.

## 1.2 Background

Scientists have been performing hydrograph separations on various scales to identify contributing reservoirs to streamflow during hydrologic events for over 50 years. This paper contributes to the methodology of obtaining a new water concentration to be used in a snowmelt hydrograph separation by accounting for spatial and temporal variability in snowmelt chemistry.

Hydrograph separations based on the mass balance equation using a conservative tracer must consider all five assumptions summarized by Buttle (1994).

1. There is a significant difference between the isotopic chemistry of the new and old components of streamflow.
2. The isotopic signature of new water is constant in space and time, or any variations can be accounted for.
3. The isotopic signature of old water is constant in space and time, or any variations can be accounted for.
4. Contributions of water from the vadose zone must be negligible, or the isotopic content of soil water must be similar to that of groundwater.
5. Contributions to streamflow from surface storage are negligible.

Also implied by the hydrograph separation equation is an instantaneous delivery assumption, which assumes that melt chemistry measured anywhere in the catchment will affect the stream chemistry immediately. The instantaneous delivery assumption is referred to as assumption 6 in this thesis.

Two problem assumptions with respect to snowmelt isotopic hydrograph separation that are addressed in this thesis are: 1) both the spatial and temporal variability of assumption 2, and 2) instantaneous delivery implication of assumption 6.



### 1.2.1 Assumption 2: New water is Temporally and Spatially Constant.

Variability in the isotopic chemistry of snowmelt originates from phase changes in water.  $^{18}\text{O}$  is an isotope of water that occurs far less often than  $^{16}\text{O}$ . The  $\delta^{18}\text{O}$  of precipitation depends on the history of that water in terms of origin and temperature during phase changes. Since  $^{18}\text{O}$  is a heavier atom, water molecules with  $^{18}\text{O}$  form stronger bonds with other water molecules. Water molecules with  $^{16}\text{O}$  will therefore preferentially melt from ice and evaporate from water leaving a parent phase enriched in  $^{18}\text{O}$ . Colder environments facilitate larger degrees of fractionation because the molecular structure of water is more organized and more specific to allowing  $^{16}\text{O}$  into it. When water is warmer, the molecular structure is less specific, and allows  $^{18}\text{O}$  to be interchangeable with  $^{16}\text{O}$ . Negative concentrations of  $\delta^{18}\text{O}$  reflect the fact that most terrestrial water originates by evaporating from the ocean, thus being depleted in  $^{18}\text{O}$  compared to the parent oceanic water.

Methods used to quantify the new water chemistry during snowmelt events have evolved steadily. Little attention was paid to melt chemistry as early studies used an average isotopic value from snow cores collected on one day. Now, studies are beginning to account for complex temporal and spatial isotopic variations in melt water.

#### 1.2.1.1 Snow Cores

Early studies collected and melted bulk snow cores to represent the new water chemistry, which was assumed constant in time and space (Rodhe, 1981); (Bottomley, Craig, and Johnston, 1986). However, Taylor, et al. (2002) and Hooper and Shoemaker (1986) conducted field experiments indicating a significant difference in isotopic content

between meltwater and snow samples. It is therefore necessary to collect melt samples to characterize new water chemistry.

#### 1.2.1.2 Temporal Variability of $\delta^{18}\text{O}$ Meltwater

Melt chemistries collected over time from one location are reported by Martinec (1975) and Dincer, Payne, Florkowski, Martinec and Tongiorgi (1970). Both studies assume a constant mean chemistry value for the new water and state that there is little areal and time variations about the mean value. Genereux (1998) and Hooper and Shoemaker (1986), however, observed an isotopic signal that varies significantly over time. Taylor, Feng, Kirchner, Osterhuber, Klaue, and Renshaw (2001) conduct laboratory and field experiments on temporal variations in  $\delta^{18}\text{O}$  and observe an isotopic enrichment during snowmelt (Figure 1.1). Taylor et al. (2002) quantify the errors associated with neglecting the observed isotopic enrichment and show that the hydrograph separation underestimates old water contributions during early melt and overestimates old water during late melt. Therefore, measurements of snowmelt must be made repetitively throughout the event to sufficiently represent new water concentrations.

#### 1.2.1.3 Spatial Variability of $\delta^{18}\text{O}$ in Melt Water

Many studies have implied spatial variations in isotopic chemistry by using more than one melt collection location. Moore (1989) collected meltwater from eight melt lysimeters during a melt event and reported daily averages between  $-20.05\text{‰}$  and  $-17.41\text{‰}$  with standard deviations between  $0.66\text{‰}$  and  $0.76\text{‰}$ . However, the study uses a grand mean from all lysimeters on all days as a constant new water value because temporal variations in chemistry and routing of new water could not be accounted for.

This approach takes into account some spatial variation, but does not consider time variations in melt chemistry.

Hooper and Shoemaker (1986) use isotopic chemistry from two melt lysimeters to represent new water in a 0.42 km<sup>2</sup> watershed. An average isotopic value is used when samples are taken from both locations at the same time. Spatial variability is reported to average 3.8‰ in deuterium between the two sampling points, which are approximately 300 m apart in distance and 220 m apart in elevation. Differences in isotopic values are attributed to rain events that occurred regularly during the melt event.

Shanley, Kendall, Smith, Wolock, and McDonnell (2002) collect melt water from four locations with different aspects in a 0.41 km<sup>2</sup> basin. Small scale variability is reported to range between 1‰ and 3‰ in  $\delta^{18}\text{O}$ . Variability was accounted for by taking a daily arithmetic mean  $\delta^{18}\text{O}$  value stating that the variability is small compared to  $\delta^{18}\text{O}$  differences between meltwater and groundwater.

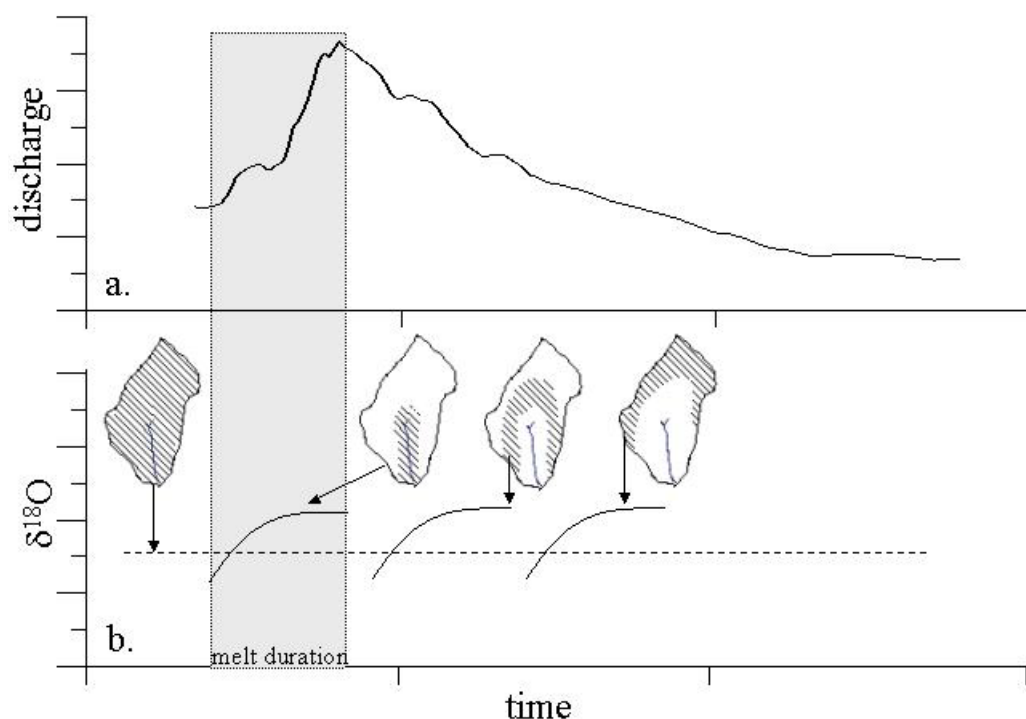
The use of daily means is the first step in taking into account basin wide snowmelt chemistry over time, but very few collection locations are sampled in large basins. Melt  $\delta^{18}\text{O}$  is difficult to characterize because many factors can effect the melting processes in the snowpack and thus affect the  $\delta^{18}\text{O}$  concentration of the snowmelt. Catchment scale factors such as elevation, aspect, wind redistribution, vegetation, and slope culminate with smaller scale factors such as melt pathways and local topography to give a significantly variable  $\delta^{18}\text{O}$  signal in time and space.

#### 1.2.2 Assumption 6: Instantaneous Delivery of Snow Melt to the Stream.

A spatially and temporally constant new water  $\delta^{18}\text{O}$  value does not require accounting for melt water travel times for different parts of the catchment. The constant

new water  $\delta^{18}\text{O}$  value is simply used for the entire hydrograph event, even though the actual snowmelt period covers a relatively short fraction of the event hydrograph (Figure 1.2 a.). The horizontal dashed line in Figure 1.2 b represents the constant  $C_n$  value to be used in the hydrograph separation if the measured melt  $\delta^{18}\text{O}$  is time constant. The constant  $\delta^{18}\text{O}$  value represents areas close to the stream early in the hydrograph event and represents areas with greater distance to the stream later in the event.

Time variations in  $\delta^{18}\text{O}$  values force one to distribute a new water chemistry signal across a catchment according to a travel time to the stream (Figure 1.2). The  $\delta^{18}\text{O}$  enrichment in the shaded box represents the  $C_n$  values measured from melt samples during the melt event. That same enrichment curve then needs to be distributed in time to account for the time it takes melt to move from the hill slope to the stream.



**Figure 1.2. Plot demonstrating the effect of a time varying new water  $\delta^{18}\text{O}$  signal compared to a constant  $\delta^{18}\text{O}$  value. Time varying new water curves are distributed in time according to the distance that the snowmelt must travel to the stream.**

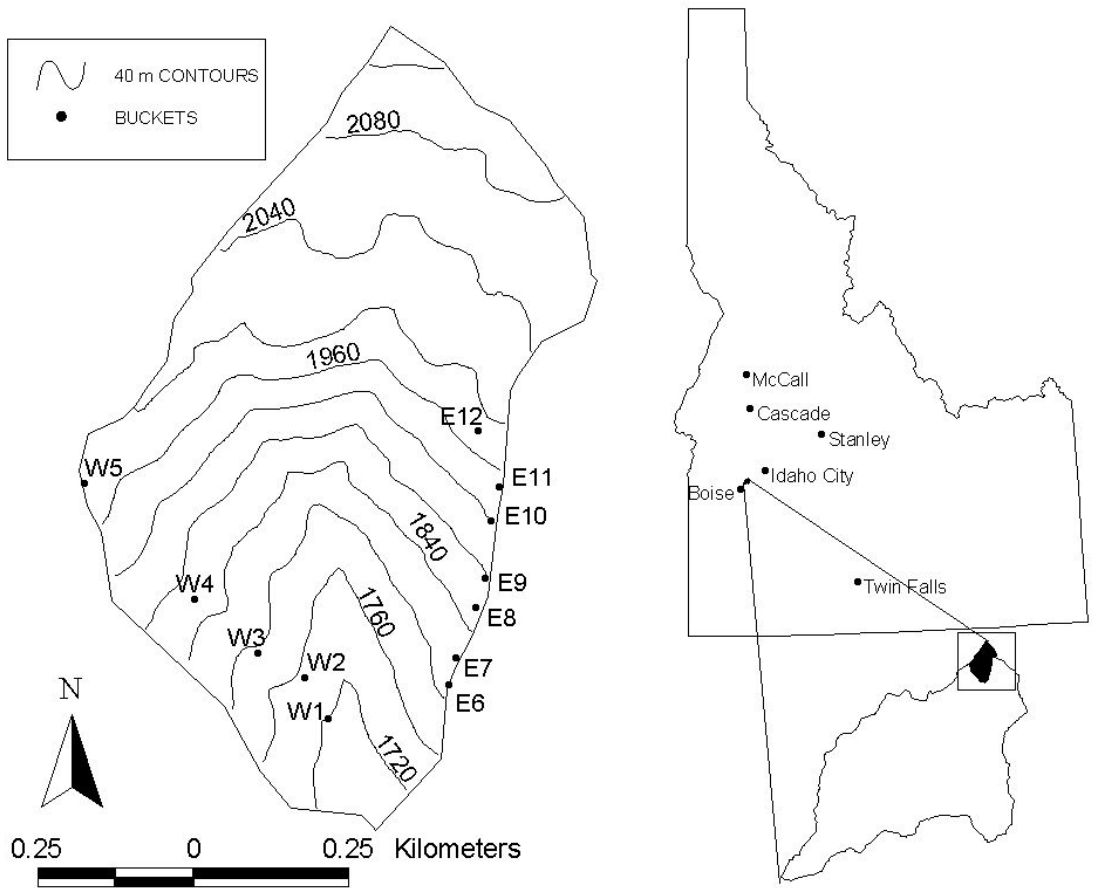
Several authors have dealt with the instantaneous delivery assumption by acknowledging that melt from one day does not completely exit the basin on the same day. The melt at the basin outlet is represented as the sum of receding discharge series, each of which represent the melt from one of the previous days (Martinec, 1975); (Martinec, Siegenthaler, Oeschger, and Tongiorgi, 1974). The use of a receding discharge series infers that it takes some amount of time for melt chemistry measured in the basin to affect the stream. However, the receding discharge series is never used to account for variable melt chemistry moving through the basin. It is used to model the flow at the basin outlet and an average snowpack chemistry value is used in the hydrograph separation.

Determining a reliable new water input chemistry is also complicated by the need to distribute point measurements across the entire basin (Taylor, et al., 2002). This thesis develops a method of constructing, distributing, and delivering a snowmelt chemistry time series to the stream and avoids the instantaneous delivery assumption.

## 2. SITE DESCRIPTION

### 2.1 Geographic Location

The Bogus Experimental Catchment (BEC) is located approximately 16 kilometers north of Boise, Idaho in Boise County (Figure 2.1). It is the northern most headwater catchment within the Dry Creek Experimental Watershed.



**Figure 2.1. Location Map of the Bogus Experimental Catchment showing the location of melt buckets and elevation.**

## 2.2 Physical Description

The BEC is a 0.6 square kilometer headwater basin ranging in elevation from 1684 meters to 2135 meters. It is underlain by fractured granite typical of the Idaho Batholith. Soils are described as the Zimmer-Eagleson Complex by the SSURGO Soil Survey conducted in 1976 by the U.S. Department of Agriculture, Natural Resources Conservation Service. The soils overlying the granitic bedrock are thin (approximately 0.5m) and coarse (between sandy loam and loamy sand). The steep northern headwalls of the basin are mostly exposed, weathered granite, while the ridges, valley bottom, and east and west slopes have varying depths of soil.

Vegetation is typical of forests and rangelands of mid elevation Boise Front Mountains. Large trees cover a very small portion of the basin and are exclusively *Pseudotsuga menziesii* (Douglas Firs) and *Pinus ponderosa* (Ponderosa Pines), while the majority of the basin is covered with *Ceanothus spp.* (buck brush) and *Prunus spp.* (bitter and choke cherry shrubs).

The average temperature at the Bogus Experimental Watershed was 6.47°C during the 2003 melt season, slightly higher than the 6.17°C 5-year average as recorded by the NRCS Bogus Basin SNOTEL site, approximately 200 meters north of the basin. The maximum snow depth was 58.2 cm, lower than the 5 year average of 65.4 cm. Annual total precipitation was 69.3 cm, above the 5 year average of 67.6 cm.

The perennial pool drop stream in the Bogus Experimental Catchment originates from one dominant spring in the rocky headwall, and is fed subsequently by 2-3 lesser springs originating as swampy marshes within a meter of the stream. Several water

tracks also feed the stream during snowmelt that quickly stop flowing as the snow pack decreases. Average daily discharge from the 2003-2004 water year is  $0.0028 \text{ m}^3/\text{s}$ .



### 3. METHODS

An  $\delta^{18}\text{O}$  signal of snowmelt that effects stream chemistry during a snowmelt event is constructed as an input to a two-component hydrograph separation equation. The hydrograph separation for the 2003 snowmelt event is performed using a mixing model based on the steady state form of the mass balance equation and mass balance equation with a conservative tracer:

$$Q_s(t) = Q_o(t) + Q_n(t), \quad (2)$$

$$Q_s(t)C_s(t) = Q_o(t)C_o(t) + Q_n(t)C_n(t), \quad (3)$$

where  $Q$  is the discharge,  $C$  is the tracer concentration,  $t$  is the time, and the subscripts  $s$ ,  $n$ , and  $o$  refer to the total streamflow, the new component of flow, and the old component of flow respectively (McNamara, et al., 1997). The portion of streamflow from old water reservoirs at any time  $t$  is solved by substituting Equation 2 into Equation 3 and yields:

$$Q_o(t) = Q_s \frac{C_s(t) - C_n(t)}{C_o(t) - C_n(t)}. \quad (4)$$

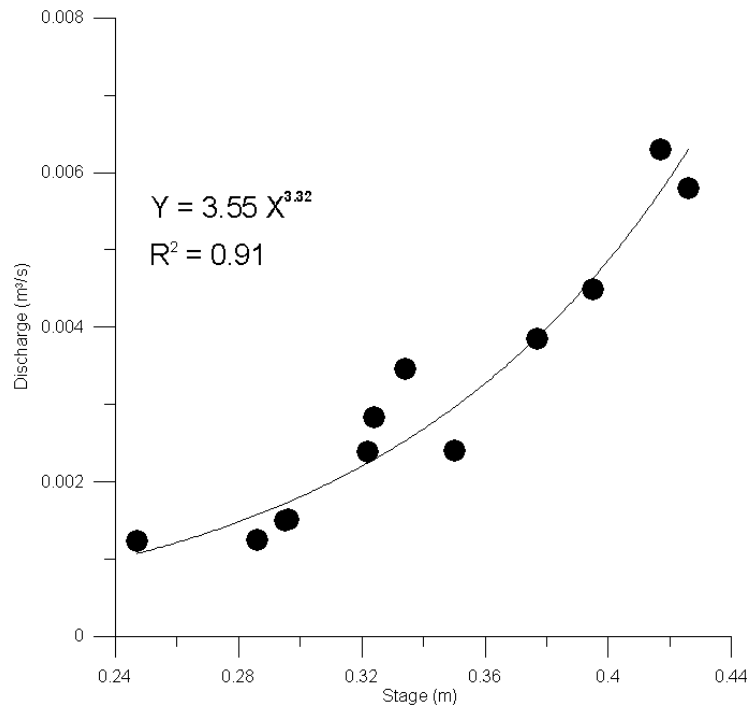
All variables in Equation 4 must be quantified in order to complete a successful hydrograph separation.

The focus of this thesis is to develop a method to account for the spatial and temporal variability of  $C_n$  (Section 4.2). We derive methods for calculating a  $C_n$  time series that incorporates temporal and spatial variability as well as delivery time, which ultimately leads to an estimation of  $Q_o$ . The performance of the isotopic hydrograph

separation is evaluated by comparing the results to a separation of the same event using silica as a tracer.

### 3.1 $Q_s$ : Stream Gauging

The Bogus Experimental Catchment is defined by the location of a gauging station on the Bogus Stream. The gauging station consists of a Global Water WL400-15 pressure transducer and Campbell Scientific 547A conductivity / temperature probe in conjunction with a Campbell Scientific CR10X data logger. The pressure transducer is placed in a constrained feature in the stream where it is unlikely that the shape of the stream will change. Discharge is calculated by the use of a depth-discharge rating curve constructed by simultaneously measuring depth and discharge (Figure 3.1). Dilution gauging was employed to measure discharge because the stream is commonly too small to gauge with a conventional flow meter (Dingman, 2002). A discharge hydrograph is



**Figure 3.1. Rating curve of the Bogus Stream relating stream stage to stream discharge.**

constructed from the stage hydrograph based on the rating curve, which is the best fit function to the stage discharge points.

### **3.2 C<sub>s</sub>: Stream Water Chemistry**

Stream water chemistry is collected from the stream by hand or by an autosampler. Water sampled for  $\delta^{18}\text{O}$  is collected in 20 ml glass vials with inverted cone caps to ensure the complete volume of the container is full of melt and no evaporative fractionation can take place. Bottles are clearly marked with a permanent marker and stored at room temperature until being shipped to University of Alaska Fairbanks Stable Isotope Facility to be analyzed.  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values are measured using pyrolysis-EA-IRMS. This method utilizes a ThermoFinnigan MAT high temperature elemental analyzer (TC/EA) and ConFlo III interface with a Delta+XL Mass Spectrometer. Two to three replicates were run for quality control on all melt and stream samples.

Samples for silica are collected in high-density polyethylene bottles, filtered through 0.7  $\mu\text{m}$  filters, and acidified with hydrochloric acid. Bottles are clearly marked with a permanent marker and refrigerated until being shipped to Utah State University Analytical Laboratories (USUAL) where cations are identified by flow injection analysis with a ThermoFinnigan Inductively Coupled Plasma Machine and Chloride was measured using a Lachat Quickchem 8000.

### **3.3 C<sub>o</sub>: Old Water Chemistry**

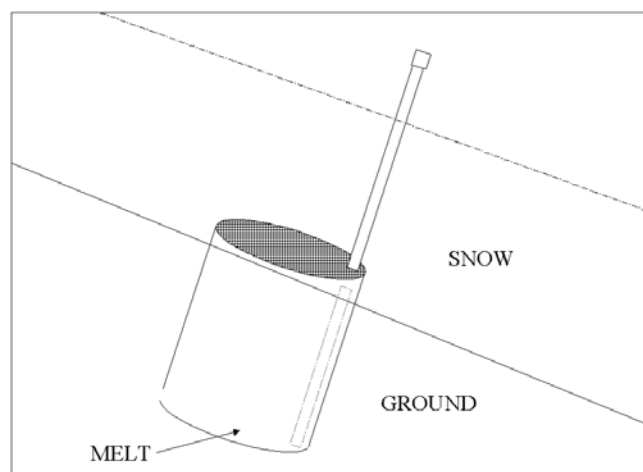
Old water chemistry is assumed to be the stream water chemistry during low flow conditions before the melt event (La Sala, 1967). It is assumed that the only reservoir contributing to stream flow during low flow conditions is a well-mixed old water

reservoir. A discussion of this assumption follows in section 5.1.3. Samples were treated the same as described in Section 3.2.

### 3.4 C<sub>n</sub>: New Water Chemistry

#### 3.4.1 Collection of Melt

Twelve 5-gallon melt buckets were installed in the Bogus Experimental Catchment to evaluate new water chemistry on the catchment scale. Buckets were buried before an accumulation of snow during the fall of 2002 for the spring of 2003 melt season. A melt bucket consists of a screened bucket equipped with a 5 foot section of capped pvc pipe, which serves as a conduit through the snow pack for melt water collection (Figure 3.2). Buckets were buried such that a few centimeters remained above the ground surface to inhibit any overland flow from entering. Buckets were positioned according to 2 major goals: 1) to capture potential elevational fractionation effects of snowmelt  $\delta^{18}\text{O}$ , and 2) for accessibility during sample collection. Five buckets were positioned along a transect of the western slope ranging in elevation from 1718 to 1983 meters, and the remaining 7 were buried along the east ridge between 1807 and 1985



**Figure 3.2. Diagram showing melt bucket construction and position in the hillside.**

meters (Figure 2.1). A peristaltic pump with 5 mm diameter tube was utilized to extract all melt water from the buckets during the 2003 spring melt. Samples were treated as described in Section 3.2.

In addition, a group of eighteen 2.5-gallon melt buckets were buried at 2 locations on a ridge during the fall of 2004. The eighteen melt buckets were used to evaluate meter-scale melt water chemical variability. Site one consisted of ten melt buckets were buried on a ridge top. The buckets were equally spaced along a circle with a 20-meter circumference on a flat area of uniform vegetation and aspect. Site two consisted of a group of 8 melt buckets were buried in a circle on an adjacent hillside with varying aspect and vegetation. Buckets at site two were spaced identically to buckets at site one, but were positioned on a hill slope hollow. Half of the buckets faced southeast and the other half faced northeast. Vegetation at site two ranged from fully covered with *Ceanothus spp.* to bare soil. Bucket locations covered a range of aspects, elevations, vegetation covers, and slopes. Buckets were constructed and melt was collected in the same manner as the previous year. Melt collection did not begin until all of the collection tubes were visible at the surface of each site (April 1<sup>st</sup> for the site two and April 5<sup>th</sup> for the site one).

#### 3.4.2 Spatial Variability in New Water Chemistry

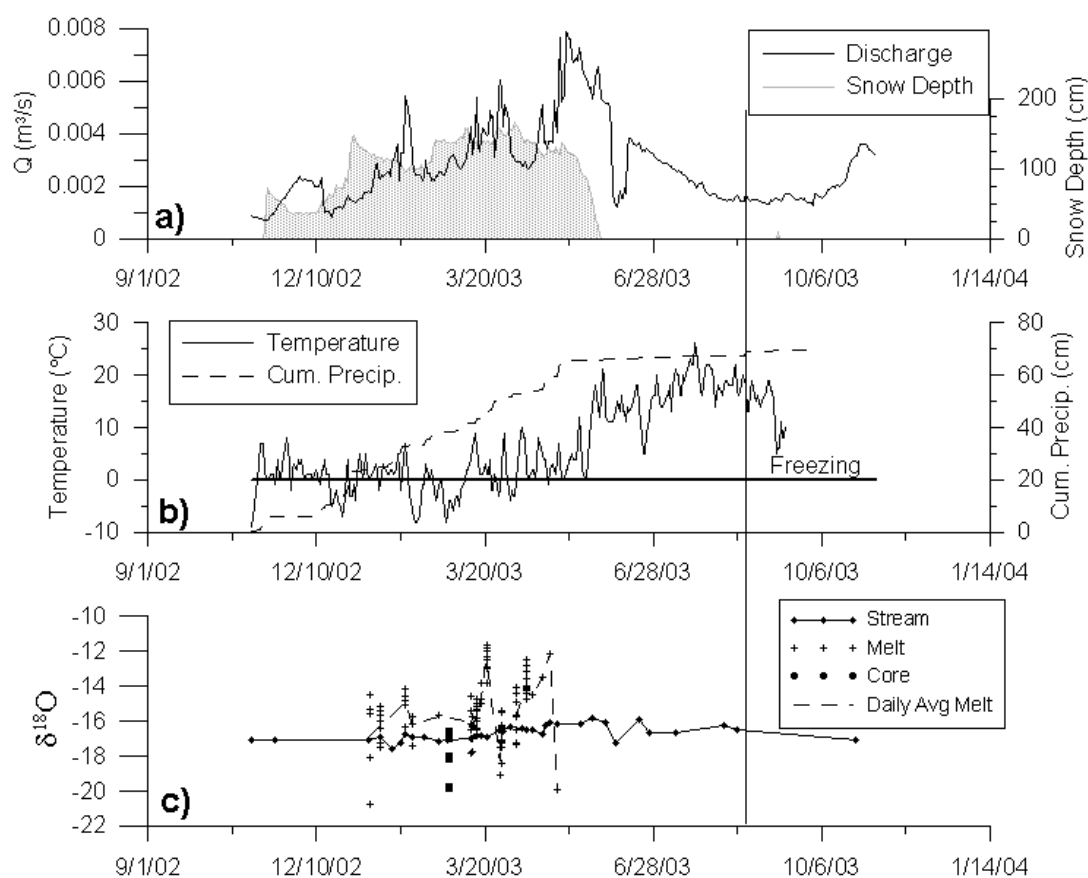
Histograms are constructed to demonstrate the variability in melt  $\delta^{18}\text{O}$  on the catchment and meter scale.

### **3.5 Weather Data**

Temperature, cumulative precipitation, and snow depth are measured at a NRCS SNOTEL site approximately 200 m north of the BEC. Data is assumed to sufficiently represent conditions present in the catchment for comparative purposes.

## 4. RESULTS

The 2003 water year is complicated by highly fluctuating winter temperatures after snowpack accumulation, late rain on snow events, and an unexplained return to baseflow conditions during the hydrograph recession (Figure 4.1). The snowmelt collected from the BEC under the highly variable melt conditions resulted in highly variable isotopic chemistry on the catchment scale.



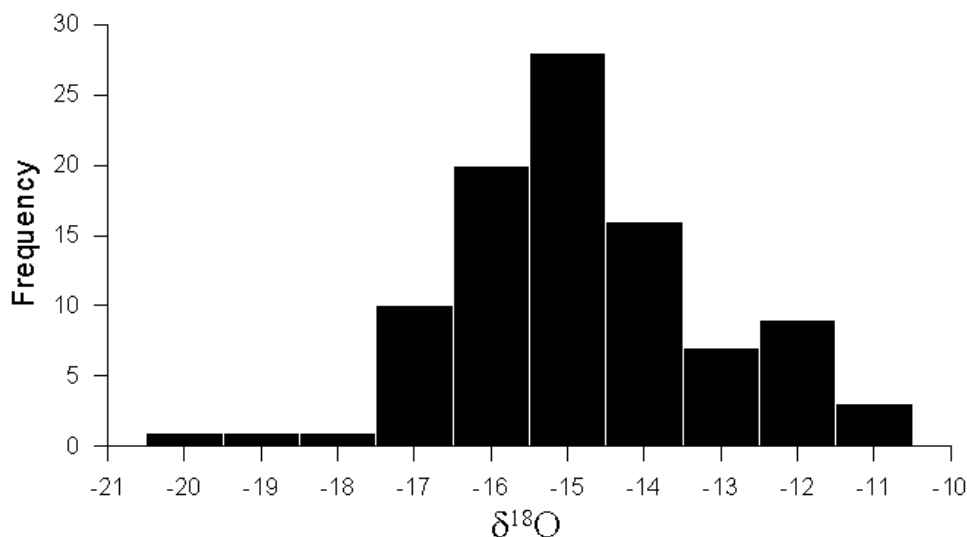
**Figure 4.1. Graphs showing the complicated nature of the 2003 water year at the BEC including: a) Hydrograph and snow depth, b) average daily temperature and cumulative precipitation, and c) stream and melt  $\delta^{18}O$ . Vertical line shows the end of the melt event for this separation.**

## 4.1 Variability of Snowmelt Chemistry

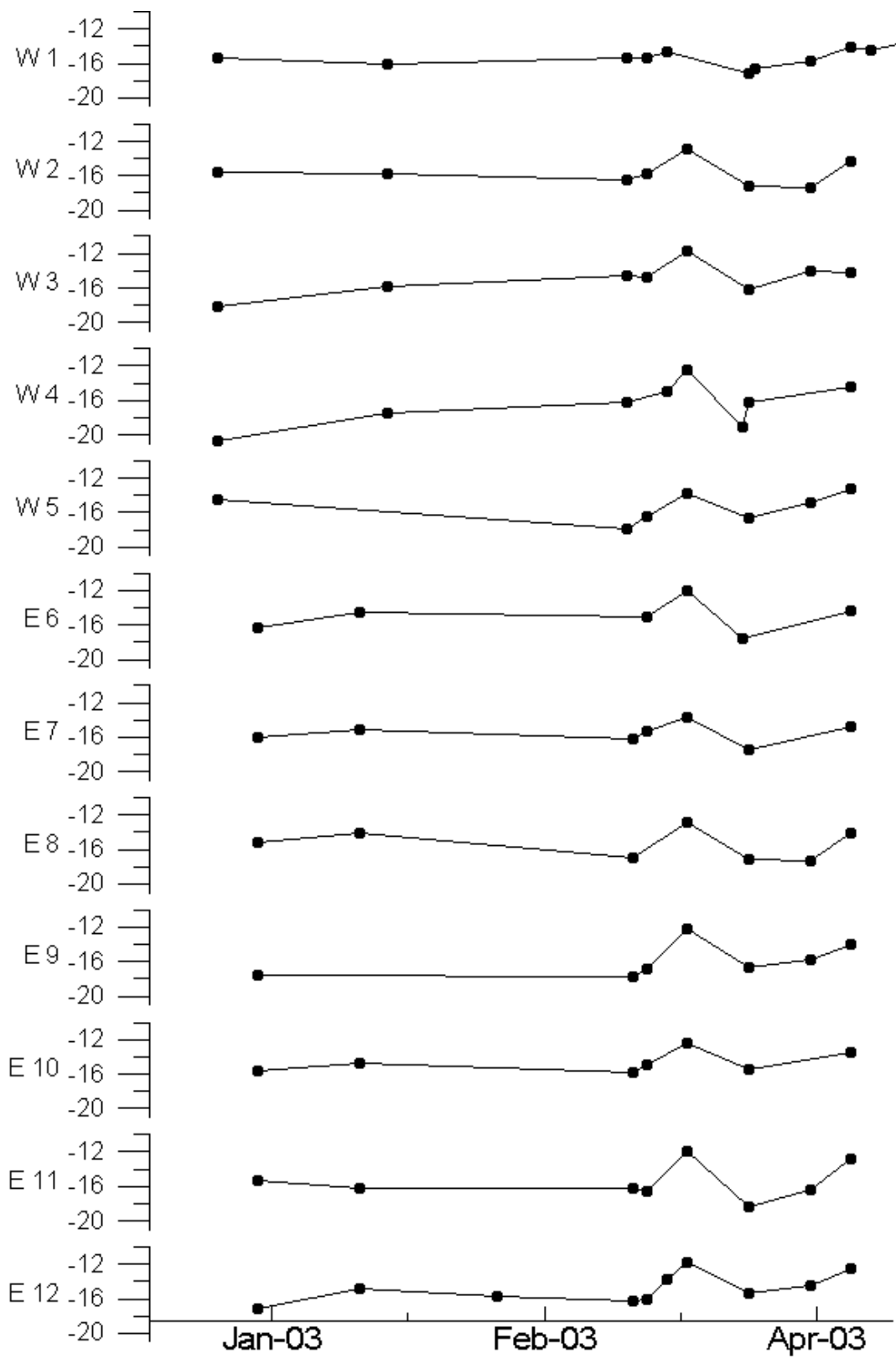
### 4.1.1 Catchment Scale Spatial Variability in Snowmelt $\delta^{18}\text{O}$

Figure 4.2 is a histogram of melt  $\delta^{18}\text{O}$  values collected during the spring of 2003 melt event showing a significant range of isotopic values. Melt chemistries range in value from  $-10.26\text{‰}$  to  $-11.57\text{‰}$  with a grand mean of  $-15.32\text{‰}$ . The histogram takes into account temporal and spatial variability on the catchment scale (Figure 4.3). Table 4.1 gives statistics from all buckets on individual days showing that there is significant spatial variability in  $\delta^{18}\text{O}$  on these days.

Spatial variation in snowmelt chemistries has been observed to follow predictable patterns based on elevation, distance from ocean, latitude, and duration of precipitation events (Siegenthaler and Oeschger, 1980); (Ingraham and Taylor, 1986); (Dansgaard, 1964); (Ingraham, 1998). The most common fractionation effect observed on a similar scale to the BEC is the depletion in  $\delta^{18}\text{O}$  concentrations with elevation. Figure 2.1 shows the elevation of the Bogus Catchment and the location of the 12 melt buckets. Melt



**Figure 4.2. Histogram of all melt chemistry sampled from the 2003 snowmelt in the BEC.**



**Figure 4.3. Graphs of  $\delta^{18}\text{O}$  over time of all meltwater buckets in the Bogus Experimental Catchment.**



buckets are positioned to capture depletion with elevation, however, there is no correlation between elevation and  $\delta^{18}\text{O}$  concentrations (Figure 4.4).

Snowmelt  $\delta^{18}\text{O}$  is also compared to aspect and slope to try to account for different melt timing and rates, as well as redistribution effects, none of which accounted for  $\delta^{18}\text{O}$  variability (Figure 4.4). One explanation for this is that a snowpack is an accumulation of snow from many different precipitation events, each of which is expected to have a different  $\delta^{18}\text{O}$  signature. Many factors other than elevation, aspect, and slope may exert an equal or stronger control on the melt  $\delta^{18}\text{O}$  concentration, such as redistribution by winds and vegetation cover. Accounting for these different chemistries and the physical processes that effect  $\delta^{18}\text{O}$  that occur within the snowpack during melt is nearly an

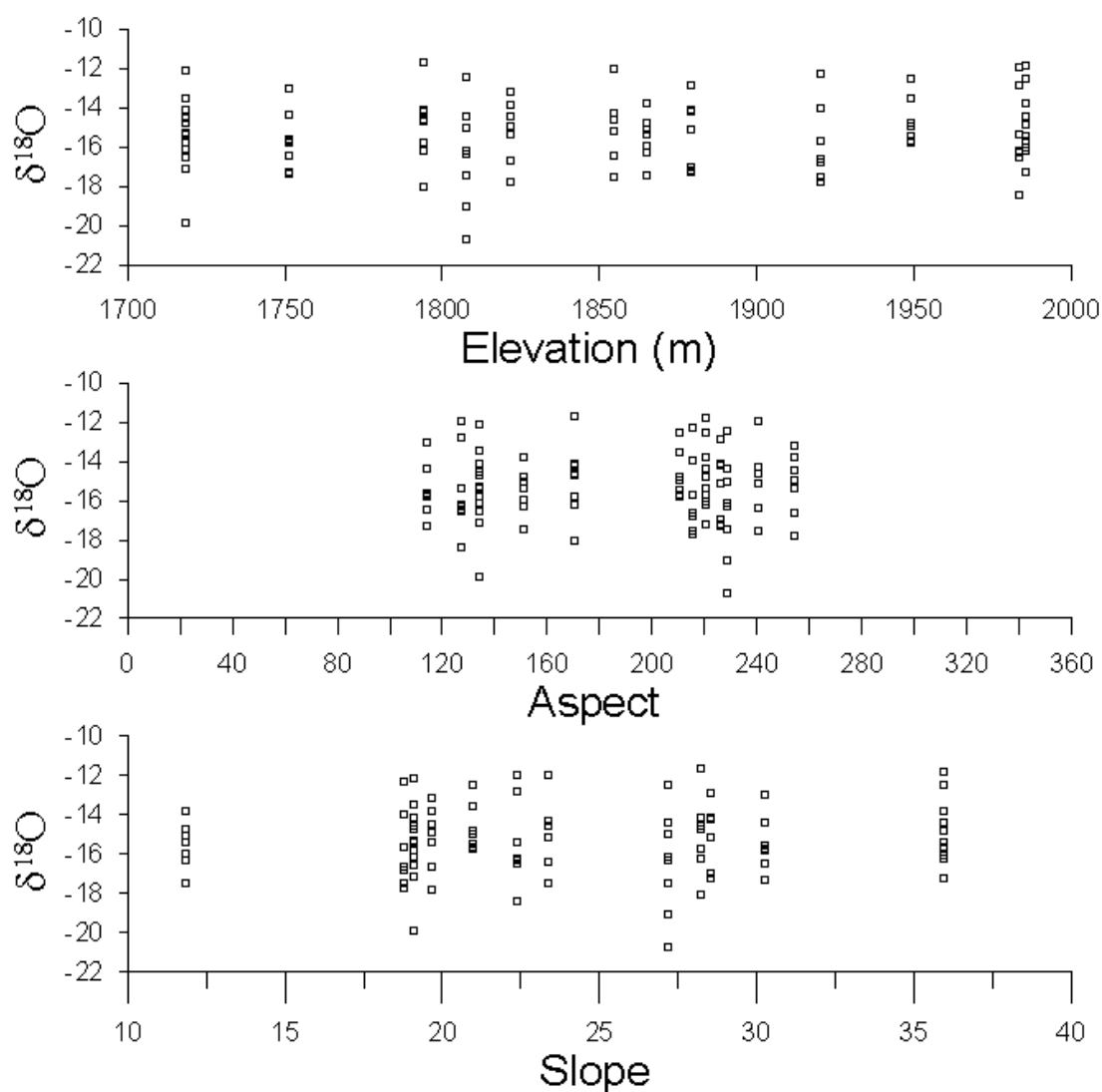
**Table 4.1. P-values, maximum values, minimum values, and standard deviations listed for days of melt collection and buckets involved showing that isotopic concentrations vary spatially.**

Date	Buckets / Sample Origin	Mean	Min	Max	Standard Deviation
01/11/03	W1, W2, W3, W4, W5 / melt	-16.83	-20.71	-14.46	2.54
01/17/03	E6, E7, E8, E9, E10, E11, E12 / melt	-16.18	-17.50	-15.12	0.91
02/01/03	E6, E7, E8, E10, E11, E12 / melt	-14.95	-16.28	-14.19	0.71
02/05/03	W1, W2, W3, W4 / melt	-16.25	-17.44	-15.69	0.82
02/27/03	W1, W2, W3, W4, W5, E6, E7, E9, E10, E11, E12 / cores	-15.66	-19.82	-16.55	1.14
03/12/03	W1, W2, W3, W4, W5 / melt	-16.08	-17.80	-14.59	1.21
03/13/03	E7, E8, E9, E10, E11, E12 / melt	-16.53	-17.75	-15.76	0.71
03/15/03	W1, W2, W3, W5, E6, E7, E10, E11, E12 / melt	-15.70	-16.77	-14.71	0.71
03/18/03	W1, W4, E12 / melt	-14.51	-15.00	-13.79	0.63
03/21/03	W2, W3, W4, W5, E6, E7, E8, E9, E10, E11, E12 / melt	-12.55	-13.81	-11.66	0.74
3/30/2003	W1, W2, W3, W4, W5, E7, E8, E9, E10, E11, E12 / melt	-16.73	-18.39	-15.39	0.88
4/8/2003	W1, W2, W3, W5, E8, E9, E11, E12 / melt	-15.74	-17.32	-14.10	1.22
4/14/2003	W1, W2, W3, W4, W5, E6, E7, E8, E9, E10, E11, E12 / melt	-13.85	-14.74	-12.50	0.69

impossible task. Since commonly observed patterns based on physical characteristics of the catchment are not observed in the 2003 melt data, typical methods of using a hypsometric or other curve can not be used to predict  $\delta^{18}\text{O}$  concentrations in the catchment. For this reason,  $\delta^{18}\text{O}$  is assumed to be randomly distributed over the basin.

#### 4.1.2 Small Scale Spatial Variability in Snowmelt $\delta^{18}\text{O}$

Melt chemistries from the meter-scale sites were variable. Histograms constructed display significant variations in time and space exist on the meter scale.  $\delta^{18}\text{O}$



**Figure 4.4. Plot of  $\delta^{18}\text{O}$  versus catchment scale controls showing no correlation.**

data from the 2004 meter scale experiment range from  $-14.62\text{‰}$  to  $-18.1\text{‰}$  and average  $-15.86\text{‰}$ . Table 4.2 gives the average and standard deviation  $\delta^{18}\text{O}$  from both sites for 2 days. Such a high degree of spatial variability provides sufficient reason to consider melt chemistries collected on the same day at different locations as random samples from a population. For this reason, individual melt chemistries are combined into one daily averaged new water  $\delta^{18}\text{O}$  value (Figure 4.5).

#### 4.1.3 Temporal Variability of Snowmelt $\delta^{18}\text{O}$

Figure 4.3 and Figure 4.5 show that temporal variability exists in melt  $\delta^{18}\text{O}$  for the spring of 2003 in the BEC. Past studies observe  $\delta^{18}\text{O}$  values from one location to become enriched with time as the snow pack ripens and evaporative fractionation takes place (Taylor, et al., 2001). This is apparent in the melt chemistries from each bucket, however, a distinct depletion is also recorded between March 21<sup>st</sup> and March 29<sup>th</sup> in response to a rain event (Figure 4.5).

### 4.2 Construction of a New Water Input Chemistry

Results show that snowmelt isotopic chemistry is spatially and temporally variable, which violates assumption 2 (Section 1.2). However, a hydrograph separation

**Table 4.2 Averages and standard deviations of  $\delta^{18}\text{O}$  from the 2004 snowmelt experiment to quantify meter-scale variability. n is the number of melt samples.**

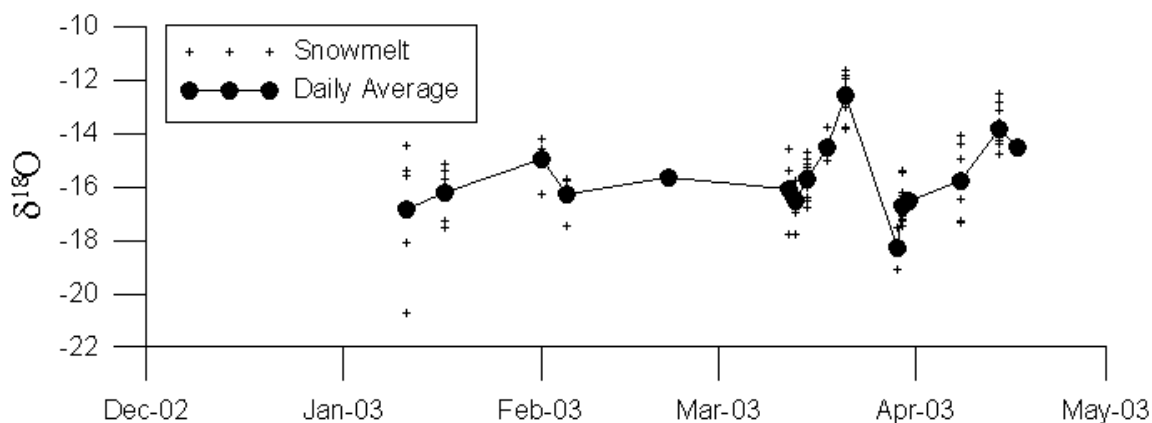
Date	n	Average	Standard Deviation	Site
4/7/2004	7	-11.33	1.29	2
4/8/2004	8	-17.11	0.57	1
4/4/2004	5	-15.43	0.49	2
4/9/2004	9	-16.55	0.4	1

can be performed if the variability can be taken into account. The solution is a new water time series of melt  $\delta^{18}\text{O}$  ( $C_n$ ) that effects the stream at time  $t$ . A new water input chemistry is created from melt water chemistry measured throughout the basin (spatial) during the entire snowmelt period (temporal). A daily average enrichment curve is first created by taking the daily averaged  $\delta^{18}\text{O}$  values of snowmelt from all 12 melt buckets in the BEC (Figure 4.5). The daily average enrichment curve is then distributed across the basin according to distance from the stream, and combined to represent the melt chemistry input to the stream. The daily average enrichment curve is lagged according to the distance to stream and Darcy Velocity, which assumes that down slope movement of water occurs through a porous media and does not consider preferential or overland flow.

A Darcy Velocity,  $q$ , of approximately 0.160 m/hr was used for the whole basin by using:

$$q = \frac{K}{n_e} \frac{dh}{dl}, \quad (5)$$

where  $K$  is the hydraulic conductivity,  $dh/dl$  is the hydraulic gradient, and  $n_e$  is the



**Figure 4.5. Plot of the daily averaged snowmelt used as the daily average enrichment curve for the construction of the new water input curve for the hydrograph separation.**

effective porosity. A hydraulic conductivity of  $1.25 \times 10^{-1}$  m/hr and an effective porosity of 0.435 is used based on soil types present in the basin (NRCS, 1997). A hydraulic gradient of 0.446 is obtained by averaging the surface slope for every 10 m pixel in the basin. Surface slope is used because the water table is assumed to follow the topography of the land surface. A distance to stream distribution is constructed for the BEC by using the flow distance to the stream for each pixel. A travel time for each pixel is obtained by dividing the flow distance by the Darcy Velocity. Implications of assumptions associated with a constant Darcy Velocity are discussed in Section 5.1.2.

The daily average enrichment curve is lagged in time for each pixel from a 10-meter digital elevation model of the study site. Pixels are grouped into bins representing the basin area that contributes melt to the stream for each two-day period. A daily average enrichment curve including late melt chemistries from W1 is used for pixels up to 50 meters away from the stream (Figure 4.5). The valley bottom remained covered with snow for a longer period as described by this curve, and 50 m is a good approximation of the extent of the valley bottom. The daily average enrichment curves are then combined by:

$$\delta^{18}O(d) = \frac{\sum_{b=1}^n [(\delta^{18}O_b)(w_b)]}{\sum_{b=1}^n (w_b)} \quad (6)$$

where  $\delta^{18}O_b$  is the isotopic value on day  $d$  in bin  $b$ ,  $w_b$  is the weight assigned to each days input curve based on the percent basin area in bin  $b$ , and  $n$  is the number of bins effecting stream chemistry on day  $d$ . The resulting new water chemistry input is shown in Figure 4.6.

### 4.3 Hydrograph Separation

An isotopic hydrograph separation calculates old water fraction of total streamflow. The value or time series used to represent the new water concentration greatly affects the outcome of the hydrograph separation. Table 4.3 shows results from hydrograph separations using different methods of accounting for the new water chemistry in the BEC. The separation was calculated 25 times using a constant new water chemistry and 14 times using a new water chemistry that varies in time. Twelve separations are performed using the  $\delta^{18}\text{O}$  values obtained by melting snow cores for new water chemistry at different locations within the basin. Snow core chemistries are depleted with respect to the majority of melt samples resulting in old water contributions to streamflow between 25% and 99%. Thirteen other separations were calculated using constant melt chemistry values as new water chemistry concentrations. Results from those separations range from 44% to 81% and a basin average of 74% old water. These values show the range in results that could occur if the separation is conducted with one or few melt samples, and the time variability in melt chemistry is not taken into account. Thirteen more separations were calculated using time varying  $\delta^{18}\text{O}$  signals in melt, one from each sampling location in the basin, and one that uses a daily average  $\delta^{18}\text{O}$  signature. Minimum and maximum separation results from single locations in the basin range from 78% to 90% old water, and the daily average  $\delta^{18}\text{O}$  signature results in 80.5% old water. These results assume an instantaneous delivery. Without distributing the time series across the basin, the new water input ends before the hydrograph peaks. By default, the rest of the hydrograph is assumed to be old water. Methods that assume an instantaneous delivery of melt to the stream poorly represent the

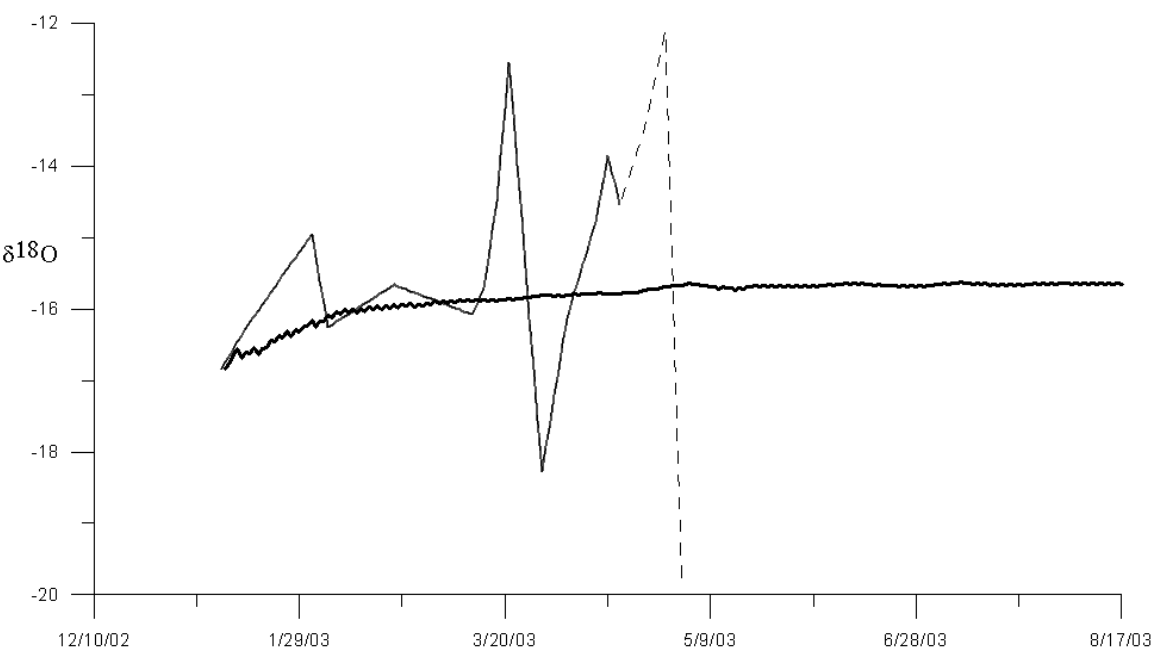
movement of water in a catchment.

A hydrograph separation conducted using methods proposed in this thesis result in 68% old water (Figure 4.7). By accounting for temporal variability, spatial

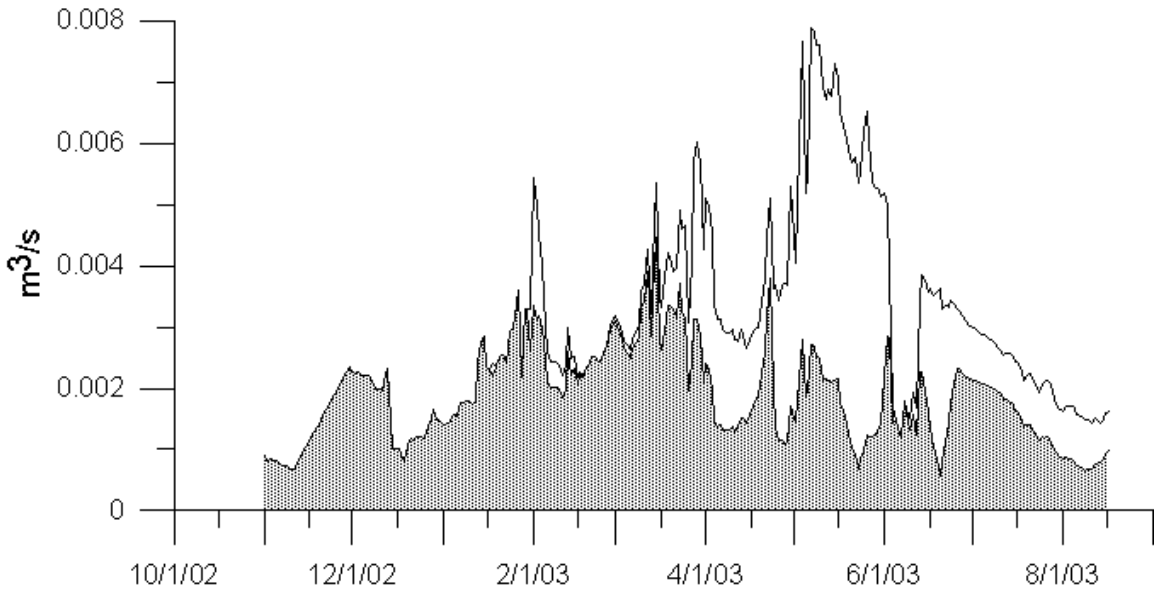
**Table 4.3. Results from hydrograph separations attained by using a variety of methods for the new water isotopic chemistry.**

location	time	sample type	statistic	% old water
w1	constant	core	1 sample	39
w2	constant	core	1 sample	99
w3	constant	core	1 sample	36
w4	constant	core	1 sample	99
w5	constant	core	1 sample	99
e6	constant	core	1 sample	25
e7	constant	core	1 sample	99
e9	constant	core	1 sample	42
e10	constant	core	1 sample	99
e11	constant	core	1 sample	99
e12	constant	core	1 sample	99
basin	constant	core	grand mean	98
w1	constant	melt	daily mean	73
w2	constant	melt	daily mean	68
w3	constant	melt	daily mean	79
w4	constant	melt	daily mean	45
w5	constant	melt	daily mean	74
e6	constant	melt	daily mean	79
e7	constant	melt	daily mean	71
e8	constant	melt	daily mean	73
e9	constant	melt	daily mean	65
e10	constant	melt	daily mean	81
e11	constant	melt	daily mean	71
e12	constant	melt	daily mean	80
basin	constant	melt	grand mean	74
w1	variant	melt	Lin. Interp. Series	80
w2	variant	melt	Lin. Interp. Series	87
w3	variant	melt	Lin. Interp. Series	87
w4	variant	melt	Lin. Interp. Series	84
w5	variant	melt	Lin. Interp. Series	84
e6	variant	melt	Lin. Interp. Series	85
e7	variant	melt	Lin. Interp. Series	81
e8	variant	melt	Lin. Interp. Series	85
e9	variant	melt	Lin. Interp. Series	78
e10	variant	melt	Lin. Interp. Series	90
e11	variant	melt	Lin. Interp. Series	85
e12	variant	melt	Lin. Interp. Series	89
basin	variant	melt	daily average	81
basin	variant	melt	distributed series.	68

variability, and travel time from the hill slope to the stream, a hydrograph separation is performed that accounts for physical process taking place in the basin.



**Figure 4.6. Graph of the daily average enrichment curve and the combined new water input signal. The dashed line is an extension to the daily average enrichment curve that is the melt chemistry from W1 used to represent pixels the valley bottom.**



**Figure 4.7. Hydrograph separation of the 2003 melt event in the BEC showing the old water fraction of streamflow as shaded.**



#### 4.4 Verification and Error Analysis

A hydrograph separation using silica concentrations for new, old, and stream water (Figure 4.8) is conducted to evaluate results of the hydrograph separation using  $\delta^{18}\text{O}$  (Figure 4.9). Lack of silica data restricts the separation to the time period of November 1<sup>st</sup> 2002 to May 31<sup>st</sup> 2003. While much of the falling limb is not included in the hydrograph separation using silica, the climbing limb and peak are included and the separation is considered sufficient to evaluate results from the  $\delta^{18}\text{O}$  separation. The averaged measured snowmelt silica value of 0.21 mg/l results in 77% old water compared to the hydrograph separation using  $\delta^{18}\text{O}$  conducted on the same time period, which results in 69% old water.

A hydrograph separation using silica is complicated by the nonconservative nature of silica as a tracer. As melt water moves through the catchment toward the stream, silica from the granitic soils will be dissolved in the new water resulting in a higher silica concentration, and thus a higher apparent old water percentage. Wels, Cornett, and Lazerte (1991) observed a sharp increase in silica concentrations from zero to 2.5 mg/l within 6 days and then a very small increase in silica concentrations thereafter. Therefore, the silica hydrograph separation resulting in 77% old water is a maximum old water percentage, and the true answer is expected to be less. For example, a hydrograph separation conducted with new water silica concentration of 2.5 mg/l instead of the observed value of 0.21 mg/l results in 70% old water.

Errors in the old water calculations are estimated by following the methods of Genereux (1998). The calculated errors are the confidence in the calculated fraction of

old water.  $\delta^{18}\text{O}$  errors are much bigger than silica errors because the differences in stream, old, and new water  $\delta^{18}\text{O}$  are small, whereas the differences in silica concentrations are large. 69% of the stream water  $\pm 43\%$  at 95% CI ( $\pm 17.6\%$  at 70% CI) is old water based on  $\delta^{18}\text{O}$  data. 77% of the stream water  $\pm 1.25\%$  at 95% CI ( $\pm 0.63\%$  at 70% CI) is old water based on silica data. Methods of Genereux (1998) do not consider the nonconservative behavior of silica, but assume the only errors to be analytical.

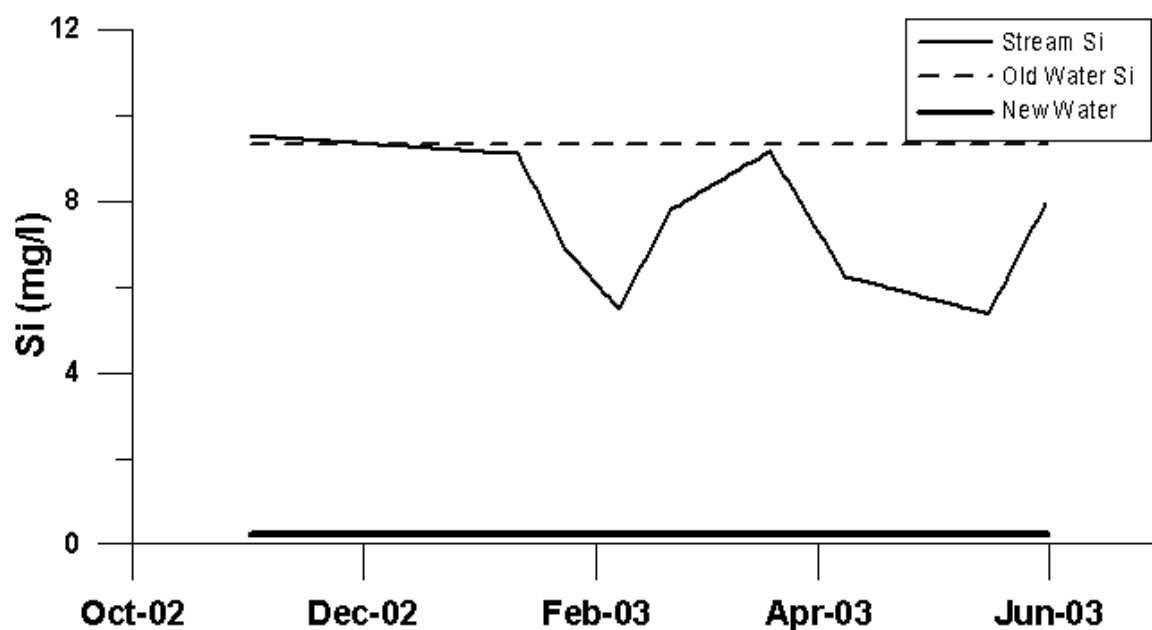
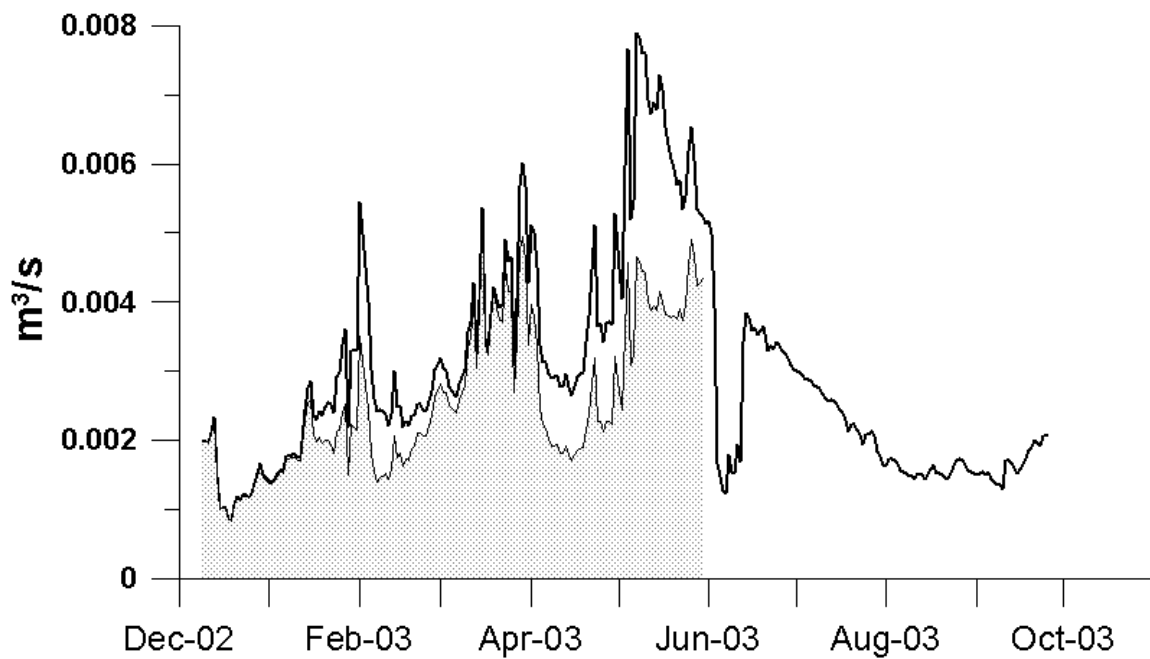


Figure 4.8. Silica concentrations used to perform the hydrograph separation in 4.9.



**Figure 4.9. Hydrograph separation using Silica showing the fraction of old water shaded.**

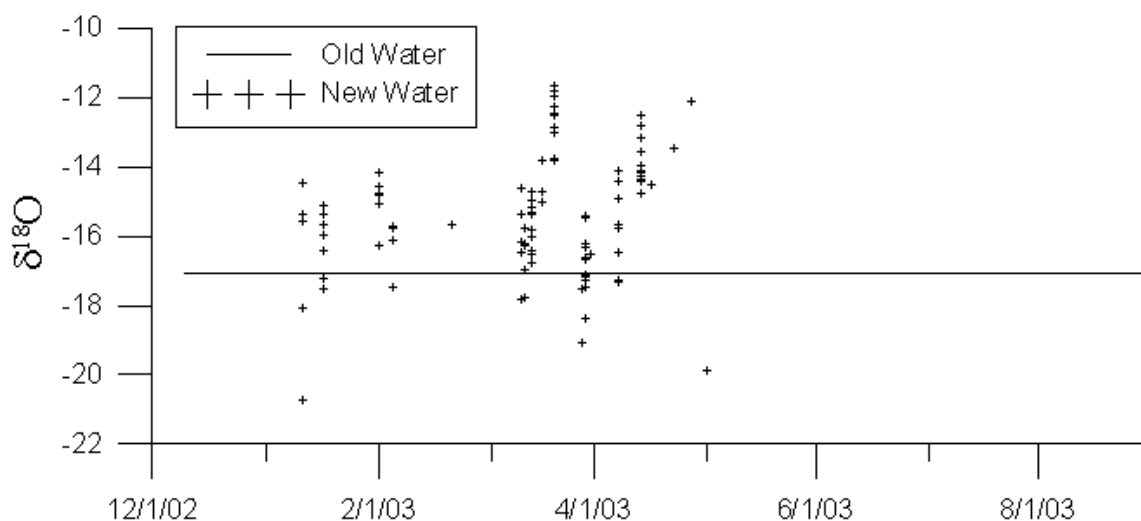
## 5. DISCUSSION

### 5.1 Hydrograph Separation Assumptions

A tracer-based hydrograph separation must meet all five of the assumptions summarized by Buttle (1994) and the instantaneous delivery assumption proposed in this thesis. Only one of the six assumptions is met without consideration, which is the lack of surface storage contributing to streamflow. The following discussion will address each of the six assumptions and methods employed to evaluate them.

#### 5.1.1 Assumption 1: Significant Difference Between New and Old Water Chemistries

The assumption that there is a significant difference between the isotopic content of the new and old water components is met only after the new water input is combined and distributed. Figure 5.1 illustrates the extent that raw snowmelt chemistry data overlaps the assumed old water chemistry. The high variability of the melt chemistry is



**Figure 5.1. Plot of baseflow and snowmelt  $\delta^{18}\text{O}$  showing overlap.**

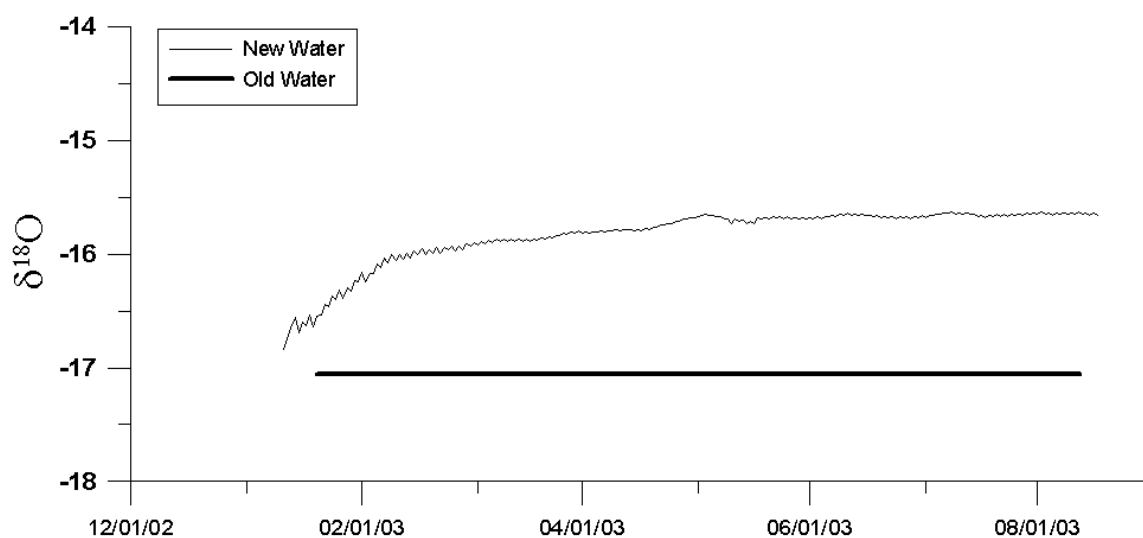
smoothed out after it is combined to give a new water input curve that is significantly enriched with respect to the old water signature (Figure 5.2).

### 5.1.2 Assumptions 2 and 6: New Water is Constant in Time and Space, Instantaneous Delivery

Results show new water melt chemistry is temporally and spatially variable. The construction of a daily average enrichment curve accounts for temporal and spatial variability of new water.

Daily melt chemistries from the entire basin are combined into a daily average enrichment curve because of an uneven distribution of melt sampling points in the basin with respect to distance from the stream, and a similarity of bucket chemistries in time. Figure 5.3 is a histogram of distance to stream distribution in the BEC and frequency of buckets within that distance class.

The similar pattern from individual snowmelt buckets consist of a steep enrichment of  $\delta^{18}\text{O}$  from March 12-18, a subsequent depletion from March 18-30, and another enrichment until snow was melted (Figure 4.4). Bucket W1 is located in the

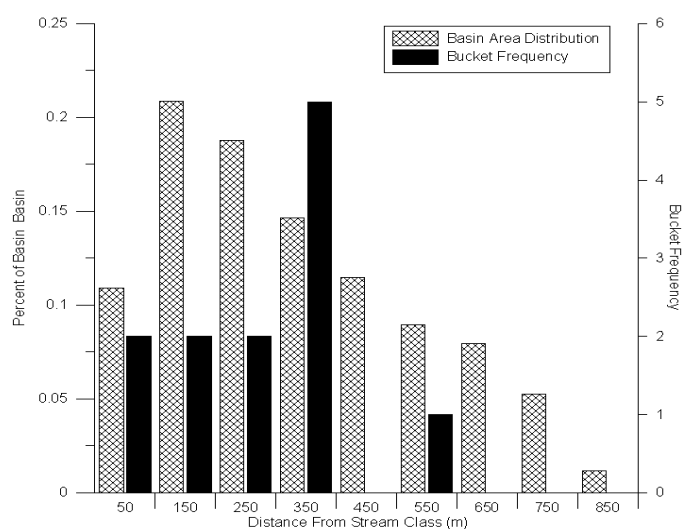


**Figure 5.2. Plot of baseflow and combined input  $\delta^{18}\text{O}$  showing no overlap.**

valley bottom, which maintained snow cover longer than the valley slopes. A daily average enrichment curve constructed including late melt chemistries from bucket W1 is constructed separately from the daily average enrichment curve used for the rest of the catchment. It is depicted as a dashed line extension onto the signal used for the rest of the basin in Figure 4.5.

Construction of the new water chemical input recognizes that melt water entering the basin during the melt event does not all exit the basin immediately when the snow is melted. Instead the basin retards the flow of meltwater to the stream and it is delivered to the stream throughout the hydrograph recession.

Several assumptions are made in constructing the new water isotopic input curve. Assuming a constant Darcy Velocity for melt water assumes that the hill slope is saturated from the first day of melt to the last day of the melt event, and that flow is moving through a uniform porous soil with no preferred pathways. There is also a point in time that decreases in the hydraulic gradient from soils draining, and soil tension slow



**Figure 5.3. Histogram showing distribution of buckets compared to basin area.**

down and eventually stop the movement of melt water to the stream. The hydrograph separation was cut off at August 17<sup>th</sup> 2003 to account for the slowing of the flow to the stream because the stream returned to baseflow. At this point, the new water stored in the basin would become old water to be lost from the basin by evaporation and transpiration, or released to the stream during baseflow or another event.

By weighting the daily average input curves exclusively with fraction of basin area, no attempt is made to weight inputs by volume. By not taking volume into account, the assumption is made that melt volume is equal in time and space during the melt period.

#### 5.1.3 Assumption 3 and 4: Old Water Chemistry is Constant in Time and Space, Soil Water Contributions are Negligible

A constant old water  $\delta^{18}\text{O}$  value is commonly used when post event stream concentrations return to preevent concentrations after the event (Dincer et al., 1970); (Pinder and Jones, 1969). A constant value of  $-17.06\text{‰}$  is used as the old water concentration in the BEC. This method assumes baseflow concentrations represent old water concentrations (Bonell, Pearce, and Stewart, 1990). The use of baseflow concentrations as old water chemistry is supported by observations by Hooper and Shoemaker (1986), who observe deuterium values from piezometers that are indistinguishable from baseflow stream values.

The use of a constant old water  $\delta^{18}\text{O}$  value does not consider the possible contribution of vadose water to the system. The assumption that soil water is not a considerable contributor to streamflow as stated in assumption 4 is questionable in the majority of hydrograph separation studies. Soil water is often much more enriched in

isotopes compared to groundwater as a result of evaporation and transpiration (Sklash and Farvolden, 1979). Kennedy, Kendall, Zellweger, Wyerman, and Avanzino (1986) state that it is impossible for groundwater close to the stream to contribute large quantities to streamflow based on bedrock permeability of many previously studied basins. Instead it is thought that a rise in the water table mobilizes a significant quantity of preevent soil moisture.

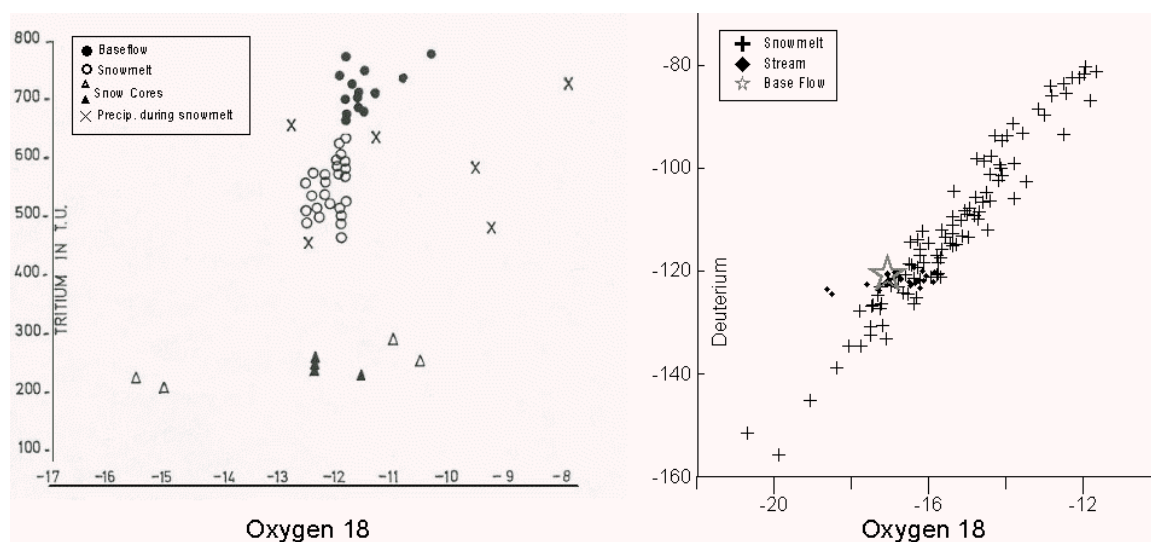
Hooper and Shoemaker (1986) assumed soil water contributions to be negligible because of the thin and highly porous unsaturated zone in a catchment in New Hampshire. Sklash and Farvolden (1979) also assumed negligible soil water contributions based on a combination of low topographic relief and high hydraulic conductivity of soils of a one square kilometer watershed in northern Quebec. They also observe  $\delta^{18}\text{O}$  values of soil groundwater (-12.8) and bedrock groundwater (-11.9) to be very similar to summer (-11.9) and winter (-12.6) baseflow (Sklash and Farvolden, 1979).

An end member mixing diagram is constructed using  $\delta^{18}\text{O}$  and deuterium to evaluate assumption 4 using methods described in Dincer et al. (1970) and Moore (1989) (Figure 5.4). According to this method, a source other than baseflow and new water contributing to streamflow would show up as a shift in the stream water away from the line connecting the new water concentration and the baseflow concentration. Figure 5.4 a shows the snowmelt runoff chemistry from a catchment in northern Czechoslovakia occurring between the baseflow (old water) and snow core (new water) points on the mixing diagram (Dincer, et al., 1970). Soil water contributions to streamflow are not expected in this case because there is no deviation from a line connecting new and old water. Figure 5.4b is a mixing diagram from the BEC showing no distinct line between



the snowmelt concentration (new water) and baseflow (old water). It is impossible to determine if soil water is contributing to streamflow from this method.

Another end member mixing diagram is constructed using discharge versus  $\delta^{18}\text{O}$  to evaluate the presence of soil water in streamflow. According to Sklash and Farvolden (1979), the presence of soil water in streamflow should cause a deviation in  $\delta^{18}\text{O}$  during the falling limb towards enrichment compared to the rising limb. Figure 5.5a is a schematic of an expected deviation in streamflow chemistry if soil water is contributing to streamflow. Figure 5.5b is data from the BEC showing no expected pattern in stream chemistry to evaluate the presence or absence of soil water contributions to streamflow. Figures 5.4 and 5.5 give insufficient evidence to conclude that there is a distinguishable, separate soil water contribution to streamflow. However, the thin sandy soils overlying fractured bedrock would not provide a sufficient reservoir for soil water in the BEC.



**Figure 5.4. End member mixing of isotopic stream chemistries between baseflow and snowmelt comparing: a) a previously published model using tritium and  $\delta^{18}\text{O}$ , and b) deuterium and  $\delta^{18}\text{O}$  data from the Bogus Experimental Catchment showing a wide variation in melt chemistries. Stream points should lie on a line between melt points and the baseflow point represented by the star (Modified from Dincer, 1970).**

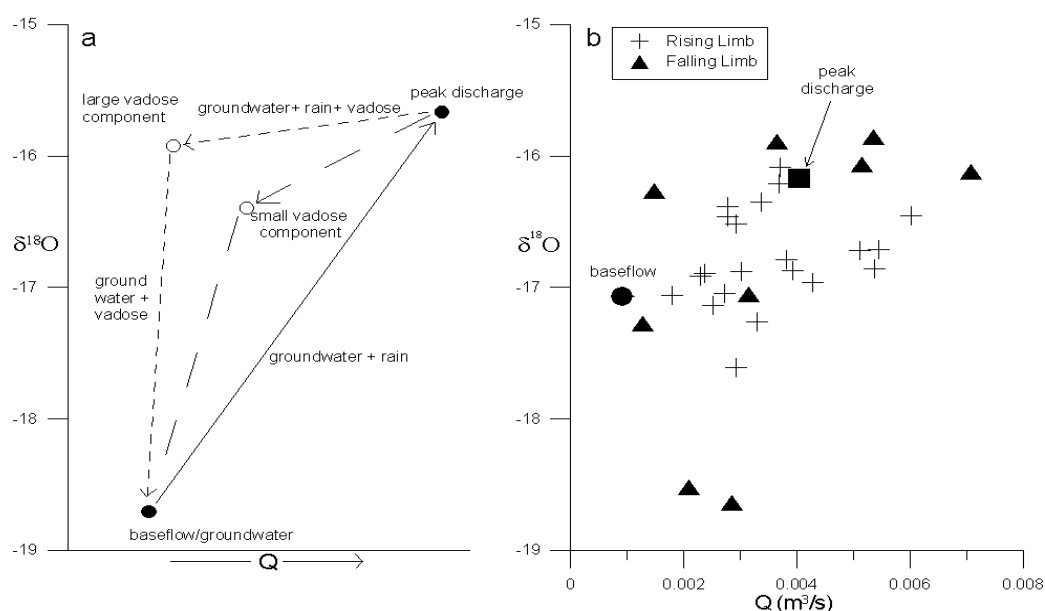
Summers typical of the Boise Front are also hot and dry, which would significantly reduce the volume of soil water through evaporation and transpiration.

#### 5.1.4 Negligible Contribution of Surface Storage.

Surface storage is not a significant contributing source of streamflow based on the catchment having sandy soils with a very high permeability. Physical evidence indicating the existence of surface storage is never observed.

### 5.2 Hydrograph Separation Input Data

Snowmelt from the spring of 2003 is enriched with respect to the baseflow  $\delta^{18}\text{O}$ . The vast majority of other studies observe melt concentrations that are depleted with respect to baseflow as a result of evaporative enrichment that occurs throughout the summer months. This observation may be a result of old water in the basin originating from melt with distant, high elevation origins where the temperature is lower. Another possibility is that the old water has a long mean residence time and originates from



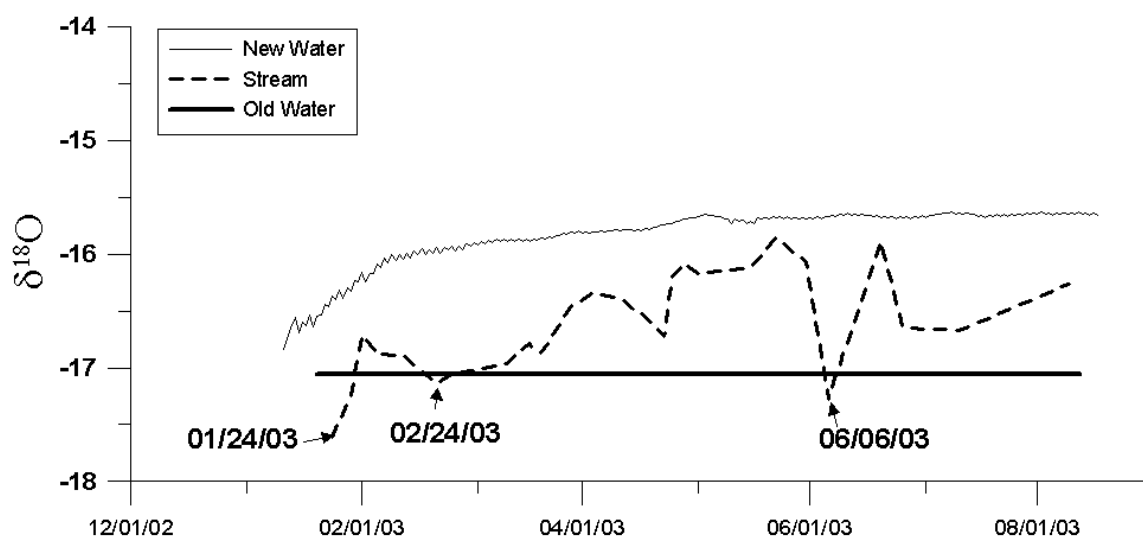
**Figure 5.5. Mixing diagram of  $\delta^{18}\text{O}$  vs. discharge comparing a) a theoretical model and b) data from the Bogus Experimental Catchment showing a lack of clear linear trend. (Modified from Sklash and Farvolden (1979)).**

historically colder winters.

Figure 5.6 shows that stream samples collected on January 24<sup>th</sup>, February 24<sup>th</sup>, and June 6<sup>th</sup> lie below the assumed old water concentration. Errors during the time when stream  $\delta^{18}\text{O}$  concentrations are more depleted than old water result in over 100% old water fraction of total streamflow. Old water fraction to streamflow is assumed to be 100% for these times (Huth, Leydecker, Sickman, and Bales, 2002).

The stream  $\delta^{18}\text{O}$  depletion on June 6<sup>th</sup> occurs at the same time as a dramatic decrease in stream discharge (Figure 4.1). There is no reason to expect that this is equipment failure as the pressure transducer records an increase back to normal recession levels in the absence of anyone servicing the equipment. No seismic disturbance is recorded during this time and there is no climatic reason for the decrease in flow and  $\delta^{18}\text{O}$ . Stream conductivity records show nothing out of the ordinary.

Another reason for the late depletion in stream water on June 6<sup>th</sup> may be explained by the late melt chemistry of bucket W1, which is located in the valley bottom.



**Figure 5.6.  $\delta^{18}\text{O}$  of baseflow, melt, and stream showing streamflow concentrations dropping below the baseflow concentrations.**

Melt from W1 on May 2<sup>nd</sup> 2003 has an  $\delta^{18}\text{O}$  of  $-19.87$  (Figure 4.1). If the late depletion from W1 is representative of the snow remaining on the valley bottom, there may have been a significant enough snowpack remaining on the valley bottom to deplete the stream when it melted. The daily average input curves that include late melt from W1 do a good job of representing depleted late melt, however, when it is combined with the daily average curves representing the rest of the basin, the new water input curve does not depict this depleted melt water input. The errors in the hydrograph separation resulting from stream  $\delta^{18}\text{O}$  on January 24<sup>th</sup> and February 24<sup>th</sup> being lower than baseflow  $\delta^{18}\text{O}$  occur during the rising limb of the hydrograph when old water contributions are usually close to 100%. Total errors due to overlap of  $\delta^{18}\text{O}$  during the 2003 melt event at the BEC occupy only 4.6% of the event flow.

### 5.3 The Hydrograph Separation

The water year of 2003 for the Bogus stream is characterized by 3 flow pulses (Figure 4.6). The first pulse, centered on January 12<sup>th</sup>, is the result of temperatures climbing above zero for the better part of January. The majority of the first flow pulse is composed of old water being pushed out of the basin by new meltwater. Temperatures climbing well above zero in March and April cause the second flow pulse, of which the majority of is also old water. The third flow pulse represents the main melt event. Temperatures climb and stay above zero in the middle of April. Much of the main melt event is composed of new water that is assumed to have worked through the basin from all three melt pulses.

## 6. CONCLUSIONS

Hydrograph separations using a variety of methods to account for the new water chemistry result solutions ranging from 25% to 99%. By accounting for the spatial and temporal variability of melt water chemistry, and travel time of melt water from the hill slope to the stream, an isotopic hydrograph separation can be performed on a snowmelt event with complicated hydroclimatic conditions. Reliability of the isotopic hydrograph separation is dependent on sampling snowmelt throughout the entire melt period in many locations within the basin.

Melt  $\delta^{18}\text{O}$  is highly variable in time and space. Catchment scale controls, such as elevation, aspect, and slope do not account for  $\delta^{18}\text{O}$  variability in the BEC. Small-scale experimentation reveals that significant variability in  $\delta^{18}\text{O}$  exists within approximately two meters. The most effective way to characterize melt  $\delta^{18}\text{O}$  is to sample from many locations within a catchment throughout the melt event.

Streamflow during melt events in semiarid environments is composed mostly of old water: 68% in the case of the BEC in the Dry Creek Experimental Watershed. Timing of melt water in the stream is characterized by delivery of old water to the stream during the rising limb and into the peak of the hydrograph, then new water dominating the hydrograph during the recession. Early snowmelt simply infiltrates into the hill slope and moves down slope, which increases the hydraulic gradient and displaces old water into the stream. As melt continues and the hydrograph peaks, new water from early melt

has moved through the hill slope and toward the stream. Late melt keeps the hill slope saturated and connected as well as maintains the hydraulic gradient.

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