THE HYDROLOGY OF HEADWATER CATCHMENTS FROM THE PLAINS TO THE CONTINENTAL DIVIDE, BOULDER CREEK WATERSHED, COLORADO

By

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THE HYDROLOGY OF HEADWATER CATCHMENTS FROM THE PLAINS TO THE CONTINENTAL DIVIDE, BOULDER CREEK WATERSHED, COLORADO

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form met acceptable presentation standards of scholarly work in the above mentioned discipline

ABSTRACT

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The Hydrology of Headwater Catchments from the Plains to the Continental Divide, Bolder Creek Watershed, Colorado

Thesis directed by Professor Mark W. Williams

Isotopic composition of precipitation, snow cover, snow melt, and stream flow were determined in three snow dominated headwater catchments to quantify the spatial variability and processes that alter stable isotope (oxygen-18, ^{18}O and deuterium, ^{2}H) composition across an elevational gradient and between open and under canopy environments. Across the three catchments there was no significant difference in $\delta^{18}O$ in precipitation but a significant difference was found within the snow pack and snow melt. Within each of the catchments there was no significant difference in $\delta^{18}O$ in precipitation landing in open and under canopy environments. At the two lowest elevation sites significant differences between open and under canopy snow pack $\delta^{18}O$ were observed but there was no significant differences in $\delta^{18}O$ of snow melt between open and under canopy settings at any location.

Additionally, isotopic ($\delta^{18}O$ and ^{3}H (tritium)) and geochemical (Na^{+}, Si, and DOC) tracers were used to investigate residence times, source waters, and flow paths in four headwater catchments along a 2,310 m elevational gradient within the Boulder Creek Watershed. The amount and type of precipitation occurring across the elevational gradient was also produced. Precipitation totals from 2009 ranged from 563 mm at 1800 m to a high of 1214 mm at 3528 m. The precipitation was 85% snow at the highest elevation and only 32% snow at the lowest elevation. Application of a convolution integral to the $\delta^{18}O$ values in precipitation and stream waters produced relatively short mean residence times ranging from 1.12 years in the alpine to

2.08 years in the lower montane ecosystem. Tritium analysis indicated relatively young surface water ages and supported the results from the residence time calculations. Two-component mixing models were run using $\delta^{18}O$ to identify new and old waters and Silica (Si) to identify reacted and un-reacted waters. All streams consisted of greater then 50% old and greater than 50% reacted waters with the peaks in new and un-reacted water occurring during hydrograph recession. These results indicate that headwater catchments within Boulder Creek Watershed have relatively short groundwater residence times and that groundwater plays an important role in stream flow generation.

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Isotopic Variation of Precipitation, Seasonal Snow Cover, and its Melt Across an Elevational Gradient in Boulder Creek Watershed, Colorado

Abstract

Isotopic composition of precipitation, snow cover, snow melt, and streamflow was determined in three snow dominated headwater catchments to quantify the spatial variability and processes that alter stable isotope (oxygen-18, ^{18}O and deuterium, ^{2}H) composition across an elevational gradient and between open and under canopy environments. Three catchments spanning a 1500 m elevational gradient were instrumented prior the start of the study. Meteorological data, precipitation, snow melt, and streamflow were continuously monitored during the study. Isotopic analysis of precipitation and snow pack were conducted weekly through the 2009-2010 winter season. Values of $\delta^{18}O$ varied between -29.3 and -9.4 ‰, and δD varied between -220.2 and -58.8 ‰ for winter precipitation. Isotope concentrations from snowpack samples varied between -27.2 and -18.1 ‰ for $\delta^{18}O$, and between -202.7 and 129.3 ‰ for δD. Isotopic concentrations from snow melt samples varied between -21.2 and -12.8 ‰ for $\delta^{18}O$, and between -157.4 and -89.5 ‰ for δD. These ranges reflect differences in precipitation, accumulation, sublimation, and melting of the snow cover across a wide range of conditions within the watershed. Across the three catchments there was no significant difference in $\delta^{18}O$ in precipitation but a significant difference was found within the snow pack and snow melt. Within each of the catchments there was no significant difference in $\delta^{18}O$ in precipitation landing in open and under canopy environments. At the two lowest elevation sites significant differences between open and under canopy snow pack $\delta^{18}O$ were observed but there was no significant differences in $\delta^{18}O$ of snow melt between open and under canopy settings at any location. This study will provide a useful index of the isotopic composition of precipitation, snow pack, and snow melt across headwater catchments that span from the montane to the alpine in the Colorado Front Range.

1.1 Introduction

An important part of the water supply in the western United States comes from stream runoff fed by mountain snowmelt (Cayan, 1996; Lee et al., 2009; Nayak et al., 2010). In addition to significant surface water contributions, snowmelt is also the largest contributor to groundwater recharge in many northern and alpine environments (Koeniger et al. 2008). The precipitation in mountains at mid-latitude in the Northern Hemisphere is strongly winter dominant and therefore snow accumulation (along with storage in the soil and groundwater) is the primary physical mechanism by which winter precipitation is stored and then transferred to surface waters during the relatively dry summers typical of the western United States (Hamlet et al., 2005).

A study at the Green Lakes Valley, Colorado by Caine (1995) showed that snowmelt provides upwards of 80% of the total annual water budget for alpine areas of the Front Range of Colorado. If predicted climate warming over western North America results in trends towards more rain and less snow, that may alter spatial distributions of snow accumulation and the timing of melt (Nayak et al., 2010) with consequent changes in groundwater recharge and flow in streams. Hamlet et al. (2005, 2007), Mote et al. (2005), and Stewart et al. (2005) have all demonstrated that sizable changes in spring snow accumulation and runoff timing have accompanied twentieth century warming across much of the western United States, making a compelling argument that advances in understanding the spatial and temporal dynamics of snow properties will greatly increase our understanding of the susceptibility of mountain ecosystems to changes in climate. Since snow dynamics are highly variable in space and time (Lundquist et al., 2002; Erickson et al., 2005) and in relation to vegetation structure and density (Molotch et al., 2009), it is appropriate to study how such changes in snow dynamics will impact hydrological processes across a spread of climactic conditions at the watershed scale.

One of the more recent advances in understanding hydrological processes has come through the analysis of stable water isotopes ($\delta^{18}O$ and δD) to study water cycles and movement through watersheds, e.g. studies in evapotranspiration (ET), groundwater recharge, and runoff (Campbell et al., 2002; Unnikrishna et al., 2002; Lui et al. 2004). The isotopic composition of localized precipitation tends to plot on or near the global meteoric water line (GMWL) (Dansgaard, 1964), and areas with distinct seasonality receive rain that is isotopically heavier than snow (Clark and Fritz, 1997). If the isotopic compositions of inputs to a watershed (rain and snow melt) along with those of ground water and surface waters are known, then theoretically mixing models can be used to determine the relative contributions of rain and snow to the hydrological processes of groundwater recharge and stream flow generation. However, care must be taken in defining end-member isotopic compositions derived from snow because in alpine and mountain environments a variety of processes including isotopic fractionation from evaporation, isotopic exchange between liquid water and ice, and isotopic exchange between vapor and ice, can all affect isotopic composition (Taylor et al., 2001; Earman et al., 2006; Zhou et al., 2008; Lee et al., 2009). Therefore it is necessary to decipher which physical and climactic variables regulate the isotopic exchange processes and to what extent those variables change across a watershed.

In regards to elevation, research conducted across many mountain regions of the world have shown that, in general, the stable isotopes of precipitation become more depleted with increasing elevation (i.e. Siegenthaler and Oeschger, 1980; Niewodniczanski et al., 1981), but neither the existence of an "isotopic lapse rate" has been reported for the Colorado Front Range.

The Colorado Front Range does experience a decrease in temperature with elevation (Barry, 1973), which may alter evaporation rates across the watershed. Chowdhurry et al., (2008) suggests that examining the slope of the $\delta^{18}O$- δD regression line in surface waters reveals information about the amount of evaporation that has occurred to the water relative to the local meteoric water line (LMWL) of incoming precipitation. For example, a study conducted in mountain regions of Idaho and Montana by Cecil et al., (2005) found surface waters had decreased slopes relative to the LMWL and suggested that recharge, dominated by winter precipitation, had undergone evaporative fractionation during infiltration.

Interestingly, recent work conducted in the southwestern United States by Earman et al., (2006) reports that high snow pack sublimation rates are responsible for decreasing the slope of the $\delta^{18}O$- δD relationship and that the isotopic composition of snow tends to change depending on time spent on the ground. Additional work conducted in the Fraser experimental forest in Colorado by Stottlemyer and Troendle (2001) showed that up to 36% of snowfall can be intercepted by tree canopies and research in the sub-alpine forests of the Colorado Front Range by Molotch et al., (2007) found that average daily sublimation rates of intercepted snow were 1.6 times greater than rates of sublimation from snow on the ground. The increased sublimation rates and increased potential for vapor ice exchange from canopy interception may also be linked to isotopic enrichment of the resulting throughfall. Claassen and Downey (1995) found that in a high altitude (3500 m) watershed in the Colorado Rocky Mountains median enrichments observed in throughfall of snow intercepted on evergreens were observed to be 2.1‰ in $\delta^{18}O$ and 13‰ in δD.

However, recent research by Zhou et al., (2008), Lee et al. (2009) and others show that a similar change in isotopic enrichment may occur because of phase changes associated with the melting of snow. Lee et al., (2009) suggests that the slope of liquid water in snow melt will be significantly lower than the slope of the LMWL due to the isotopic exchange between ice and the liquid water that is generated by melt at the surface as it flows through the snowpack by percolation.

Previous research has clearly shown that the variety and magnitude of processes influencing the isotopic evolution of snow from new precipitation to melt are both interactively dynamic and widespread. It is unclear to what degree the above mentioned processes are occurring and interacting at the watershed scale in the Colorado Front Range, and if the resulting variations are significant enough to affect hydrologic mixing models parameterized with stable water isotopes.

In this research we investigate the isotopic variations in precipitation and the isotopic evolution of the resulting snowpack, snowmelt and surface waters. Intensive sampling was conducted from January 1, 2009 until May 31, 2010 across three headwater catchments spanning a 1,596 m elevational gradient from the montane forests to the continental divide in the Colorado Front Range. Sampling occurred in both open and under canopy environments at locations below treeline. Specifically, this research investigates changes of $\delta^{18}O$ and δD compositions of snow across the headwater catchments to quantify how elevation and forest vegetation influences stable water isotopes during the many transitions between incoming precipitation and outgoing surface waters.

The specific research questions are:

1. How does the isotopic composition ($\delta^{18}O$ and δD) of precipitation vary with elevation at both annual and seasonal time scales?

2. How does the isotopic evolution of snow pack vary with elevation and between open and under canopy environments?

3. How does the isotopic composition of snow pack at maximum accumulation vary with elevation?

4. How does the isotopic evolution of snow melt vary with elevation and between open and under canopy environments?

5. How does the magnitude and timing of snow melt vary with elevation and between open and under canopy environments?

6. How does the isotopic composition of surface waters vary with elevation and in relation to snow melt and precipitation inputs?

1.2 Study Area

The Boulder Creek Watershed is located on the eastern side of the Colorado Front Range, is about 1160 km^2 in area, and extends from an elevation of 4,120m at the Continental Divide to about 1,480 m on the eastern plains (Figure 1.1). Here we focus on three headwater catchments of the Boulder Creek Watershed: 1) the alpine Green Lakes Valley, 2) the sub-alpine Como Creek, and 3) the montane Gordon Gulch. Research activities at these sites are supported by a combination of the Niwot Long Term Ecological Research (NWT LTER) program and the Boulder Creek Critical Zone Observatory (BC-CZO). The underlying bedrock is similar among the four catchments, Precambrian crystalline rock that is primarily granodiorite, with nearly equal percentages of gneiss and schists in the alpine and becoming predominantly gneiss in the montane (Braddock and Cole, 1990).The upper Green Lakes Valley is an east-facing glacial valley, headed on the Continental Divide in the Colorado Front Range (40°030N, 105°350W). Named for a series of shallow paternoster lakes, the Green Lakes Valley is the headwaters of North Boulder Creek and lies within the City of Boulder Watershed. The upper valley is approximately 225 ha in area, and the elevation ranges from 4084 m at the Continental Divide to 3515 m at the outlet of Green Lakes 4 (GL4) (Figure 1.1). The catchment is dominated by steep rock walls above talus slopes and rock glaciers with a stepped valley floor of glacially scoured bedrock. GL4 is a typical alpine headwater catchment in the Colorado Front Range where active and inactive rock glaciers are indicative of underlying permafrost (Janke, 2005). Patterned ground and active solifluction lobes are also common in parts of Niwot Ridge and Green Lakes Valley, especially on ridgelines (Benedict, 1970). Permafrost has been verified above 3500 m on Niwot Ridge (Ives and Fahey, 1971) and more recently by geophysical methods near Green Lake 5 (Leopold et al., 2008). All of the catchment is above treeline, with about 20% of the catchment covered by soils: Cryic entisols and inceptisols on hillslopes, with histosols found on wetter sections of the valley floor (Williams et al., 2001). Coarse debris, including talus slopes, blockslopes, and rock glaciers, cover about 45% of the GL4 catchment. This coarse debris is poorly sorted, generally unconsolidated and includes a range of particle sizes from clays to boulders more than 2 m in diameter (Williams et al., 1997).

Como Creek originates just to the North and East of Green Lakes valley on the southeast flank of Niwot Ridge approximately 8 km east of the Continental Divide and 26 km west of Boulder, CO (Figure 1.1). The catchment falls within the Niwot Ridge Biosphere Reserve, has an area of 664 ha, and ranges in elevation from 2900 m to 3560 m. Approximately 80% of the catchment is below treelike (Lewis & Grant, 1979). The catchment is primarily coniferous forest that is about 100 years old and has a mixture of trees dominated by Engelmann spruce (*Picea engelmannii*), sub-alpine fir (*Abies lasiocarpa*), limber pine (*Pinus flexilis*) and lodgepole pine *(Pinus contorta)*, with some aspen (*Populus tremuloides*). The landscape near treeline is characterized by high-elevation meadows bounded by ribbon forest. These meadow soils are classified as a mixed Type Humicryepts, sandy-skeletal in texture (Williams et al., 2009). Texture is a loamy sand to gravel with little clay content and is moderately well-drained. Within and adjacent to the catchment there are three sites which collect research information, the Saddle site, Soddie site, and C-1 (Figure 1.1). The Saddle site (40º 03’ 17” N; 105º 35’ 21” W; 3528 m) is located in alpine tundra with research infrastructure including snow and soil lysimeters, a subnivean laboratory, a snow-fence experiment, and an aerometrics wet-chemistry precipitation collector, which is part of the National Atmospheric Deposition Program (NADP) (site CO02). Groundwater wells were installed at the Saddle site in the fall of 2005. Wells were drilled to a depth of 9 m, cased, and screened at the bottom 1.6 m. The Soddie site (40º 02’ 52” N; 105º 34’

15” W; 3345 m) is located in the treelike ecotone within the Como Creek catchment. This site also has an aerometrics wet-chemistry precipitation collector that is sampled simultaneously with the NADP sites but is not part of the official NADP program. The C-1 site (40º 02’ 09” N; 105º 32’ 09” W; 3021 m) is part of a long-term meteorological study that has recorded continuous climate measurements since the 1950’s (e.g. Williams et al., 1996) and participates in the Ameriflux program (Monson et al., 2002). The site at C-1 also contains an NADP site (CO90) that was established in 2006. The site has a mean annual temperature of 1.5 °C and receives about 800 mm of precipitation annually, with 60% in the form of snow and 40% in the form of rain (calculated from a 10-year average).

Gordon Gulch is a small (1.014 km^2) sub-catchment in a mixed conifer montane ecosystem at 2500 m elevation (range 2400 to 2650m) (Figure 1.1). Gordon Gulch is a predominantly west to east drainage resulting in distinct north and south facing slopes representing distinctly different vegetation communities. The north aspect slopes are dominated by Lodgepole pine (*Pinus contorta)* stands of nearly uniform size and age characteristics, along with the more shade tolerant Rocky Mountain Douglas-fir (*Psuedotsuga menziesii* var. *glauca*) and Colorado Blue Spurce (*Picea pungens*). The south aspect slopes have a more open and mosaic patchwork of Ponderosa pine (*Pinus ponderosa*), interspersed with Rocky Mountain Juniper (*Juniperus scopulorum*) and common shrubs including Mountain-mahogany (*Cercocarpus spp*.) and Hawthorn (*Crataegus spp*.). Gordon Gulch is characterized by the low-relief remnants of a dissected Tertiary erosion surface. Results from applied geophysical characterization of the subsurface show that unconsolidated materials are generally 1 to 2 m thick while weathered bedrock profiles extend to depths of 11 to 15 m (Befus, 2010).

Precipitation measurements for Gordon Gulch are collected at the Sugarloaf NADP site (CO94) located about 2 km away in an adjacent catchment at 2524 m.

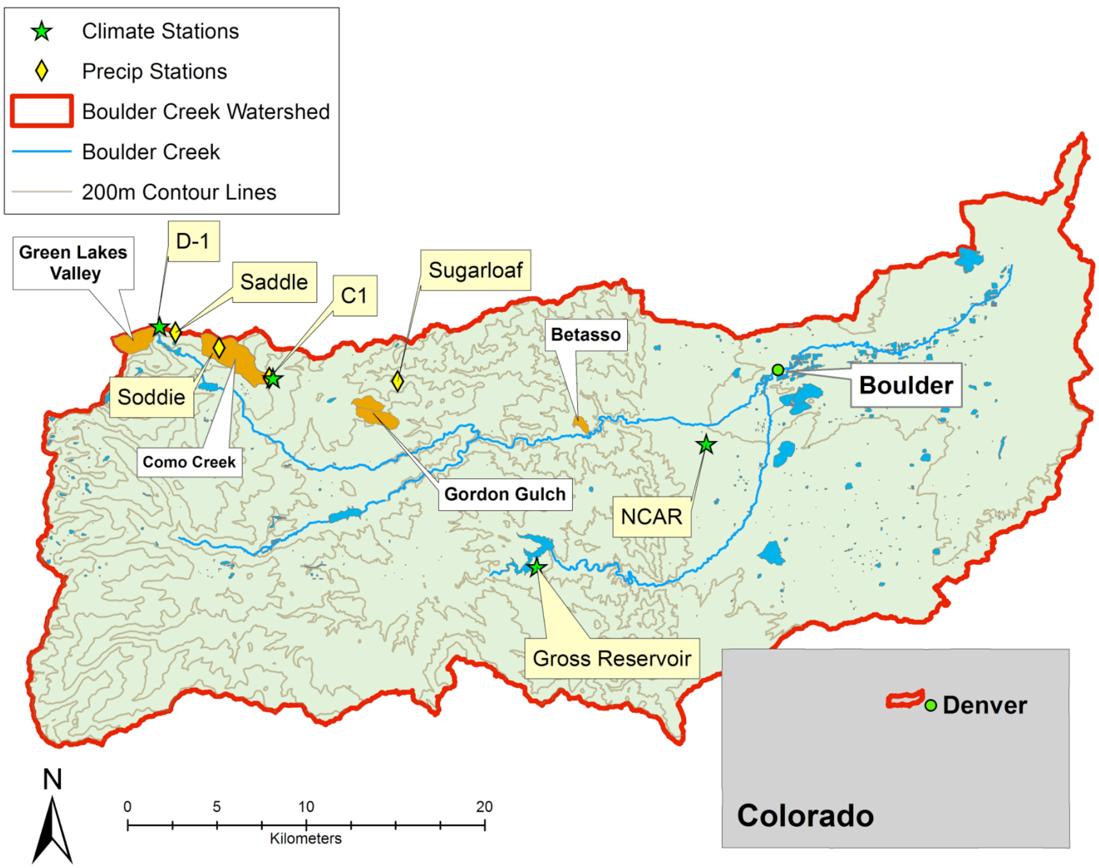

Figure 1.1: Boulder Creek watershed showing locations of each of the four headwater catchments along with the locations of climate and precipitation measurement stations. All snow pack and snow melt sampling occurred adjacent to the precipitation stations except Gordon Gulch where sampling occurred within the catchment near the gauging station rather than at the Sugarloaf precipitation station. The elevation of the watershed ranges from a high of 4120 m along the western boundary to a low of 1420 m in the eastern plains.

1.3 Data and Methods

1.3.1 Precipitation sampling

The Niwot Ridge/Green Lakes Valley LTER site participates in the National Atmospheric Deposition Program (NADP), which operates about 200 wet precipitation collectors throughout the continental United States. NWTLTER operates NADP sites at the Saddle alpine ecosystem (CO02, elevation 3525 m), the sub-alpine ecosystem (CO90, elevation 3021 m), and montane ecosystems (CO94, elevation 2524 m). Another unofficial NADP site using the same instruments and protocols is located just below treeline at the Soddie site (elevation 3345 m). Samples are collected weekly and analyzed using the same protocols, so that precipitation chemistry may be compared among sites. The NADP program does not analyze for stable water isotopes. This research analyzed splits of the NADP samples for stable water isotopes.

These precipitation samples were complemented by additional measurements to evaluate the potential changes in the isotopic values of winter precipitation caused by canopy interception of snowfall from 1 October 2009 to 31 May 2010. Buckets open to the atmosphere, and similar in design and shape to those used by the NADP aerochem metrics, were placed in the open and under tree canopies, located adjacent to the NADP collection towers, to collect through-fall and/or canopy intercepted precipitation before it reached the ground. Due to easier access to sampling sites at the lower elevation Gordon Gulch site, additional precipitation collectors were placed under canopies of each of the dominant coniferous tree species to provide a more detailed under canopy sample set at this location. The buckets collecting precipitation in an open setting were placed directly on or adjacent to the NADP collection stands to test for compatibility of experimental design. All additional buckets were sampled on the same weekly time steps as the

NADP collections and the under-canopy sampling buckets were located beneath the nearest canopy to the open collection sites to minimize spatial variability. Precipitation amounts were recorded by a Belfort precipitation gauge located adjacent to the precipitation collection tower at each site. Each collection tower is also co-located with standard meteorological instruments. Due to the over-collection of winter precipitation (October-May) in the form of blowing snow at the Saddle site (CO02), the winter precipitation amounts at the Saddle were reduced by 39% following the recommendations of Williams et al. (1998).

1.3.2 Snowpack Sampling

The snowpack in all catchments was sampled approximately weekly throughout the 2009-2010 winter season when the snowpack depth was greater than 30cm. Snow pits were sampled for chemical content, physical properties, and oxygen isotopes following the protocol of Williams et al (2009). Snow samples were collected for chemical and oxygen isotopic analysis using beveled PVC tube (50-mm diameter, 500-mm long), which had been soaked in 10% HCL and then rinsed at least five times with deionized water. Duplicate, vertical, contiguous cores were collected from the snow-air interface to the snow-ground interface. Snow was transferred from the cores into new polyethylene bags and transported to our analytical laboratory the same day as collection.

Approximately once a month each of the pits was analyzed further by collecting snow samples for every 10 cm interval from the snow-air interface to the snow-ground interface using a Snometrics density sampler. The snow was transferred into new polyethylene bags and transported to the laboratory for analysis of water isotopes. Additionally, a one-time sampling of the snowpack in open- and under- canopy settings was conducted on April 12, 2010. The under-canopy snow pits were located adjacent to the regularly sampled open locations and were co-located with the under-canopy precipitation collectors. All snow pits sampled on April 12, 2010 were analyzed following the same procedure outlined for the monthly sampling.

1.3.3 Snow Melt Sampling

The chemical and isotopic content of snowmelt was continuously measured by collecting snowpack melt-water in lysimeters before contact with the ground. At the Saddle site melt water was collected in 1.0-m^2 lysimeters and flowed by gravity through PVC pipes into a subnivian laboratory where melt volumes were recorded using tipping bucket rain gauges attached to a Campbell Scientific CR10X data logger and melt water was collected in 250 mL HDPE bottles at approximately daily intervals throughout the melt season (Williams et al. 1999) At the Soddie site, melt water was collected in 0.2-m^2 lysimeters and flowed by gravity through PVC pipes into a subnivian laboratory, were melt volumes were measured using tipping bucket rain gauges attached to a Campbell Scientific CR10X data logger (Williams et al. 2009). Melt water for isotopic analysis was collected in 250-mL HDPE bottles at approximately daily intervals throughout the melt season. At Gordon Gulch, melt water was collected in 0.2-m^2 lysimeters and flowed by gravity through PVC pipes directly into 1-L HDPE collection bottles that were changed out on a weekly basis throughout the winter snowmelt season. Due to limitations in sampling design at Gordon Gulch the melt volumes were not recorded by tipping buckets. At both the Soddie site and Gordon Gulch snowmelt lysimeters were placed in open meadows and under canopies of the most common tree species. The melt lysimeters were placed under the same canopies as the precipitation collectors to minimize spatial variations in the isotopic content of falling snow.

1.3.4 Surface and Groundwater Sampling

Collection of water samples for chemical and isotopic analyses followed the sampling protocols presented in Williams et al. (2006; 2009). Surface water samples for chemical analyses were collected weekly as grab samples from GL4 outlet, Como Creek, and Gordon Gulch, at the same location as discharge measurements. Water samples for isotopic analysis were collected un-filtered in cleaned, 25-mL, borosilicate bottles with no-headspace lids to avoid any evaporation or fractionation. Samples were collected about 10-cm below the water surface in turbulent areas where the water column was well mixed. Groundwater was sampled weekly during ice-free months and monthly during the winter at the alpine Saddle site from observation wells approximately 100 m from the Como Creek watershed. Sampling was performed with a 1-m teflon bailer to minimize chemical contamination and followed the protocol of surface water collection.

1.3.5 Analytical methods

All samples were analyzed at the Kiowa wet chemistry laboratory operated by the NWT LTER program, following the protocols presented in Williams et al. (2006). Samples were analyzed for ^{2}H and ^{18}O using an L1102-i Isotopic Liquid Water Analyzer developed by Picarro Incorporated. The analyzer is based on Picarro's unique Wavelength- Scanned Cavity Ring Down Spectroscopy (WS-CRDS), which is a time-based measurement using near-infrared laser to quantify spectral features of molecules in a gas contained in an optical measurement cavity. Isotopic compositions are expressed as a δ (per mil) ratio of the sample to the Vienna Standard Mean Ocean Water (V-SMOW), as shown for $^{18}0$:

$$\delta^{18}O = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{VSMOW}}{(^{18}O/^{16}O)_{VSMOW}} \times 1000$$

(Equation 1.1)

The precision for $\delta^{18}O$ was ±0.05‰ and for D was ±0.1‰

1.3.6 Statistical Methods

Measured values of $\delta^{18}O$ were compared between locations and settings (open or under canopy) using a one-way analysis of variance (ANOVA) to test for significant differences between sample populations. Additionally, an analysis of covariance test (ANCOVA) was used to test for significant changes in the δD -$\delta^{18}O$ relationship between different sample populations.

1.4 Results

1.4.1 Precipitation

The annual volume weighted mean (VWM) $\delta^{18}O$ values in precipitation tended to decrease with elevation (Figure 1.2). The lowest elevation site, Sugarloaf, had a VWM $\delta^{18}O$ value of -16.9 ‰, which was the most enriched signal. The annual VWM value continued to become more depleted with elevation as C1 VWM was -17.1 ‰, while the Soddie VWM was -17.7 ‰, and the highest site, the Saddle, had the most depleted mean $\delta^{18}O$ of -18.2 ‰ (Figure 1.2). However, the decrease in VWM $\delta^{18}O$ values was not significant across the elevation gradient (p = .72). The 'lapse rate' for the annual VWM $\delta^{18}O$ concentrations in precipitation was approximately a 0.13 ‰ decrease with every 100 m increase in elevation.

Winter (October through May) VWM isotopic values in precipitation were lower than those of the summer (June through September) (Figure 1.2) The VWM $\delta^{18}O$ of winter precipitation was not significantly different (p = .68) across elevation, with the highest-elevation site at the Saddle having a VWM value of -17.6‰, Soddie –18.8‰, C1 -19.4‰, and the lowest-elevation site at Sugarloaf was -19.1‰. In contrast to winter precipitation, the VWM $\delta^{18}O$ of summer precipitation did increase with elevation but not significantly (p = .92), with Saddle having the most depleted $\delta^{18}O$ value of -12.5 ‰, Soddie -11.9 ‰, C1 -11.7 ‰, and Sugarloaf having the most enriched summer VWM of -10.5 ‰.

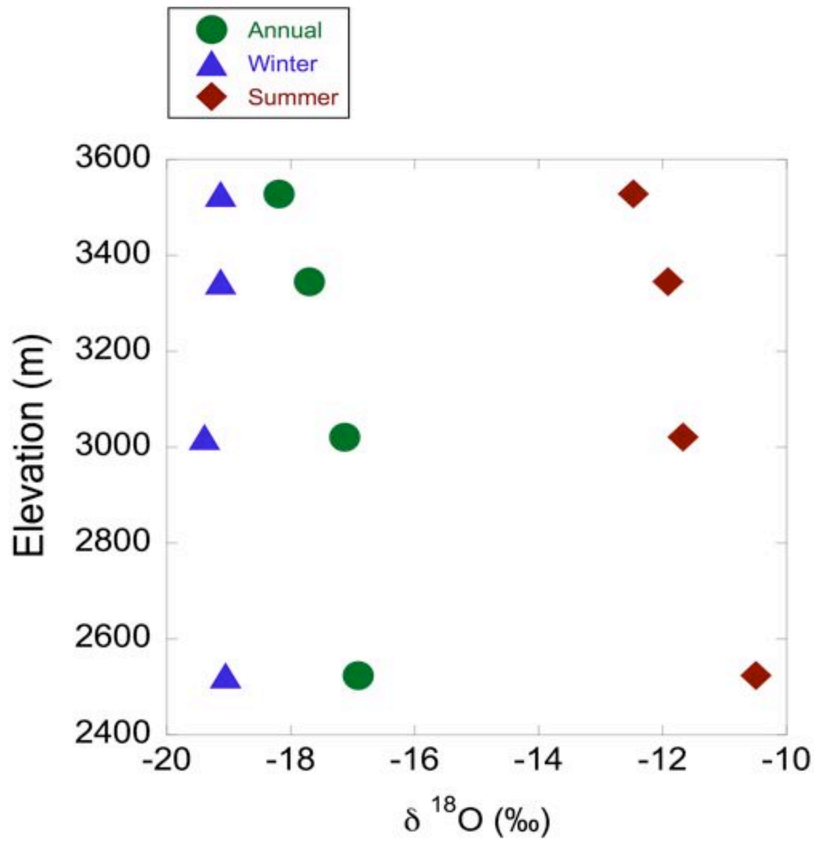

Figure 1.2: Volume weighted mean $\delta^{18}O$ of precipitation for 2009, shown for the entire year and for winter (October - May) and summer (June - September) seasons.

The possible importance of evaporation and other processes that can cause fractionation of the isotopic content of water can be evaluated by investigating the $\delta^{18}O$ - δD relationship in snow and surface waters. Empirical results have shown that δD and $\delta^{18}O$ values in precipitation co-vary and are generally described by the relationship (Craig, 1961):

$$\delta D = 8\ \delta^{18}O + 10 \qquad \text{(Equation 1.2)}$$

Which is defined as the Global Meteoric Water Line (GMWL). Deuterium values in precipitation at all four sites were highly correlated with $\delta^{18}O$ (Figure 1.3). The slopes of the $\delta^{18}O$ - δD for incoming precipitation all plot close to the GMWL and range from a low of 7.7 at

Sugarloaf to a high of 7.9 at the Saddle site. An analysis of covariance (ANCOVA) test showed no significant difference (p = .93) in the slope of $\delta^{18}O$ vs. δD across the elevational gradient. The deuterium excess of 10.2 ‰ at the Saddle site is similar to the 10 ‰ characteristic of the GMWL, while the deuterium excess at the Soddie, C1, and Sugarloaf were slightly below the global average at 8.6 ‰, 8.7 ‰ and 6.7 ‰. I selected the mid-elevation C1 site to represent the local meteoric water line (LMWL).

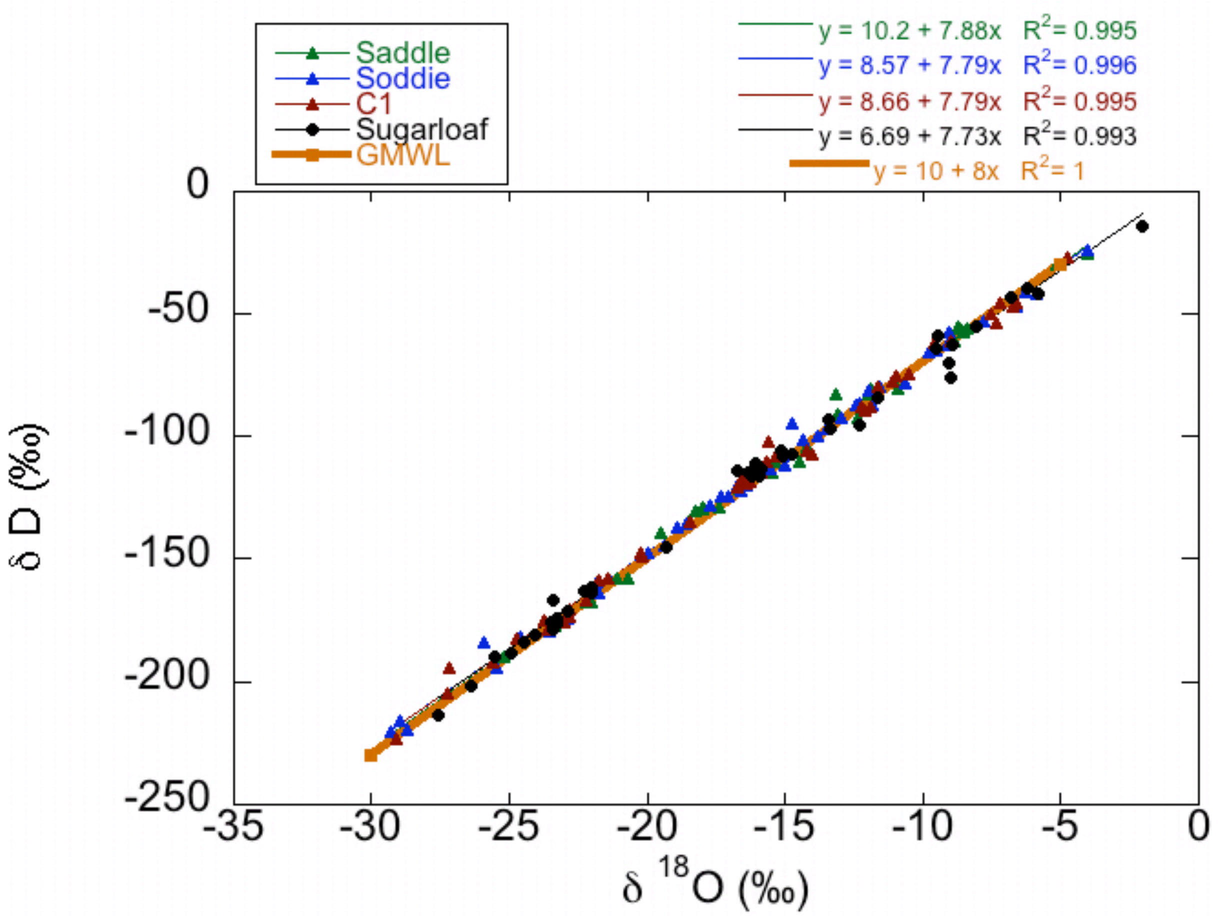

Figure 1.3: A plot of δD versus $\delta^{18}O$ from all precipitation samples, compared to the Global Meteoric Water Line (GMWL).

Looking just at cold season precipitation, there was a trough-shaped trend in weekly values of $\delta^{18}O$ (Figure 1.4). In general, values of $\delta^{18}O$ became lower moving from fall to winter months, than rose again towards the spring months. In general, the weekly $\delta^{18}O$ values in precipitation tracked each other reasonably well. However, there were large changes in $\delta^{18}O$ values from week to week. For example, at Gordon Gulch the $\delta^{18}O$ value increased from -27 ‰ the week of 1 March to -12 ‰ the week of 14 March. Moreover, Gordon Gulch went from having the lowest $\delta^{18}O$ of the four sites the week of 1 March to the highest value of the four sites the week of 14 March.

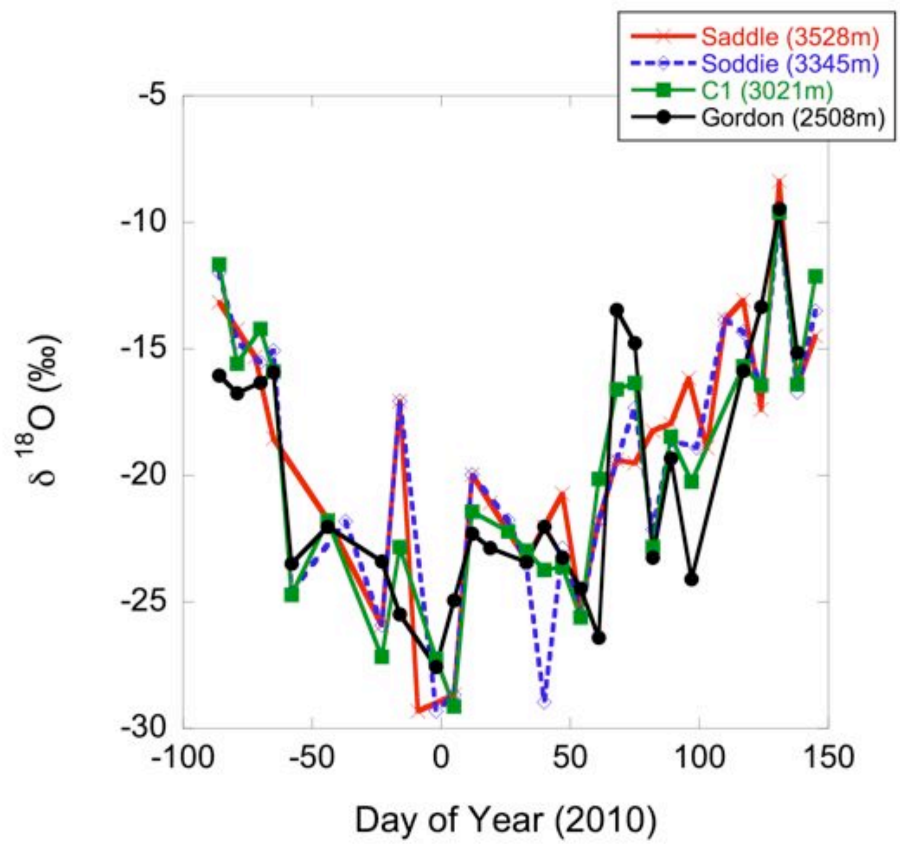

Figure 1.4: Weekly $\delta^{18}O$ values of cold season precipitation (October through May) for the 2009 to 2010 season at four elevations within the Boulder Creek Watershed.

To evaluate the possible role of canopy interception in changing the values of stable water isotopes in snowfall, I compared the slopes of the $\delta^{18}O$ vs. δD relation between that of snow collected weekly in open areas versus under tree canopy areas (Figure 1.5). Using identical open top collection buckets for open and under canopy collection across all sampling locations minimized sampling bias. Additionally, a paired-difference t-test for $\delta^{18}O$ samples collected in the open buckets and in the NADP collectors at each site showed no significant difference (all $p > .15$) between the experimental and official NADP sample collection types during cold season precipitation.

The slopes of the $\delta^{18}O$ vs. δD relation between that of snow collected weekly in open areas versus under tree canopy areas at each sampling site were compared by applying an ANCOVA test to each paired set of samples. At the Soddie site the slope decreased significantly ($p = .005$) from 8.0 in the open to 7.6 under canopy while the upper montane C1 site the slope actually increased significantly ($p = .038$) from 8.6 in the open to 9.0 under canopy. At the lower montane Gordon Gulch site the slope in the open was 7.7 and increased to 7.9 under canopy but the difference was not significant ($p = .28$).

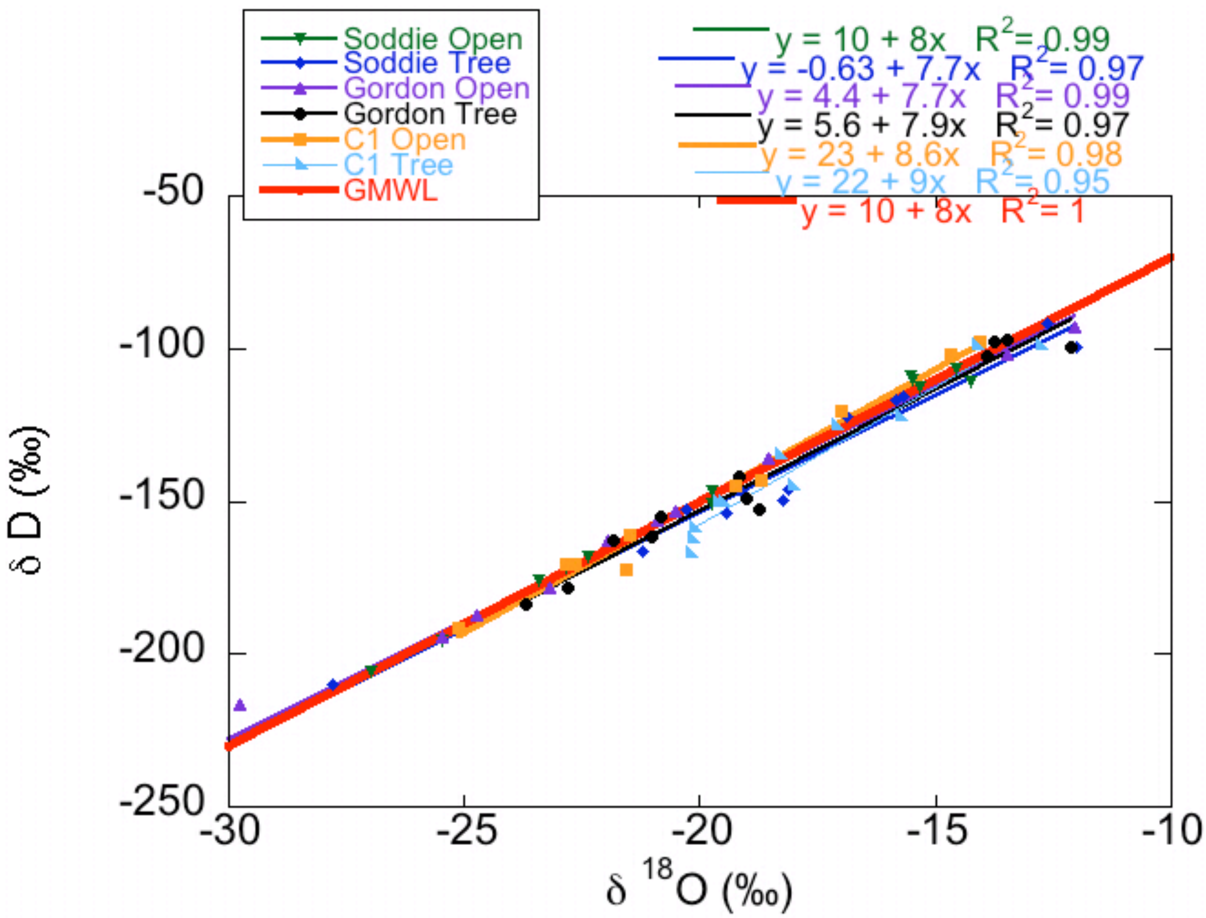

Figure 1.5: The δD versus $\delta^{18}O$ diagram for weekly precipitation sampling from open and under canopy environments during the 2009-2010 snowfall season.

A more intensive under canopy precipitation collection campaign was performed in Gordon Gulch. Figure 1.6 shows results from Gordon Gulch in which additional open and under canopy precipitation collections were performed to investigate the effects of aspect and tree species on the $\delta^{18}O$ - δD relationship. All slopes were close to the GMWL with the open south facing collection site having the highest slope of 8.2 and all other collection sites having slopes ranging from 7.7 to 7.9 and falling just below the GMWL. There was no significant difference in slope across all collection locations within the catchment ($p = .06$) nor was there a significant difference in slope between precipitation falling on south facing and north facing slopes ($p = .39$). Additionally, there was no significant difference in the $\delta^{18}O$ - δD relationship of precipitation coming through the 3 dominant types of coniferous vegetation occurring in Gordon Gulch (p = .56).

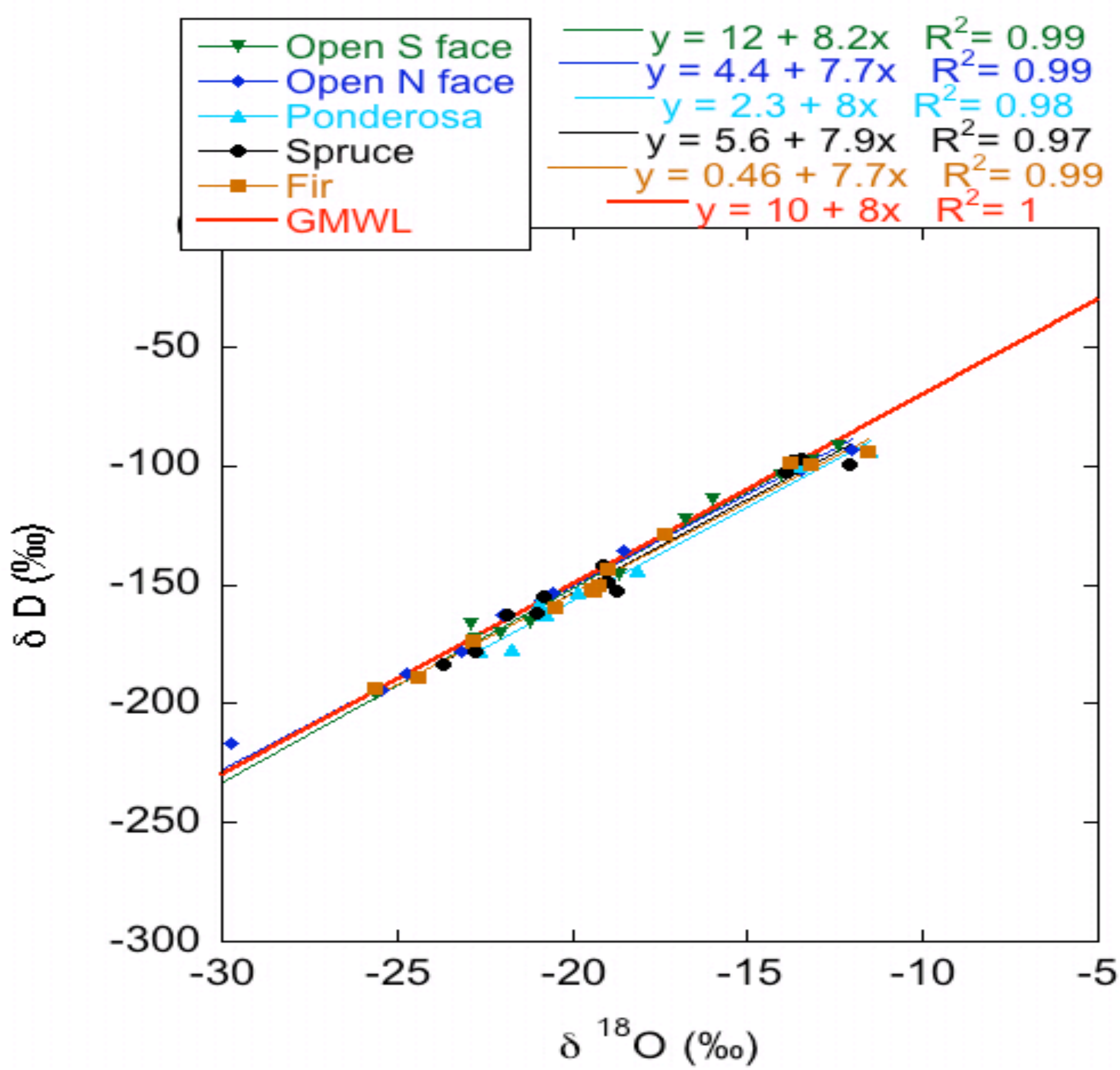

Figure 1.6: The δD versus δ^{18}O diagram for weekly cold season precipitation sampling in Gordon Gulch. Precipitation samples were collected from open meadows on both north and south facing aspects and from beneath the canopies of three dominant coniferous tree species: Ponderosa pine (*Pinus ponderosa*), Rocky Mountain Douglas-fir (*Psuedotsuga menziesii* var. *glauca*) and Colorado Blue Spurce (*Picea pungens*).

1.4.2 Snow Pack Evolution

The depth integrated mean $\delta^{18}O$ of the snowpack on the ground ranged from -18.6‰ to -26.4‰ on January 20, 2010 at the beginning of the accumulation season, but only ranging from -19.8‰ to –23.8‰ on April 12, 2010 when snow pack sampling ended at the C1 and Gordon Gulch sites (figure 1.7). Sufficient snow pack remained at the Saddle and Soddie sties to continue sampling until June 9, 2010 when the Saddle had a mean $\delta^{18}O$ of -18.7‰ and the Soddie had a mean $\delta^{18}O$ of -24.2‰.

Over the entire snow season there was a significant difference ($p < .0001$) in the depth integrated mean $\delta^{18}O$ of the snow pack between all open sites ($p < .0001$) with the Saddle having a mean of -20‰, the Soddie having a mean of –24.5‰, C1 having a mean of -22.1‰, and Gordon Gulch having a mean of -24.6‰. Similarly, there was a significant difference in the seasonal depth integrated mean $\delta^{18}O$ of the snow pack between all under canopy sites ($p = .007$) with the Soddie having a mean of -22.2‰, C1 having a mean of -19.0‰, and Gordon Gulch having a mean of -18.2‰.

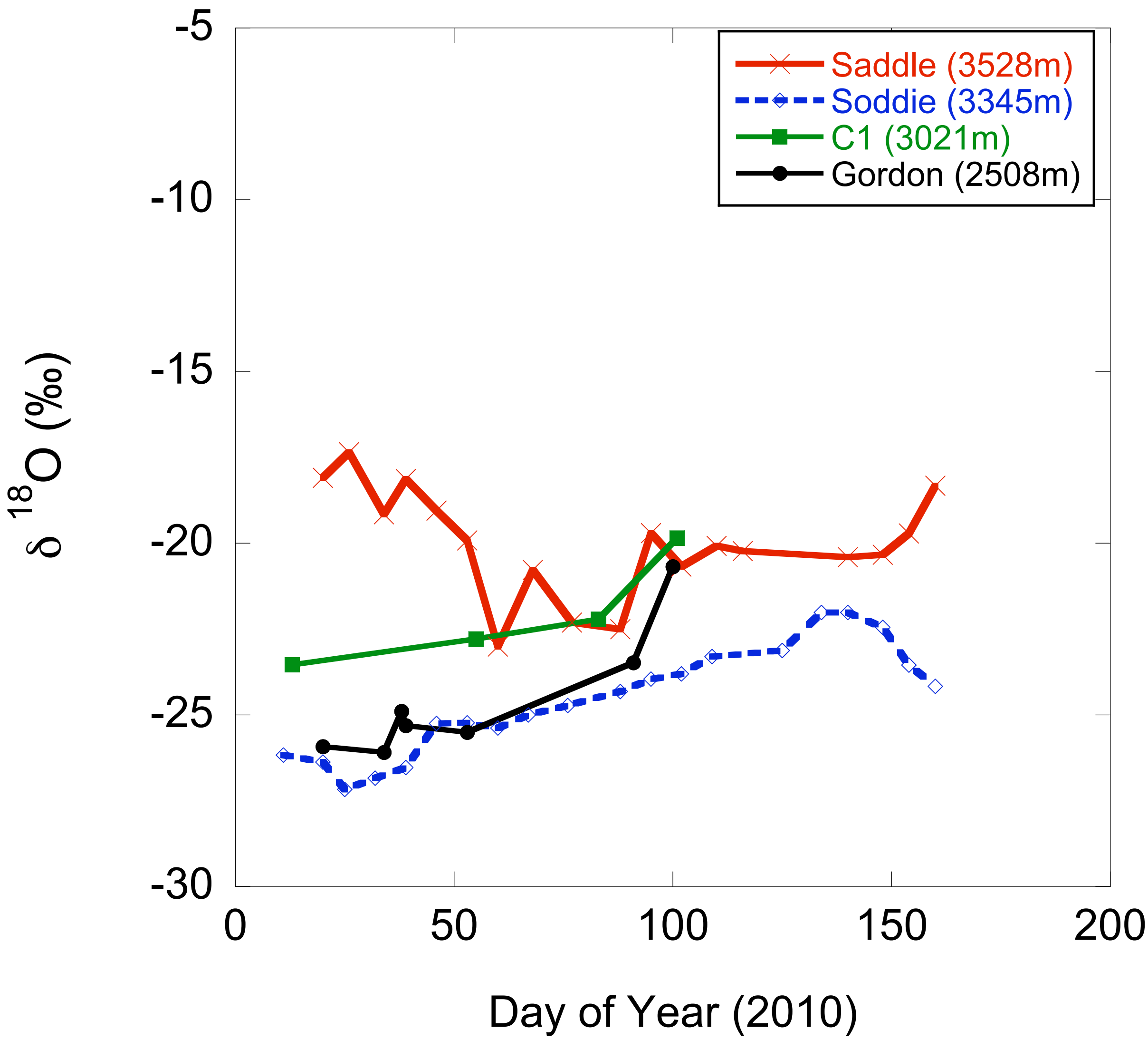

Figure 1.7: Time series of the depth integrated mean $\delta^{18}O$ of Snow pack samples collected in the open at each sampling location.

To evaluate possible differences in the values of stable water isotopes in seasonal snow pack across all sampling sites, I compared the slopes of the $\delta^{18}O$ vs. δD relation between that of weekly depth integrated mean snowpack samples collected at each location (Figure 1.8). The slopes within the snow pack across all sites were significantly different ($p <. 001$) ranging from a high of 8.5 at the alpine Saddle site to a low of 6.7 at the C1 site. There was no significant difference ($p = .15$) in the slopes at Gordon (6.9) and C1 (6.7), the lowest two sites, but then the slopes became greater moving into the sub-alpine (7.1) and the alpine (8.5). The δD excess at the Saddle (22.9‰) was greater then the local precipitation, while the δD excess at the Soddie, C1 and Gordon was well below the local precipitation at -6.8‰, -19.9‰, and -15.2‰ respectively.

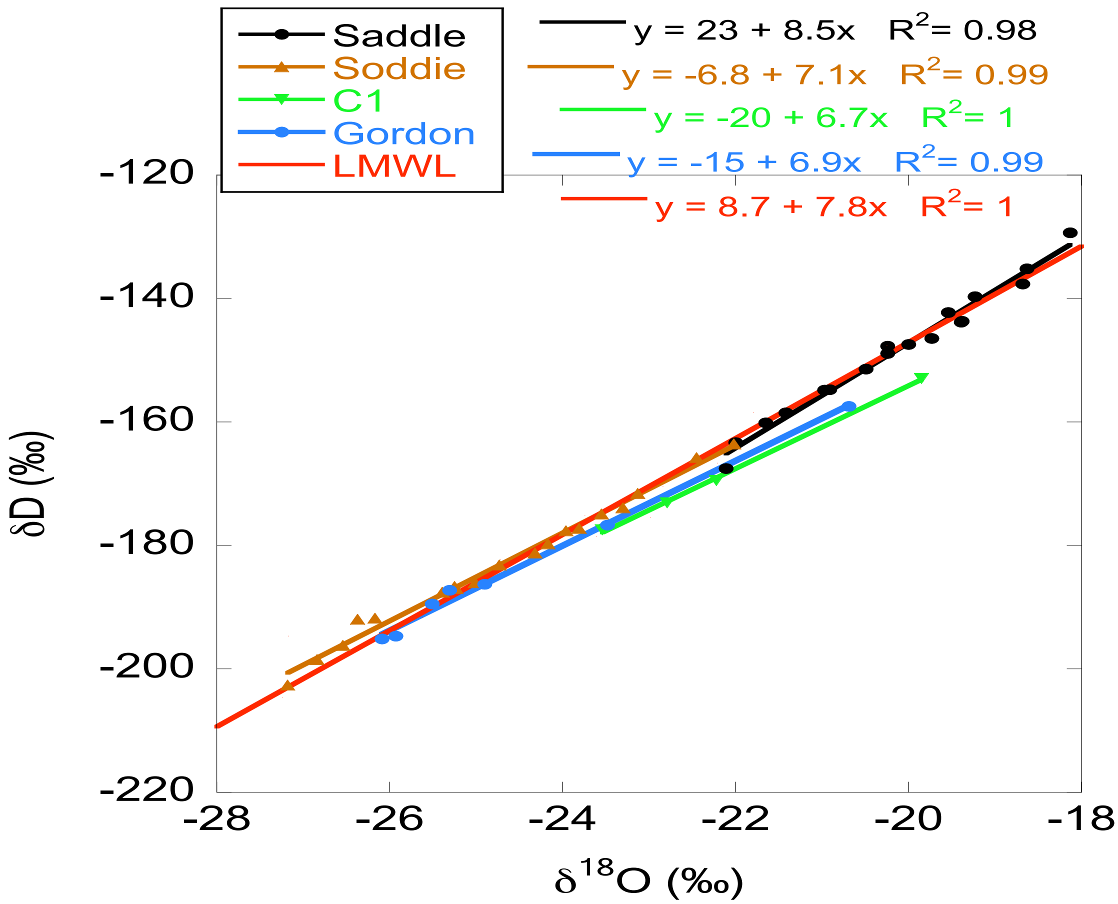

Figure 1.8: The δD versus δ^{18}O diagram for weekly depth integrated snow pack samples from open sampling locations at each site.

In addition to the weekly depth integrated sampling, monthly isotopic sampling of the entire vertical profile of the snowpack can be seen in Figure 1.9. The Saddle snow pack had no significant change ($p = .92$) in vertical profile δ^{18}O composition with a mean and standard deviation δ^{18}O of -19.8±6.7‰ in January and -19.7±3.17‰ in April. The Soddie snow pack had no significant change ($p = .1$) in vertical profile δ^{18}O composition with a mean and standard deviation $\delta^{18}O$ of -25.7±4.2‰ in January and -23.4±2.8‰ in April. The C1 snow pack had no significant change (p = .16) in vertical profile $\delta^{18}O$ composition with a mean and standard deviation $\delta^{18}O$ of -23.5±1.5‰ in January and -19±0.8‰ in April. Contrary to the other sites the Gordon Gulch snow pack had a significant change (P= .03) in vertical profile $\delta^{18}O$ composition with a mean and standard deviation $\delta^{18}O$ of -25±3.0‰ in January and -20.9±0.7‰ in April.

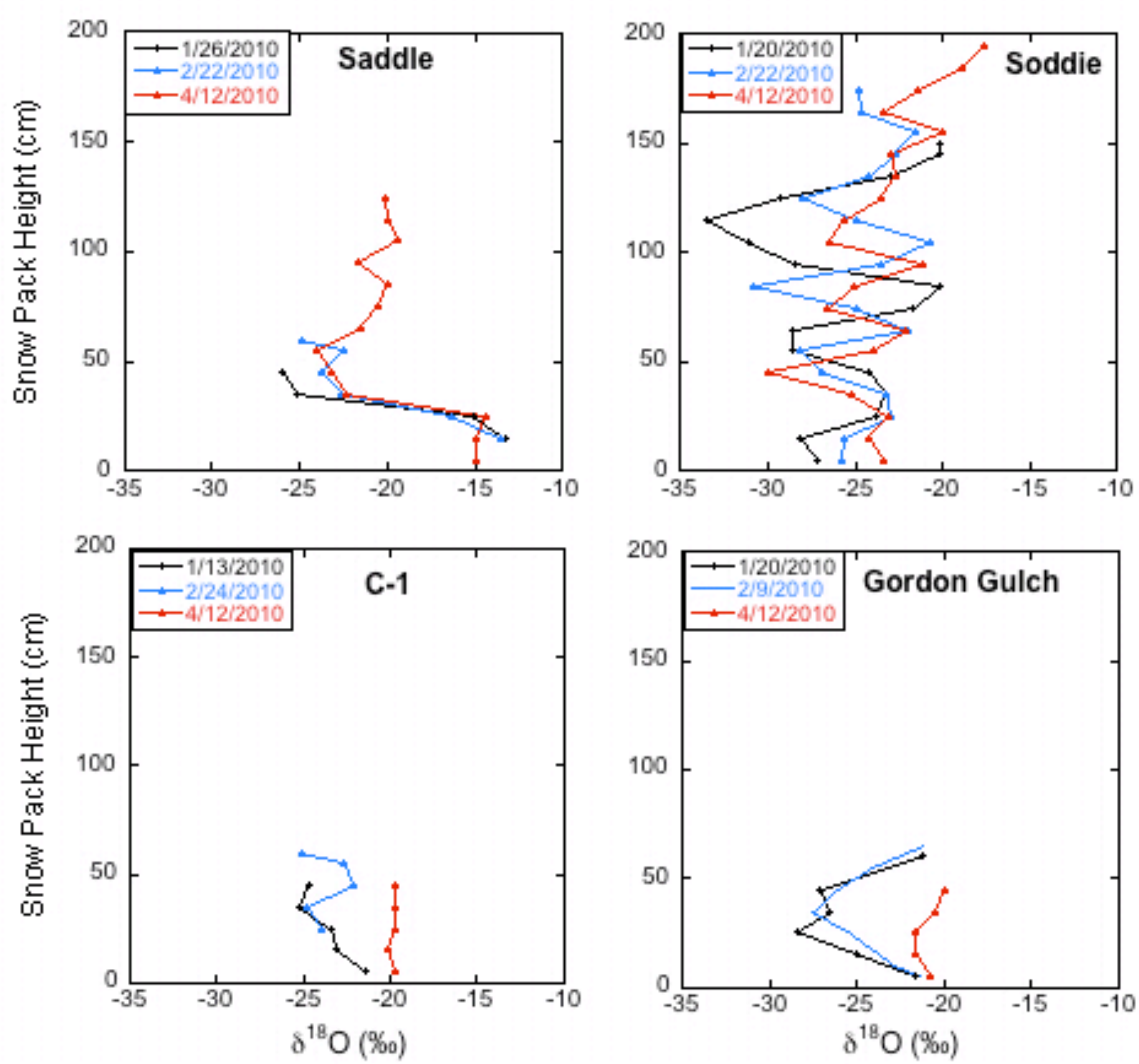

Figure 1.9: Snow pack $\delta^{18}O$ (‰) profiles throughout the snow season of 2010 at the Saddle, Soddie, C1, and Gordon Gulch sites.

The snow pack sampling on April 12, 2010 was intended to capture maximum accumulation of winter precipitation across the entire watershed. Due to the large climactic variability across the elevational gradient in the study the snow pack had already begun to decrease at the lower elevations (Figure 1.9) so it was determined necessary to acquire a one time snap shot of the snow pack across all sampling sites in both open and under canopy settings (Figure 1.10). The Saddle site vertical profile $\delta^{18}O$ composition had a mean and standard deviation of -19.7±3.17‰ and was still showing the high $\delta^{18}O$ values at the base of the snow pack from early season precipitation. At the Soddie there was no significant difference ($p = .28$) between the mean $\delta^{18}O$ of the open (-23.4±2.8‰) and under canopy (-22.2±2.3‰) snow packs, but the snow pack depth in the open meadow (198 cm) was more than twice the depth under canopy (94 cm). At C-1 there was a significant difference ($p = .04$) between the mean $\delta^{18}O$ of the open (-19.8±0.2‰) and under canopy (-19±0.8‰) snow packs but the snow pack was isothermal in both locations and melt had already begun so the results may have been influenced by the melting process. At Gordon Gulch there was also a significant difference ($p = .001$) between the mean $\delta^{18}O$ of the open (-20.9±0.7‰) and under canopy (-18.2±0.4‰) but again results should be taken with caution because the snow pack was isothermal and melting had begun.

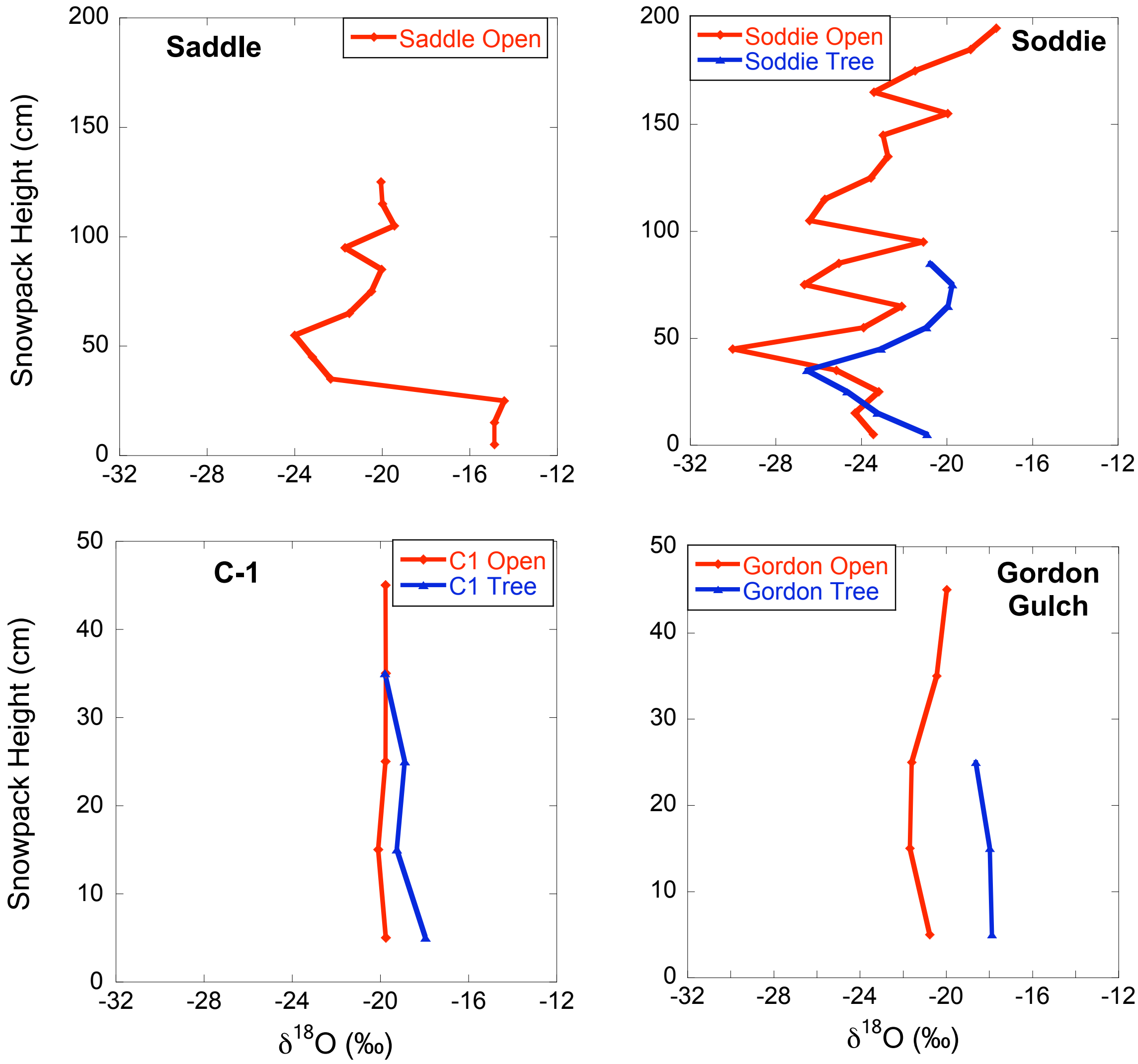

Figure 1.10: Vertical profile of snow pack $\delta^{18}O$ in open and under canopy locations on April 12, 2010 at Saddle, Soddie, C1, and Gordon Gulch.

In addition to the weekly sampling at the Saddle there is an annual snow survey that takes place every year near maximum snow accumulation to measure snow pack properties in the alpine Green Lakes Valley watershed. The annual snow survey occurs around the second week of May and includes depth integrated snow pack sampling at several locations with elevations greater then the Saddle site. In the interest of extending snow pack isotopic characterization beyond the elevational extent of the current study, Figure 1.11 shows the depth integrated mean $\delta^{18}O$ of snow packs over three consecutive snow surveys from 2008 to 2010. The mean $\delta^{18}O$ of snow packs increases from -23.1±0.6‰ at the Soddie site (3345m) up to -16.9±0.1‰ just below the Arikaree Glacier (3785m).

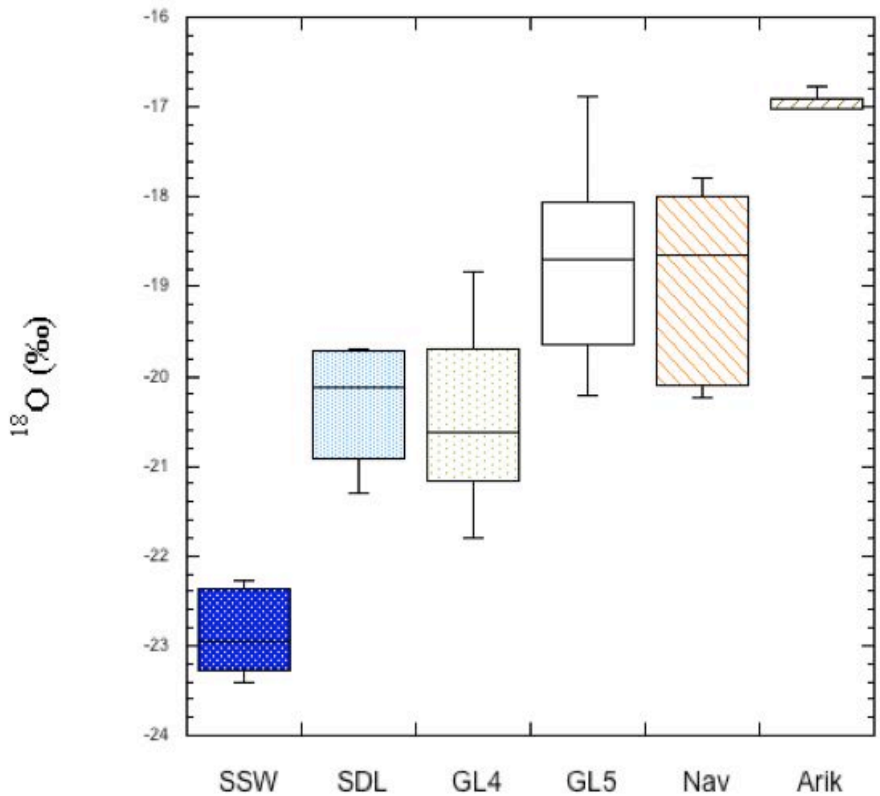

Figure 1.11: Volume weighted mean of snow pack samples taken during the past three annual Green Lakes Valley snow surveys. The elevations of the sample locations are: Soddie (SSW 3345 m), Saddle (SDL 3528 m, Green Lake 4 (GL4 3550 m), Green Lake 5 (GL5 3620 m), Navajo bench (Nav 3720 m), and below Arikaree Glacier (Arik 3785 m). The snow survey occurred during the second week of May in 2008, 2009, and 2010. Boxes represent the range of values within the 25th to 75th percentiles of the median and the whiskers represent the minimum and maximum values.

1.4.3 Snowmelt Evolution

Measurable quantities of snow melt first appeared at the lowest elevation, Gordon Gulch, on March 2, 2010 and melt at Gordon Gulch continued until May 19, 2010 (Figure 1.12). The $\delta^{18}O$ of melt under canopy and in the open at Gordon ranged from –20.8‰ and -16.0‰ at the beginning of melt to -12.8‰ and -14.1‰ at the end of melt respectively. At the Soddie measurable quantities of melt in the open began on April 27, 2010 with a mean $\delta^{18}O$ of -19.4‰ and ended on June 1, 2010 with a mean of -17.0‰. Under canopy melt at the Soddie began on May 18, 2010 with a mean $\delta^{18}O$ of -19.8‰ and ended on June 7, 2010 with a mean $\delta^{18}O$ of -18.2‰. Measurable melt at the Saddle also began on May 18, 2010 with a mean $\delta^{18}O$ of -16.6‰ and ended on June 7, 2010 with a mean $\delta^{18}O$ of -16.2‰. The $\delta^{18}O$ of melt was significantly different in the open ($p = .0002$) and under canopy ($p = .02$) across the three elevations, but was not significantly different between the open and under canopy melt occurring at both the Soddie and Gordon Gulch ($p = .5$ and $p = .43$ respectively). There is also no significant difference ($p = .17$) between the $\delta^{18}O$ in melt water at the sub-alpine Soddie site and the Alpine Saddle site.

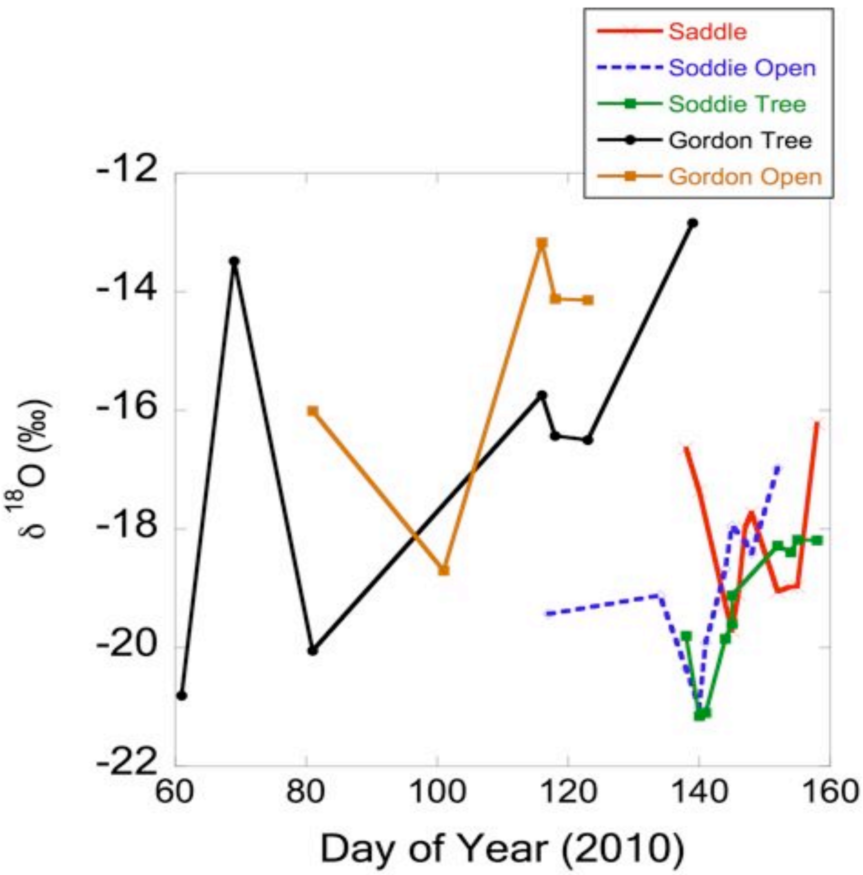

Figure 1.12: Time Series of the $\delta^{18}O$ of melt water at all snow melt lysimeter locations at the Saddle, Soddie, and Gordon Gulch sites.

The δD versus $\delta^{18}O$ relationship for all snowmelt samples collected throughout the snow season was also analyzed to further investigate changes in isotopic composition during snowmelt (Figure 1.13). The slopes for melt in Gordon Gulch (9.5 open and 8.5 tree) were significantly different ($p = .015$) from each other but both remain close to and slightly above the slope of the local snow pack. The slopes for melt at the Soddie (6.5 open and 5.3 tree) were significantly different ($p = .007$) from each other and both plot well to the right of the slope of the snow pack (7.1). The slope for melt at the Saddle was 4.9 and the δD excess was the most negative of all samples at -45.8‰.

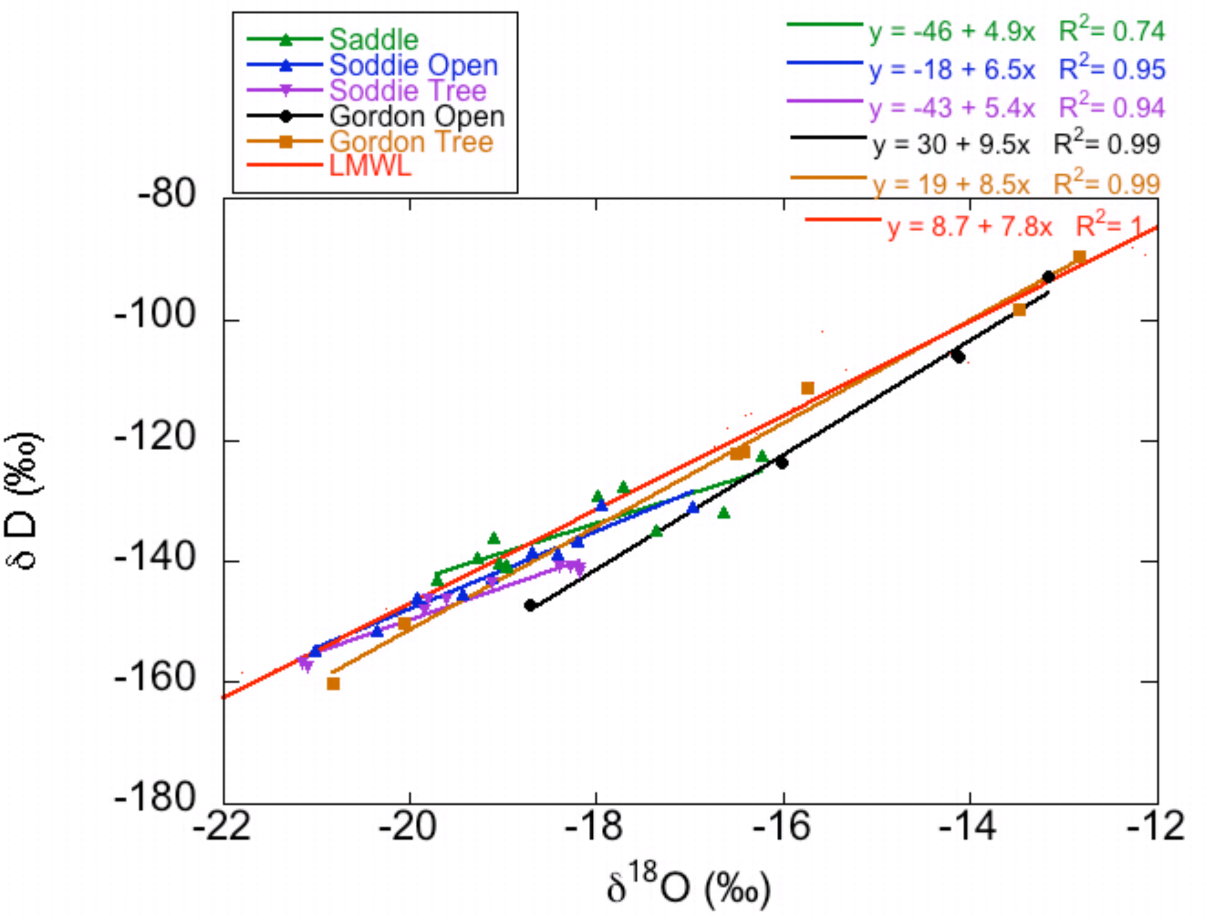

Figure 1.13: The δD versus δ^{18}O diagram for all snowmelt samples collected throughout the season at both open and under canopy locations, plotted with the local meteoric water line.

To examine the evolution of δ^{18}O in melt water, figure 1.14 shows the volume weighted mean δ^{18}O of melt water in relation to the fraction of total water melted at each location where melt volumes were continuously recorded. After an initial decrease in the δ^{18}O content during the fist 10% of melt, all three locations show a sustained increase or enrichment through the remainder of melt. To compare the isotopic evolution of snow melt to the rate of melt, Figure 1.15 shows a time series of the mean δ^{18}O stacked on top of the daily specific melt (mm) at the Saddle and in open and under canopy locations at the Soddie. To further emphasize the rate at which the snow packs melted at the Saddle and Soddie sites, Figure 1.16 shows a time series of the percentage of snow pack melted. The melt rates were similar at all three locations with the higher elevation Saddle lagging behind the Soddie melt by less then 5 days and the final 40% of melt at the Soddie occurring faster in the open then under canopy.

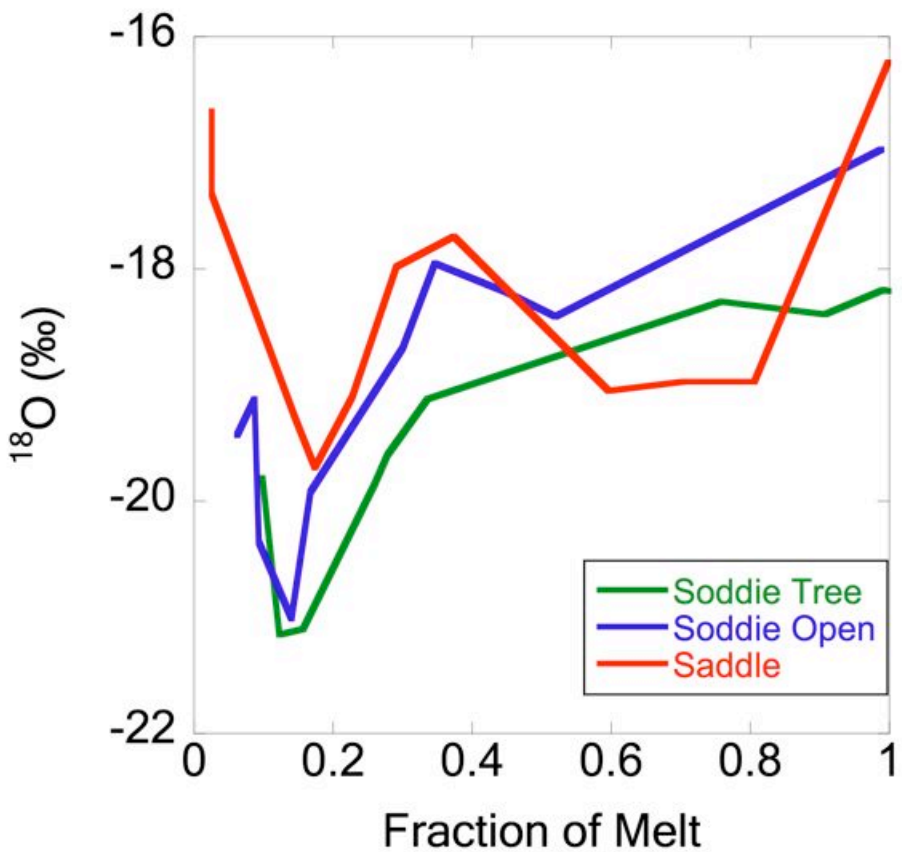

Figure 1.14: Volume weighted mean δ^{18}O of snow melt relative to the fraction of total melt throughout the season.

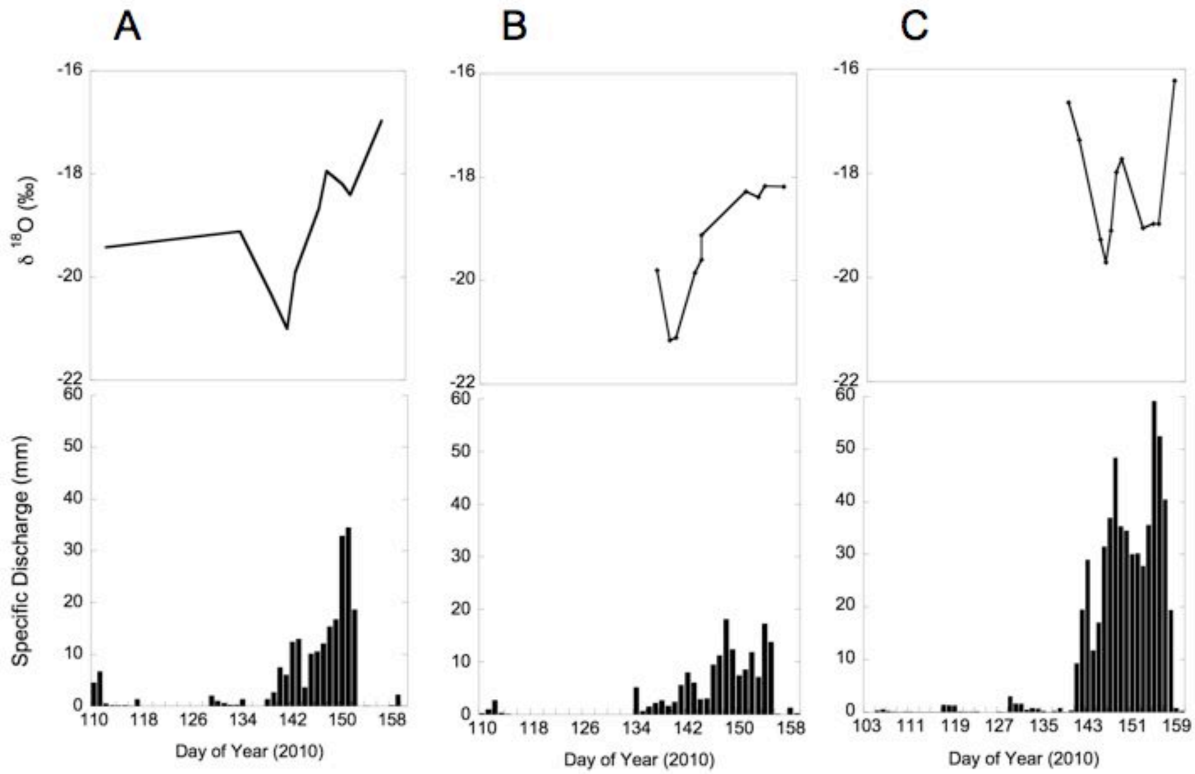

Figure 1.15: Top panel shows a time series of the volume weighted mean $\delta^{18}O$ of snowmelt. Bottom panel shows the daily specific discharge (mm) from the melt lysimeter for A) Soddie open meadow, B) Soddie under canopy, and C) Saddle.

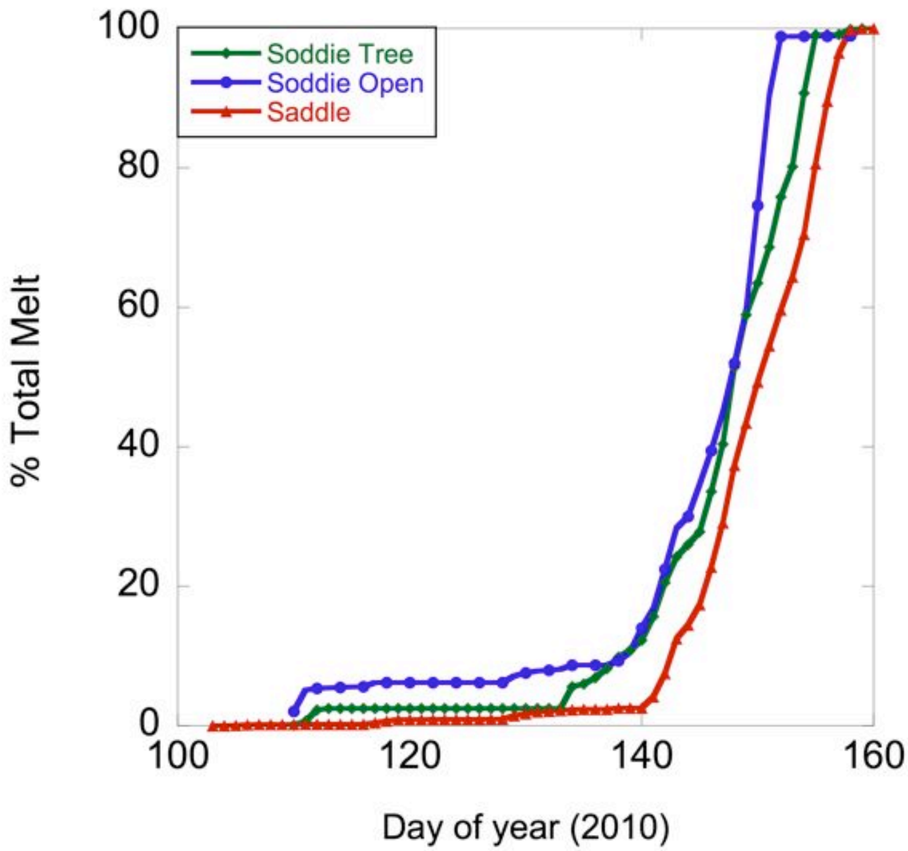

Figure 1.16: Time series of the percentage of total melt measured at the Saddle and in open and under canopy locations at the Soddie site.

1.4.4 Surface water

A final analysis of the δD and $\delta^{18}O$ relationship found in the surface waters of each of the three headwater catchments is shown in Figure 1.17 along with the local meteoric water line. The surface water isotope ratios all plotted to the right of the LMWL and had slopes that were significantly different ($p = .0001$) then the LMWL. Additionally, the δD excess was lower then the LMWL, ranging from -5.0 to -12.1‰ in the three streams. Interestingly, the δD and $\delta^{18}O$ relationships and δD excess values found in the surface waters for GL4 and Como Creek fall between the values in annual precipitation and the values of seasonal snow melt in each respective catchment, while the surface waters in Gordon Gulch plot to the right of both the local precipitation and the seasonal snow melt.

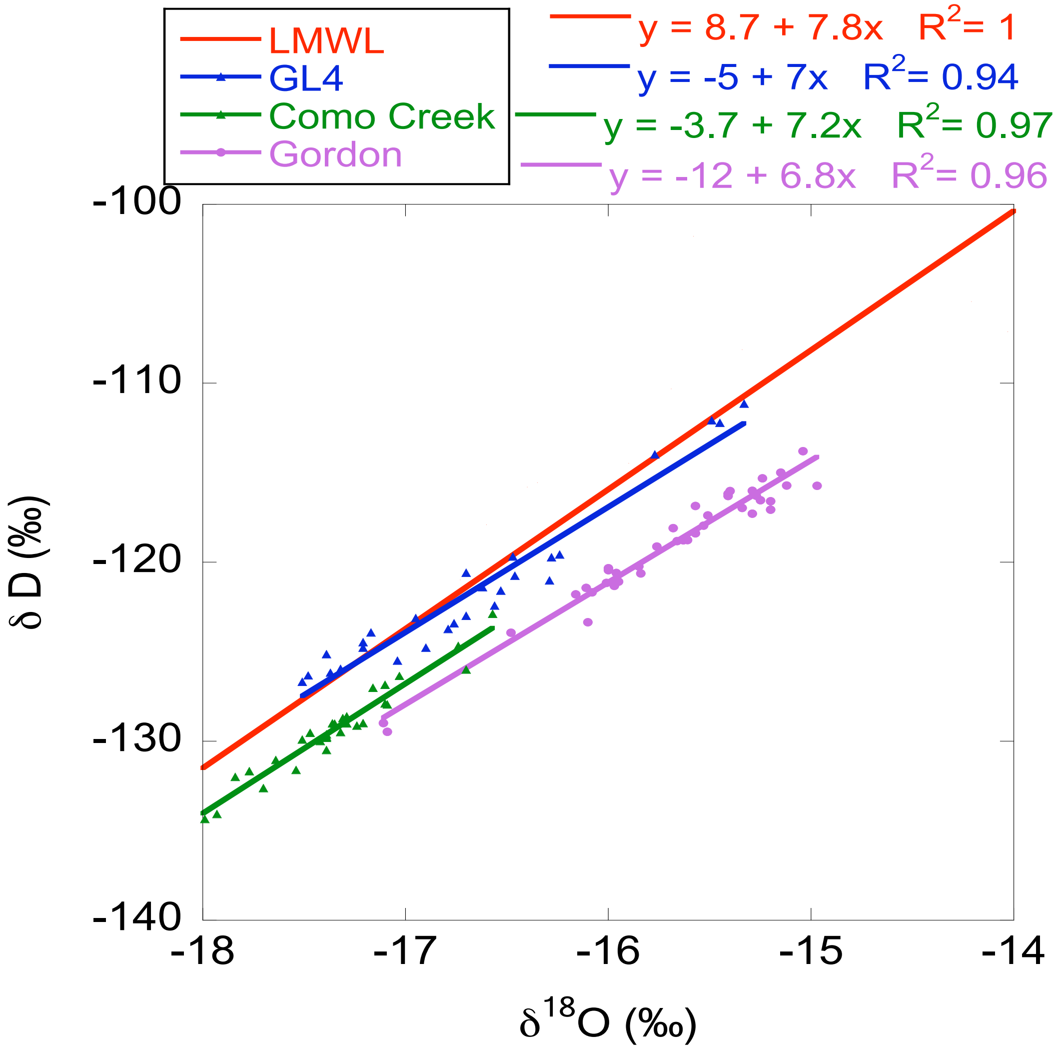

Figure 1.17: The δD versus δ^{18}O diagram for stream waters collected in 2009 at each of the headwater catchments plotted with the Local Meteoric Water Line (LMWL).

1.5 Discussion

1.5.1 Precipitation

Local precipitation at all elevations was close to the GMWL suggesting that the isotopic composition of precipitation falling in Boulder Creek Watershed had undergone similar processes as those studied and established through global isotopic studies (i.e. Clark and Fritz, 1997). The isotopic variations found in the local precipitation indicated that the precipitation was similar to that of the global meteoric water line defined by Craig (1961) and that it did not show signs of disproportional fractionation beyond what is expected due to the "continental effect" described in Cecil et al. (2005). The results of this study show that there was no significant difference in the annual or seasonal composition of $\delta^{18}O$ across the study sites, which was most likely due to large deviations in $\delta^{18}O$ values from storm to storm at any one site. However, the annual volume weighted mean $\delta^{18}O$ of precipitation calculated for all the catchments did suggest that a small lapse rate could be calculated on an annual time scale. The measured lapse rate for $\delta^{18}O$ of 0.1‰/100 m was similar to an altitude effect of 0.2‰/100 m for precipitation found in the alps by Siegenthaler and Oeschger (1980) but considerably smaller then the range of 0.6‰ to about 1.0‰ per 100 m of elevation found in four mountain regions (the South American Andes, the Central Asian Hindu Kush, the Himalaya, and Mounts Kenya and Kilimanjaro in Africa) by Niewodniczanski et al. (1981).

To try and understand why the lapse rate of $\delta^{18}O$ is different for different high elevation environments it is necessary to try and understand the processes that actually control the isotopic variations in precipitation falling across the watershed. Stewart (1975) showed that the isotopic composition of raindrops in clouds are primarily determined by equilibrium fractionation processes, which by definition means that there are two dominant factors controlling the stable isotopic composition of precipitation: the isotopic composition of the parent vapor and temperature. Since all study catchments were located within a 30 km radius on the eastern side of the Continental Divide in the Front Range of Colorado, it is probable that all catchments were receiving precipitation that was generated from the same parent vapor mass. The small changes that did occur may therefore have been related to the micro-scale temperature variability experienced by the precipitation as it traveled the short distance from the cloud to the ground. The lower elevation areas will generally have lower snow covered area (and thus lower albedo) potentially creating higher near surface air temperatures that could accelerate fractionation of precipitation just before landing on the ground. Further dissection of precipitation into individual storm events (requiring more frequent sampling then NADP protocol), coupled with the identification of storm trajectories (i.e. up-slope or westerly) may confirm parent vapor mass uniformity and allow for a more isolated analysis of temperature influences on isotopic composition. As seen in Figure 1.5 there were small variations in $\delta^{18}O$ in precipitation from week to week but there was no consistent trends in relation to elevation at any point throughout the cold season again suggesting that factors other than elevation were controlling isotopic values during individual events.

The lack of a significant difference in the mean $\delta^{18}O$ composition and the $\delta^{18}O$ - δD relationship of incoming precipitation between open and under canopy environments at the lowest elevation catchment suggests that there was not a significant amount of fractionation occurring during canopy interception. One reason may be that at the lower elevation snowfall totals were lower and therefore there was less opportunity for significant amounts of canopy interception leading to lower rates of sublimation and/or secondary evaporation and ultimately less fractionation. Additionally, Andreadis et al., (2009) stated that intercepted snow could be removed from the canopy by sublimation, mass release, or melt water drip. Melt water drip generally only accounts for a small portion of the overall release of water from canopy interception and the mass release of snow is driven by either mechanical wind effects or by melt and is thus governed by the adhesion of intercepted snow to tree branches (Andreadis et al., 2009). Therefore, knowing that only small amounts of fractionation were occurring to intercepted snow at the lower elevation sites it is suggested that mass release was the major contributor to moving snow from the canopy to the forest floor. The mass release process may have been driven by warmer cold season air temperatures (Figure 1.18) at the lower elevations such as Gordon Gulch, preventing sufficient adhesion of snow to the branches for long enough to promote increased fractionation of snow fall in the forested areas.

These results are in slight contradiction to previous research by Classen and Downey (1995) and Molotch et al. (2007), which showed that snow interception by forest canopies could lead to high rates of sublimation and additional fractionation of precipitation prior to infiltration into the subsurface. Their results suggest to the possible scenario of a decrease in the δD and $\delta^{18}O$ slope and deuterium excess in lower elevation catchments that have a greater percentage of forested area then the sub-alpine and alpine catchments. The differing results from this study and those by Classen and Downey (1995) and Molotch et al. (2007) may be due to the elevational differences between studies. The Gordon Gulch catchment is at 2500 m while the other two studies were conducted at 3000 m and 3500 m respectively, suggesting that a transition occurs between these elevations in which the duration of canopy interception may be sufficiently different to account for changes in amount of isotopic fraction of intercepted snow. Additionally, this study did not directly measure the changes in SWE between open and under canopy settings so no quantitative comparison with the other studies can be made.

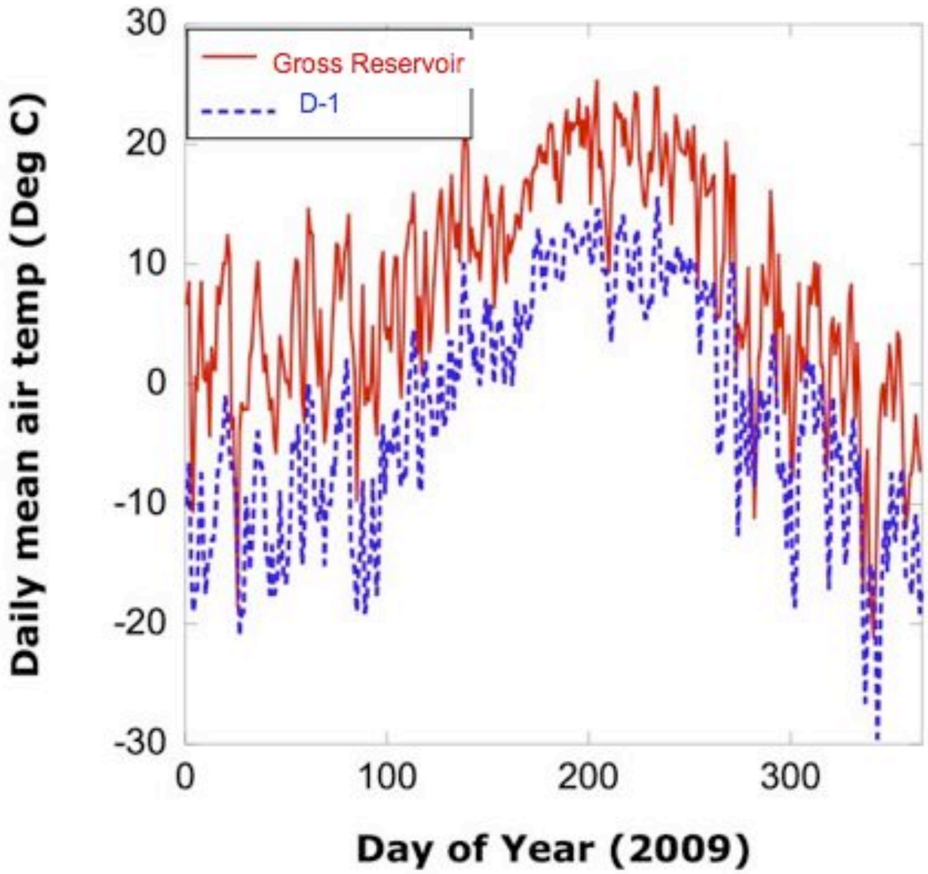

Figure 1.18: 2009 Daily mean air temperatures at the montane Gross Reservoir climate station (2426 m) and the alpine climate station D-1 (3739 m).

1.5.2 Snow Pack Evolution

The large spread in initial $\delta^{18}O$ composition of snow packs (Figure 1.7) can be attributed to the fact that the early cold season precipitation was received at all elevations but melted out at all sites except the highest elevation Saddle site. The colder temperatures at the alpine site (Figure 1.19) allowed the initial snow to remain on the ground and become part of the seasonal snowpack, whereas at the lower sites the early storms melted out before being covered by additional storms and therefore did not become part of the seasonal snowpack.

The monthly vertical profiles of snow pack (Figure 1.9) demonstrate that at all elevations the standard deviation of $\delta^{18}O$ decreased throughout the accumulation season, which supports the notion of a homogenization of the snow pack throughout the winter. Additionally, at all locations except the Saddle the mean $\delta^{18}O$ increased and became more enriched throughout the accumulation season, further indicating a homogenization that could be attributed to the well understood processes of equilibrium fractionation (Craig et al., 1963; Horita and Wesolowski, 1994).

At the Saddle, the lack of enrichment in mean $\delta^{18}O$ in the snowpack over the cold season can again be attributed to the relatively enriched $\delta^{18}O$ in early cold season snowfall generating a enriched $\delta^{18}O$ mean in the initial snow pack sample, which was similar to the enriched $\delta^{18}O$ mean value appearing at the end of the accumulation season after homogenization had occurred. However, the standard deviation of $\delta^{18}O$ values in the Saddle snow pack did decrease through time indicating that the upper layers of the snow pack become more enriched throughout the accumulation season, thereby becoming more similar to the values in the early season snow fall.

Overall, both the open and under canopy mean $\delta^{18}O$ of snow packs varied significantly with elevation, which was not observed in incoming precipitation. Therefore it appears that the processes driving isotopic fractionation during snow pack evolution are significantly varied across the elevational gradient within the watershed. It is therefore necessary to observe if the isotopic variations with elevation are preserved through the snow melt phase and as it travels towards the surface waters.

1.5.3 Snow Melt

Across the study sites there remained a significant difference in the $\delta^{18}O$ of melt water with elevation. This difference is seen by comparing either the open or under canopy results across the elevational gradient (Figure 1.12). Interestingly, within sites there was no significant difference between the mean $\delta^{18}O$ of melt water in open and under canopy environments, further indicating that the processes driving isotopic evolution of water varied with elevation but that those processes were similar within sites between canopy and open settings during snow melt.

To further examine the isotopic compositions of melt water it is necessary to look at the evolution of that melt water through time. At all locations where snowmelt was measured there was evidence of enrichment of the isotopes as the melt season progressed (Figure 1.12), which is in agreement with Lee et al (2009) who found that the initial snowmelt was depleted in the heavier isotope due to fractionation as compared to later season melt. The study conducted by Lee et al (2009) showed that melt occurs at the surface of the snowpack and then percolates down through the pack and eventually enters the ground. As the water moves through the snow pack it is continuously transitioning between the liquid and solid phases as it melts and refreezes along its path. Isotopic fractionation during freezing is known to occur due to preferential incorporation of the rare, heavy isotopic species of water ($^{1}H^{1}H^{18}O$ and $^{1}H^{2}H^{16}0$) into the ice phase relative to the common light species ($^{1}H^{1}H^{16}O$) (Moser and Stichler, 1980). As a result the melt water reaching the bottom of the snowpack first will be depleted with respect to $\delta^{18}O$ and δD and then as the melt season progresses more and more of the heavy isotopes that were left in the solid phase will melt and cause the resulting melt water to become more enriched in the heavy $\delta^{18}O$ and δD isotopes with time. The results of this study were also in agreement with previous work by Sokratov (2009) which suggested that continuous phase transitions inside snow (recrystallization) are the processes responsible for the isotopic content change because they are the primary mass-exchange mechanism between the snow mass and the surrounding environment.

Interestingly, Figures 1.14 and 1.15 show that at the Soddie and Saddle sites the initial 10% to 15% of melt water had relatively enriched $\delta^{18}O$ values, then the melt water quickly became more depleted in $\delta^{18}O$ before showing a steady enrichment trend throughout the later part of melt. This scenario is most likely due to piston-flow displacement of the enriched $\delta^{18}O$ liquid water from the base of the snowpack by the snowmelt that infiltrated from above. Even though melt occurs from the top down, it is feasible to have some liquid water at the base of the snowpack because the snow-soil interface remains near isothermal throughout the snow season. This process was not observed at Gordon Gulch due to periodic melting of snow pack throughout the entire season with individual melt samples often consisting of a mixture of the entire snow pack that had accumulated since the previous sample.

Evidence of this process was strongest at the Saddle site where, as seen in Figure 1.10, the bottom of the snowpack was significantly enriched in $\delta^{18}O$ as an artifact of enriched $\delta^{18}O$ early cold season snowfall that was preserved throughout the season and then pushed out as liquid water in the early stages of melt. It can be inferred that when the rates of melt increased (Figure 1.17) the melt water was efficiently moving from the top of the snowpack downward and enabling the liquid water and Ice fractionation to occur thus producing the steady enrichment in $\delta^{18}O$ seen in Figure (1.15).

As a whole the mean $\delta^{18}O$ of melt water was enriched relative to the snow pack at all locations within the watershed. The most likely mechanism for enrichment would have been through sublimation of the snow during time spent on the ground. The enrichment of $\delta^{18}O$ was largest at the lower elevations sites with the mean $\delta^{18}O$ at Gordon Gulch changing from -24.6‰

to -16.3‰, and smallest at high elevations where the mean $\delta^{18}O$ at the Saddle only changed from -20‰ to -18.2‰. The result is again consistent with warmer air temperatures at the lower elevations promoting greater rates of sublimation leaving behind a more isotopically enriched snow pack. The results also suggest that the significant variations in isotopic compositions of snow packs with elevation are not only preserved by also magnified by the isotopic evolution of snowmelt. Additionally, the results suggest that the presence or absence of tree canopies did not significantly alter the δD and $\delta^{18}O$ compositions of water as it evolved from precipitation to snow pack to snow melt at the same elevation.

The final step in the analysis of δD and $\delta^{18}O$ compositions of water moving through snow dominated catchments was to observe the δD and $\delta^{18}O$ compositions of stream water leaving the catchment to see if it resembled either incident precipitation or snowmelt.

1.5.4 Surface waters

Many isotope hydrology studies have shown that the stable isotope composition of rivers and streams can be substantially different than that of incident precipitation (Dutton, 2005). These differences have been variously attributed to regional water budgets dominated by snowmelt at high elevations that is highly depleted in ^{18}O (Friedman *et al*., 1992), regional effects of evapotranspiration that enrich surface waters in ^{18}O and ^{2}H (Simpson and Herczeg, 1991; Gremillion and Wanielista, 2000), and to water budgets that are dominated by snow isotopic compositions due to insufficient infiltration of precipitation during the warmer months when evapotranspiration is high and/or enhanced infiltration of winter precipitation occurs under the snow pack (Fritz *et al*., 1987; Simpkins, 1995).

Plotting the LMWL alongside the δD and $\delta^{18}O$ values found in the surface waters in each of the headwater catchments shows that the surface waters isotopic compositions (Figure 1.17) were not the same as the average annual precipitation (Figure 1.3) or snow melt (Figure 1.13). All of the surface waters had a lower slope of the δD and $\delta^{18}O$ ratios relative to the LMWL, which may have been caused by the kinetic fractionation of evaporation occurring to water in the unsaturated zone while on its way to recharging groundwater (Cecil et al, 2005). To fully understand the degree to which water in the sub-surface is undergoing evaporation it becomes necessary to understand the flowpaths and sub-surface residence times of water moving through the catchments, which will be discussed in greater detail in the second chapter of this thesis.

To take another approach, it may be even more interesting to look at the deuterium excess (δD excess) (defined as $\delta D - 8^* \delta^{18}O$ by Dansgaard, 1964) values for surface waters within the watershed. According to Cui et al. (2009) the deuterium excess values can potentially fingerprint evaporation more reliably then the δD - $\delta^{18}O$ slope of the surface waters since the slope of the evaporating body could be greater then the slope of precipitation when the recharging sources are variable. In this study the δD excess increased from precipitation to snow in alpine, but decreased at all lower elevations. The δD excess then continued to decrease from snow pack to snow melt in the alpine and sub-alpine but increase in the lower elevation montane system. Water that reached the stream channel in the alpine and sub-alpine had δD excess values that were between the values found in precipitation and the values found in snowmelt. However, in the lower elevation Gordon Gulch catchment the surface water δD excess was lower then both incoming precipitation and melt water. The results suggest that at Gordon Gulch evaporation was continuing to occur as water moves through the subsurface between the point of infiltration (as snowmelt or rain) and reemergence as surface water.

At the alpine and sub-alpine sites the δD excess increased between snowmelt infiltration and surface water reemergence suggesting that sub-surface evaporation may not have occurred, but rather that the melt water was mixing with some less fractionated (higher δD excess) water on its way to the stream. One potential explanation is that summer precipitation directly entered the subsurface, unfractionated, and then mixed with snowmelt water causing overall δD enrichment before it reached the stream. A second hypothesis is that throughout the cold season a small amount of unfractionated melt water was continuously being produced at the base of the snow pack and infiltrating into the subsurface where again it mixed with snowmelt in the groundwater reservoir and raised the δD excess values prior to the water reaching the stream channel. The deep snow packs in the alpine and sub-alpine would have provided sufficient insulation of the bottom layers of the snow pack, allowing it to remain near isothermal, facilitating slow but consistent melt. Additionally, there were inevitable limitations in snow melt lysimeter design which may have inhibited their ability to capture the potential season long melt. Mainly, the lysimeters were designed to capture melt water beneath a snow pack on an impervious surface that was above the ground but beneath the snow pack. The result was a separation between the snow-ground interface with a barrier that could have inhibited processes such as temperature gradient metamorphism and thus stopped melt form occurring.

Shifting back to the $\delta^{18}O$ variations in surface waters in relation to snow melt, we actually observed a potentially different story. Focusing on the $\delta^{18}O$ alone, there was enrichment in $\delta^{18}O$ from snow melt to surface waters across all catchments. However, the enrichment was significant in both the GL4 and Como Creek catchments (both $p <. 0001$) but not significant in Gordon Gulch ($p = 0.16$). These results are contradictory to the δD excess results that supported the notion that higher air temperatures at lower elevations increased evaporation rates and evaporative fractionation as the water traveled from the point of infiltration to the stream channel. The answer may lie in the additional variable of time and its influence on the magnitude of isotopic fractionation within the snow pack and as liquid water moving through the subsurface. For Gordon Gulch the snow pack may simply not last long enough on the ground to undergo fractionation before it melts and follows various pathways to the stream channel. Therefore the information provided by both the $\delta^{18}O$ and δD excess results may not provide sufficient insight into the time component of the fractionation of water isotopes. Therefore, to properly understand this dynamic it is necessary to understand the flow paths and residence times of the water moving through the catchments, which will be addressed in chapter 2.

1.6 Conclusion

The air temperature and precipitation values measured during the study were both within 15% of the long-term averages across the Boulder Creek watershed, suggesting that 2009 was a near average year with respect to climate. Therefore, the detailed monitoring of winter precipitation, snow cover, snow melt, and stream flow in three headwater catchments in Boulder Creek watershed during the 2009-2010 snow season accurately demonstrated the normal variability in isotopic composition of water moving through the watershed. Across the three catchments there was no significant difference in the annual or seasonal composition of $\delta^{18}O$, which was most likely due to large deviations in $\delta^{18}O$ values from storm to storm at any one site. This study also suggests that there was no significant fractionation of isotopes during canopy interception of snow in any of the catchments.

Analysis of the seasonal snow pack indicated that the mean $\delta^{18}O$ generally became more enriched throughout the accumulation season while the standard deviation of $\delta^{18}O$ decreased throughout the accumulation season, which demonstrated a homogenization of the snow pack throughout the winter. Overall, both the open and under canopy mean $\delta^{18}O$ of snow packs varied significantly with elevation, which was not observed in incoming precipitation, indicating that the processes driving isotopic fractionation during snow pack evolution are significantly varied across the elevational gradient within the watershed.

Across the study sites there remained a significant difference in the $\delta^{18}O$ of melt water with elevation. Interestingly, within sites there was no significant difference between the mean $\delta^{18}O$ of melt water in open and under canopy environments, further indicating that the processes driving isotopic evolution of water varied with elevation but that those processes were similar within sites between canopy and open settings during snow melt. Lastly, all surface water samples showed signs of either continued isotopic fractionation after snow melt entered the subsurface or a mixing of waters with differing isotopic compositions before exiting the catchments as steam flow. These findings indicate that understanding the processes driving isotopic evolution of snow packs and subsequent melt may be more relevant then simply knowing the isotopic composition of precipitation, especially if the isotope signals are to be used as tracers for understanding watershed scale hydrologic processes.

Use of Isotopic and Geochemical Tracers to Estimate Flowpaths, Source Waters, and Groundwater Residence Times in Headwater Catchments Across an Elevational Gradient in Boulder Creek Watershed, Colorado

Abstract

Isotopic ($\delta^{18}O$ and ^{3}H (tritium)) and geochemical (Na^{+}, Si, and DOC) tracers were used to investigate residence times, source waters, and flow paths in 4 headwater catchments along a 2,310 m elevational gradient within the Boulder Creek Watershed in the Front Range of Colorado. A baseline characterization of the amount and type of precipitation occurring across the elevational gradient was also produced. Precipitation totals from 2009 ranged from 563 mm at 1800 m to a high of 1214 mm at 3528 m. The precipitation was 85% snow at the highest elevation and only 32% snow at the lowest elevation. Application of a convolution integral to the $\delta^{18}O$ values in precipitation and stream waters produced relatively short mean residence times ranging from 1.12 years in the alpine to 2.08 years in the lower montane ecosystem. Tritium analysis indicated relatively young surface water ages and supported the results from the residence time calculations. Two-component mixing models were run using $\delta^{18}O$ to identify new and old waters and Silica (Si) to identify reacted and un-reacted waters. All three streams consisted of greater then 50% old and greater than 50% reacted waters with the peaks in new and un-reacted water generally occurring during the receding limb of the hydrographs. Additionally, runoff efficiency decreases with elevation from a high of 75.9% in the alpine to a low of just 12.2% at the lowest elevation catchment. The runoff efficiency calculations were made to better understand the connections between surface water discharge and the recharge and residence times of subsurface flow. These results indicate that headwater catchments within Boulder Creek Watershed have relatively short groundwater residence times and that groundwater plays an important role in streamflow generation. An overall improvement in understanding the spatial-temporal variations of streamflow generation under predicted changes in climactic conditions will become increasingly important as hydrologic inputs change drastically and outputs are increasingly needed for human consumption.

2.1 Introduction

The hydrology of the western United States and many other semi-arid regions of the world are dominated by snowmelt runoff (Serreze et al. 1999). In general, the western United States is predicted to face warmer temperatures, more frequent and prolonged droughts, and more precipitation falling in intense storms (Doherty et al., 2009). When these factors combine we can expect to see a decrease in annual snow pack, earlier onset of snowmelt, and increased evaporation (Stewart et al., 2005; Clow, 2010; Pielke et al., 2005). Understanding changes in streamflow generation, and surface groundwater interactions, under these changing climatic conditions will become increasingly important as water availability becomes limiting for domestic, municipal, and agricultural uses. An outstanding question for snowmelt-dominated watersheds of the western US is the role groundwater plays in streamflow generation. We know little about mountain aquifers because they commonly involve structurally complicated rocks, extreme head gradients (ground slope angles 10-40°), and dramatically fluctuating recharge driven by seasonal snow melt (Liu et al., 2004; Manning & Caine, 2007). Groundwater flow occurs primarily through fractures in these crystalline catchments, reducing the effectiveness of the classic porous medium approach for understanding surface-groundwater interactions (Hazen et al., 2002).

The course-grained nature of the surface geological material and steep slopes in alpine catchments has led to the common assumption that these basins have little water-storage capacity resulting in rapid movement of water through the subsurface (Clow, 2003). There are also many traditional views held that high altitude basins effectively act as “teflon” basins where snowmelt travels directly to streams with little or no chemical or physical interaction with the subsurface. Recent studies of alpine areas (Williams et al., 1997; Mitchel et al., 2000; Sueker et al., 2000;

Liu et al., 2004) have dispelled the myth of a "teflon" basin and established that subsurface waters are contributing to streamflow, even in alpine settings. These studies have focused on landscape controls on stream water composition and have sought to characterize the source waters and flow paths in alpine catchments. The research of Liu et al. (2004) showed that the stable isotope composition of mountain surface waters could be substantially different than that of the local precipitation. These differences have been attributed to regional water budgets dominated by snowmelt at high elevations that contains highly depleted $\delta^{18}O$ values (Friedman et al., 1992). The groundwater in these systems can also be dominated by isotopic compositions consistent with cold season precipitation due to lack of infiltration of precipitation during the warmer months when evapotranspiration is high (Fritz et al., 1987; Simkins, 1995). Conversely, there are regional effects of evapotranspiration that enrich surface waters in $\delta^{18}O$ and δD (Gremillion and Wanielista, 2000). From a biogeochemical standpoint Hood et al. (2003a) reported that along an elevational gradient on North Boulder Creek in the Colorado Front Range hydrologic flowpaths were responsible for changes in the quantity and quality of dissolved organic carbon (DOC) in stream water.

Watersheds above tree line have seen lots of research on surface-groundwater interaction (Liu et al., 2004; Manning & Caine, 2007). However, there has been little research exploring surface-groundwater interaction in sub-alpine and montane ecosystems. A lack of research at lower elevation mountain headwater catchments results in few studies that span large elevational gradients and that investigate both seasonally snow-packed and intermittently snow covered catchments within the same watershed.

An improved understanding of the magnitude and timing of groundwater contributions to streamflow in headwater catchments that span a large elevational gradient will enhance our ability to predict runoff and streamflow generation in response to changes in climate. Additionally, detailed understanding of the amount and type of precipitation entering the system under current climactic conditions will aid in modeling future hydrologic conditions created by perturbations like climate change and the mountain pine beetle epidemic. The over arching hypothesis is that space, in the form of the elevational gradient, can be substituted for time in terms of predicting how future changes in climate may affect the local hydrology. For example, Fleischer and Sternberg (2006) demonstrated the "space for time" approach by showing that changes in climactic conditions are simulated by comparing areas that naturally differ in their climatic regimes. Additionally, Nayak et al. (2010) measured temperature, precipitation, snow, and streamflow data for valley bottom, mid-elevation, and high-elevation sites within the Reynolds Creek Experimental Watershed, located in the state of Idaho, United States to evaluate the extent and magnitude of the impact of climate warming on the hydrology and related resources in the interior northwestern United States. They report that there is a significant elevation gradient in either timing or magnitude in the length of the seasonally snow-covered season and the amount of snowfall. Therefore the current inputs to lower elevation mountain catchments provide insight into what may be received by higher elevation catchments in the future.

Care must be taken when extrapolating physical processes from lower elevations to higher elevations along an altitudinal gradient. In terms of local hydrological cycling there are two categories of environmental changes with altitude: those physically tied to meters above sea level, such as atmospheric pressure, temperature and incoming solar radiations; and those that are not generally altitude specific, such as the underlying geology and even human land use changes. The confounding of the first category by the latter has introduced confusion in the scientific literature on the altitude phenomena (Korner, 2007). Therefore, in addition to the altitude driven climate variables it is also important to recognize that the condition of the land surface and the structure of the subsurface may play a significant role in the above-mentioned surface and groundwater interactions at the catchment scale. The first step is to identify the differences in sub-surface architecture, which are likely to occur across the elevational gradient of a mountain watershed, and then recognize how the various conditions are influencing the current state of water movement through the subsurface. Knowing that changes to the structure of the subsurface occur on much longer geologic time scales then current rates of climactic change, the subsurface can be treated as in relatively steady state when predicting hydrologic changes on the decade to century scale. The result is an ability to apply the space for time concept to changes in temperature and precipitation and then use those projected changes to infer how surface and groundwater interactions will respond at the catchment scale across entire watersheds. The results from catchment scale studies can then be applied to larger mountain range scale assessments if subsurface structure is understood and climactic conditions can be linked to elevation.

The goal of this research is to first establish a baseline characterization of the amount and type of precipitation occurring across an elevational gradient in Boulder Creek Watershed for calendar year 2009. Additionally, the isotopic ($\delta^{18}O$, δD and ^{3}H (tritium)), geochemical (Na+, Si) and biological (DOC) signatures occurring in the precipitation and surface waters of 4 distinct headwater catchments will be analyzed to calculate the relative contributions of source waters and to understand the flowpaths and mean residence times of subsurface water. An improved understanding of the current catchment scale surface and groundwater interactions across the elevational gradient will then allow for application of the space for time hypothesis to predict future hydrologic conditions in the Boulder Creek Watershed.

The specific research questions are:

1. How does the amount and type of precipitation falling in the catchments change with elevation?

2. How does runoff efficiency change with elevation?

3. How do sub-surface residence times vary between alpine, sub-alpine, and montane catchments of Boulder Creek?

4. What are the relative contributions of sources waters to streamflow generation across the three catchments?

5. How do flowpaths vary across the three catchments?

2.2 Study Area

The Boulder Creek catchment (BCC) is about 1160 km^2 in area and drains the Colorado Front Range from the Continental Divide (4120m) to the eastern plains (1480m) (Figure 2.1). Here we focus on four headwater catchments of the Boulder Creek Watershed: long-term data collected by the NWT LTER program at the Green Lakes Valley and Como Creek catchments, and the Gordon Gulch and Betasso catchments which the Boulder Creek Critical Zone Observatory (BC-CZO) began instrumenting in the fall of 2008. The BCC encompasses four climatic zones: alpine, sub-alpine, montane, and foothills (Table 2.1). The underlying bedrock is similar among the four catchments, Precambrian crystalline rock that is primarily granodirite, with nearly equal percentages of gneiss and schist in the alpine and becoming predominantly gneiss in the montane (Braddock and Cole, 1990).

Table 2.1: Sampling site descriptions with site abbreviation, elevation at the basin outlet (m), catchment area (ha), dominant landscape type with percent of forest cover, mean annual air temperature **(°C)**, and mean annual precipitation (mm). Mean air temperature and precipitation values are long-term averages from each site.

Site	**Elevation (m)**	**Catchment Area (ha)**	**Landscape Type/ (% Vegetation Cover)**	**Mean Annual Air Temperature (°C)**	**Mean Annual Precipitation (mm)**
Green Lake 4 Outlet	3550	225	Alpine (0.09%)	-3.8	1000
Como Creek	2910	664	Sub-alpine (81%)	4.0	800
Gordon Gulch	2588	101	Montane (68%)	6.83	536
Betasso	1810	45	Foothills (55%)	10.72	476

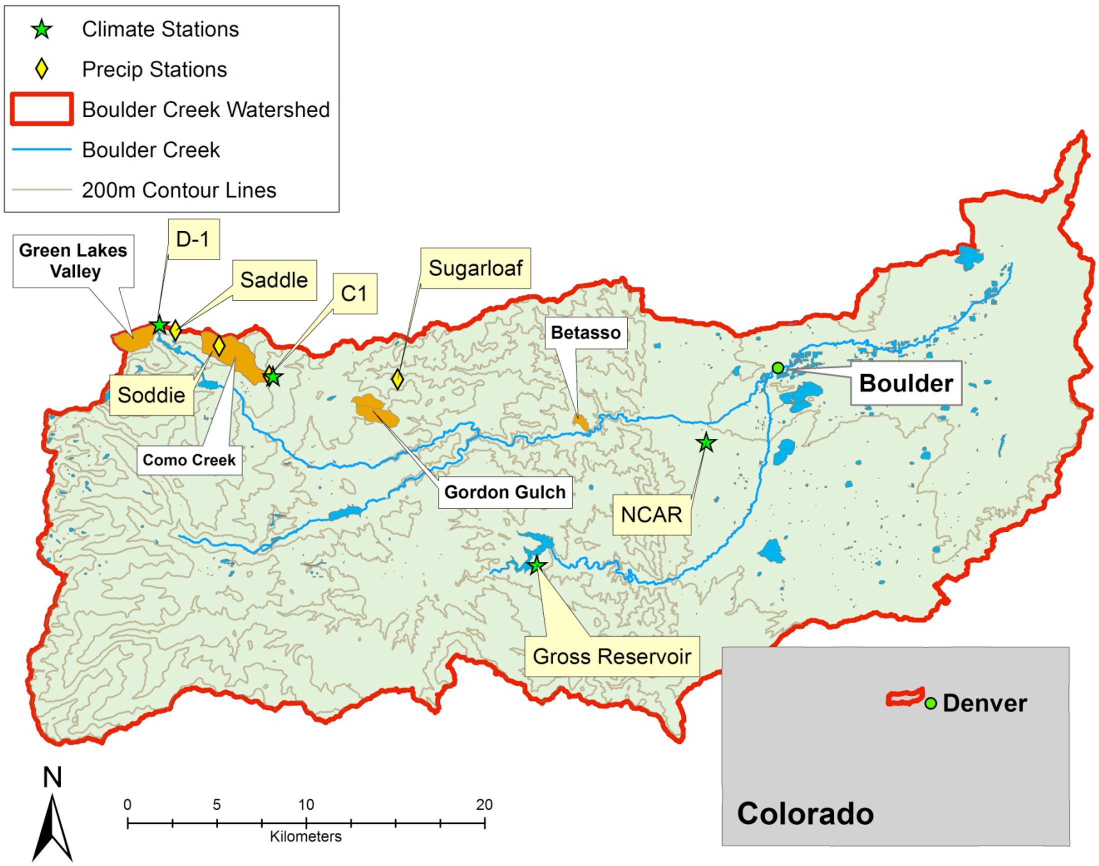

Figure 2.1: Boulder Creek watershed showing locations of each of the four headwater catchments along with the locations of climate and precipitation measurement stations. All snow pack and snow melt sampling occurred adjacent to the precipitation stations except Gordon Gulch where sampling occurred within the catchment near the gauging station rather than at the Sugarloaf precipitation station. The elevation of the watershed ranges from a high of 4120 m along the western boundary to a low of 1420 m in the eastern plains.

The upper Green Lakes Valley is an east-facing glacial valley, headed on the Continental Divide in the Colorado Front Range (40°030N, 105°350W). Named for a series of shallow paternoster lakes, the Green Lakes Valley is the headwaters of North Boulder Creek and lies within the City of Boulder Watershed. The upper valley is approximately 225 ha in area, and the elevation ranges from 4084 m at the Continental Divide to 3515 m at the outlet of Green Lakes 4 (GL4) (Figure 2.2) (Table 2.1). GL4 is a typical alpine headwater catchment in the Colorado

Front Range where active and inactive rock glaciers are indicative of underlying permafrost (Janke, 2005). Patterned ground and active solifluction lobes are also common in parts of Niwot Ridge and Green Lakes Valley, especially on ridgelines (Benedict, 1970). Permafrost has been verified above 3500 m on Niwot Ridge (Ives and Fahey, 1971) and more recently by geophysical methods near Green Lake 5 (Leopold et al., 2008). The catchment consists of steep rock walls above talus slopes and rock glaciers with a valley floor of glacially scoured bedrock. Exposed bedrock makes up 29% of the basin area, talus 33%, vegetated soils 29%, the Arikaree glacier 4%, and the two lakes (GL4 and Green Lakes 5) make up the final 5% (Erickson et al., 2005). The alpine vegetation is growing on moderately well developed soils, exhibiting Oe, A, and 2Bw horizons, most of which are located in the valley bottom (Litaor, 1988). Geophysical and drilling data collected on the slopes of Niwot ridge, the northeastern border of the catchment, show that the depth to bedrock ranges from 4 to greater than 10 m, with the top 1 to 2 m consisting of soils and unconsolidated materials overlaying either bedrock or periglacial slope deposits that vary from 1 to 8 m thick (Leopold et al., 2008). Additionally, the Green Lakes Valley is located on the western edge of the Lake Albion mining district that contains a series of well-developed faults (Williams et al., 2006), indicating the potential for additional faults providing considerable secondary porosity within the catchment.

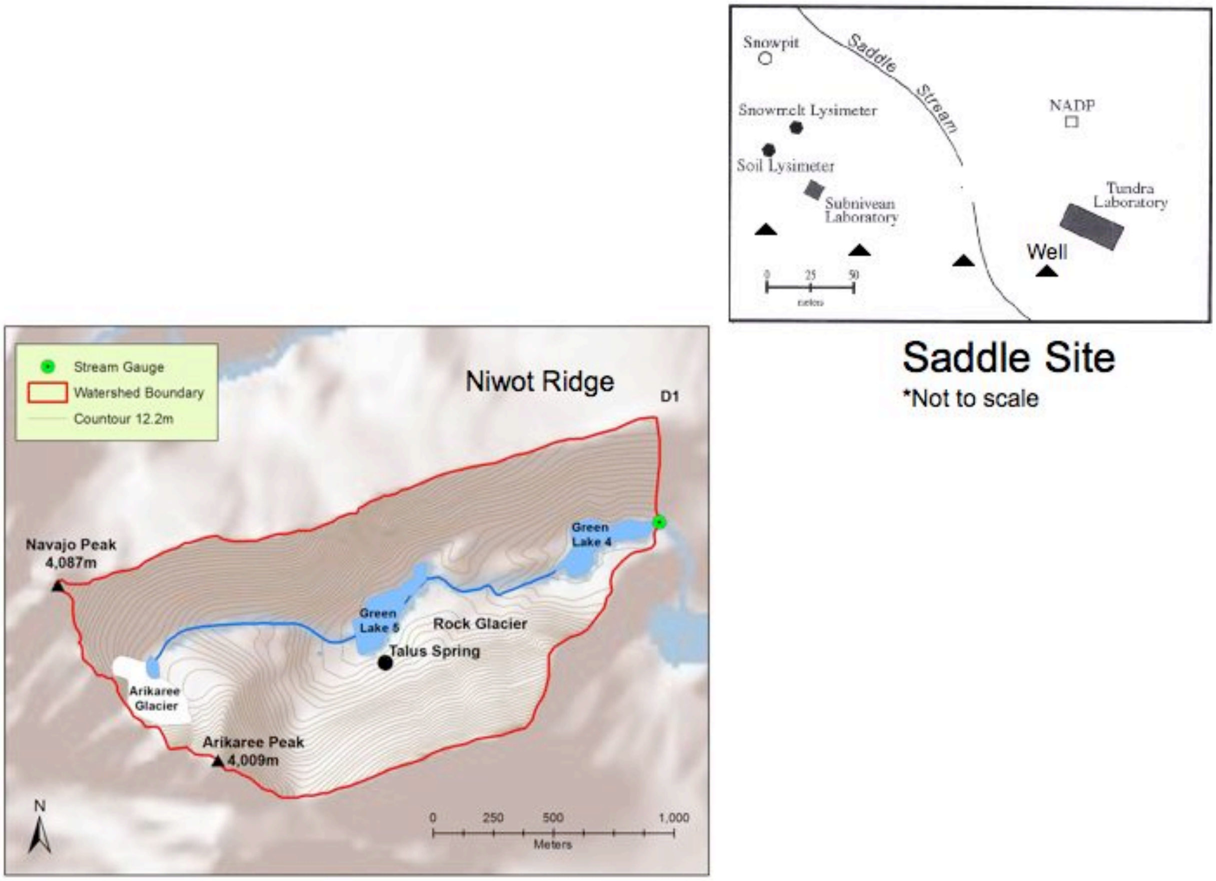

Figure 2.2: Contour map of the Green Lake 4 catchment and enlargement of the Saddle experimental study located on Niwot Ridge 3 km east of the D1 climate station. The saddle site inset shows the locations of the NADP wet-chemistry collector, groundwater sampling wells, snow melt lysimeters, and the snow pits. The Green Lake 4 catchment map shows locations of the stream gauge, talus slope spring, the Arikaree glacier, and the Green Lake 5 rock glacier.

Climate is characterized by long, cool winters and a short growing season (1-3 months). Since 1951, mean annual temperature is -3.8°C, and annual precipitation is 1000m (Williams et al., 1996). About 80% of the annual precipitation occurs as snow. Streamflows are markedly seasonal, varying from < 0.05 m^3 s^{-1} during the winter months to > 3.0 m^3 s^{-1} at maximum discharge during snowmelt. Surface waters are dilute, with acid neutralizing capacities (ANC) generally < 200 μeqL at all sampling sites (Williams et al. 2001).

The Saddle site (40º 03' 17" N; 105º 35' 21" W; 3528 m) is located in alpine tundra on the northern ridge of Green Lakes Valley with research infrastructure including snow and soil lysimeters, a subnivean laboratory, and an aerometrics wet-chemistry precipitation collector, which is part of the National Atmospheric Deposition Program (NADP) (site CO02) (Figure 2.2). Groundwater wells were installed at the Saddle site in the fall of 2005. Wells were drilled to a depth of 9 m, cased, and screened at the bottom 1.6 m.

Como Creek originates just to the north and east of Green Lakes Valley on the southeast flank of Niwot Ridge, approximately 8 km east of the Continental Divide (Figure 2.3). The catchment falls within the Niwot Ridge Biosphere Reserve, has an area of 664 ha, and ranges in elevation from 2900 m to 3560 m (Table 2.1). The Como Creek catchment differs from the nearby Green Lake 4 catchment in two important respects: 1) There are no paternoster lakes, and 2) there is no talus, exposed bedrock, steep cliffs, or periglacial features such as rock glaciers. The area was glaciated during the Pleistocene and the lower half of the Como Creek catchment resides primarily on the Arapaho moraine (USGS Ward quadrangle). Soil development varies throughout the catchment with a mean of 60 cm and a maximum of about 200 cm, but is deeper in areas composed of glacial till (Lewis and Grant, 1978). Neither the spatial extent nor thickness of glacially deposited materials have been directly measured within the Como Creek catchment, though the USGS ward quadrangle estimates the moraine thickness at about 10 m. A recently installed sampling well near the C-1 site was drilled to a depth of 33 m and did not encounter bedrock, further indicating significant depths of glacial deposits within the Como Creek catchment.

Approximately 80% of the catchment is below tree line and consists of primarily coniferous forest that was last deforested nearly a century ago, but has seen minimal human disturbance since that time (Lewis & Grant, 1979). The forest has a mixture of trees dominated by Engelmann spruce (*Picea engelmannii*), sub-alpine fir (*Abies lasiocarpa*), limber pine (*Pinus flexilis*) and lodgepole pine *(Pinus contorta)*, with some aspen (*Populus tremuloides*).

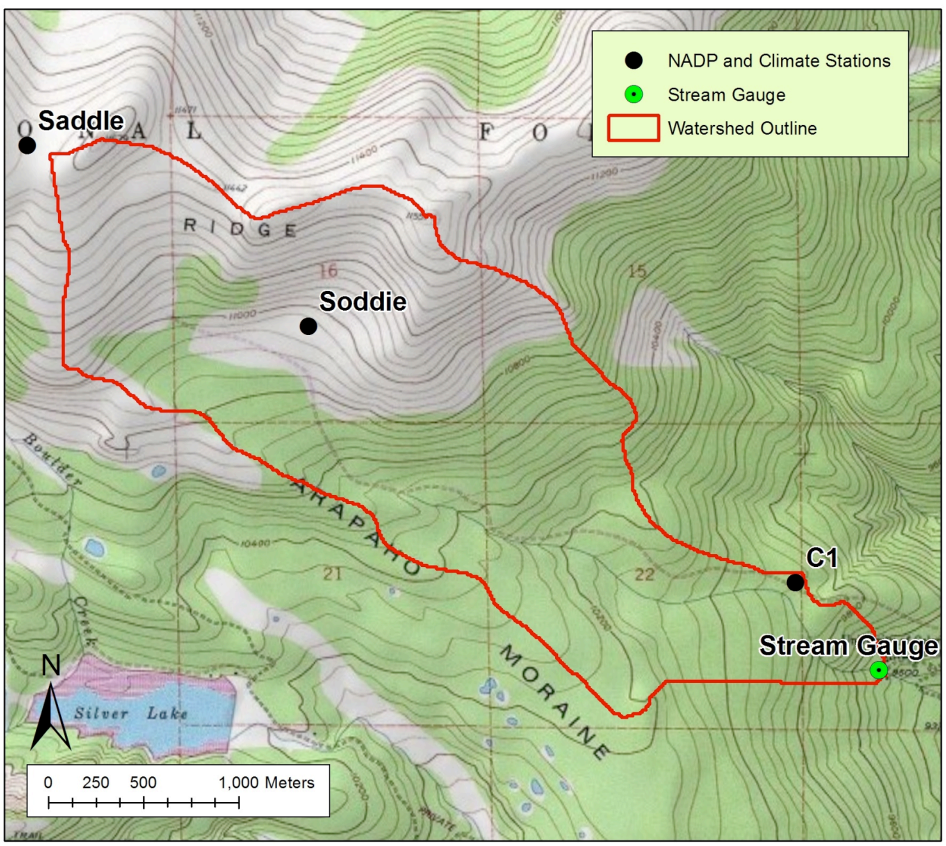

Figure 2.3: Como Creek catchment showing relative locations of sampling locations and the stream gauge.

The Soddie site (40º 02’ 52” N; 105º 34’ 15” W; 3345 m) is located near the upper extent of Como Creek catchment just below the treeline ecotone. This site has an underground laboratory 10'x30'x8' in size, line power, with an array of snow lysimeters and zero-tension soil lysimeters. Adjacent to the soil lysimeters is a suite of meteorological instruments sufficient to close the energy balance. (Williams et al. 2009). Snow pits were sampled about weekly for physical and chemical parameters. NWTLTER also operates an unofficial NADP wet chemistry collector at the Soddie site, using the same instruments and protocols that the NADP program uses.

The C-1 site (40º 02’ 09” N; 105º 32’ 09” W; 3021 m) within the lower part of the Como Creek catchment is part of a long-term meteorological study that has recorded continuous climate measurements since the 1950's (Williams et al. (1996). The mean annual temperature is 4ºC and mean annual precipitation is 800 mm (Monson et al. 2002). The C-1 site contains an NADP site (CO90) that was established in 2006 and also participates in the Ameriflux program (Monson et al., 2002). The SnoTel network operates the NIWOT 663 site here (http://www.wcc.nrcs.usda.gov/snotel/snotel.pl?sitenum=663&state=co).

Gordon Gulch is a small (101.44 ha) sub-catchment in a mixed conifer montane ecosystem at 2500 m elevation (range 2400 to 2650m) (Table 2.1). Gordon Gulch is a predominantly west to east drainage resulting in distinct north and south facing slopes representing distinctly different vegetation communities (Figure 2.4). The north aspect slopes are dominated by Lodgepole pine (*Pinus contorta)* stands of nearly uniform size and age characteristics, along with the more shade tolerant Rocky Mountain Douglas-fir (*Psuedotsuga menziesii* var. *glauca*) and Colorado Blue Spruce (*Picea pungens*). The south aspect slopes have a more open and mosaic patchwork of Ponderosa pine (*Pinus ponderosa*), interspersed with

Rocky Mountain Juniper (*Juniperus scopulorum*) and common shrubs including Mountain-mahogany (*Cercocarpus spp.*) and Hawthorn (*Crataegus spp.*). Gordon Gulch lies within the low-relief post-Laramide surface below the glacial limit (Bradley, 1987). Apparently inconsistent for this type of rolling upland surface, Gordon Gulch contains steep topography with many bedrock exposures of Precambrian granites, gneisses and schists. Geophysical characterization of the subsurface using shallow seismic refraction shows that slow velocity materials (taken to be unconsolidated materials) are generally less than 1m thick while weathered bedrock profiles extend to depths of 11 to 15 m (Befus, 2010). Soil pits dug on north and south facing slopes (n = 6) show that soil development was generally 30 cm to 60 cm thick on the north and south facing slopes and marginally deeper in soil pits (n = 3) located in riparian areas at the bottom of the catchment near the stream channel.

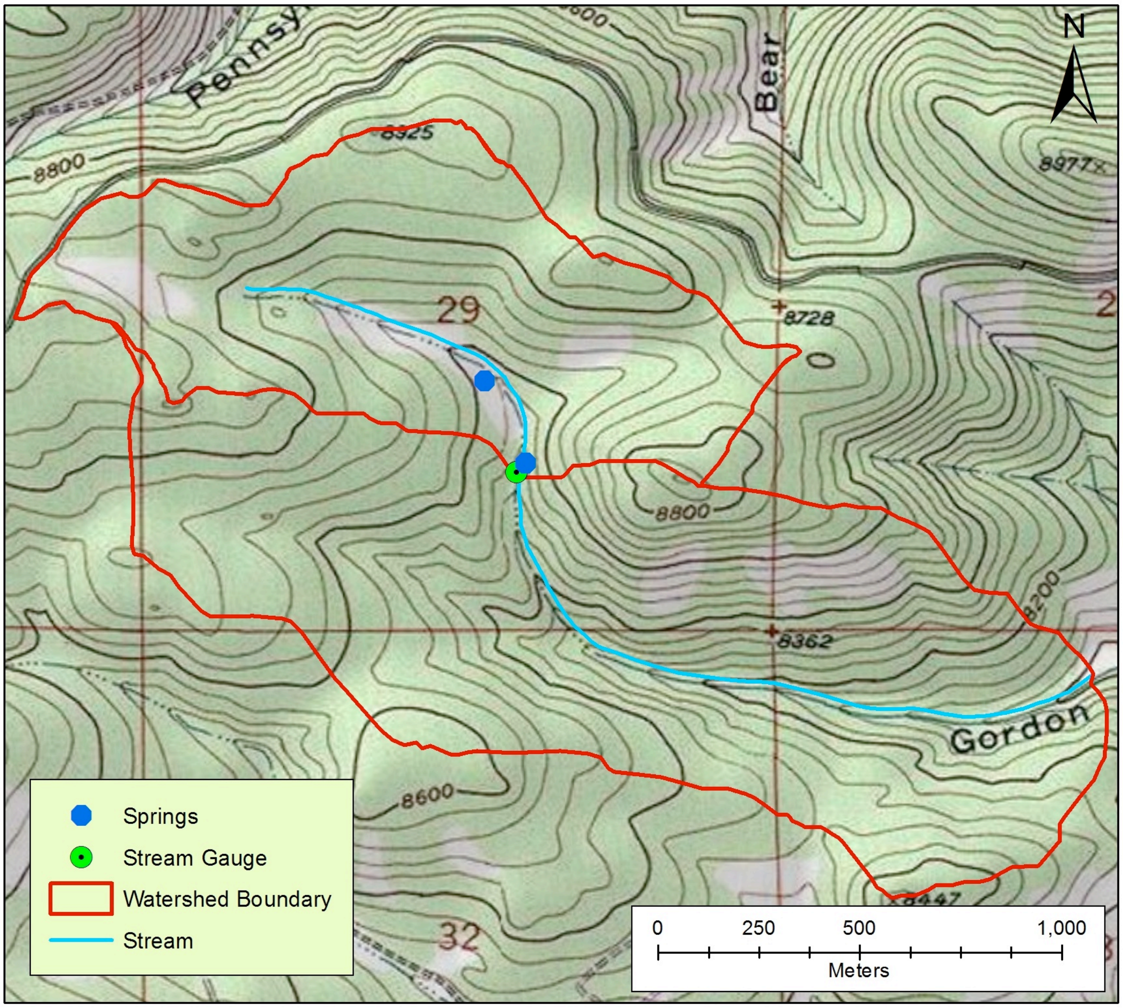

Figure 2.4: Gordon Gulch Catchment showing the locations of the stream gauge and springs sampled. This study only focused on the upper basin due to a longer discharge record for the gauge measuring flow exiting the upper basin.

The Sugarloaf NADP site (CO94) (39.9939 N; -105.48 W; 2524 m) is located about 2 km to the northeast of Gordon Gulch and was used to collect both meteorological and precipitation data for Gordon Gulch (see Figure 2.1).

Betasso is the lowest of the four headwater catchments, ranging in elevation from 1810 m to 2024 m, and is representative of a foothill montane ecosystem with Ponderosa pine (*Pinus ponderosa*) the dominant vegetation type (Table 2.1). Betasso is the smallest of the studied catchments with an area of 45 ha and is situated in lower Boulder Canyon about 10 km west of the city of Boulder and about 6 km downstream of the knick zone of Boulder Creek (Figure 2.5). The upper portion of the Betasso catchment looks similar to the Gordon Gulch landscape with gentle rolling slopes that are remnants of the post-Laramide surface. In contrast, the lower portion of the Betasso catchment is steeply incised and is drained by an ephemeral channel that is a tributary to the main channel of middle Boulder Creek. These steep slopes were formed over the last 5 million years by renewed bedrock channel incision progressing headward from the plains, cutting into the post-Laramide surface (Anderson et al., 2006).

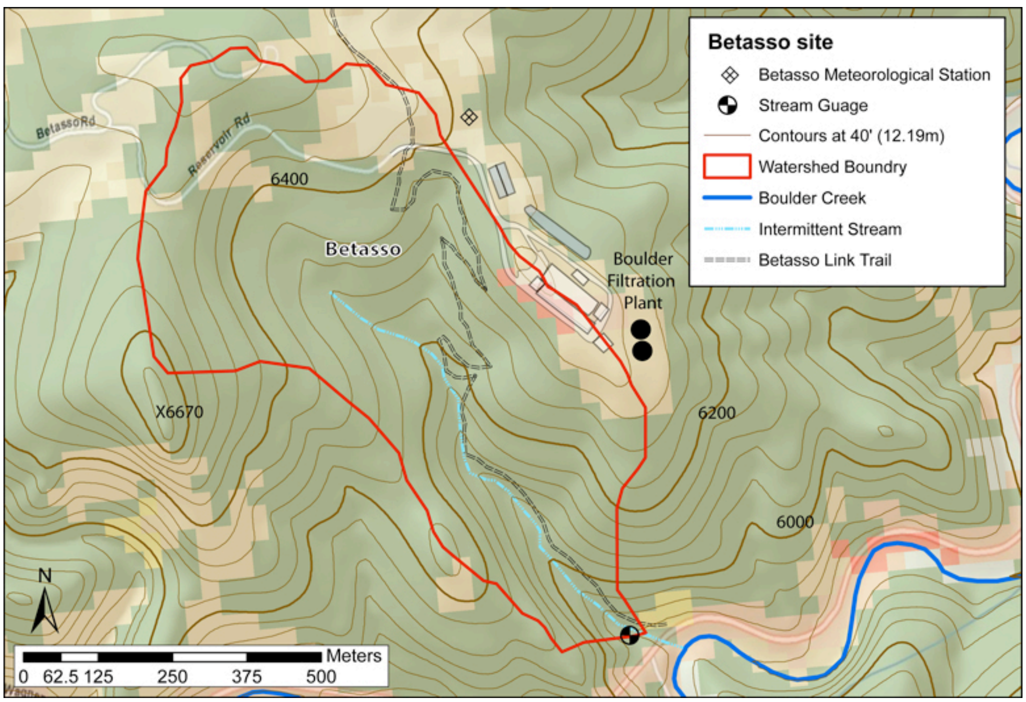

Figure 2.5: The Betasso catchment showing the relative locations of the meteorological tower and stream gauge.

2.3 Data and Methods

2.3.1 Climate and meteorological measurements

Climate data has been recorded at the D1 and C1 stations on Niwot Ridge since the early 1950's. D1 is located in alpine tundra at an elevation of 3700 m, 2.6 km from the Continental Divide. The C1 climate station is located in sub-alpine forest at an elevation of 3,005 m, 9.7 km east of the Continental Divide. Climate data for Gordon Gulch is represented by the Gross Reservoir station at an elevation of 2,309 m, which has continuous measurements since 1978 and was compiled from the Western Regional Climate Center (http://www.wrcc.dri.edu). For Betasso, we used the climate data compiled from the National Center for Atmospheric Research (NCAR) climate station (1670 m), which has continuous measurements since 1893 and was also obtained from the Western Regional Climate Center. For all climate station sites, we report the 2009 annual precipitation and mean annual temperatures and compare 2009 to the long-term averages for each site. Daily precipitation totals for 2009 were classified as either snow, mixed, or rain based on temperature records during precipitation events. If the local air temperature was greater then 2°C then the precipitation was classified as rain. If the temperature changed during the precipitation event and crossed the 2°C point in either direction, or if there were multiple events during one day where at least one event is in the opposite of all the others for that day then the precipitation was classified as mixed. If the air temperature was less than 2°C then the precipitation was classified as snow. Due to the over-collection of cold season precipitation (October-May) in the form of blowing snow at the Saddle site, the winter precipitation values at the Saddle were reduced by 39% following the recommendations of Williams et al. (1998).

The snowpack was sampled approximately weekly for chemical content, physical properties, and oxygen isotopes of water from 2009 to 2010 following the protocols of Williams et al. (1999; 2009). Here we report values for the Saddle site, Soddie, C1, and Gordon Gulch sampled at the time of maximum snow depth and prior to snowmelt, when maximum loading of solutes stored in the seasonal snowpack occurs (Williams et al. 2009). Snow samples were collected for chemical and oxygen isotopic analyses using beveled PVC tubes (50-mm diameter, 500-mm long), which had been soaked in 10% HCl and then rinsed at least five times with deionized water. Duplicate, vertical, contiguous cores in increments of 40-cm were collected from the snow-air interface to the snow-ground interface. Snow was transferred from the cores into new polyethylene bags and transported about 3 km to our analytical facilities the same day as collection. The depth-integrated concentrations of solutes in the snowpack for each duplicate core were determined by calculating the volume-weighted mean concentrations (VWM) as in Williams and Melack (1991a,b) and Williams et al. (1996, 1999). Here we report the mean value of the two cores collected at maximum accumulation each year. At the Saddle, Soddie, and C-1 sites snow melt was also collected and analyzed following the same methods outlined in chapter one of this paper.

2.3.2 Surface and Groundwater Sampling

Stream samples were collected as grab samples following the protocol of Williams et al. (2009). Samples were collected weekly during the ice-free season from about May 1 to October in Green Lakes Valley and Como Creek. At Gordon Gulch and Betasso, samples were collected weekly April-July 2009 and biweekly on the recession curve of the hydrograph during the later summer and fall (August-October 2009), to provide more samples during the period where the hydrograph was changing the most. Samples were collected in cleaned HDPE bottles after rinsing three times with sample water at the time of collection. Samples were transported within a few hours of collection to the Kiowa Environmental Chemistry Laboratory, where sub samples were immediately filtered through pre-combusted glass fiber filters with a nominal pore size of 0.7 μm and stored in the dark at 4°C prior to analyses. Samples for DOC analyses were collected in pre-combusted amber glass bottles with Teflon-lined caps. Water samples for isotopic analysis were collected un-filtered in cleaned, 25-mL, borosilicate bottles with no-headspace lids to avoid any evaporation or fractionation. On an approximately quarterly basis water samples were also collected as grab samples in 1L HDPE bottles and analyzed for ^3H (Tritium).

Groundwater was sampled weekly during ice-free months and monthly during the winter at the alpine Saddle site from four observation wells located on Niwot ridge along the north west boundary of the Como Creek watershed. Sampling was performed with a 1-m teflon bailer to minimize chemical contamination after purging three well volumes, and then followed the protocol for surface water collection. Additionally, a talus spring was sampled weekly during summer months in GL4 to analyze sub-surface water from within the alpine catchment (Figure 2.2). In Gordon Gulch two springs, one on a predominantly north facing slope and one on a predominantly south facing slope, were also sampled weekly to analyze sub-surface water in the absence of wells (Figure 2.4).

2.3.3 Discharge

Water level was measured with a pressure transducer and converted to volumetric discharges by empirical rating curves at the outlets of the four catchments (Table 2.1). For GL4 and Como Creek catchments, I used established rating curves developed by NWTLTER. For

Gordon Gulch and Betasso I developed new protocols for measuring discharge. In Gordon Gulch and Betasso rectangular weirs with stilling wells were constructed in the fall of 2008. Stage height was measured with a Solinst Levelogger Gold pressure transducer. At all catchments the transducers were installed and removed annually due to the possibility of freezing in the stilling well, which resulted in variations in the start and end dates of discharge measurements across the catchments. However, the discharge not measured by the transducers was primarily during ice-on conditions and thus assumed to represent an insignificant amount of total annual discharge (e.g. Liu et al. 2004).

2.3.4 Laboratory Analyses

All precipitation and water samples were analyzed for pH, acid-neutralizing capacity (ANC), specific conductance, H^+, NH_4^+, Ca^{2+}, Na^+, Mg^{2+}, K^+, Cl^-, NO_3^-, SO_4^{2-}, Si, DOC, dissolved organic nitrogen (DON) and total nitrogen (TN) at the Kiowa Environmental Chemistry Laboratory in Boulder, CO. Detection limits and instrumentation are as presented in Williams et al. (2009); in general detection limits for all solutes were less than 1 μeq L^{-1}.

Samples were also analyzed for D and ^{18}O using an L1102-i Isotopic Liquid Water Analyzer, developed by Picarro Incorporated. The analyzer is based on Picarro's unique Wavelength- Scanned Cavity Ring Down Spectroscopy (WS-CRDS), which is a time-based measurement using near-infrared laser to quantify spectral features of molecules in a gas contained in an optical measurement cavity. Isotopic compositions are expressed as a δ (per mil) ratio of the sample to the Vienna Standard Mean Ocean Water (V-SMOW), as shown for $^{18}0$:

$$\delta^{18}O = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{VSMOW}}{(^{18}O/^{16}O)_{VSMOW}} \times 1000$$ (Equation 2.1)

The precision for $\delta^{18}O$ was ±0.05‰ and for D was ±0.1‰.

Tritium was analyzed at the USGS Tritium Laboratory in Menlo Park California by electrolytic enrichment and liquid scintillation counting. Distilled sample water was reduced electrolytically in electrolysis cells to 10 mL from an initial 200 mL in a cooling bath. This increases the concentration of tritium by a factor of 16. The remaining liquid is mixed with a scintillation cocktail of known tritium concentrations to improve baseline values. The sample is then counted in a Packard scintillation counter. Tritium concentrations are reported in "tritium units," or TU, with a precision of ±0.4 TU. 1 TU is defined as equal to 1 tritium atom per 10^{18} hydrogen atoms. The detection limit is reported as twice the precision.

2.3.5 Residence Time

Average residence time for subsurface flow can be calculated by comparing the smoothing of the $\delta^{18}O$ input (precipitation) and output (streamflow) using a convolution algorithm (Maloszewski et al., 1983; Pearce et al., 1986). The time series of incoming $\delta^{18}O$ values from precipitation can be approximated as a sinusoidal function:

$\delta^{18}O_{in}(t) = A\sin(wt) + M$ (Equation 2.2)

Where: A is the amplitude of $\delta^{18}O$ variation in precipitation,
w is the period
M is the mean of the $\delta^{18}O$ variation.
t is time

If your period is 1 year then w is equal to 2π as sin functions units are in radians. Similarly the isotopic variation of streamflow can be characterized by:

$\delta^{18}O_{out}(t) = B\sin(wt + \varphi) + M$ (Equation 2.3)

Where: B is the amplitude of $\delta^{18}O$ variation in streamflow
φ is the phase shift.

By assuming a well mixed and exponential flow system the convolution integral has the form:

$$\delta_{out}(t) = \frac{1}{T}\int_0^{\infty}\delta_{in}(t - t')\exp(-t'/T)dt' \quad \text{(Equation 2.4)}$$

Where: T is the mean residence time
t′ is the lag time between input and output composition

Solving the integral produces the following solution:

$$T = \frac{1}{w}\sqrt{\left(\frac{A}{B}\right)^2 - 1} \quad \text{(Equation 2.5)}$$

This isotope-based age estimate includes the groundwater age, mixing, and transit time in the unsaturated zone (Plummer et al. (2001)). The convolution also assumes an exponential mixing model, which was introduced to hydrology by Eriksson (1958) who made the assumption that the distribution of transit times of water in the outflow of a system is exponential and corresponds to a probable situation of permeability decreasing with aquifer depth. Given the structural complexity and general lack of detailed investigations of mountain aquifers it is difficult to confirm or reject this assumption but it is recognized that deviations from this situation, such as preferential flow through fractures, are not specifically accounted for when using the convolution algorithm.

Additionally, the residence time can be constrained by measuring the amount of tritium found in surface and groundwater. Tritium enters the groundwater system through recharge initially derived from precipitation. An analysis of tritium concentrations in groundwater and surface water samples can provide information concerning the time since the water was isolated from the surface (i.e. recharge date). The activity of tritium available to form precipitation in the atmosphere greatly exceeded natural levels due to above-ground nuclear weapons testing in the 1950's and early 1960's. Tritium is a radioactive atom with a half-life of 12.33 years (Maloszewski et al., 1983) and thus is an ideal tracer for identifying relatively young groundwater. Since tritium is a part of the water molecule it does not undergo any substantial chemical reactions once the water has entered the subsurface and thus is an ideal hydrological tracer (Rose, 1996). One basic approach to estimating the age of a water source since recharge is to apply its radioactive decay equation with N(t) being the number of nuclei present after a certain time t:

$$N(t) = N_0 \, e^{-\lambda t} \qquad \text{(Equation 2.6)}$$

Where: N_0 is the initial number of nuclei present (incoming precipitation)
λ is the decay constant = $(\ln 2)/ T_{1/2}$
$T_{1/2}$ is the half life for Tritium = 12.33 years

2.3.6 Hydrograph Separation Models

A two-component mixing model can be used to determine the relative contribution of streamflow from old and new sources (Sklash and Farvolden, 1979; Bottomley et al., 1986; Liu et al., 2004) or reacted and unreacted sources (Caine, 1989; Williams et al., 1993; Liu et al., 2004). Using stable isotopic tracers such as $\delta^{18}O$ and δD we can differentiate between old and new contributions to streamflow. Similarly, streamflow can be separated between reacted and unreacted water sources using concentrations of solutes such as sodium (Na+) or silica (Si). Reacted water is defined as water that has infiltrated into the subsurface and collected mineral weathering products from the soil matrix. Conversely, unreacted water is defined as water that travels directly into the stream without interacting with the sub-surface. Mathematically this can be represented using a simple mass balance approach:

$$Q_T = Q_1 + Q_2 \qquad \text{(Equation 2.7)}$$

and

$$C_T\, Q_T = C_1\, Q_1 + C_2\, Q_2 \qquad \text{(Equation 2.8)}$$

Where: Q_T is total discharge
Q_1 and Q_2 are the discharge from each respective source
C is the concentration of the tracer from each reservoir

By solving for Q_1 and Q_2, using equations 2.7 and 2.8, the contribution from each source can be determined. Several conditions must be met for this two-component model, including (e.g., Sueker et al. (2000)): (1) Tracer values of each component must be significantly different; (2) there are only two components contributing to streamflow; and (3) the tracer composition of each component is constant for the duration of the event, or variation is known from measurements. If the tracer composition of an end-member is not constant then the value applied to the mixing model can be mathematically adjusted based on measurements of that end-member's concentrations over the time period to which the mixing model is being applied. In order to assess the overall validity of the two-component mixing model, we evaluated for each time step whether the contribution of each component to streamflow had a reasonable range from 0 to 100%, and calculated the ratio of these successful solutions to the total number of stream samples collected in 2009 (SR equals success ratio).

2.4 Results

2.4.1 Climate and meteorological measurements

The annual mean 2009 air temperature for Green Lakes Valley measured at the D1 climate station was -3.2°C (Table 2.2), within 15% of the 50-year mean of -3.7°C (Table 2.1). The annual mean temperature at the C1 climate station was 4.3°C, warmer than, but within 15% of the 50-year mean of 4.0°C. The mean temperature the GG site, as measured at Gross Reservoir was 5.1°C, slightly colder then the long-term mean of 6.8°C. The 2009 mean annual temperature at the NCAR climate station was 12.3°C, slightly warmer than the long-term average of 10.7°C. Calendar year 2009 was thus about average with respect to air temperature.

Table 2.2: Climate results from 2009.

Site	Annual air temperature (°C)	Annual Precipitation (mm)	Percent of annual precip as snow	Specific Discharge (mm)	Runoff Efficiency (%)
Betasso	+12.3	563	32	68.5	12.2
Gordon Gulch	+5.1	519	59	196	37.7
Como Creek	+4.3	842	70	168	20.0
Green Lake 4	-3.2	1214	86	921	75.9

Changes in the values of daily mean air temperature with elevation are illustrated using the high-elevation D1 climate station and the montane Gross Reservoir climate station (Figure 2.6). At the D1 site, winter temperatures were consistently below freezing at about -10°C, with daily mean air temperature rising to 0°C on about May 10. Air temperature than reached a maximum of near 12°C on August 24, before decreasing below freezing in late October. In contrast, daily mean air temperatures at Gross Reservoir were about 10°C higher than at D1.

Daily mean air temperatures fluctuated above and below freezing until about 1 February, when daily mean air temperature became consistently above freezing. Air temperature than reached a maximum of near 25°C on July 20, before decreasing towards freezing in December.

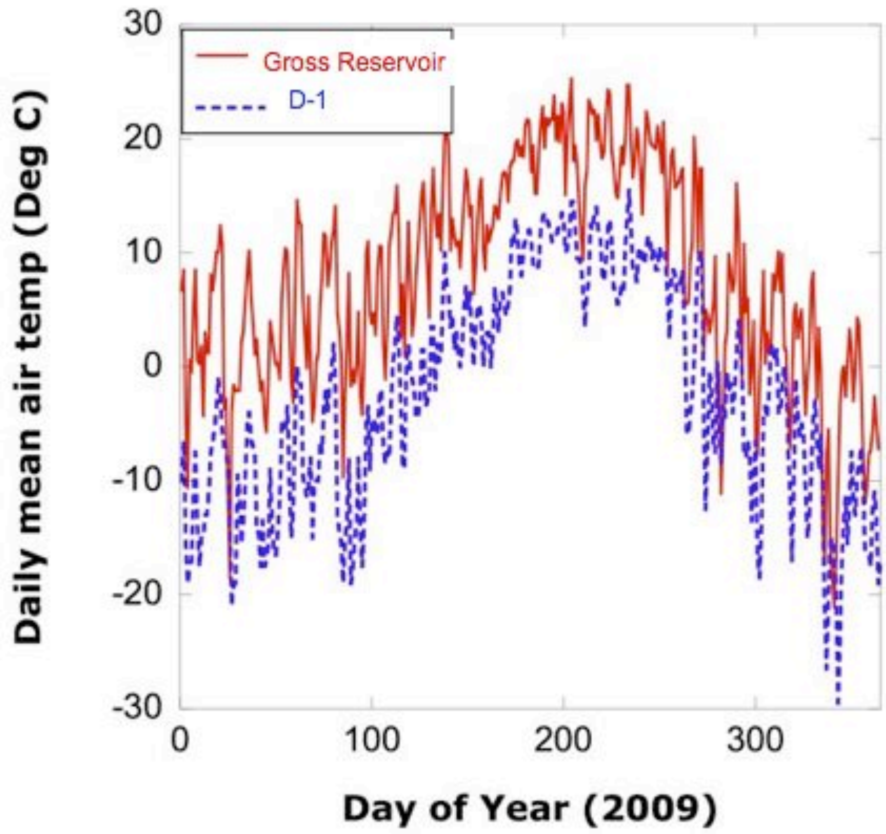

Figure 2.6: 2009 Daily mean air temperatures at Gross Reservoir climate station (2426 m) and the alpine climate station D-1 (3739 m).

In 2009 the annual precipitation and the amount of annual precipitation falling as snow generally increased with increasing elevation across the Boulder Creek watershed (Table 2.2) (Figure 2.7). The alpine Saddle site received 1214 mm of annual precipitation, with 85% falling as snow, 7% as mixed snow and rain, and 8% as rain. The sub-alpine Soddie site at 3345 m received 842 mm of precipitation, with 86% falling as snow, 5% as mixed, and 9% as rain. The upper montane C1 site at 3021 m received 804 mm of precipitation, with 70% falling as snow, 14% as mixed, and 16% as rain. The montane Sugarloaf site at 2524 m received 519 mm of precipitation, with 59% falling as snow, 14% as mixed precipitation, and 27% as rain. The lower montane Betasso site at 1800 m received 563 mm of precipitation with only 32% falling as snow, 28% as mixed precipitation, and 40% as rain. As with air temperature, these values were within 15% of the long-term averages for each site (Table 2.1), suggesting that 2009 was a near average year with respect to annual precipitation.

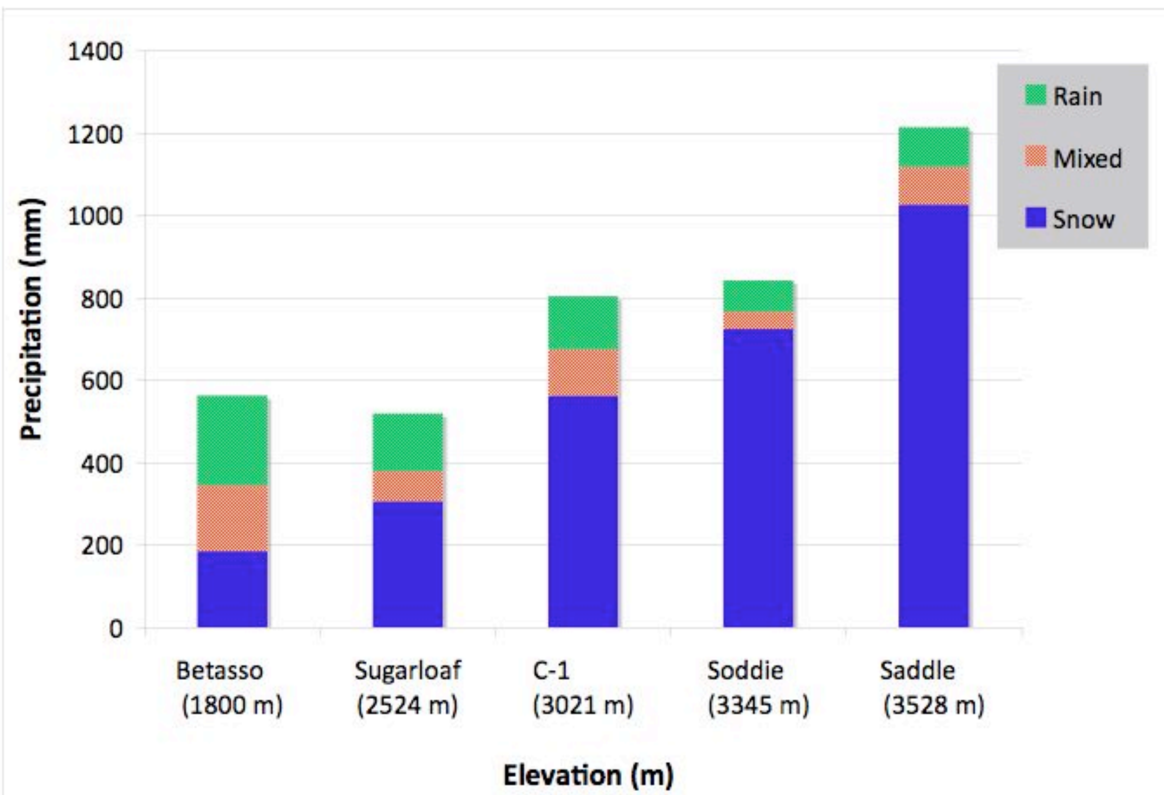

Figure 2.7: Amount and type of precipitation collected at five locations within Boulder Creek Watershed.

2.4.2 Discharge

Stage-discharge rating curves

Here we illustrate the rating curves for Como Creek and Gordon Gulch catchments; the GL4 rating curves have been available for many years from the NWTLTER program. For Como Creek, 23 measurements of discharge were made at stage heights ranging from 5 cm to 34 cm in 2009, effectively spanning the range of recorded stage heights. Discharge was calculated as a power function:

$$Q= 0.0575\ X^{2.3826} \qquad \text{(Equation 2.9)}$$

where Q is discharge in L s^{-1} and X is the stage height in cm (figure 2.8). The fit was acceptable with an R^2 of 0.97.

For Gordon Gulch, the velocity-area method of calculating discharge was supplemented with a salt dilution technique in low flow conditions due to limitations of the pygmy meter at low flow conditions. For Gordon Gulch, 10 measurements of discharge were made at stage heights ranging from 6 cm to 20 cm. The stage-discharge relationship for Gordon Gulch was calculated as a logarithmic function (Figure 2.9a):

$$Q = -80.6 + 106.32\log(x) \qquad \text{(Equation 2.10)}$$

The fit was acceptable with an R^2 of 0.95 for all stage heights greater than 5.8 cm, but failed to accurately represent low flow conditions. Therefore, an additional 6 measurements of discharge were made at stage heights ranging from 1 to 4 cm and the discharge at stage heights lower than 5.8 cm was calculated as a second logarithmic function (Figure 2.9b):

$$Q = -0.7507 + 9.3652\log(x) \qquad \text{(Equation 2.11)}$$

The fit was acceptable with an R^2 of 0.99. The stage height of 5.8 cm was chosen as the transition between the 2 curves because equation 2.10 failed to produce positive discharge values below this stage height.

In 2009 the pressure transducer at Gordon Gulch was not installed until day 90, which, based on weekly manual stage height measurements, was after the start of the spring snowmelt runoff. By analyzing daily mean air temperatures in Gordon Gulch (Figure 2.6), in relation to the timing of increased stage height measurements, it was determined that the most probable start to the rising limb of the hydrograph was around day 60 when air temperatures remained well above freezing for several days. In order to calculate an annual discharge for Gordon Gulch, a baseflow value, consisting of the average daily discharge measured in late fall prior to removal of the pressure transducer (days 250-320), was applied to the remainder of 2009 and the beginning of 2009 up until day 60. Daily discharge from day 60 until the sensor install on day 90 was then linearly interpolated to provide a reasonable estimated daily discharge for the beginning of the rising limb of the hydrograph.

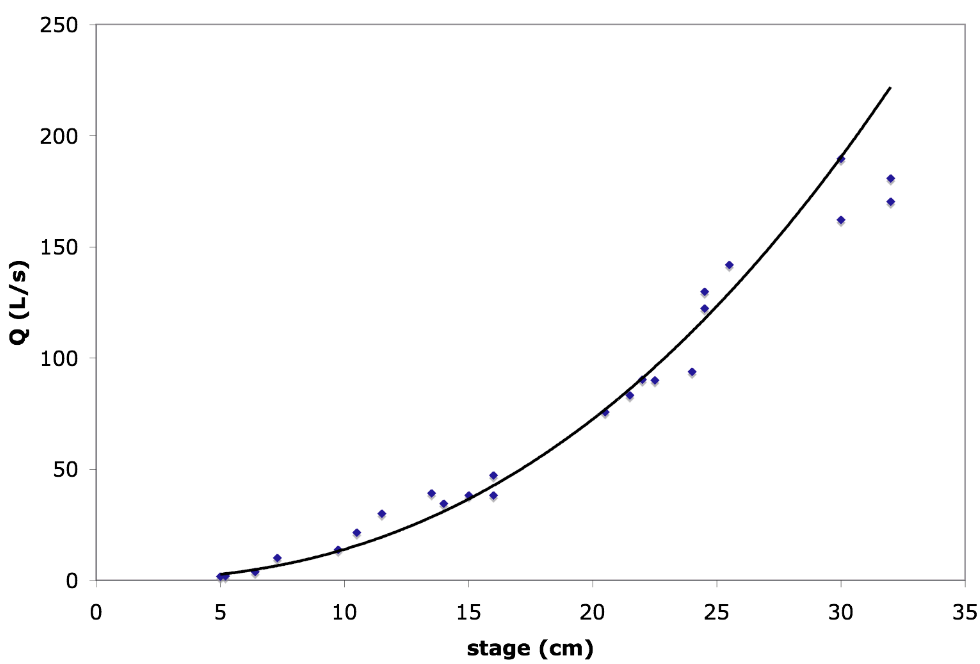

Figure 2.8: Stage-discharge rating curve for Como Creek in 2009.

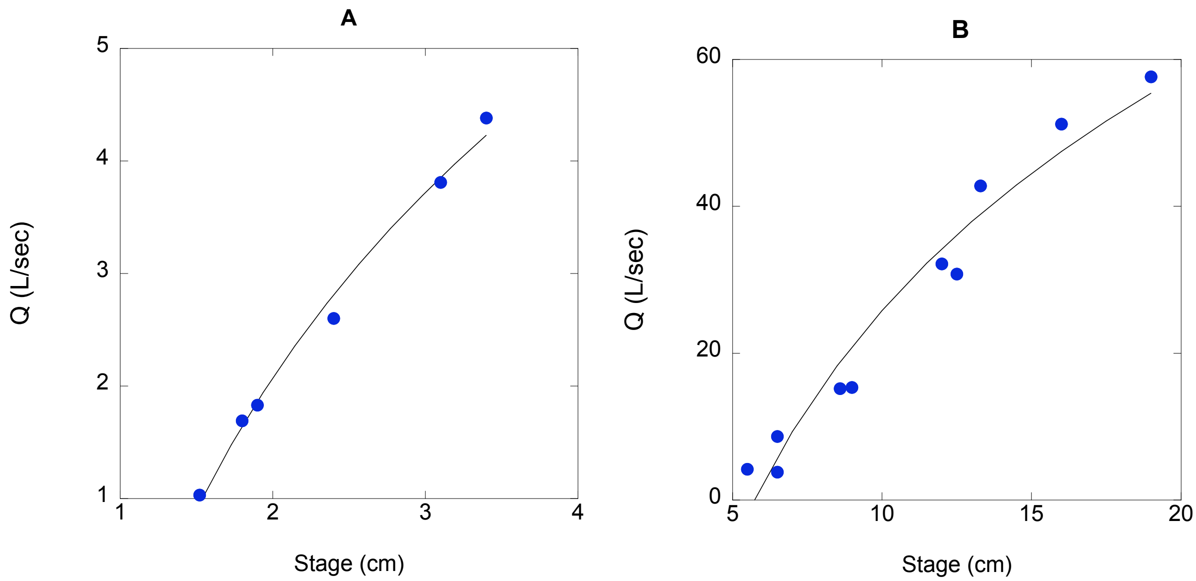

Figure 2.9: Stage-discharge rating curves for Gordon Gulch in 2009. Panel A is stage heights less than 5.8cm and panel B is stage heights greater then 5.8 cm.

At Betasso the design and location of the rectangular weir and associated pressure transducer turned out to be insufficient for capturing total discharge. Comparison of weekly hand discharge measurements to the pressure transducer data confirmed that some discharge, especially during low flow conditions, was being lost to flow under the weir. Additionally, it was determined that the barometric pressure offset was nearly ten fold greater then the pressure created by the small discharge throughout most of the year, which created difficulty in correcting the pressure transducer readings for atmospheric influences. Therefore, it was determined that the most accurate representation of discharge for Betasso would be to use hand measurements taken at daily time steps during the snowmelt pulse and at bi-weekly to weekly time steps throughout the remainder of 2009.

The complete daily discharge record was then calculated by linear interpolation between each of the manual measurement points. This method was not ideal but provides a reasonable estimation of discharge owing to the fact that weekly manual measurements and notes insured that interpolations were never made for greater then a one week period. The drawback to this approach is that discrete events lasting on the order of hours to days may be missed by weekly measurements.

Discharge Timing and Magnitude

The specific discharge hydrographs in all four catchments are characteristic of snowmelt-dominated watersheds with steep rising limb driven by snowmelt runoff in April, May and June (Figure 2.10). Interestingly, while the montane Gordon Gulch site exhibited a characteristic snowmelt hydrograph, during the summer months there were large increases in discharge in response to summer rain events. In contrast, the recession limb was relatively long and gradual for alpine GL4 and sub-alpine Como Creek, with only small increases in discharge from summer rains. Betasso differs from the other catchments in that it is an intermittent stream characterized by discharge only after precipitation events. In Betasso the hydrograph showed a rapid response to melt from a large April storm and then returned quickly to near baseflow conditions within only a few days.

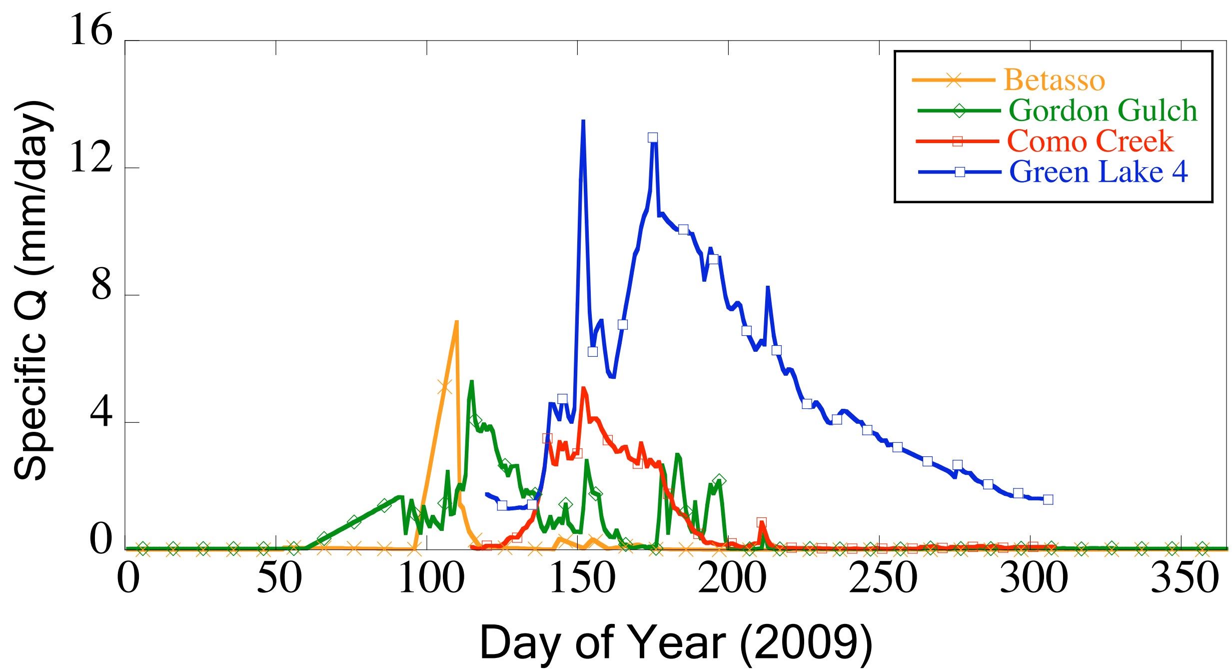

Figure 2.10: 2009 Specific daily discharges for Betasso, Gordon Gulch, Como Creek and Green Lake 4.

The specific discharge measurements show a lag in the timing of peak discharge with increasing elevation, with discharge occurring earlier at the lowest elevation sites compared to the higher elevation sites. The seasonal discharge for Betasso in 2009 was 30,817 m^3, with a peak discharge of 3,223 m^3 occurring on April 20, 2009. The majority of discharge in Betasso occurred during the April snow melt pulse, with the stream going entirely dry from September 19, 2009 until November 2, 2009, when discharge resumed following a significant precipitation event on October 30, 2009. The seasonal discharge for Gordon Gulch in 2009 was 198,020 m^3, with a peak daily discharge of 5,341 m^3 occurring on April 25, 2009.

At Como Creek and GL4 discharge was limited to seasonal measurements from about the beginning of May until the end of October due to freezing of water in the stilling well containing the pressure transducer. In 2009 Como Creek seasonal discharge was measured from April 20 to November 4 with a total recorded discharge of 1,113,900 m^3, which peaked at 33,755 m^3 on June

1. At GL4 seasonal discharge was measured from May 1 to October 31, 2009. The 2009 seasonal discharge was 2,072,178 m^3, which peaked at 29,254 m^3 on June 24. There was a very sharp but short-lived peak in discharge (30,317 m^3) occurring on day 152 that is believed to be the result of an ice dam release upstream of the gauge from Green Lake 5 and thus is not considered to be the true peak in the spring runoff.

2.4.3 Runoff Efficiency

To provide an analysis on the relationship between water entering a catchment as precipitation and leaving the catchment as surface waters, the runoff efficiency was calculated. Runoff efficiency (K) for each catchment was calculated as:

$$K = Q\ (\text{mm}) / P\ (\text{mm}) \qquad \text{(Equation 14)}$$

Where Q is measured as the seasonal specific discharge for the catchment and P is the annual water entering the catchment as rain and snow. Table 2.2 shows the results for each of the catchments with the alpine site (GL4) having the highest efficiency at 75.9 % and the foothills site (Betasso) having the lowest runoff efficiency at just 12.2%.

2.4.4 Residence Times

<u>Seasonal Variation in $\delta^{18}O$</u>

The $\delta^{18}O$ values from all available precipitation and surface water samples (Figure 2.11) were analyzed to find the yearly range (amplitude), mean and standard deviations, which were applied to the convolution algorithm to calculate a mean residence time for GL4, Como Creek, and Gordon gulch (Table 2.3). All incoming precipitation showed similar amplitude in isotopic compositions ($\delta^{18}O$ ‰) with the Saddle precipitation having the smallest average amplitude of

23.7 ‰ while the Sugarloaf precipitation had the largest amplitude of 28.9 ‰. All outgoing surface waters had largely damped amplitudes with GL4 being the largest at 3.3 ‰ and Como Creek and Gordon Gulch both at 2.2 ‰. At GL4 the residence times calculated for individual years ranged from 1.0 to 1.9 years producing a mean of 1.12 years. For Como Creek residence times were calculated using data from each individual year (2002-2009) and for years 2002-2004, 2002-2006, and 2002-2009 to test the sensitivity of the residence time calculations to the length of the data set. Residence times calculated from individual years of data ranged from 1.11 to 2.41 years while residence times using 3, 5, and 7 years of data only ranged from 1.72 to 1.88 years. The mean residence time for Como Creek calculated from all available data was 1.8 years. Gordon Gulch stream sampling commenced in the fall of 2008 so only one year of precipitation and stream data was analyzed to produce a mean residence time of 2.11 years.

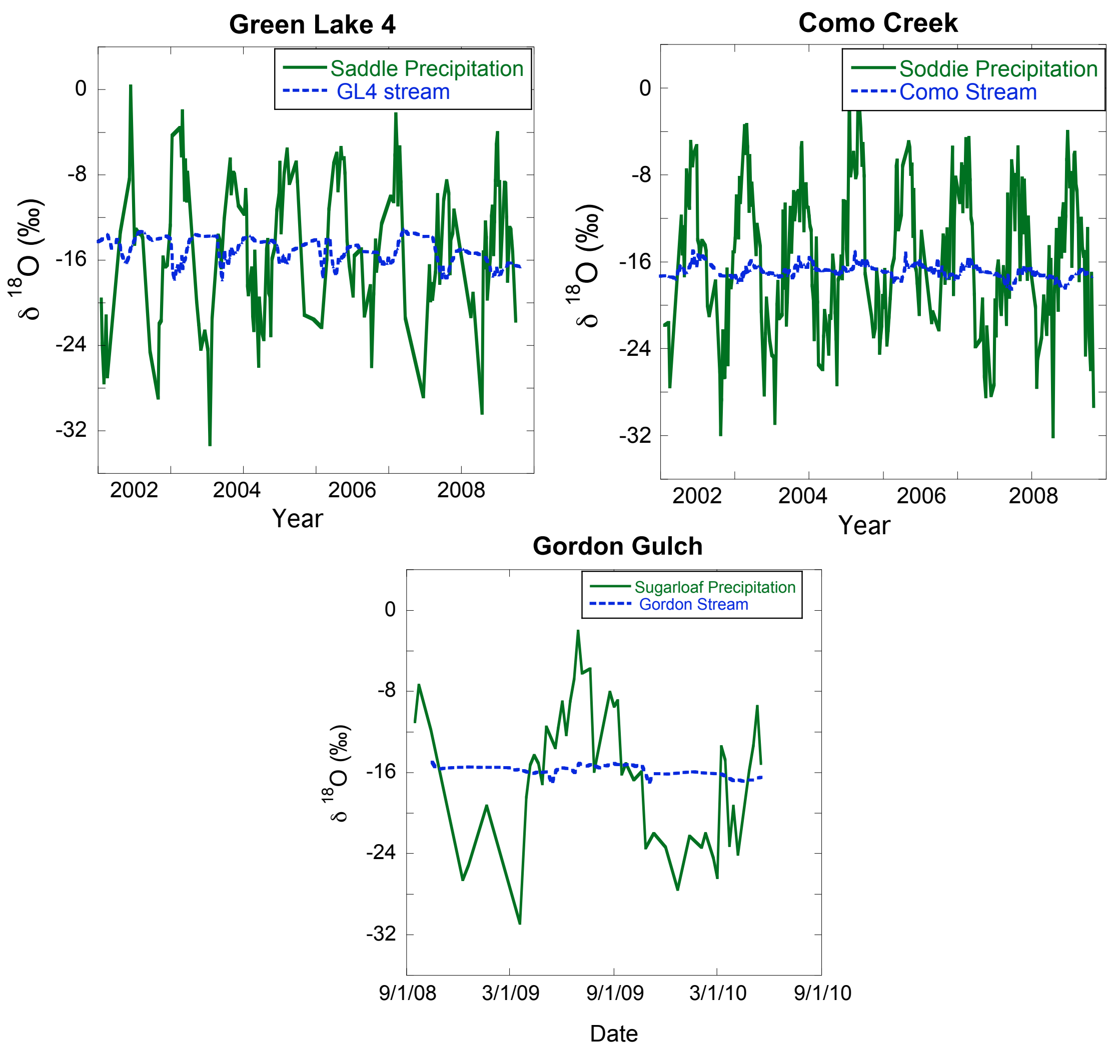

Figure 2.11: Time series of δ^{18}O values from precipitation and stream water for Green Lake 4 and Como Creek from 2002 to 2009 and for Gordon Gulch since sampling began in 2008.

Table 2.3: Values of $\delta^{18}O$ applied to convolution algorithm to calculate catchment residence time. The precipitation and stream water amplitudes (amp) and mean $\delta^{18}O$ concentrations are reported in units of per mil (‰) relative to Vienna Standard Mean Ocean Water, and residence times are in years.

Green Lake 4

year	Saddle Precip amp	Mean $\delta^{18}O$ Precipitation	STDEV $\delta^{18}O$ Saddle	GL4 stream amp	Mean $\delta^{18}O$ GL4	STDEV $\delta^{18}O$ GL4	Residence Time
2002	27.84	-16.71	7.74	2.93	-14.72	0.90	1.5
2003	26.94	-14.13	7.83	4.22	-15.87	1.40	1
2004	26.8	-15.78	6.65	4.11	-14.91	0.97	1.02
2005	20.4	-14.67	6.19	2.16	-15.46	0.79	1.49
2006	16.93	-12.52	5.78	3.61	-15.51	1.07	0.72
2007	23.71	-12.66	6.87				
2008	20.25	-15.53	5.33	3.87	-16.06	1.35	1.47
2009	26.32	-14.01	5.50	2.18	-16.66	0.63	1.9
Combined	23.65	-14.50	6.49	3.30	-15.60	1.01	1.06

Como Creek

year	Soddie Precip amp	Mean δ18O	STDEV δ18O	Como Steam amp	Mean δ18O	STDEV δ18O	Residence Time
2002	22.62	-13.56	5.86	2.6	-16.50	0.74	1.38
2003	28.57	-16.06	7.71	1.99	-16.98	0.48	2.28
2004	25.86	-15.81	6.29	1.92	-16.74	0.48	2.14
2005	27.53	-14.64	7.57	2.13	-16.57	0.43	2.05
2006	19.48	-14.68	6.13	2.77	-16.74	0.57	1.11
2007	22.03	-13.77	6.10	1.9	-16.81	0.50	1.84
2008	23.04	-16.75	6.50	2.16	-17.24	0.57	1.69
2009	28.10	-15.46	6.36	1.85	-17.49	0.45	2.41
2002-2004	25.68	-15.14	6.62	2.17	-16.74	0.57	1.88
2002-2006	24.81	-14.95	6.71	2.28	-16.71	0.54	1.72
2002-2009	24.65	-15.09	6.57	2.17	-16.88	0.53	1.8

Gordon Gulch

year	Sugarloaf precip amp	Mean δ18O	STDEV δ18O	Grordon stream amp	Mean δ18O	STDEV δ18O	Residence Time
2009	28.87	-12.26	6.71	2.17	-15.66	0.50	2.11

<u>Tritium Age estimates</u>

Tritium (^{3}H) concentrations found in surface waters throughout 2009 were compared to the current level of atmospheric ^{3}H entering the catchments in the seasonal snowpack at maximum accumulation (Figure 2.12). The mean concentration of ^{3}H in incoming winter precipitation was 10.1 TU, but current levels of ^{3}H in summer rains had not been analyzed at the time of this report. Previous work by Rozanski (1991) indicated that levels of ^{3}H in precipitation may vary slightly on an annual scale with the ^{3}H content of monthly precipitation in northern temperate zones showing a distinct summer maximum most likely caused by the spring rise of the tropopause at these latitudes. Therefore a reasonable estimate for ^3H values of current precipitation would be a range from winter lows of 10 TU to summer highs of 11 or 12 TU.

During mid-winter baseflow conditions Como Creek tritium levels were at a high of 13.6 TU and then return to levels close to incoming precipitation during the spring and summer snowmelt runoff season. Applying the apparent age function used by Manning and Caine (2007) to the baseflow value in Como Creek suggests an average age of 8 years for water entering the stream in mid-winter. On the other hand, Gordon Gulch tritium levels drop to a low of 8.1 TU during winter baseflow and then return to levels close to incoming snow during the spring and summer snowmelt runoff season. Applying the basic decay function (Equation 2.9) to the baseflow value at Gordon Gulch suggests an average age of 4 years for the water entering the stream in mid-winter. The surface water at both GL4 and Betasso show little annual variation in ^3H concentration and thus remains close to incoming precipitation values throughout the year. All results suggest that most of the waters throughout the headwater catchments are relatively new because they show neither little sign of decay nor signs of containing significant amounts of bomb spike water.

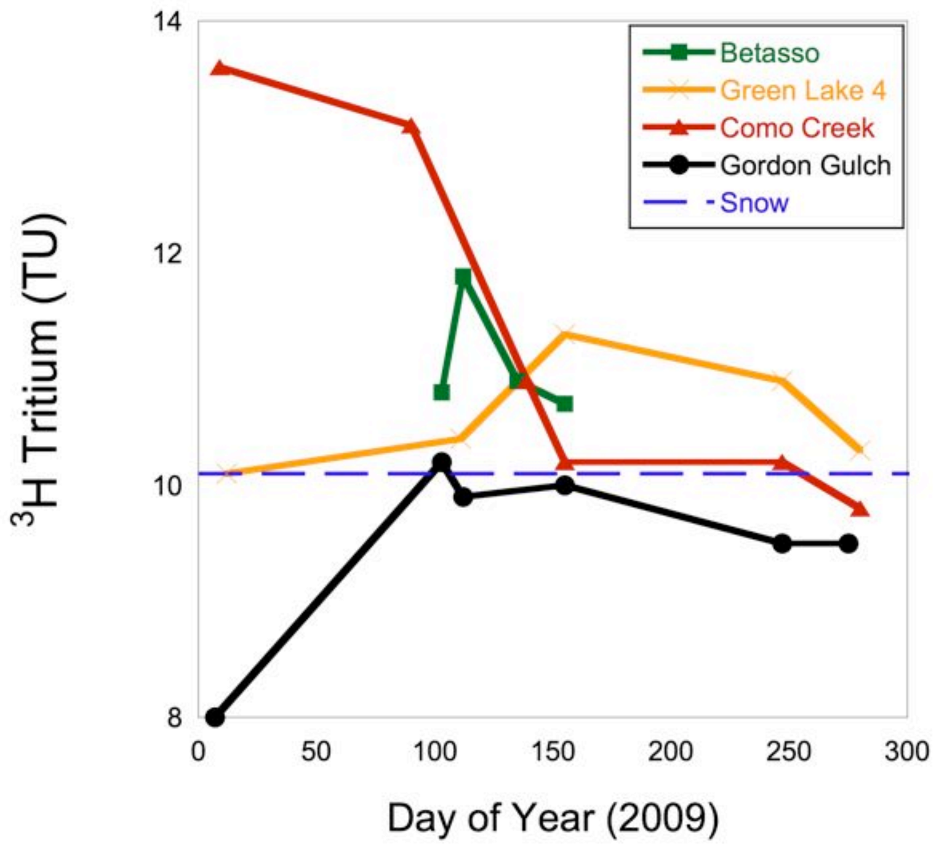

Figure 2.12: Tritium concentrations reported in tritium units (TU) from winter precipitation and surface waters throughout 2009.

2.4.5 Two Component Mixing Models

Mixing model analysis was performed for GL4, Como Creek, and Gordon gulch using $\delta^{18}O$ and reactive silicate (Si) as conservative tracers. Analysis was not performed for Betasso due to insufficient precipitation and snow pack data for the catchment during the sampling period. To verify the applicability of the chosen tracers and to identify the correct end members, binary plots of $\delta^{18}O$ versus Si were constructed for all stream waters collected in 2009 along with potential end members for GL4 and Como Creek (figure 2.13). In both catchments the potential end members had distinct $\delta^{18}O$ and Si values. Additionally, the binary plots of $\delta^{18}O$ versus Si show that stream waters generally plot on mixing lines between the snowpack values and baseflow, thus justifying the application of two-component mixing models.

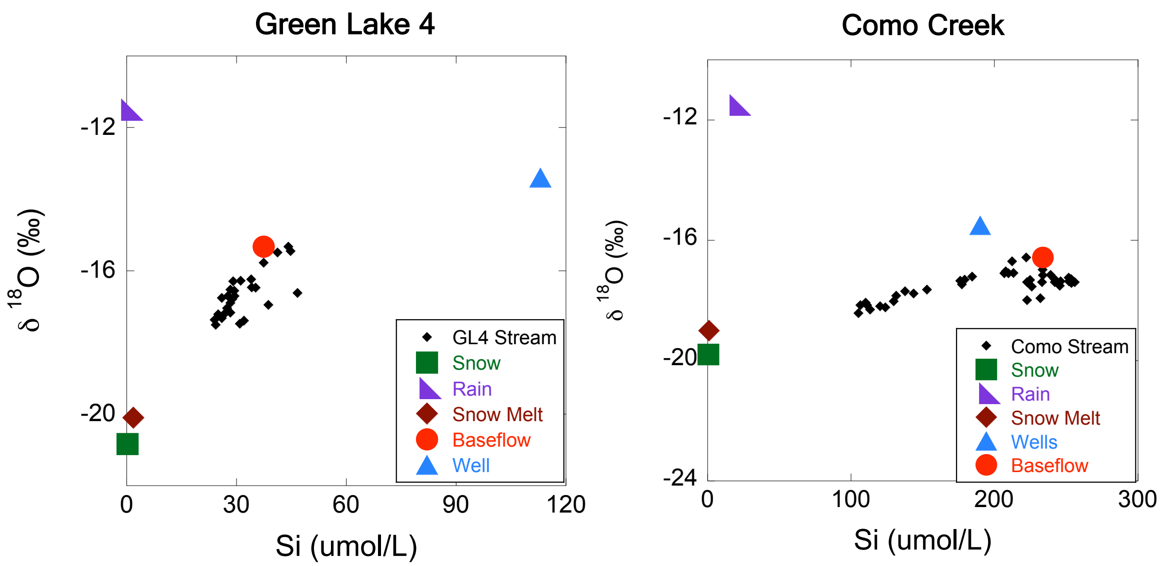

Figure 2.13: Binary Plots of $\delta^{18}O$ versus Si for Green Lake 4 and Como Creek.

For Gordon Gulch the $\delta^{18}O$ of weekly stream samples were more enriched and more depleted then the baseflow on a seasonal basis (Figure 2.14) and thus were not consistently bracketed by two distinct end member values. During summer months the $\delta^{18}O$ of stream samples were likely influenced by the relatively enriched summer rain $\delta^{18}O$ values. Therefore, successful application of a two component mixing model required calculation of a unique precipitation end member for each stream sample. The precipitation end member was calculated on an event basis based on the most recent precipitation values prior to the stream sample date.

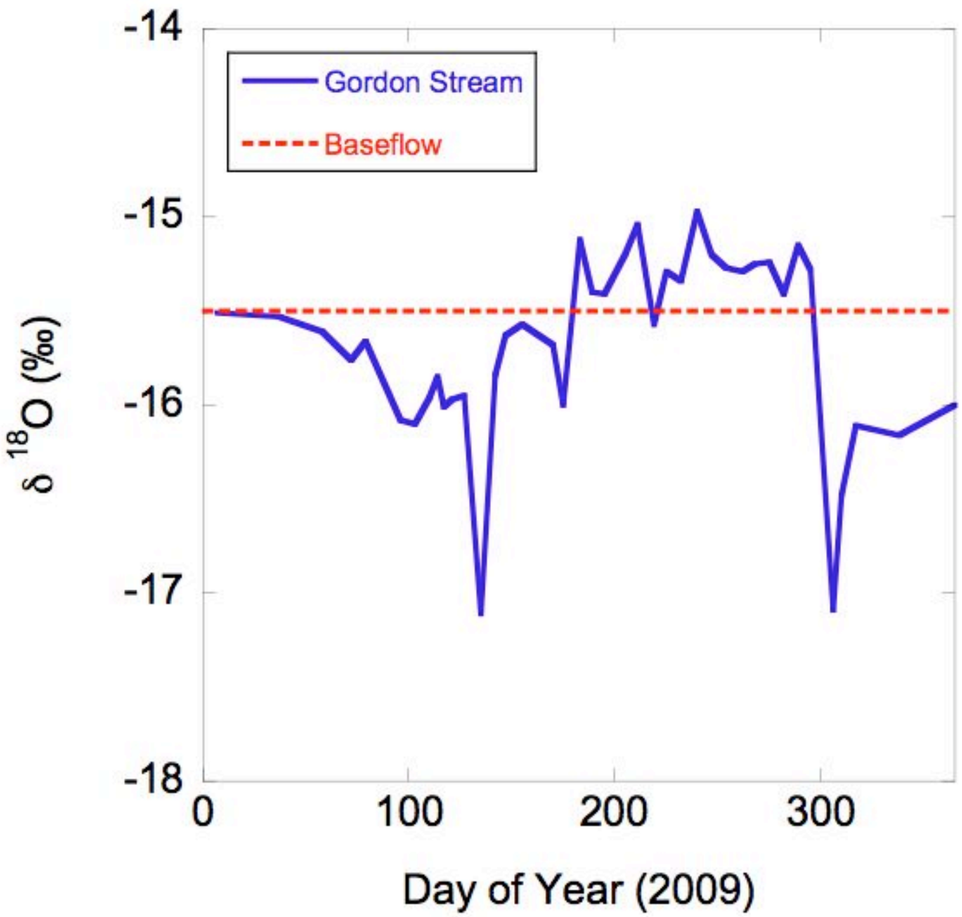

Figure 2.14: 2009 Time series of $\delta^{18}O$ in Gordon Gulch stream waters plotted with the baseflow value chosen for mixing model analysis.

Snow end-member selection

The snowpack values for GL4 ($\delta^{18}O$ is -20.8 ± 0.2 ‰, Si is 0.26 ± 0.1 μmol/L), were taken as a mean of two depth integrated sample from the Saddle snow pit dug at maximum accumulation on April 20, 2009. The $\delta^{18}O$ and Si snow values were both within one standard deviation of the volume weighted mean values of the Saddle snow melt ($\delta^{18}O$ -20.1 ± 1.0 ‰, Si 1.8 ± 1.5 μmol /L).

The snowpack values for Como Creek ($\delta^{18}O$ -19.8 ± 0.15‰, Si 0.66 ± 0.1 μmol /L) were taken as a mean of two depth integrated samples from the C-1 snow pit dug on April 12, 2009. Snow melt was not measured at C-1 but the April 12 snow pack values at C-1 compare well to the volume weighted mean of snow melt at the Soddie site ($\delta^{18}O$ -19.0 ± 1.2 ‰, Si 1.1 ± 0.6 μmol /L) and thus accurately represent the snow end-member.

Due to higher air temperatures (Figure 2.6), and a lower ratio of snow to total precipitation (Figure 2.7), at the montane Gordon Gulch site there was not a continuous accumulation of snow pack, therefore it was determined that end member values for winter precipitation would be most accurately represented as the cumulative volume weighted mean of winter precipitation from December 1, 2008 until the date of each successive surface water sample. The cumulative volume weighted mean of winter precipitation was used as an end member constraining stream samples collected through June 15 (day 166), at which point the hydrograph indicates an end to the spring runoff pulse and a return to near baseflow conditions. For stream samples collected after June 15 a precipitation end-member was calculated as the volume weighted mean $\delta^{18}O$ and Si from the most recent precipitation event.

<u>Baseflow selection</u>

For GL4, the stream sample collected during baseflow conditions on February 19, 2009 had a $\delta^{18}O$ value of -15.3 ‰, which was the most enriched value of the year and was thus chosen to represent the baseflow end member. Using the most enriched $\delta^{18}O$ stream sample as one end member and the max accumulation snow pack $\delta^{18}O$ as the second end member, the SR was 100% for hydrograph separation of new and old waters in GL4. For GL4, the Si concentration (37.5 μmol /L) in the stream sample collected just prior to melt on April 21, 2009 was chosen to represent baseflow. There were higher concentration of Si in the winter samples from GL4 but they were believed to be higher than true stream values at that time due to an unavoidable sampling bias during the winter season. The bias arose when GL4 was frozen and samples were collected through a hole in the ice as a grab sample from just below the lower extent of the ice. The conditions found at GL4 were assumed to be similar to those studied by Pugh et al. (2003) who concluded that solutes in the liquid water sample are cryoconcentrated because they are left behind as the crystalline lattice structure of ice continues to grow. The value collected on April 21 was believed to be most representative of a baseflow end member due to the cryoconcentration in mid-winter, and because the value was similar to the average stream concentrations in the late fall before GL4 became completely iced over. Using the Si concentrations on April 21, 2009 as the baseflow end member and the snowpack Si concentrations from April 20, 2009 as the second end member the SR was 81% for hydrograph separation of reacted and unreacted waters in GL4 for 2009. However, removing the cryoconcentrated winter values from the analysis increases the SR to 96% for hydrograph separation of reacted and unreacted waters in GL4 for 2009.

For Como Creek the stream sample collected during baseflow conditions on October 16, 2009 had a $\delta^{18}O$ value of -16.6 ‰, which was the most enriched value of the year and was thus chosen to represent the baseflow end member. Using the most enriched $\delta^{18}O$ stream sample as one end member and the April 12 snowpack $\delta^{18}O$ as the second end member, the SR was 100% for hydrograph separation of new and old waters in Como Creek. For Como Creek, the Si concentration (234 μmol/L) in the stream sample collected on November 4, 2009, the final day of measured discharge was chosen to represent baseflow. Late fall baseflow Si values were chosen to avoid cryoconcentration during winter when the stream is iced over. Additionally, a late fall baseflow $\delta^{18}O$ value was chosen as most enriched signal because during winter isotopic fractionation between stream water and overlying ice leaves more of the heavy isotopes in the ice phase and the remaining stream water is isotopically depleted. Fortunately, the removal of the pressure transducer in winter eliminates the need for hydrograph separation during those months. As a result, using the Si concentration on November 4 as the baseflow end member and the max accumulation snow pack $\delta^{18}O$ as the second end member, the SR was 100% for hydrograph separation of reacted and unreacted waters in Como Creek.

For Gordon Gulch the time series of $\delta^{18}O$ in the stream (Figure 2.14) suggests that the most appropriate baseflow value of -15.51‰ occurs on day 7 when the stream is in a steady baseflow state. This baseflow value is further supported by the streams $\delta^{18}O$ concentration returning close to the winter baseflow value around day 175 when the spring runoff pulse has ended but before summer rains start reaching the stream.

Source Waters

The relative contributions of old and new waters were calculated for each of the three catchments (Figures 2.15, 2.16, 2.17; top panel). In all three catchments the overall snowmelt contributions to stream flow are less than 50% with the greatest contributions coming just after peak discharge and then often approaching zero during late fall and winter baseflow conditions. In 2009, GL4 consisted of 27% new water and 73% old water with a peak in percent new water (39.5%) occurring on day 210 during the receding limb of the hydrograph. For 2009 Como Creek consisted of 48% new water and 52% old water with a peak in the new water contribution (56%) occurring on day 171 during the receding limb of the hydrograph. For 2009 Gordon Gulch consisted of 11% new water and 89% old water with a brief peak in the percent new water contribution (52%) occurring on day 135 during the receding limb of the hydrograph.

Flow Paths

The relative contributions of reacted and unreacted waters were calculated for each of the three catchments (Figures 2.15, 2.16, 2.17; bottom panel). The percentage of unreacted water varies seasonally with the largest contributions also coming after peak discharge during the receding limb of the hydrograph and then diminishing to near zero during most baseflow conditions. In 2009, GL4 consisted of 21% unreacted water and 79% reacted water with a peak in percent unreacted water (36%) occurring on day 204 during the receding limb of the hydrograph. In 2009, Como Creek consisted of 49% unreacted water and 51% reacted water with a peak in percent unreacted water (55%) occurring on day 170 during the receding limb of the hydrograph. In 2009, Gordon Gulch consisted of 8% unreacted water and 92% reacted water with a peak in percent unreacted water (20%) occurring on day 114, one day prior to peak discharge.

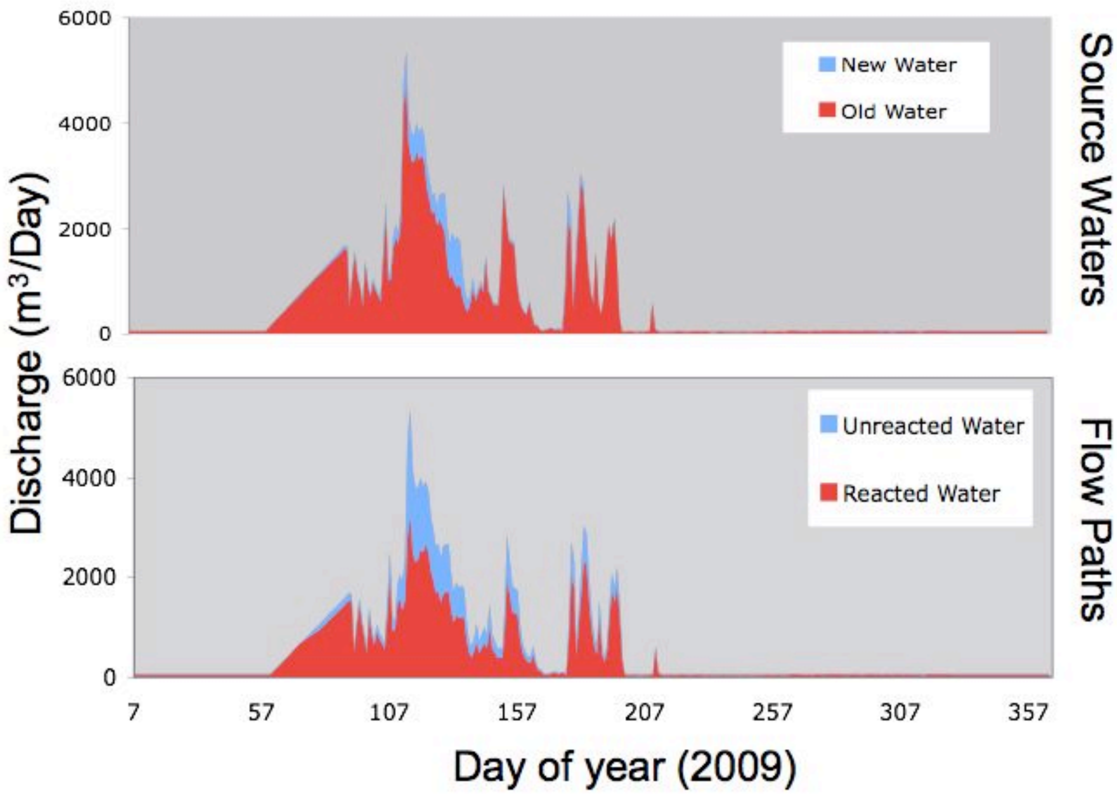

Figure 2.15: Gordon Gulch hydrograph separation into source waters and flow paths.

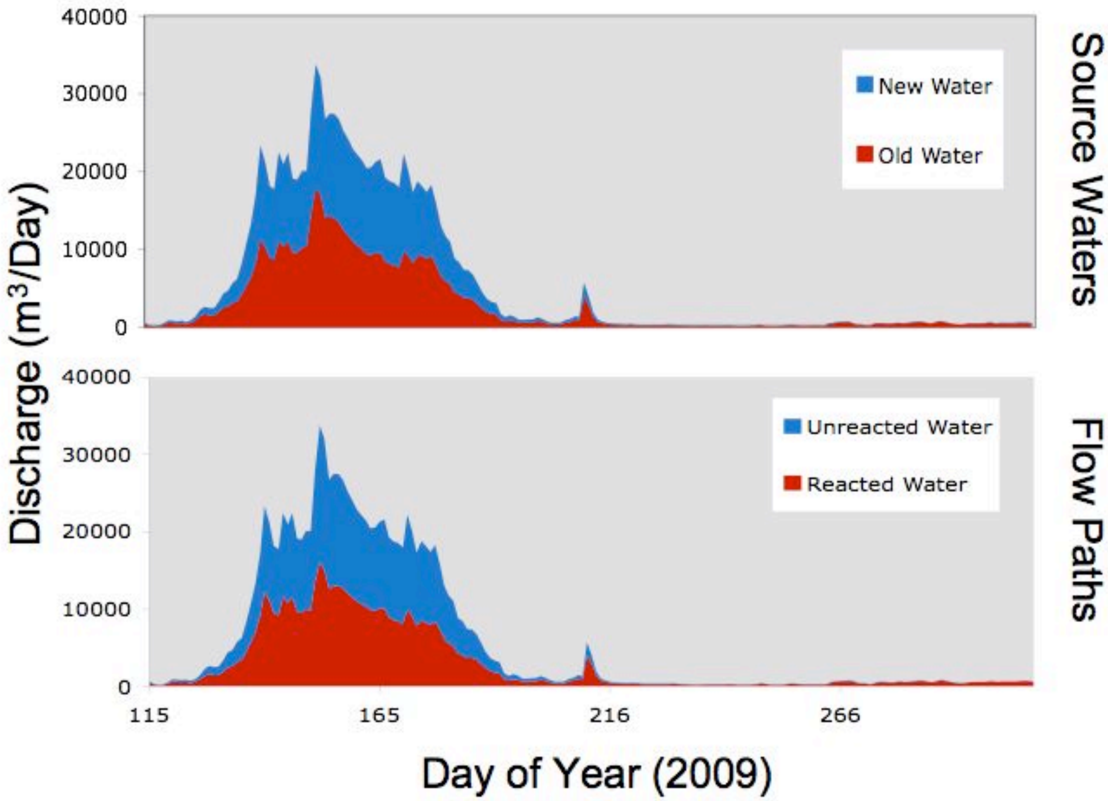

Figure 2.16: Como Creek hydrograph separation into source waters and flow paths.

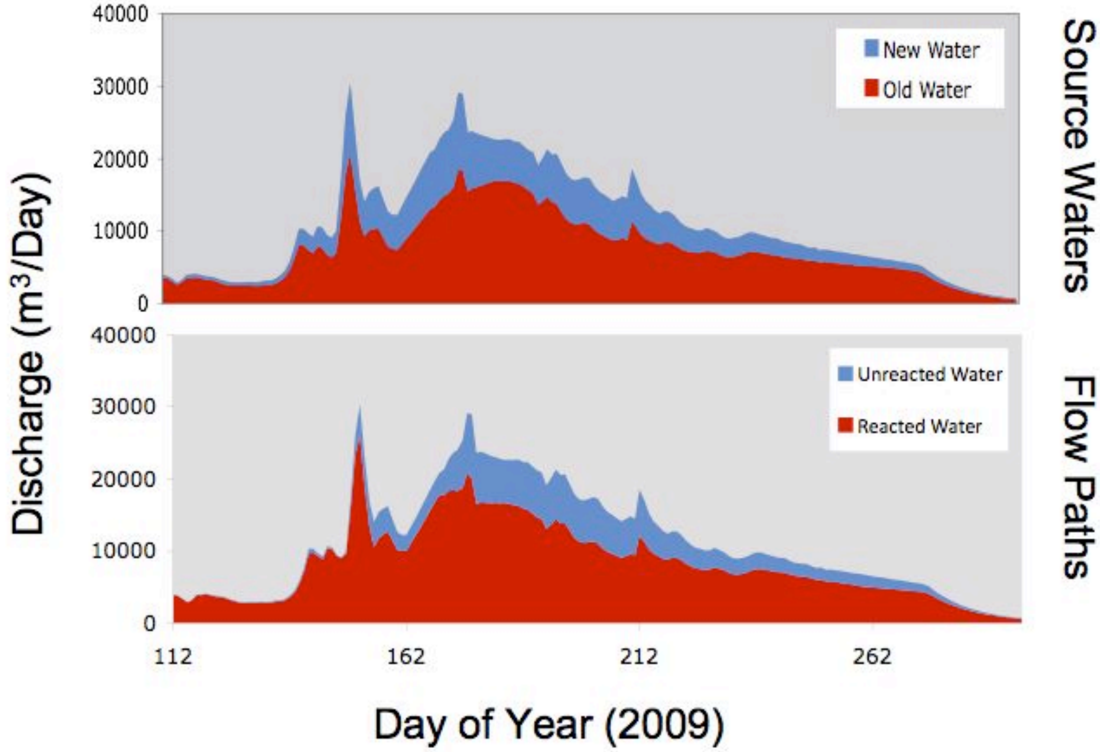

Figure 2.17: Green Lake 4 hydrograph separation into source waters and flow paths.

To further examine flowpath generation in GL4, Como Creek, and Gordon Gulch time series plots of δ^{18}O and dissolved organic carbon (DOC) in surface waters were plotted alongside values measured from available sources of sub-surface flow for each catchment. The Como Creek watershed contained both deep and shallow wells that directly sampled sub-surface waters, but due to the inability to install wells in GL4 and Gordon Gulch, springs were sampled as proxies for wells in an attempt to characterize the isotopic and geochemical signatures of subsurface flow in those catchments. At GL4 a spring on the talus slope above the main channel was sampled regularly during summer months and was found to have both DOC and δ^{18}O concentrations that were similar to stream waters during the recession limb of the hydrograph (Figure 2.18).

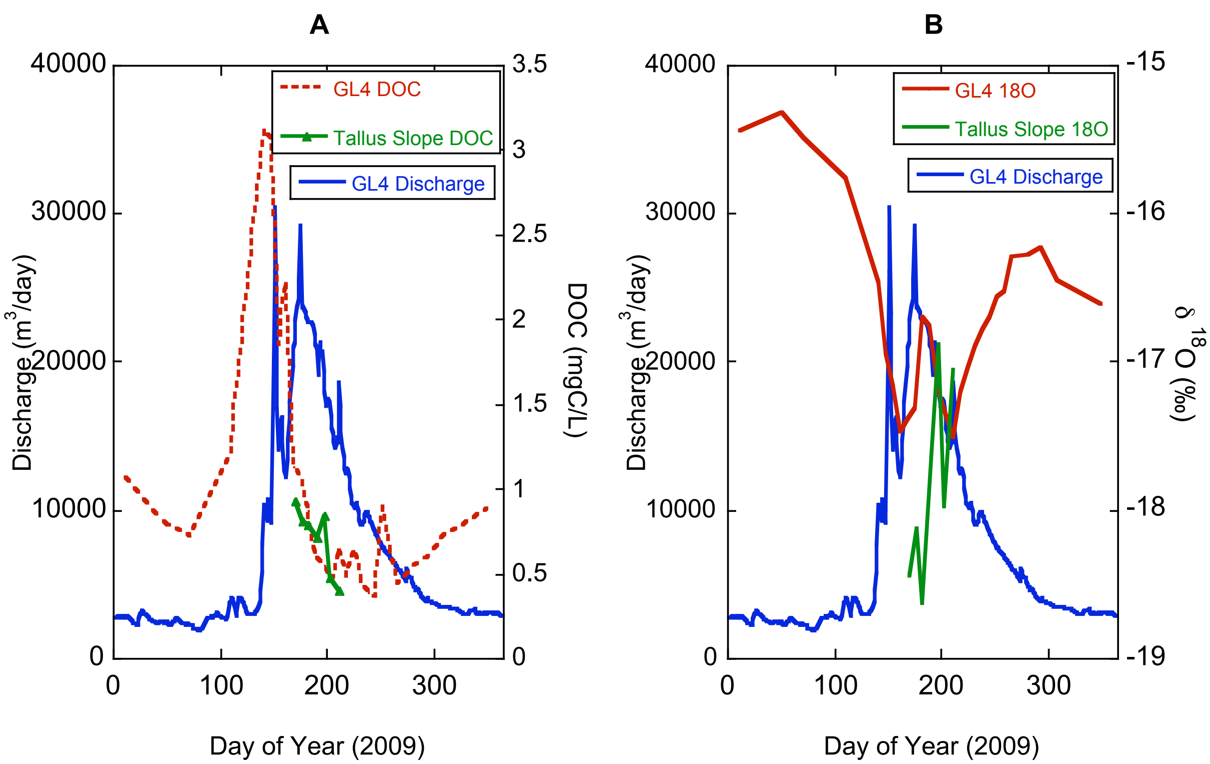

Figure 2.18: Time series of A) DOC concentrations and B) δ^{18}Oconcentrations, In GL4 stream and from a talus slope spring.

At Como Creek a deep (8-9 m screen depth) and a shallow (1-2 m screen depth) well located at the Saddle site (Figure 2.2) near the western edge of the catchment were sampled throughout the year and the DOC and δ^{18}O concentrations were compared to those measured in the steam channel (Figure 2.19). The DOC concentrations in the shallow well compare well to the stream values during the recession limb while the δ^{18}O concentrations in the deep well are most similar to the stream waters late in the summer when the stream has returned to baseflow.

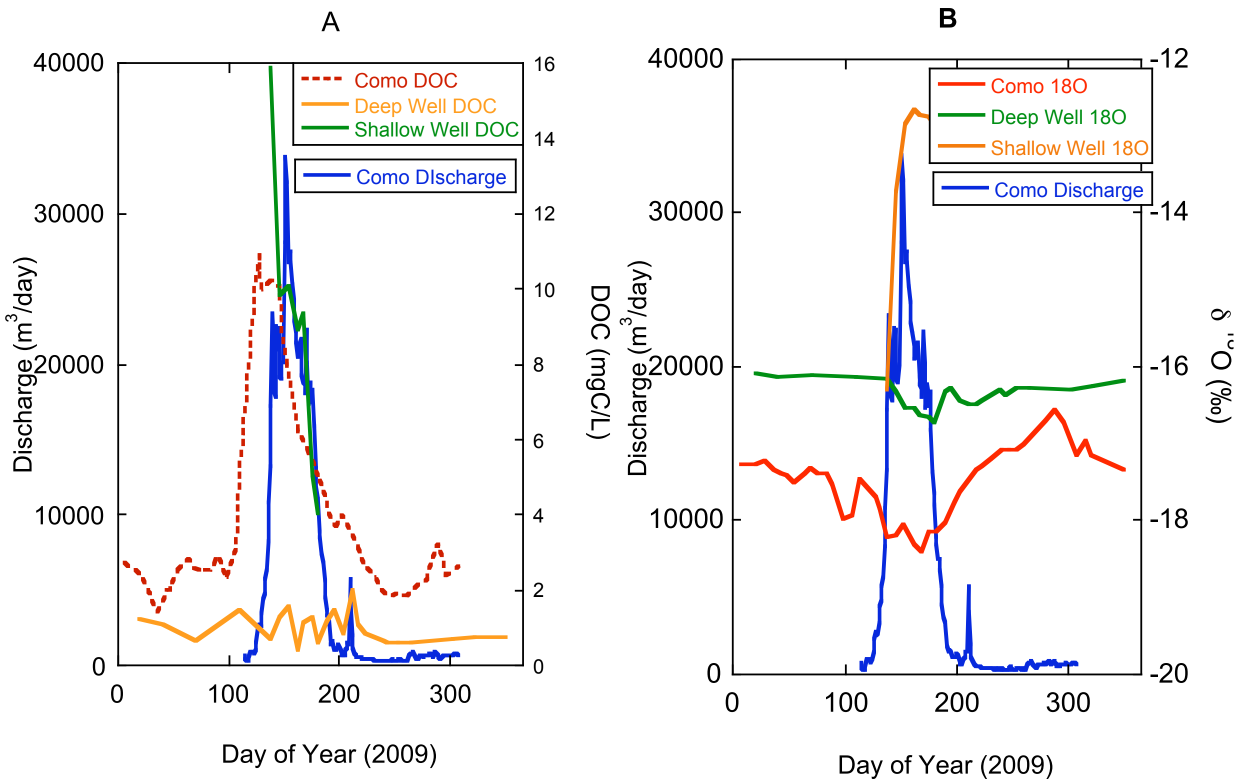

Figure 2.19: Time series of A) DOC concentrations and B) δ^{18}O concentrations, in Como Creek and from deep and shallow wells located near the Saddle site.

In Gordon Gulch DOC and δ^{18}O concentrations measured in two routinely sampled springs located on north and south facing slopes were compared to DOC and δ^{18}O concentrations measured in the stream channel (figure 2.20). The variations in DOC and δ^{18}O concentrations in the stream channel were more similar to the variations measured in the spring draining the south facing slope, while the DOC and δ^{18}O concentrations in the north facing spring were less varied throughout the year.

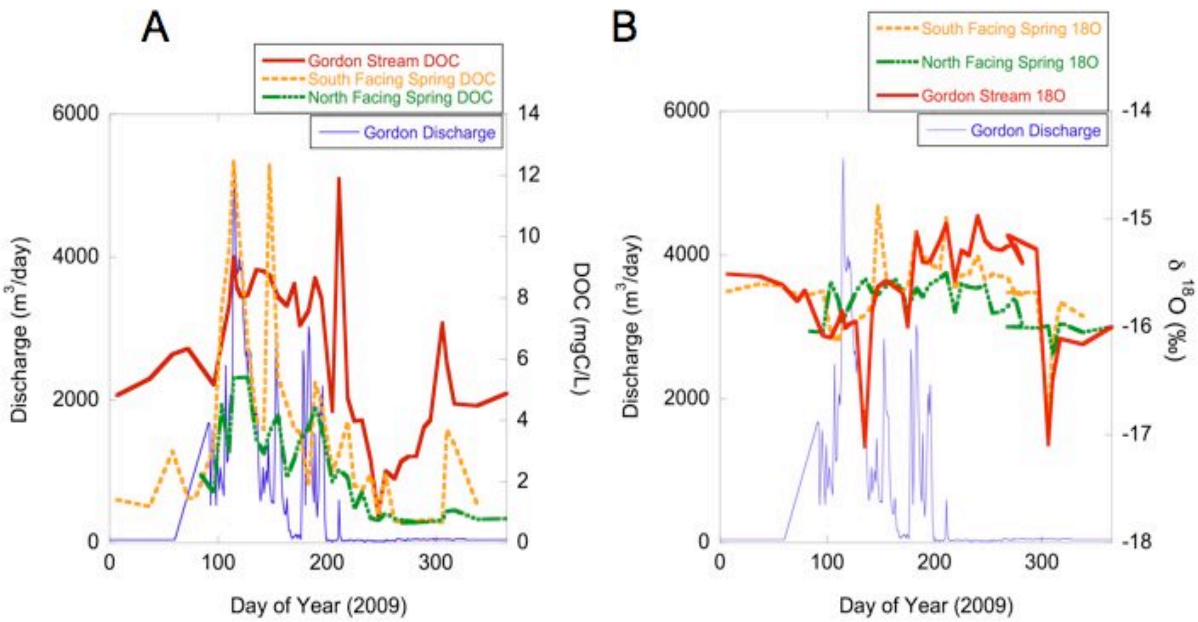

Figure 2.20: Time series of A) DOC concentrations and B) δ^{18}Oconcentrations, in Gordon Gulch stream and from a North facing and south facing spring.

2.5 Discussion

2.5.1 Precipitation

The analysis of precipitation across a large elevation gradient from a high of 3528 m near the Continental Divide down to 1800 m shows large variations in both the total annual amount of precipitation and in the amount that falls as rain or snow. Results indicate that at elevations close to the Continental Divide, precipitation totals can be at least two times greater than in the foothill and montane ecosystems 1000 m lower in elevation. The total precipitation measured at the alpine site (1214 mm) in 2009 was slightly higher than the 1,186 mm measured in 1996 by Liu et al (2004) and the fifty-year average of 1,000 mm (Williams et al., 1996). The record of 804 mm of precipitation at C1 in 2009 is also backed by Monson et al. (2002), which reported a 10-year average of 800 mm of precipitation at C1. There was also great variation in the amount of precipitation that fell as snow across the catchments. The calculated 86% snow at the Soddie site agrees well with the 80% snow value reported by Caine (1996) for the same location and the 70% snow at the C1 site also agrees well with the 60% value reported for C1 by Monson et al. (2002). Due to the relatively course grained nature of the method used to classify precipitation type, there will be some uncertainty in the ratio of types especially when air temperatures remain close to the 0°C inflection point during large precipitation events. The consistency between the 2009 precipitation record and previously published records provides confidence that the results are representative of the present day conditions across Boulder Creek watershed. At the Sugarloaf site there is an almost even annual distribution of snow and rain/mixed precipitation, which agrees well with the annual precipitation volume weighted mean $\delta^{18}O$ of -16.49 ‰ being roughly in the middle between winter precipitation values of -20 to -25 ‰ and summer rains being -5 to -10 ‰. The near even distribution of rain and snow totals for Gordon Gulch should also improve the accuracy of the residence times calculated from the convolution algorithm since the input signal is assumed to be a sinusoidal function with equal contributions across the entire spread of the amplitude. The lowest elevation site, Betasso, received slightly more total precipitation then Gordon Gulch and also had the highest percent of precipitation falling as rain (39%) and the smallest percent of precipitation falling as snow (33%). These results are consistent with higher air temperatures creating more rain at the lower elevation and with greater total precipitation being attributed to the large upslope spring storms producing precipitation totals that actually decrease with elevation.

2.5.2 Discharge

Each of the four headwater catchments represent snowmelt dominated hydrographs with low winter baseflow followed by a steep rising limb during spring snowmelt and a slightly more gradual receding limb returning to baseflow by late summer (Figure 2.10). The specific discharge is similar in magnitude for Betasso, Gordon Gulch, and Como Creek but is about twice the magnitude for GL4, which can be partially explained by the greater amount of total precipitation in the alpine catchment. Como Creek has similar magnitude to Gordon Gulch but a longer duration of snowmelt pulse discharge therefore the total yield is larger in Como Creek. Betasso actually had a greater specific discharge then Gordon Gulch and Como Creek during the initial snowmelt pulse due to greater precipitation totals during the spring upslope storm followed by warm temperatures driving a rapid melt response. However, the high specific discharge in Betasso was followed by a very rapid recession limb that quickly returned to near baseflow discharge, producing a smaller total specific yield than all the other catchments.

Interestingly, Gordon Gulch has much greater variability in summer discharge, suggesting more rapid and pronounced responses to summer storm events than seen in the higher elevation catchments. Most of the discharge spikes occur in June and July with no significant increases in discharge occurring after August 1 suggesting that the water table may have remained high enough to interact with summer rain events throughout the first half of summer. In Gordon the snow melt pulse has a short recession limb while in Como Creek the receding limb is more drawn out as can be seen by the greater area under the discharge curve (Figure 2.10). This suggests that although the snow melt pulse has subsided in Gordon Gulch the water table has remained near the surface and thus kept the unsaturated zone moisture levels high enough that during rain events the soils are quickly reaching field capacity and causing soil water to be pushed out and into the channel. In Como Creek, the rain events of June and July may still contribute to increases in discharge but they are masked by the continued inputs from the snowmelt pulse and thus not visible at daily time steps. Additionally, a lower vegetation density in Gordon Gulch, especially on south facing slopes, which can lead to lower canopy interception during storm events and a therefore quicker delivery of incoming water to the sub-surface and stream channel, could explain the flashier response in Gordon Gulch then in Como Creek.

A final comparison of the discharge hydrographs across the three catchments show that peak discharge in Betasso occurred on April 20 while peak discharge at GL4 did not occur until June 24, suggesting an approximately 2 month lag in peak discharge over the 1800 m elevation change across the Boulder Creek Watershed.

2.5.3 Residence Times

<u>Lump parameter transit time approach</u>

Our estimates of residence times are similar to that of other forested catchments with Plummer et al. (2001) reporting 5 years in the Appalachians and McGuire et al. (2005) reporting 0.8 - 3.3 years in the Cascade Mountains. For GL4 the residence time of 1.1 years was the shortest of the catchments studied suggesting that the alpine basin does have surface-groundwater interactions but that most of the water is moving through the shallow subsurface and then quickly returning to surface flows. In the case of Como Creek, with an average residence time of 1.8 years, greater soil development and greater potential subsurface water storage within the unconsolidated glacial deposits may lead to increased residence time and potentially larger groundwater reservoirs. Where Campbell et al. (1995) found that snowmelt infiltration exceeded groundwater supplies and shallow groundwater had short residence times in the Loch Vale watershed in the northern Front Range of Colorado, Como Creek may have larger groundwater reservoirs leading to deeper flowpaths and longer subsurface residence times. This difference is likely indicative of geomorphic differences between basins but a more detailed analysis of sub-surface architecture would be necessary to draw further conclusions. This also suggests that changes in climatic conditions at Como Creek may have longer hydrologic impacts (i.e. greater lag time) than in other high elevation areas where residence times are shorter.

The calculated residence time of 2.1 years for Gordon Gulch suggest that the subsurface architecture, controlled by the weathering rates and erosion history, may dictate the depths of developed soils and weathered profiles that will ultimately provide significant flowpath variability and generate even longer mean subsurface residence times then found at the higher elevation sites. Further research currently being conducted by the Boulder Creek Critical Zone

Observatory will help to better quantify the geomorphic structure and subsurface composition of each of these headwater catchments. Combining the structural information of the critical zone with hydrologic and geochemical data will ultimately create a more robust understanding of the flowpaths and residence times of sub-surface water across these headwater catchments. Greater knowledge of sub-surface hydrological processes are necessary because current modeling efforts to predict future hydrologic changes have focused on spatial changes in snow cover and have neglected to address changes in the subsurface hydrological component (Bavay et al., 2009). Future application of additional isotopic and geochemical analysis techniques such at those used by Manning and Caine (2007) will also aid in uncovering the complexity of the sub-surface flow systems and provide enhanced understanding of groundwater ages and residence times.

An additional comparison between catchment groundwater residence time and catchment area present some interesting results. The Como creek catchment has an area of 664 ha and a calculated residence time of 1.8 years while Gordon Gulch encompasses only 101 ha and has a calculated residence time of 2.11 years. The residence times may not be significantly different but there is a six-fold difference in catchment area suggesting that residence time is more influenced by factors such as critical zone development then by the size of the catchment. These results are consistent with the recent findings of Rodgers *et al*. (2005) and McGlynn et al. (2003), which both suggest that landscape organization rather than catchment area plays a more dominant role as a first-order control on catchment residence times.

<u>Tritium age estimates</u>

The mean concentration of ^{3}H in incoming winter precipitation was 10.1 TU, similar to the mean ^{3}H values of 10.5 TU measured in snow from a previous study near Leadville, Colorado in 2006 (Wireman, 2006) and recent precipitation values from Salt Lake City as reported in Manning and Caine (2007).

The elevated levels of tritium during baseflow conditions in Como Creek are indicative of some amount of bomb spike water mixing into the system. This result suggests that during baseflow conditions some portion of the groundwater contribution is coming from deeper or longer flowpaths with greater residence times and thus containing water that was recharged from bomb spike precipitation.

The depleted levels of tritium during baseflow conditions in Gordon Gulch are potentially indicative of exponential decay of tritium while residing in the subsurface. The result suggests that at least some portion of the groundwater contribution to streamflow has spent enough time to undergo decay, but is young enough to still contain measurable levels of tritium.

The results for GL4 suggest that much of the water reacting with the sub-surface is traveling along high permeability, near surface, flowpaths with relatively short residence times allowing little time for exponential decay thus producing output ^3H levels in discharge very similar to ^3H levels in precipitation.

The results from Betasso also indicate that stream water is relatively new with short residence times, which agrees well with the hydrograph in indicating a flashy system with intermittent discharge in response to precipitation events. The suggested short residence times of water in Betasso, in conjunction with the low runoff efficiency discussed earlier, suggest that most of the water entering the catchment is subject to high rates of ET and thus only large precipitation events will truly contribute to flowpath generation at this elevation. Therefore, the timing and magnitude of water inputs to the Betasso catchment may have a more immediate impact on changes in surface water production then in Gordon Gulch and Como Creek catchments were residence times are longer.

It is important to remember that the tritium values represent an average value for all water contributing to streamflow. Therefore the results do not provide a quantitative analysis of the age of groundwater but do provide confidence in the age estimates generated using the lumped parameter transit time approach. Overall the tritium values do constrain the convolution results and suggest the each of the headwater catchments are dominated by relatively young groundwater that follows shallow sub-surface flowpaths.

2.5.4 Two-component Mixing Models: Source waters

The two-component mixing models show that old water accounted for greater than 50% of total streamflow throughout the year in all three catchments. There was also consistency in the timing of peak percentage contribution of new water in all three catchments occurring after peak discharge. The amount of unreacted water was highest on the receding limb of the hydrograph because at this time sufficient volumes of snowmelt had infiltrated and saturated the soils thereby effectively bringing the water table up to the ground surface. As a result of the higher water tables and soils being at or exceeding field capacity, infiltration still occurred but infiltrating water was quickly forced back to the surface creating the appearance of overland flow. The water that quickly returned to the surface had undergone little if any fractionation of $\delta^{18}O$ and thus still resembled new water when it reached the stream channel. An increase in snowpack accumulation with elevation implies that more of the annual water inputs to the higher elevation catchments will occur during the short snowmelt period and thus its expected to see greater contributions of new waters occurring at higher elevations especially during spring melt.

Interestingly, the percentage of new water was actually higher in Como Creek then in GL4, which could have been caused by shallower groundwater tables in that catchment resulting in more rapid saturation of the sub-surface during melt and thus more new water flowing overland directly into the stream channel. Additionally, in GL4 the binary diagram (Figure 2.13) indicates that the Si concentrations were less tightly coupled to the two component mixing line, which suggests that a third end member with a different Si signal may be contributing to streamflow. Earlier research by Liu et al. (2004) suggested that talus water (which is considered old water) was the additional end member that significantly contributed to sub-surface flow. Therefore, the additional contributions from talus slopes, which are not present below the alpine zone, may have reduced the new water contributions to stream flow at GL4. Performing three component mixing models using End Member Mixing Analysis (EMMA) would have provided more detailed analysis of both source waters and flow paths but were beyond the scope of this study.

2.5.5 Two-component mixing models: Flow Paths

Reacted water was responsible for greater than 75% of total streamflow in both GL4 and Gordon Gulch and greater than 50% of total streamflow in Como Creek, confirming the importance of subsurface flowpaths and reservoirs in surface water production. The increase in unreacted water during the summer is consistent with results from Sueker et al. (2000) who suggested this phenomenon is a likely result of diminished adsorption capacity within the soils. The adsorption capacity is diminished due to the flushing of solutes during the snowmelt infiltration pulse resulting in reacted waters entering the stream in late summer that have lower solute concentrations then during other times of the year, and thus appear to look more like unreacted waters.

The fact that subsurface contributions showed no relationship to drainage area suggest that other factor besides basin size controlled flowpath dynamics across the watershed. This coincides well with the residence time estimates from the convolution approach in which there was also no relationship between groundwater residence times and basin area.

The time series plots of $\delta^{18}O$ and dissolved organic carbon (DOC) found in surface waters and in springs and wells representing sub-surface water provide some additional insight on flowpath generation. In GL4 the talus spring sampled during summer months indicated that talus water DOC and $\delta^{18}O$ concentrations closely resemble the GL4 stream during late season flows, showing that indeed shallow sub-surface flow through the talus may be a significant contributor of reacted water particularly during late summer discharge. This result suggest that in the alpine setting sub-surface water may be coming from near surface sources in addition to draining of the saturated zone, ultimately leading to shorter average residence times.

For Como Creek there appears to be a strong correlation between the shallow well DOC and stream channel DOC during the receding limb of the hydrograph followed by a late season switch to surface water concentrations becoming more similar to the DOC concentrations in the deeper well. The results support the notion that the stream is receiving water resembling a shallow flow path signal during the receding limb of the snowmelt pulse then switching to late season baseflow that looks like deeper groundwater. The $\delta^{18}O$ concentrations in the stream continue to move towards those found in the deep well throughout the summer, further indicating that subsurface flow becomes a significant contributor to late season streamflow in Como Creek.

In Gordon Gulch the water in the springs show fluctuations in $\delta^{18}O$ and DOC concentrations that are simultaneously occurring with fluctuations in stream waters, thus indicating a tight coupling between steam flow and sub-surface water coming out of the springs.

The DOC fluctuations further indicate that the Gordon stream has a very flashy response to precipitation events in which storm water is infiltrating but then following relatively short flow paths and showing up in the stream shortly after storm events. Both graphs in Figure 2.20 also indicate that the stream response is more similar in direction and magnitude to the response of the spring on the south-facing slope, especially during late summer and fall precipitation events. Conversely, the north-facing slope spring appears to maintain a more stable $\delta^{18}O$, indicative of a more consistent recharge source, potentially coming from a more sustained spring snowmelt pulse on those slopes. The north facing spring also has consistently lower DOC levels, which suggest deeper flow paths (at least to that spring) then on the South facing slopes. These results suggest that the flowpaths in Gordon Gulch could vary depending on hillslope aspect with north facing slopes more heavily influenced by snowmelt infiltration to deeper depths and south facing slopes having less infiltration to depth and therefore more rapid transport of water to the stream channel.

2.5.6 Potential Impacts of Changing Climate on Surface-Groundwater Interactions

Climate predictions suggest that warming temperatures and CO_2 concentrations in the atmosphere may increase the total precipitation for areas of the Rocky Mountains by 50-100% (Baldwin et al, 2003). With the increase in temperature, snowmelt onset will occur earlier and likely 50% less precipitation will fall as snow (Baldwin et al, 2003). It is known that global changes in temperatures directly affect the hydrology of the land surface through changes in the accumulation and ablation of snow, as well as in evapotranspiration (ET) (Nijssen et al., 2001).

Unfortunately, there is little agreement on the direction and magnitude of historical and future ET trends (Barnett et al., 2005).

Recent research in Boulder Creek Watershed by Molotch et al (2009) shows that commencement of the growing season was coincident with melt-water input to the soil. This suggests that with earlier snowmelt the vegetation will “turn on” earlier in the year ultimately lengthening the summer growing season thereby increasing the total amount of ET occurring in the system. The result will be a greater loss of water out of the system through the ET pathway especially during the snowmelt pulse. If more water is leaving the system as ET then there is less available to contribute to discharge and groundwater recharge, ultimately reducing runoff efficiency. The results of this study show that runoff efficiency decreases with a decrease in elevation, and it also shows that lower elevations have higher air temperatures and earlier snowmelt. Therefore, this research supports the notion that warmer temperatures lead to earlier snowmelt, potentially increasing overall ET, which can lead to decreased stream discharge and lower runoff efficiency. Additionally, the elevational gradient in this study may serve as an indicator for future hydrologic conditions where the processes currently occurring at the lower elevations will continue to move up in elevation as climate change leads to more warming at the higher elevations. Ultimately, understanding surface-groundwater interactions under current hydrologic conditions will enhance our ability to predict how future natural and anthropogenic perturbations will impact sub-surface water resources in headwater catchments.

2.6 Conclusion

There was an increase in both precipitation and the percent falling as snow with an increase in elevation across the Boulder Creek watershed in 2009. Snowmelt dominated hydrographs were observed across all elevations with peak discharge occurring later in the season at higher elevations. The duration of the snowmelt pulse increased with elevation, while the lower elevation sites showed greater response to summer rains. Runoff efficiency was greatest in the alpine and lowest in the foothills but did not vary linearly with elevation, indicating that additional variables besides temperature and precipitation could be influencing this process.

Each of the headwater catchments studied exhibited relatively short residence times, while also showing that significant portions of streamflow had reacted with the subsurface. The results therefore suggest relatively rapid movement of water through the subsurface, especially during snowmelt. During baseflow conditions stream water in Como Creek and Gordon Gulch potentially contained older water that may have been following longer or deeper subsurface flow paths, whereas baseflow at GL4 and Betasso did not show signs of containing significantly older water.

To conclude, the results of this research suggest that within Boulder Creek watershed elevation strongly influences the climactic conditions of temperature and precipitation. The research also suggests that other variables such as subsurface architecture, landscape evolution, and even vegetation structure play an important role in controlling the hydrologic processes occurring in headwater catchments. Therefore the space for time hypothesis can be applied to predicting and understanding the impacts of climate change on watershed hydrology, but accurate application requires a sound understanding of all the variables influencing surface and groundwater interactions across many scales. A warmer climate will surely produce less annual snowfall in mountain watersheds, but we are unlikely to see a uniform hydrologic response that is predictable by elevation alone.

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