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Streamflow and Groundwater Response to Precipitation Variability in a Snow-Dominated, Subalpine Headwater Catchment, Colorado Rocky Mountains, USA

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STREAMFLOW AND GROUNDWATER RESPONSE TO PRECIPITATION VARIABILITY IN A SNOW-DOMINATED, SUBALPINE HEADWATER CATCHMENT, COLORADO ROCKY MOUNTAINS, USA

by

KELSEY RAE DAILEY

B.S., Geological Sciences, The Ohio State University, 2013

A thesis submitted to the Faculty of the Graduate School of the University of Colorado in partial fulfillment of the requirement for the degree of Master of Science Environmental Studies Program 2016
This thesis entitled:

Streamflow and groundwater response to precipitation variability in a snow-dominated, subalpine headwater catchment, Colorado Rocky Mountains, USA

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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 meet acceptable presentation standards of scholarly work in the above mentioned discipline
ABSTRACT

Dailey, Kelsey Rae (M.S. Environmental Studies)

Streamflow and groundwater response to precipitation variability in a snow-dominated, subalpine headwater catchment, Colorado Rocky Mountains, USA

Thesis directed by Professor Mark W. Williams

Snow-dominated mountainous watersheds of the western US that provide vital freshwater resources are facing increased precipitation variability due to climate change, including changes in the timing and amount of snowmelt. During years of low snow accumulation, groundwater can supply a large portion of streamflow that natural and human ecosystems rely on, yet groundwater dynamics in mountainous areas are poorly understood due to complex topography and geology and heterogeneity in flow processes. Isotopic and geochemical surface water and groundwater data are used to examine groundwater recharge dynamics and hydrologic connectivity in the mixed alpine-subalpine Como Creek headwater catchment of the Boulder Creek Watershed. Interannual variations in surface water-groundwater interactions are investigated across years that exhibited near-record snowfall in Colorado (2011), the worst snow drought in decades (2012), and a rare, heavy rain event (2013), providing an opportunity to investigate the impacts of precipitation variability on mountainous hydrologic systems. Mean subalpine groundwater residence times are 2-6 years, with a mean catchment water residence time of 1.1 years. Net subalpine groundwater recharge accounts for an average of 36% of event (snowmelt, rain) precipitation. The fast turnover of the subalpine groundwater reservoir suggests it has limited storage capacity and is consistent with a high recharge, snowmelt-dominated system. Geochemical (Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Si, ANC) and isotopic (\(\delta^{18}\)O) tracers are analyzed via End-Member Mixing Analysis (EMMA) to determine the source waters contributing to streamflow over 2011-2014. Results show that mean annual streamflow is derived of 36% soil
water, 35% snowmelt, and 29% groundwater. Stream-groundwater interactions are high in the subalpine and most snow or rain infiltrates the subsurface before entering the stream. Observed recharge from the 2013 rain event indicates that the subalpine aquifer-stream system has the possibility of transitioning to a hybrid (snow-rain) influenced system with greater recharge from seasonal rains. Observed changes in hydrologic connectivity over 2011-2014, including multiple major groundwater recharge events during a year, drying out of the subsurface following snow drought, and decreased catchment water residence time due to large rain inputs, provide insight into the response of mountainous headwater catchments to precipitation variability under a changing climate.
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CHAPTER 1
Hydrologic connectivity, water residence time, and groundwater recharge in a subalpine, headwater catchment, Colorado Rocky Mountains, USA

Abstract

Geochemical surface water and groundwater data are used to examine groundwater recharge dynamics and hydrologic connectivity in the Como Creek headwater catchment of the Boulder Creek Watershed over years of precipitation variability. Stream chemistry along an elevational transect indicated that the highest elevation site near treeline was significantly different from lower sites for DOC, δ¹⁸O, and Ca²⁺ (p < 0.05). The lower stream sites were not significantly different with regards to DOC and δ¹⁸O, indicating a well-mixed hydrologic system below treeline, with large contributions from near treeline regarding groundwater discharge and recharge. The subalpine soil water δ¹⁸O record showed enrichment from summer rains while subalpine groundwater and streamflow did not, suggesting that precipitation is assimilated into subalpine soils and lost there rather than contributing to streamflow or groundwater recharge.

The δ¹⁸O compositions of precipitation, streamflow, and groundwater in the catchment were evaluated to estimate a mean catchment water residence time of 1.13 years and mean shallow (<10 m depth) and deep (>15 m depth) subalpine groundwater residence times of 2.98 years and 6.63 years, respectively. Additionally, the δ¹⁸O stream record from the catchment outlet was not significantly different from that of the subalpine groundwater wells, indicating a well-mixed system with low residence times. Net subalpine groundwater recharge is estimated to account for an average of 36% of event precipitation, with slower recharge rates and less recharge with below average snowfall. While snowmelt is commonly the only major groundwater recharge event observed in the subalpine during a year, substantial groundwater recharge was observed for the September heavy rain event that dropped 200 mm of rain on the catchment in one week and
caused devastating flooding in Colorado. Results suggest that the subalpine aquifer-stream system is recharge-driven and snowmelt-dominated, but has the possibility of transitioning to a hybrid hydroclimatic system with increased recharge from seasonal rains. Observed changes in hydrologic connectivity, including multiple major groundwater recharge events for one year, a drying out of the subsurface following snow drought, and decreased catchment water residence time due to large rain inputs, provide insight into future catchment response under a changing climate.

1.1 Introduction

Mountains supply a disproportional amount of freshwater to lowland areas, making them the “water towers of the world” (Viviroli et al., 2003). The melting of deep, seasonal snowpack in mountainous areas of the semi-arid western United States (US) provides the majority of surface runoff to adjacent lower-elevation areas during the spring and summer months when environmental and municipal demands are greatest (Mote et al., 2005). Higher air temperatures are predicted to decrease the snowfall fraction of precipitation and the subsequent mountain snowpack, which will result in earlier snowmelt in the western US, effectively reducing the region’s natural freshwater storage capacity (Knowles et al., 2006; Hamlet et al., 2005; Stewart et al., 2005). Snowmelt timing additionally controls both the amount and rate of streamflow, with major implications for water storage and flood management, temporally defined water rights, and ecosystem services (Clow, 2010). Surface and man-made reservoirs may lack the adequate storage capacity to capture surface runoff from more rain falling in place of snow, which means that more water will be passed on downstream and eventually lost to the ocean (Barnett et al., 2005).
Earlier snowmelt in snow-dominated mountainous watersheds of the western US results in earlier peak soil moisture, initiating a longer growing season for vegetation and a late summer soil moisture deficit (Tague and Peng, 2013). This deficit increases forest water stress and makes trees more susceptible to disturbances such as wildfire and insect infestation that have increased in size and severity in western US forests over the past few decades (Harpold et al., 2014a; Biederman et al., 2014; Livneh et al., 2015). For terrestrial, aquatic, and managed ecosystems alike, changing precipitation and runoff regimes will influence the system’s hydrologic connectivity, or the water-mediated transfer of matter, energy, and organisms between components of the hydrological cycle, particularly regarding the cryosphere (Pringle, 2001; Fountain et al., 2012). Given the major importance of snow-dominated, mountainous watersheds to freshwater resources in the western US, evaluating the response to precipitation variability at the watershed scale is critical for sustainable water resource management.

While snowmelt contributes most of the annual streamflow in headwater catchments of the Rocky Mountains, groundwater can account for greater than 75% of streamflow during storms and the winter baseflow period (Clow et al., 2003). Indeed, during years of low snow accumulation, groundwater can supply a substantial portion of summer streamflow in mountainous areas that supply water for agriculture, recreation, domestic water supply, and riparian and aquatic ecosystems (Tague and Grant, 2009; Liu et al., 2004). In semi-arid mountainous regions, groundwater recharge is largely driven by the melting of seasonal snowpacks, with groundwater systems effectively storing and slowly releasing snowmelt to streamflow throughout the year (Segal et al., 2014). Thus, climate changes and variability are predicted to impact groundwater resources primarily through the timing, location, magnitude, and mechanism of groundwater recharge (Ajami et al., 2012; Clow, 2010; Taniguchi and
Hiyama, 2014). Overarching ramifications of climate change on groundwater recharge in mountain watersheds range from increased recharge due to earlier infiltration when evapotranspiration (ET) rates are low to decreased recharge due to increased ET and decreased snowpack (Manning et al., 2012; Meixner et al., 2016). Yet mountain groundwater remains poorly understood as such systems are characterized by site-specific, complex topography and geology and heterogeneity in flow and transport processes, complicating regional application of existing studies (Garfias, 2009). Additionally, difficult or limited access to mountainous areas and a lack of infrastructure impede groundwater analysis, and basic questions remain regarding mountain groundwater recharge and tradeoffs with streamflow and ET in headwater catchments (Brooks et al., 2010; Tague and Peng, 2013). A small but growing body of research on mountain groundwater systems exists (Garfias, 2009; Allen et al., 2010; Spencer et al., 2014), with common focus on alpine areas (Manning and Caine, 2007; Clow et al., 2003; Liu et al., 2004; Baraer et al., 2015), valley-bottom aquifers (Smerdon et al., 2009), mountain block recharge (Magruder et al., 2009; Wilson and Guan, 2004; Wahi et al., 2008), and regional groundwater flow (Gleeson and Manning, 2008; Wolf et al., 2008). Groundwater studies in subalpine areas near treeline with greater soil and critical zone development have received less attention (Cowie, 2014; Hudson and Golding, 1997; Bearup et al., 2014), despite the awareness that these areas function as important filters for downstream ecosystems and water resources (Seastedt et al., 2004).

As one of the fastest growing states in the country over the past decade (U.S. Census Bureau, 2016), population growth and human development in Colorado are certain to increase stress on limited freshwater resources. Both near-record winter drought and snowfall have occurred in Colorado in more recent years, providing a valuable temporal context for studying
changes in mountain hydrologic partitioning and storage (Knowles et al., 2015). Anomalously dry winter conditions in 2012 contributed to some of Colorado’s largest and most destructive wildfires during the summer months of 2012 and 2013 (Hamm, 2016). Additionally, the Colorado Front Range received 20-40 cm of rainfall from September 9-16, 2013, which broke daily and multi-day rainfall records across eastern Colorado. The heavy rains caused devastating flooding that resulted in eight fatalities, the evacuation of 18,000 people, nearly $2 billion in property damage, and 1,300 landslides (Uccellini, 2014). Such an event can be used as a valuable proxy for evaluating the hydrological resilience of snow-dominated mountainous watersheds subject to future precipitation variability and extremes.

The purpose of this study is to delineate surface water-groundwater interactions in a mixed alpine-subalpine headwater catchment of the Boulder Creek Watershed (BCW) in the Colorado Front Range during a period marked by precipitation variability. With the Continental Divide as its western border, the BCW is home to more than 185,000 people and provides high quality freshwater for municipalities, agriculture, aquatic ecosystems, and recreation in an otherwise semiarid environment (U.S. Census Bureau, 2016). Previous research in the BCW headwater Como Creek catchment determined that shallow, subalpine-derived groundwater constituted a large portion of streamflow leaving the hydrologically significant area (Cowie, 2014). Yet, limited knowledge of the ability of the subalpine subsurface reservoir to mitigate impacts of changing precipitation inputs to surface waters restricts predictions of future climate and disturbance impacts on the catchment. As a result, interannual variations in surface water-groundwater interactions are assessed across years that exhibited variable precipitation regimes in Colorado, including near-record snowfall (2011), the worst snow drought in decades (2012), and a rare, heavy rain event (2013). Geochemical and isotopic surface and soil water chemistry
data are used in conjunction with groundwater depth and chemistry data to determine the subalpine response to hydrologic change and to estimate water residence times and groundwater recharge. Characterization of groundwater residence time, recharge, and storage in the subalpine Como Creek catchment during a time of precipitation variability will provide insight into how streamflow in mountain watersheds may respond to climate change.

The specific research questions for this study are:

1. How does precipitation variability affect the hydrologic connectivity within this catchment and the resulting quantity and quality of exported surface water?
2. What are the respective residence times for catchment water, shallow subalpine groundwater, and deep subalpine groundwater?
3. How does subalpine groundwater recharge and the response of the unsaturated zone change with precipitation variability?

1.2 Study Area

The Como Creek catchment is a headwater catchment of BCW draining the southeast flank of Niwot Ridge in the Colorado Rocky Mountains, USA (40°03’ N, 105°35’ W). The 5.36 km² catchment lies approximately 4-9 km east of the Continental Divide and ranges in elevation from 2900 to 3560 m a.s.l., with approximately 69% of catchment area below treeline and 31% above treeline (Figure 1.1; Knowles et al., 2015). The mean annual temperature and precipitation for the Como Creek catchment are near 4°C and 800 mm, with approximately 70 to 80% of the annual precipitation falling as snow from the base to the headwaters of the catchment, respectively (Monson et al., 2002; Williams et al., 2011). Summer precipitation is common during afternoon convective storms and can result in extreme but sporadic rainfall near Niwot Ridge (Greenland and Losleben, 2001). Climate data have been collected at the subalpine
C-1 site (40° 02’ 09” N; 105° 32’ 09” W) in the catchment since the 1950s (Williams et al., 1996b), with additional climate programs operating in the vicinity including the Niwot Snowpack Telemetry (SNOTEL) Site (#663) and a National Atmospheric Deposition Program (NADP) site (CO90). In addition to operating the NADP CO90 site, the Niwot Ridge Long-Term Ecological Research (NWT LTER) program also operates an unofficial NADP wet chemistry collector at the Soddie site (40° 02’ 52” N; 105° 34’ 15” W) near treeline in the catchment. Research in the Como Creek catchment dates back to the mid-1970s (Lewis and Grant, 1979; Hood et al., 2003ab; Darrouzet-Nardi et al., 2012; Williams et al., 2009; Cowie, 2014, Knowles et al., 2015). Residing above Como Creek is the 30 km² alpine Green Lakes Valley catchment, which is closed to the public and protected by the City of Boulder. Data from the aforementioned programs pertaining to Como Creek and Niwot Ridge can be accessed via links in the Appendix.
Figure 1.1. Map of the Como Creek catchment showing all sample locations and Niwot SNOTEL. The catchment has an area of 5.36 km² with approximately 31% and 69% of the catchment above and below treeline, respectively. Insert shows the regional location of the catchment (adapted from Knowles et al., 2015).

The subalpine portion of the Como Creek catchment is primarily coniferous forest dominated by Engelmann spruce (*Picea engelmannii*), subalpine fir (*Abies lasiocarpa*), limber pine (*Pinus flexilis*) and lodgepole pine (*Pinus contorta*), with some aspen (*Populus tremuloides*) (Williams et al., 2011). The forested area is currently in an aggradation phase after being logged over a century ago, with minimal disturbance since then (Lewis and Grant, 1979). Non-forested portions of the catchment including areas above treeline and some small seasonal wetlands are covered with grasses, forbs, sedges (*Carex*), and willows (*Salix*) (Lewis and Grant, 1979). Areas near treeline are characterized by ribbon forests and meadows comprised of moderately well-
drained soils with loamy sand to gravel textures and little clay content (Williams et al., 2009). The area was glaciated during the Pleistocene, so much of the subalpine area at and around C-1 resides on the Arapaho moraine, with a large portion underlain by Pinedale and Bull Lake glacial till (Williams et al., 2011). While the USGS Ward quadrangle estimates a moraine thickness near 10 m (Gable and Madole, 1976), a groundwater well installed in 2011 near C-1 was drilled to a depth of 28 m and was believed to only reach the bedrock-moraine interface, signifying the great extent of glacial deposits within the catchment. Soils overlying the Precambrian siliceous metamorphic and granitic bedrock are relatively thin, ranging from 60-200 cm, and are deeper in areas with glacial till (Lewis and Grant, 1979; Murphy et al., 2003). In contrast with the nearby alpine Green Lakes Valley catchment, there are no lakes, rock glaciers, talus, exposed bedrock, or steep cliffs in the Como Creek catchment (Williams et al., 2011). Como Creek is a tributary to North Boulder Creek, the source of 40% of the City of Boulder’s water supply (City of Boulder, 2016). Geochemical and isotopic surface water data were obtained from four sites along Como Creek, and groundwater, soil water, and soil moisture content data were collected near the C-1 site within the lower part of the catchment (Figure 1.2). The combination of these data represents intensive measurements at one site (C-1) and a longitudinal stretch of measurements along an elevational transect.
Figure 1.2. Groundwater wells (piezometers) and soil lysimeters near the C-1 Como Creek site within the Como Creek catchment.

1.3 Data and Methods

1.3.1 Climate

Air temperature records from the C-1 climate station in the catchment were obtained via the Niwot Ridge LTER database to calculate mean annual and 50-yr air temperatures for the subalpine. Daily precipitation amount was measured at NADP CO90 site near C-1 over the duration of the study. Additionally, precipitation was sampled weekly at both the NADP CO90 site at C-1 between 2011 and 2014 and the unofficial NADP Soddie site between 2011 and 2013. Daily snow water equivalent (SWE) and cumulative precipitation (CP) amount were measured at the Niwot SNOTEL Site (Figure 1.1). All climate data can be attained via links provided in the Appendix.

1.3.2 Surface Water

Surface water samples were collected at 4 locations along Como Creek as grab samples
according to the protocols in Williams et al. (2009). From lowest to highest in elevation, these sites correspond to a weir at the catchment outlet (Weir), a site near C-1 (C-1), a site near where the Mountain Research Station (MRS) road makes a large turn (S-Curve), and a headwater stream of Como Creek near the Soddie site located in the upper extent of the catchment just below treeline (Soddie Stream) (Figure 1.1). Samples were collected approximately weekly at the Weir since 2003 and weekly during the spring and summer months at C-1, S-Curve, and Soddie Stream since 2011. The water level in Como Creek was measured at the Weir by hand during sampling and with a continuously recording pressure transducer and converted to volumetric discharges by annual empirical rating curves according to the procedures in Knowles et al. (2015).

1.3.3 Groundwater

Subalpine groundwater wells near C-1 were sampled approximately weekly during the spring and summer months and monthly during the winter since 2010 when they were installed. The eleven wells near C-1 that were utilized for this portion of the study include four wells south of C-1 (SO, 1-4), two wells southwest of C-1 (SW, 1-2), four wells near the Niwot SNOTEL Site (ST, 1-4), and one additional well in the vicinity (BEL) (Figure 1.2; Appendix). The groundwater wells consisted of piezometers made of PVC pipes screened at the bottom 1.5 m. Well depths generally ranged from 7-8 m, with one deeper well at 28 m (SW2). All groundwater wells at C-1 resided within unconsolidated glacial deposits, mainly sand, gravel, and cobbles, and were not known to have penetrated bedrock upon installation. Depth-to-water was measured by hand with a weighted tape measurer. Groundwater well sampling was then performed using a 1 m teflon bailer after purging one full well volume and subsequently followed the protocol for surface water collection. Water level was also measured twice daily between 2013 and 2014 by
pressure transducers (Solinst 3001 Levelogger Edge) in four wells at C-1 (SW2, SO1, SO4, ST1). Water level data collected by pressure transducers were compared to manual measurements taken throughout the year and an appropriate linear function ($R^2 > 0.93$) was used to calibrate transducer measurements between manual measurements.

1.3.4 Snowpack and Soil Water

The snowpack was sampled approximately weekly from January until snowmelt at the C-1 and Soddie sites following the procedures in Williams et al. (1996b). When available, soil water was collected at the Soddie site using zero-tension soil lysimeters accessed via an underground laboratory (Williams et al., 1996b). Soil water at C-1 was sampled via tension lysimeters co-located with the three pods of groundwater wells at C-1 (Figure 1.2; Appendix). The three pods of soil lysimeters at C-1 sampled water from four depths down to 1.5 m below the ground surface and were installed in 2011.

Daily volumetric soil water content data for 2005-2012 were obtained from a vertical soil moisture array (Sentek EnviroScan Probe) connected to a datalogger (Campbell Scientific CR23X) located near the groundwater wells at C-1. Sensors are stacked at eight depths from 10 to 200 cm below the ground surface. These data can be found at the Niwot Ridge LTER link provided in the Appendix.

1.3.5 Laboratory Analyses

All precipitation and water samples were analyzed for $H^+$, $NH_4^+$, $Ca^{2+}$, $Na^+$, $Cl^-$, $Mg^{2+}$, $K^+$, $NO_3^-$, $SO_4^{2-}$, $Si$, $\delta D$, $\delta ^{18}O$, pH, acid-neutralizing capacity (ANC), specific conductance, dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and total dissolved nitrogen (TDN) at the Kiowa Environmental Chemistry Laboratory in Boulder, CO, as part of the NWT LTER Program. Laboratory methods, detection limits, and instrumentation for chemical and
nutrient analyses are as presented in Williams et al. (2009). Generally, detection limits for all solutes were less than 1 µeq/L. Samples for stable water isotopes were analyzed via a Picarro L1102-i Isotopic Liquid Water Analyzer. The precision for δ\(^{18}\)O and δD were ± 0.05‰ and ± 0.1‰, respectively. Prior to 2009, water isotopes were analyzed at the Institute of Arctic and Alpine Research Stable Isotope Laboratory in Boulder, CO.

1.3.6 Statistical Analyses

Determination of differences in Ca\(^{2+}\), NO\(_3\), DOC, and δ\(^{18}\)O distribution between Como Creek streamflow sites was performed by one-way analysis of variance (ANOVA) at the 0.05 significance level (R, 3.1.3, 2014). Since surface water data were only available during the spring and summer months at three of the sampling sites, statistical analyses were performed on data corresponding to the period between 1 May and 31 October. This approach aimed to minimize the potential for seasonality effects on the sampling distribution while still including hydrologically significant time periods such as snowmelt and the summer growing season. Additionally, ANOVA was applied to the δ\(^{18}\)O distributions of the 2003-2014 record of Como Creek streamflow at the Weir and the 2011-2014 records of all C-1 groundwater wells, snowpack within the catchment (C-1, Soddie), and soil water (C-1). Both the F-statistic, or the ratio of sum of squares to the degrees of freedom, and a p-value, derived from the cumulative distribution of F, are provided via ANOVA. If significant differences were observed (p < 0.05), multiple one-way ANOVA were performed to identify sites or waters that were significantly different from one another.

1.3.7 Residence Times

The residence time of water draining a catchment reflects a catchment’s ‘memory’ to past inputs and thus can be used a tool to understand a catchment’s hydrologic sensitivity to climate
change (McGuire et al., 2005). Estimation of the mean residence time for water in a catchment can be calculated if the seasonal variations of $\delta^{18}O$ input (precipitation) and output (e.g. streamflow, groundwater) are known. Mean residence times for water in the Como Creek catchment were calculated by examining the smoothing of the $\delta^{18}O$ input (precipitation at the Soddie site) in various outputs (Como Creek streamflow at the catchment outlet, C-1 groundwater) using the convolution algorithm approach (Maloszewski et al., 1983; Pearce et al., 1986; Plummer et al., 2001). Sinusoidal functions were used to approximate the time series for $\delta^{18}O$ values in precipitation and streamflow or groundwater, respectively:

$$\delta^{18}O_{in}(t) = A \sin(wt) + M$$  \hspace{1cm} (1.1)

$$\delta^{18}O_{out}(t) = B \sin(wt + \phi) + M$$  \hspace{1cm} (1.2)

where $t$ is the time in years, $A$ is the amplitude of $\delta^{18}O$ in precipitation, $w$ is the period in radians ($w = 2\pi$ for one year), $B$ is the amplitude of $\delta^{18}O$ in streamflow or groundwater, $\phi$ is the phase shift, and $M$ is the mean of the respective $\delta^{18}O$ variation. Assuming the catchment is characteristic of a well-mixed, exponential system, in which incoming rain mixes with existing water in storage, the convolution integral is:

$$\delta^{18}O_{out}(t) = T^{-1} \int_0^\infty \delta^{18}O_{in}(t - t') \exp(-\frac{t'}{T}) dt'$$  \hspace{1cm} (1.3)

where $T$ is the mean residence time of water in the catchment in years and $t'$ is the lag time between input and output composition. Substituting (1.1) into (1.3) and solving produces:

$$T = \frac{1}{w} \sqrt{\left(\frac{A^2}{B^2}\right)} - 1$$  \hspace{1cm} (1.4)

1.3.8 Water Table Fluctuation Method

1.3.8.1 Groundwater Recharge

The Water Table Fluctuation (WTF) method is a well-known and widely used technique.
for estimating groundwater recharge in unconfined aquifers based on the relation between changes in aquifer water storage and water table height (Meinzer, 1923). Using a water budget approach, change in saturated zone storage for a groundwater system, or “net recharge,” in a specified area can be theorized as:

\[
\Delta S_{gw} = R + Q_{gw}^{in} - Q_{gw}^{out} - Q_{bf} - ET_{gw}
\]  

(1.5)

where \( R \) is total recharge, \( Q_{gw}^{out} \) and \( Q_{gw}^{in} \) are subsurface flow away from or into the area of study, \( Q_{bf} \) is baseflow, and \( ET_{gw} \) is evapotranspiration from groundwater (Healy and Cook, 2002). All components of Equation 1.5 are expressed as rates [L/T]. The WTF method is based on the notion that a time lag exists between water arriving to the water table and the redistribution of that water to the other components in Equation 1.5. Thus, the WTF method assumes that during this lag time, all other components in Equation 1.5 equal zero and:

\[
\Delta S_{gw} = R = S_y \frac{dh}{dt} = S_y \frac{\Delta h}{\Delta t}
\]  

(1.6)

where \( S_y \) is specific yield [dimensionless], \( h \) is water-table height, and \( t \) is time (Healy and Cook, 2002). The assumption that net recharge (\( \Delta S_{gw} \)) is equal to total recharge (\( R \)) is most valid over the course of hours to days, so Equation 1.6 is best applied to individual water level fluctuations occurring within a short time if an estimate of \( R \) is desired. To analyze recharge over longer intervals, Equation 1.6 can also be used to calculate \( \Delta S_{gw} \) for major recharge events such as snowmelt. Using the depth record of a groundwater well, \( \Delta h/\Delta t \) can be calculated as the difference between the minimum and maximum observed water-level measurements that define the time period of analysis. The difference between \( R \) and \( \Delta S_{gw} \) is represented by the other components in Equation 1.5 and is realized in Equation 1.6 by using different approaches to estimate water level rise (\( \Delta h/\Delta t \)) (Healy, 2010).

The WTF method is best suited for shallow water tables with wells that display sharp
responses attributed to precipitation or melt events. If the rate at which water moves away from the water table is not significantly slower than the rate at which water arrives, the WTF method will not produce accurate estimates of recharge (Healy and Cook, 2002). The WTF method requires no requirement of assumptions on the mechanism by which water flows through the unsaturated zone and is appealing due to its simplicity and ease of use (Healy and Cook, 2002). Water levels measured in groundwater wells in unconfined aquifers are generally representative of an area of several square meters or more, so the WTF method can be regarded more as an integrated approach and less as a point measurement for determining recharge in an area. Uncertainties arising from utilization of the WTF method often deal with water table fluctuations in the water table due to causes other than precipitation infiltration (i.e. ET at the water table, changes in atmospheric pressure) (Healy and Cook, 2002).

1.3.8.2 Estimating Specific Yield

The WTF method requires an estimation of the specific yield, or drainable porosity, of the aquifer material. The water-yielding and water-keeping capacities of a rock or soil are known as the specific yield and specific retention, respectively, and together they equal the total porosity of the rock or soil (Meinzer, 1923). When laboratory or field estimates of \( S_y \) are not available, a water budget approach can be used (Healy and Cook, 2002). The water budget for a catchment can then be characterized as:

\[
P + Q^{in} = ET + \Delta S_{sw} + \Delta S_{uz} + \Delta S_{gw} + Q^{out}
\]

(1.7)

where \( P \) is precipitation, \( Q^{in} \) and \( Q^{out} \) are surface and subsurface flow into and out of the catchment, \( ET \) is total evapotranspiration, and \( \Delta S \) is the change in storage from surface reservoirs (\( sw \)), the unsaturated zone (\( uz \)), and the saturated zone (\( gw \)). For the Como Creek catchment, streamflow is in recession in the late summer and early autumn and \( ET \) and \( \Delta S_{uz} \) in Equation 1.7
are considered negligible due to relatively low temperatures, the end of the growing season, and soils relatively saturated from snowmelt. During this low flow time, streamflow exiting the catchment is derived primarily from baseflow and precipitation and all precipitation either runs off as streamflow or recharges the water table. Since the time period over which $S_y$ should be estimated for an aquifer is on the order of one week, net surface and subsurface flow ($Q^{in} - Q^{out}$) during this short low flow time are treated as negligible (Healy and Cook, 2002).

Rearranging Equations 1.6 and 1.7 accordingly yields:

$$R = \Delta S_{gw} = P - \Delta S_{sw} = S_y \frac{\Delta h}{\Delta t}$$  \hspace{1cm} (1.8)

For Como Creek during streamflow recession, $\Delta S_{sw}$ is represented mainly by surface water leaving the catchment:

$$\Delta S_{sw} = \frac{Q_{out}^{sw}}{A_{CC}}$$  \hspace{1cm} (1.9)

where $Q_{out}^{sw}$ [L$^3$/T] is streamflow measured at the catchment outlet on the last day of the analysis time period and $A_{CC}$ [L$^2$] is the area of the Como Creek catchment (5,360,000 m$^2$). The $S_y$ of the subalpine aquifer where C-1 groundwater wells reside in the Como Creek catchment can thus be estimated as:

$$S_y = \frac{P - \frac{Q_{out}^{sw}}{A_{CC}}}{\frac{\Delta h}{\Delta t}}$$  \hspace{1cm} (1.10)

where $P$ is precipitation amount measured at the C-1 NADP CO90 site over the time period of analysis ($\Delta t$) and $\Delta h$ is the associated water level decline in the groundwater well. Using Equation 1.10 to estimate $S_y$ assumes that baseflow does not change over the period of analysis (Healy and Cook, 2002). Uncertainty in recharge estimates using the WTF method is often associated with the difficulty in attaining an accurate value for $S_y$. Laboratory, theoretical, and field methods have produced considerably variable values for $S_y$ and limited progress has been
made over the last century in addressing the limitations of $S_y$ determination (Healy and Cook, 2002). It should be recognized that utilizing estimates of $S_y$ and water level rises derived from the above methods to calculate groundwater recharge is somewhat subjective. Nonetheless, estimation of $S_y$ and groundwater recharge in the subalpine across years with variable precipitation will advance scientific understanding of snowmelt-dominated mountainous groundwater systems.

1.4 Results

1.4.1 Climate and Como Creek Discharge

The mean annual air temperatures (all results reported by water year) at C-1 were -2.9°C (2014), 0.44°C (2013), 2.3°C (2012), and 2.2°C (2011), with a long-term (50-yr) mean of 1.6°C. Cumulative precipitation (CP) and snow water equivalent (SWE) as measured at the Niwot SNOTEL site in the Como Creek catchment are plotted for 2008-2014, along with the 1981-2010 CP mean and SWE median (Figure 1.3ab). Discharge for Como Creek at the Weir site near the catchment outlet is also shown for years 2008-2012 and 2014 (Figure 1.3c). Data from the years of 2008-2010 are shown as they generally demonstrate average snow and streamflow responses for the Como Creek catchment.
Figure 1.3. (a) Cumulative precipitation and (b) snow-water equivalent (SWE) at Niwot SNOTEL and (c) the Como Creek catchment hydrograph for the period 1 March to 1 October for water years 2008-2014. Note that 2012 peak discharge occurred on 8 July after snowmelt. Mean cumulative precipitation and median SWE are shown for 1981-2010. Available discharge data for 2013 are shown as black dots (adapted from Knowles et al., 2015).

Annual CP at the Niwot SNOTEL site was greatest for the water year of 2013 (940 mm), followed by 2011 (894 mm) and 2014 (785 mm). Despite anomalously low snowfall, CP in 2012 reached 719 mm due to contributions from July rains. Rainfall from 6-10 July 2012 totaled 111 mm, representing 15% of the 2012 water year CP (Figure 1.3a). During the week of 9-16
September 2013, approximately 190 mm and 208 mm of rain were recorded at the NADP CO90 and Niwot SNOTEL sites near C-1, respectively, representing roughly 20% of 2013 CP (Figure 1.3a). The majority of this rain fell on 12-13 September 2013, which resulted in the month of September 2013 experiencing nearly four times the amount of precipitation that is commonly observed during that month at the NADP CO90 site (2006-2014 record). Relative to the long-term (30-yr) precipitation record mean CP of 808 mm, the four focus years of this study represent above average (116% in 2013; 110% in 2011), near average (97% in 2014), and below average (89% in 2012) precipitation regimes. Between 2011 and 2014, peak SWE was highest in 2014 on 18 April (470 mm), followed by 2011 on 22 May (432 mm), 2013 on 11 May (424 mm), and 2012 on 12 March (279 mm). For 1981-2010, the peak median SWE (320 mm) occurred on 29 April.

For 2008-2011 and 2014, the Como Creek hydrograph was characteristic of a snowmelt-dominated watershed with a steep rising limb corresponding with snowmelt observed in April, May, or June. A larger and longer lasting snowpack observed in 2011 was reflected by a peak discharge near 539 Ls⁻¹ on 20 June, the latest observed date for peak annual discharge (Figure 1.3bc). Substantially higher flows were maintained throughout the 2011 summer in Como Creek relative to all other years. For 2012, SWE was near the long-term mean just prior to April, but an unusual low spring snowfall and early melt preceded a low peak snowmelt discharge of only 60 Ls⁻¹ on 27 April. Peak annual discharge of 75 Ls⁻¹ occurred more than two months after snowmelt on 7 July 2012, and was associated with rainfall. Despite near average annual CP, the large magnitude and early timing of 2014 peak SWE preceded the largest observed discharge on this study’s record for Como Creek corresponding to a peak discharge of 810 Ls⁻¹ on 2 June (Figure 1.3). Due to pressure transducer failure in 2013, continuous water level data were not
available for Como Creek and thus only manual measurements of water level and velocity corresponding to sample dates were available for 2013 discharge analysis. This study’s record for the Como Creek catchment indicates that peak discharge corresponds with SWE disappearance, suggesting that 2013 peak discharge occurred around the first week of June (Figure 1.3b). The highest discharge observed during this time was 295 Ls⁻¹ on 3 June (Figure 1.3c). Como Creek discharge was measured at 186 Ls⁻¹ on 16 September 2013, 3-4 days after the heaviest September rains. Subsequent bimonthly measurements suggest disappearance of the rain signal from Como Creek in about one month, with discharge returning to baseflow values near 3 Ls⁻¹ (Knowles et al., 2015).

1.4.2 Como Creek Chemistry

The isotopic (δ¹⁸O) composition of Como Creek generally was more depleted during snowmelt and became more enriched with summer rain inputs (Figure 1.4a). Concentrations of DOC were at minimum (~2 mg C/L) during baseflow and consistently peaked on the rising limb of the hydrograph, with greater concentrations observed during higher precipitation years (Figure 1.4b). Solutes throughout Como Creek generally decreased with elevation and became diluted with snowmelt, subsequently increasing on the recession limb of the annual hydrograph. While NO₃⁻ concentrations at the catchment outlet have generally peaked just prior to snowmelt, most of the samples from May-October across all years fell below laboratory detection limits (Figure 1.4c). Over an 11-yr record for Como Creek at the catchment outlet, minimum values near 70 µeq/L were consistently observed for Ca²⁺ after peak streamflow as a result of dilution from snowmelt entering the stream, with values increasing during baseflow likely as a result of cryoconcentration and increased groundwater contributions (Figure 1.4d). The 2013 flood event was observable in every record at the Weir except NO₃⁻, with the most enriched δ¹⁸O value on
record of -13.41‰ (10 September 2013), a dilution effect apparent for Ca\(^{2+}\), and a discernible second peak in DOC for the year (Figure 1.4). Similar findings of seasonal and elevation effects on stream water chemistry in the catchment are reported in previous studies (Cowie, 2014; Williams et al., 2009, 2011). The 11-yr \(\delta^{18}O\) record of Como Creek at the catchment outlet was not significantly different from the 2011-2014 \(\delta^{18}O\) record of all C-1 subalpine groundwater wells \((p = 0.20)\), while both 2011-2014 \(\delta^{18}O\) records of snowpack in the catchment and C-1 subalpine soil water were found to be different \((p \approx 0.00;\) Figure 1.5). Snowpack was much more depleted than the other three waters, while subalpine soil water showed enrichment from summer rains that did not show up in the stream and groundwater \(\delta^{18}O\) distributions (Figure 1.5).

**Figure 1.4.** Time series of a) \(\delta^{18}O\), b) DOC, c) NO\(_3^-\), and d) Ca\(^{2+}\) concentrations for 2003-2014 for Como Creek at the Weir sampling site near the catchment outlet. Samples with concentrations of NO\(_3^-\) below laboratory detection limits are included as 0.00 µM to represent the low values present in the stream.
Figure 1.5. Boxplots showing median and quartiles (box for 25% and 75%, whiskers for 5% and 95%) for 2011-2014 δ¹⁸O values for all C-1 groundwater wells (GW), C-1 soil water, streamflow (Weir; 2003-2014), and snowpack within the catchment.

The δ¹⁸O values between 2011 and 2014 for the four Como Creek surface water sites are shown in Figure 1.6. While the lower three sites track each other well, more depleted values for the highest elevation Soddie Stream site are consistently observed and are indicative of direct snowmelt influence, as previous work near the Soddie site determined the isotopic content of snow near -21‰ (Williams et al., 2009). In 2011, surface water δ¹⁸O became more depleted with snowmelt, followed by enrichment into the summer. In contrast, during 2012, Como Creek showed less depletion for δ¹⁸O with spring snowmelt due to below average snowmelt inputs, and instead was followed by greater summer enrichment relative to other years as a result of summer rain events that dominated the peak annual discharge. The 2013 September rains were observable in δ¹⁸O at the Weir and C-1 sites by the most enriched δ¹⁸O values on record of -13.41‰ and -13.52‰, respectively (10 September 2013). Soddie Stream is typically too low to be sampled in late July or early August, but in 2013, samples were available for collection for an
entire month following the September rains. Results from one-way ANOVA indicated that Soddie Stream site was significantly different from the Weir, C-1, and S-Curve Como Creek sites with regards to $\delta^{18}$O, $\text{NO}_3^-$, DOC, and $\text{Ca}^{2+}$ ($p \approx 0.00$) over May-October between 2011 and 2014 (Figures 1.6, 1.7; Table 1.1). Performing ANOVA between all sites except Soddie Stream yielded a $p$-value $>0.05$ for $\delta^{18}$O, $\text{NO}_3^-$, and DOC, indicating the Weir, C-1, and S-Curve sites were not significantly different with regard to their $\delta^{18}$O, $\text{NO}_3^-$, and DOC distribution over this time. Additionally, the S-Curve site was found to be significantly different ($p \approx 0.00$) from all other sites with respect to $\text{Ca}^{2+}$ concentrations, while no significant difference was observed between the Weir and C-1 sites ($p = 0.14$).

**Figure 1.6.** Time series of $\delta^{18}$O for 2011-2014 for all Como Creek surface water sites. From highest to lowest in elevation: Soddie Stream (SOD), S-Curve, C-1, Weir (from H. Hughes, pers. comm.).
Figure 1.7. Time series of DOC, NO$_3^-$, and Ca$^{2+}$ concentrations for 2011-2014 for all Como Creek surface water sites.

<table>
<thead>
<tr>
<th>Variable</th>
<th>df</th>
<th>F-statistic</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Sites</td>
<td>$\Delta^{18}$O</td>
<td>3</td>
<td>42.878</td>
</tr>
<tr>
<td></td>
<td>Ca$^{2+}$</td>
<td>3</td>
<td>113.065</td>
</tr>
<tr>
<td></td>
<td>NO$_3^-$</td>
<td>3</td>
<td>8.001</td>
</tr>
<tr>
<td></td>
<td>DOC</td>
<td>3</td>
<td>49.942</td>
</tr>
<tr>
<td>Weir, C-1, and S-Curve (Excludes Soddie Stream)</td>
<td>$\Delta^{18}$O</td>
<td>2</td>
<td>0.616</td>
</tr>
<tr>
<td></td>
<td>Ca$^{2+}$</td>
<td>2</td>
<td>58.479</td>
</tr>
<tr>
<td></td>
<td>NO$_3^-$</td>
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<td>0.036</td>
</tr>
<tr>
<td></td>
<td>DOC</td>
<td>2</td>
<td>2.842</td>
</tr>
<tr>
<td>Weir and C-1</td>
<td>Ca$^{2+}$</td>
<td>1</td>
<td>2.208</td>
</tr>
<tr>
<td>S-Curve and Soddie Stream</td>
<td>Ca$^{2+}$</td>
<td>1</td>
<td>124.932</td>
</tr>
</tbody>
</table>
1.4.3 Subalpine Groundwater

Groundwater levels were clearly coupled with the timing and magnitude of snowmelt in the subalpine portion of the Como Creek catchment and increased with the rising limb of the hydrograph (Figure 1.8). Water levels in the shallow wells followed similar patterns of seasonal fluctuation, with a comparable yet damped pattern observed for the deep well. Water level increased at the onset of snowmelt and subsequently declined into the autumn and winter months, operating as a gaining system before peak discharge and a losing one after. Magnitude of water level increase upon snowmelt generally corresponded to the size of annual snowpack. Increases in water levels not associated with the onset of snowmelt were only observed after the September 2013 heavy rain event, with pressure transducer data suggestive of peak water level height within one week after the rains. Though less pronounced, water levels in the deep well (SW2) also increased in late September 2013. Water level increased substantially in the deep subalpine well at the onset of 2011 and 2014 snowmelt. Yet, despite similarly high snowfall in 2013, water levels at depth increased minimally, suggestive of a drying out of the subsurface following the low snow year. Water level was consistently much lower in the deep well southwest of C-1 (SW2) as compared to the adjacent shallow well (SW1), suggesting different flowpaths influencing the two subsurface sites, perhaps resulting from the presence of intermittent, low permeability clay layers or a perched aquifer system.
No strong seasonal or interannual trends were observed in the solute chemistry of subalpine groundwater from C-1 wells between 2011 and 2014. Concentrations of DOC and NO$_3^-$ were generally below 3 mg C/L and 5 µM, respectively, in all wells. Calcium (Ca$^{2+}$) generally ranged from 100-300 µeq/L with consistently higher concentrations observed in the deep well. Conversely, the isotopic composition ($\delta^{18}$O) of groundwater showed interannual variation similar to that of nearby surface waters in that it appeared most depleted after 2011 snowmelt and relatively more enriched in subsequent years (Figure 1.9).
1.4.4 Subalpine Soil Water

The dates of soil water sampling alone indicate when water was available for sampling, which provides insight into water availability throughout the summer. In 2012, soil water samples at C-1 were collected as early as 10 April, as opposed to late May in 2011 and mid-June in 2013 and 2014. Soil water samples were available for collection at C-1 until mid-September in 2012 and 2014 and until late October in 2011 and 2013.

The $\delta^{18}$O values in soil waters at C-1 ranged from -18.26‰ to -7.7‰ between 2011 and 2014 (Figure 1.5). Concentrations of Ca$^{2+}$ generally ranged from 20-400 µeq/l, with higher concentrations observed with depth. Soil water DOC concentrations ranged from 2-25 mg C/L, while NO$_3^-$ was mainly below 10 µM. However, higher concentrations (20-75 µM) were observed for some samples from late April through July of 2012 at the SW and SO soil lysimeter.

Figure 1.9. Time series of $\delta^{18}$O for 2011-2014 for C-1 groundwater wells.
pods at C-1 (Figure 1.2). Additionally, the two soil water samples collected at the ST lysimeter pod after the September 2013 rain event in early October had NO\textsubscript{3}\textsuperscript{-} concentrations near 50 µM.

Data from a soil moisture array spanning 2 m depth at C-1 have shown substantial surface infiltration and upwelling of moisture from depth during the snowmelt time period followed by soil drainage for the years 2005 and 2007-2010 (Figure 1.10). The source of homogeneity in 2011 and 2012 data could not be identified from sensor data or field observations; regardless, upwelling from below can still be identified in 2011 as well as infiltration from heavy summer 2012 rains.

**Figure 1.10.** C-1 volumetric soil water content as an integrated time depth image for 2005-2012. Data for 2013-2014 are unavailable due to sensor failure (adapted from H. Humphries, pers. comm.).
1.4.5 Residence Times

Water residence times in the Como Creek catchment were calculated over a variation of time periods using the $\delta^{18}$O values of precipitation measured at the NWT LTER operated NADP Soddie site (input) and the $\delta^{18}$O values of Como Creek streamflow and C-1 subalpine groundwater (outputs). Residence times were calculated on both an interannual and multiannual basis to ascertain the sensitivity of the estimates to the length of the dataset. Stream $\delta^{18}$O composition was significantly damped compared to that of precipitation, with average amplitudes of 25‰ for Soddie NADP precipitation and 3.8‰ for Como Creek (Figure 1.11). The mean residence time for water in the Como Creek catchment from 2010-2014, derived from the isotopic composition of precipitation and streamflow, was 1.13 years (Table 1.2). Results from various time intervals collectively yielded a range of mean water residence times from 0.77-1.83 years. The large amplitude for $\delta^{18}$O in 2013 and the resulting residence time calculation is partially attributed to the heavily enriched 10 September 13 sample corresponding to the week of heavy rains. The $\delta^{18}$O composition of subalpine groundwater was more damped than that of streamflow and precipitation, with average amplitudes of 1.5‰ and 0.6‰ for a shallow well (SO1) and a deep well (SW2), respectively (Figure 1.9). Mean residence time for groundwater in the subalpine was 2.98 years for the shallow well and 6.63 years for the deep well (Table 1.3).
Figure 1.11. Time series of $\delta^{18}$O values from precipitation and streamflow for Como Creek catchment from 2011-2014.

Table 1.2. Estimated annual residence times for water in the Como Creek catchment. Values of $\delta^{18}$O applied to Equation 1.4 from Como Creek streamflow at the catchment outlet (Weir site) and NADP Soddie precipitation samples are shown.

<table>
<thead>
<tr>
<th>Water Year</th>
<th>SD $\delta^{18}$O (‰)</th>
<th>Mean $\delta^{18}$O (‰)</th>
<th>A $\delta^{18}$O (‰)</th>
<th>SD $\delta^{18}$O (‰)</th>
<th>Mean $\delta^{18}$O (‰)</th>
<th>A $\delta^{18}$O (‰)</th>
<th>Mean residence time (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>7.0</td>
<td>-15.6</td>
<td>25.1</td>
<td>0.5</td>
<td>-17.4</td>
<td>2.2</td>
<td>1.83</td>
</tr>
<tr>
<td>2011</td>
<td>7.1</td>
<td>-15.7</td>
<td>28.1</td>
<td>0.6</td>
<td>-17.6</td>
<td>3.0</td>
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<tr>
<td>2012</td>
<td>6.4</td>
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<td>24.1</td>
<td>0.7</td>
<td>-17.0</td>
<td>3.2</td>
<td>1.20</td>
</tr>
<tr>
<td>2013</td>
<td>7.1</td>
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<td>24.9</td>
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<td>-17.0</td>
<td>4.5</td>
<td>0.86</td>
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<tr>
<td>2014</td>
<td>5.1</td>
<td>-16.0</td>
<td>19.4</td>
<td>0.5</td>
<td>-17.2</td>
<td>2.2</td>
<td>1.37</td>
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<td>0.7</td>
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<td>4.2</td>
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<td>-17.2</td>
<td>5.6</td>
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</table>

SD = standard deviation, A = amplitude
Table 1.3. Estimated annual subalpine groundwater residence times for the Como Creek catchment. Values of $\delta^{18}$O applied to Equation 1.4 from Como Creek subalpine groundwater wells are shown. Values of $\delta^{18}$O for precipitation are shown in Table 1.2.

<table>
<thead>
<tr>
<th>C-1 deep groundwater well (SW2)</th>
<th>Water Year</th>
<th>SD $\delta^{18}$O (‰)</th>
<th>Mean $\delta^{18}$O (‰)</th>
<th>A $\delta^{18}$O (‰)</th>
<th>Mean residence time (years)</th>
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<tr>
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<td>-17.6</td>
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Cumulative Mean 6.63

<table>
<thead>
<tr>
<th>C-1 shallow groundwater well (SO1)</th>
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<th>SD $\delta^{18}$O (‰)</th>
<th>Mean $\delta^{18}$O (‰)</th>
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<th>Mean residence time (years)</th>
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<td></td>
</tr>
<tr>
<td>2011-2012</td>
<td>0.3</td>
<td>-17.5</td>
<td>1.6</td>
<td>2.83</td>
<td></td>
</tr>
<tr>
<td>2012-2013</td>
<td>0.4</td>
<td>-17.2</td>
<td>1.8</td>
<td>2.23</td>
<td></td>
</tr>
<tr>
<td>2013-2014</td>
<td>0.4</td>
<td>-16.9</td>
<td>1.5</td>
<td>2.63</td>
<td></td>
</tr>
<tr>
<td>2011-2014</td>
<td>0.5</td>
<td>-17.2</td>
<td>2.1</td>
<td>2.08</td>
<td></td>
</tr>
</tbody>
</table>

Cumulative Mean 2.98

SD = standard deviation, A = amplitude

1.4.6. Groundwater Recharge

A shallow subalpine well (SO4) was analyzed to estimate $S_y$ and recharge due to its consistent water level data record, relatively rapid response to recharge events, and similar pattern of water table fluctuation compared to other shallow subalpine groundwater wells (Figure 1.8). Equation 1.10 was applied to SO4 water level data from the late summer/early autumn for the water years between 2011 and 2014 to obtain a mean value for the subalpine groundwater
aquifer of 0.06 (Table 1.4). Morris and Johnson (1967) report $S_y$ values ranging from 0.02-0.34 for till predominated by sand and gravel, the dominant geology observed at the subalpine groundwater well sites upon installation. Thus, estimations of $S_y$ fall within the lower end of the range of previously determined $S_y$ values. Knowles et al. (2015) found that summer ET exceeded precipitation in the subalpine in Como Creek catchment. Thus, the latest dates in each water year that had the shortest time interval between manual groundwater depth measurements and complete corresponding precipitation and discharge data were chosen for each year to minimize uncertainty arising from the assumption that ET and $\Delta S_{uw}$ are negligible in Equation 1.7.

**Table 1.4.** Input values of precipitation, streamflow, and change in water level at SO4 and resultant value of $S_y$ using a water budget approach and Equation 1.9.

<table>
<thead>
<tr>
<th>P (m/d)</th>
<th>$Q_{out}/A_{CC}$ (m/d)</th>
<th>$\Delta h$ (m)</th>
<th>$\Delta t$ (d)</th>
<th>$S_y$</th>
<th>Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.0002</td>
<td>0.3</td>
<td>8</td>
<td>0.047</td>
<td>8/18-8/26</td>
</tr>
<tr>
<td>0.002</td>
<td>0.0005</td>
<td>0.1</td>
<td>6</td>
<td>0.091</td>
<td>8/22-8/28</td>
</tr>
<tr>
<td>0.003</td>
<td>0.0011</td>
<td>0.4</td>
<td>6</td>
<td>0.043</td>
<td>7/24-7/30</td>
</tr>
<tr>
<td>0.002</td>
<td>0.0004</td>
<td>0.1</td>
<td>5</td>
<td>0.061</td>
<td>9/3-9/8</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td>0.060</td>
<td></td>
</tr>
<tr>
<td>SD</td>
<td></td>
<td></td>
<td></td>
<td>0.022</td>
<td></td>
</tr>
</tbody>
</table>

$P = $ precipitation at NADP CO90 (C-1), $Q_{out}/A_{CC} = $ streamflow on last day divided by area of Como Creek catchment (5,360,000 m$^2$), $\Delta h = $ groundwater level decline, $\Delta t = $ change in time, $S_y = $ specific yield, SD = standard deviation

The WTF method was applied to the subalpine portion of the Como Creek catchment to analyze fluctuations in the water table and interannual variations in subalpine net groundwater recharge between 2011 and 2014. For 2011, 2012, and 2014, snowmelt was the only observed major recharge event for all subalpine wells. For 2013, two major recharge events were identified corresponding to snowmelt and the large rain event in September 2013 (Figure 1.8). Estimations of net groundwater recharge for a shallow subalpine well (SO4) between 2011 and
2014 are reported in Table 1.5. Reported estimations of recharge include water loss from net subsurface flow away from the area, baseflow, and ET of groundwater, and thus represent the total estimated change in subsurface storage for the recharge event, or net recharge. Net recharge from snowmelt alone was greatest in 2011 (0.18 m), followed by 2014 (0.16 m), 2012 (0.12 m), and 2013 (0.11 m). Peak SWE was highest in 2011, followed by 2014, corresponding with the magnitude of net recharge from snowmelt in 2011 and 2014. Despite the differences in SWE between 2012 and 2013, similar net recharge from snowmelt was calculated for the two years. It is notable that the snowmelt recharge event was calculated over a time period half as long in 2013 relative to 2012 based on the timing of minimum and maximum water levels in available groundwater records, resulting in a recharge rate twice as fast (Table 1.5). Substantial recharge was observed as a result of the September 2013 rains, with a corresponding recharge rate of nearly 6 mm day\(^{-1}\), roughly two to three times faster than that observed for snowmelt (Table 1.5). Net recharge for major events between 2011 and 2014 averaged 36% of CP corresponding to the recharge event (snowmelt, rains) as measured at the Niwot SNOTEL site.

<table>
<thead>
<tr>
<th>Water Year</th>
<th>Recharge Event</th>
<th>Sy</th>
<th>Δh (m)</th>
<th>Δt (d)</th>
<th>ΔS(_{gw}) (m)</th>
<th>ΔS(_{gw}) (m/d)</th>
<th>ΔS(_{gw})* (m)</th>
<th>P (m)</th>
<th>P (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>snowmelt</td>
<td>0.06</td>
<td>3.0</td>
<td>77</td>
<td>0.18</td>
<td>0.0023</td>
<td>0.18</td>
<td>0.4</td>
<td>42</td>
</tr>
<tr>
<td>2012</td>
<td>snowmelt</td>
<td>0.06</td>
<td>2.0</td>
<td>74</td>
<td>0.12</td>
<td>0.0016</td>
<td>0.12</td>
<td>0.3</td>
<td>43</td>
</tr>
<tr>
<td>2013</td>
<td>snowmelt</td>
<td>0.06</td>
<td>1.9</td>
<td>36</td>
<td>0.11</td>
<td>0.0032</td>
<td>0.11</td>
<td>0.4</td>
<td>26</td>
</tr>
<tr>
<td>2013</td>
<td>extreme rains</td>
<td>0.06</td>
<td>1.5</td>
<td>15</td>
<td>0.09</td>
<td>0.0059</td>
<td>0.09</td>
<td>0.2</td>
<td>41</td>
</tr>
<tr>
<td>2014</td>
<td>snowmelt</td>
<td>0.06</td>
<td>2.6</td>
<td>42</td>
<td>0.16</td>
<td>0.0037</td>
<td>0.16</td>
<td>0.5</td>
<td>33</td>
</tr>
</tbody>
</table>

|               | Mean     | 0.2     | 0.3   | 36     |
|               | SD       | 0.04    | 0.1   | 7.2    |

\(S_y\) = specific yield, \(\Delta h\) = water level rise, \(\Delta t\) = change in time, \(\Delta S_{gw}\) = net recharge rate, \(\Delta S_{gw}^*\) = net recharge, \(P\) = annual SWE or CP for event (Niwot SNOTEL), SD = standard deviation
1.5 Discussion

1.5.1 Water Residence Time

The calculated mean catchment water residence time of 1.13 years for 2010-2014 is similar to but less than that reported by Cowie (2010) of 1.8 years for Como Creek from 2002-2009. McGuire et al. (2005) investigated mean catchment water residence time over diverse geologic and geomorphic conditions ranging from <1-62 km$^2$, reporting 0.8-3.3 years, and found no correlation of residence time with basin area. Instead, residence time was correlated with catchment terrain indices such as flowpath distance and gradient, suggesting topography acts as a dominant control over catchment-scale transport of water. Cowie (2010) also observed a decrease in catchment water residence time with elevation, regardless of catchment size, reporting 1.12 years for the alpine and 2.11 years for the montane catchments surrounding Como Creek. Therefore, the surface and subsurface complexities of mountainous areas and level of critical zone development are the dominant influences on catchment residence time even in small (<6 km$^2$) catchments like Como Creek (Rodgers et al., 2005). Removal of the $\delta^{18}O$ value for the 10 September 2013 Como Creek stream sample in residence time calculations yielded a mean residence time of 1.78 years for 2013, twice as long as with the outlier (Table 1.2). Removing the 2013 outlier also increases the residence time cumulative mean to 1.38 years for the Como Creek catchment. Overall, 2012 and 2013 had the shortest residence times for water in the catchment, demonstrating the effect of a drought snow year and anomalously large rain event on stream $\delta^{18}O$ that may be indicative of future climate (e.g. Clow, 2010). As many biogeochemical reactions are time-dependent, residence times for water in a catchment have important implications for water quality (McGuire et al., 2005).

Differences in $\delta^{18}O$ variability between the two subalpine groundwater depths (Figure
1.9) are likely driven by differing amounts of younger water, with wells that sample shallower paths more likely to change seasonally due to greater accessibility to younger precipitation inputs on the surface (Segal et al., 2014). Estimated mean groundwater times of 2.98 years for shallow (<10 m depth) and 6.63 years for deep (>15 m depth) subalpine groundwater are within range of those calculated in other mountainous studies utilizing the convolution integral method for $\delta^{18}O$. Plummer et al. (2001) reported a mean groundwater residence time of 5 years for a forested catchment in the Appalachian Mountains. Zeliff (2013) observed a mean groundwater residence time ranging from 2.1-4.2 years for piezometers in a bedrock aquifer (8 m depth) of the Saddle alpine catchment just above Como Creek from 2006-2011, reporting a shorter groundwater residence time for most piezometers during the above average snow year of 2011. The relatively short mean groundwater residence times in Como Creek coupled with the decreases observed in catchment residence time due to precipitation variability have major implications for hydrologic cycling in the catchment under climate change. Decreases in catchment water residence time as a result of both rapidly increased (2013) and slowly decreased (2012) precipitation inputs suggests increased fragmentation of hydrologic connectivity, with important consequences for groundwater recharge and ecosystem water availability.

1.5.2 Groundwater Recharge and Subsurface Storage

Temporal variability in groundwater response to surface precipitation inputs, upwelling of water from the subsurface during snowmelt, and highly variable groundwater recharge rates were all observed in the subalpine aquifer of the Como Creek catchment over a period of precipitation variability. Isotopic analysis suggests that substantial groundwater input to Como Creek, represented by enriched $\delta^{18}O$ values $>\text{-}18\%_\text{o}$, is occurring between Soddie Stream and S-Curve. Previous work suggested that the groundwater in Como Creek is recharging within the
glacial deposits overlying the local bedrock somewhere near treeline within the catchment (Cowie, 2014). Due to the high demand for water within the forest upon snowmelt (Monson et al., 2002), it is unlikely that groundwater recharge is occurring at this time far below treeline or Soddie Stream. The $\delta^{18}$O distribution of subalpine soil water near C-1 exhibited enrichment from summer rains, yet this rain signal did not show up in groundwater or the stream. This suggests that rain in the subalpine area generally does not make it to streamflow or result in groundwater recharge but instead is assimilated into the soil system. For potential recharge at treeline, the $\delta^{18}$O differences at Soddie Stream could reflect groundwater discharge to the surface below, with this site geochemically “disconnected” from the other sites.

Net groundwater recharge was found to account for a mean of 36% of CP for major recharge events between 2011 and 2014. While subalpine groundwater recharge was observed with the early and slow meltout of the 2012 below average snowpack (Figure 1.8; Table 1.5), recharge was not noticeable as a result of the 2012 summer rains that dominated the annual Como Creek hydrograph. Knowles et al. (2015) measured Como Creek catchment ET as accounting for over 70% of annual precipitation in 2012, reporting reduced runoff efficiency and discharge relative to less dry years. These observations suggest that surface water demands including ET and streamflow during a summer following low snowfall may take precedent over groundwater recharge, with important implications for long-term hydrological resilience of the catchment. Although net recharge was not calculated for the deep subalpine well (SW2), Figure 1.8 depicts that after the low snow year of 2012, there was much less recharge at depth compared to shallow wells from 2013 snowmelt. Lower recharge at depth and lower shallow net recharge from snowmelt in 2013 relative to other high snow years suggests a drying out of the subsurface and possibly less recharge potential in the subalpine following a low snow year. On the other
hand, 2014 saw very high stream discharge (Figure 1.3c), suggesting subsurface reservoirs had reached storage capacity following recharge from both the September 2013 rains and 2014 snowmelt. Observed groundwater recharge from the autumn rains likely carried over late season soil moisture to the spring of 2014, resulting in a higher level of antecedent soil moisture at snowmelt, and resulting in a quicker saturation of the subsurface. The magnitude and high rate of the 2014 Como Creek streamflow, coupled with observations suggesting subsurface saturation in 2014, have major implications for future catchment flooding following years with multiple major recharge events.

The major recharge events for 2011 and 2012 (snowmelt only) and their recharge amounts of 0.18 m and 0.12 m, respectively, can also be compared to annual CP to estimate annual net recharge (Table 1.5; Figure 1.3a). Net recharge for 2011 constitutes 20.1% of annual CP while net recharge for 2012 accounts for 16.6% of annual CP. Knowles et al. (2015) calculated a change in catchment water storage for Como Creek using precipitation, ET, and discharge measurements of 16.6% in 2011 and 9.7% in 2012, slightly lower than values reported here yet very similar given the vast difference in methods utilized. Knowles et al. (2015) attributed the change in storage to changes in subsurface reservoirs, seepage to bedrock flowpaths, blowing snow, or measurement uncertainty. The low intensity of the 2012 snowmelt event likely introduced some uncertainty into this study’s net recharge estimate since infiltration from snowmelt or summer rains could have been of similar magnitude as drainage away from the water table. Thus, 2012 recharge values should be treated with such caution. Previous work in the alpine of the Niwot Ridge study area utilized the WTF method to estimate total mean annual recharge in a fractured rock aquifer of 52% of precipitation during 2006-2010 (King, 2012). Based on the graphical method of calculation chosen for the WTF method, total recharge
estimates vary from net recharge estimates by not including losses from ET of groundwater, baseflow, or net subsurface flow from the site, thus resulting in higher values for reported recharge (Healy, 2010). Other groundwater studies utilizing the WTF method report groundwater recharge at 21% of annual precipitation in forested watersheds of Minnesota, 56% in a coastal plain of North Carolina, and 24% in a fractured bedrock aquifer of Pennsylvania (Delin and Risser, 2007). While no other studies are known to have used the WTF method to estimate groundwater recharge in snow-dominated, mountainous groundwater systems, there are estimates in mountain regions from the use of other methods. Huntley (1979) estimated groundwater accounted for 14-38% of precipitation in two mountain provinces of the San Luis Basin in Southern Colorado, while Lee et al. (2006) reported more than 20% of precipitation recharging groundwater in the mountains of Taiwan.

Previous work calculated the annual runoff efficiency, or the amount of annual discharge relative to annual precipitation (Q/P), as 19% for the subalpine portion of the Como Creek catchment compared to 40% for the alpine portion of the catchment between 2008 and 2012, suggesting increased importance of ET in the subalpine (Knowles et al., 2015). Lower annual runoff efficiencies were also observed for the Como Creek catchment as a whole (24%) compared to the adjacent alpine Green Lakes Valley catchment (88%) (Cowie, 2014). While one significant recharge event per year corresponding to snowmelt was observed for the fractured bedrock aquifer in the nearby alpine catchment (King, 2012) and for the Como Creek subalpine aquifer for all other years, a second major subalpine recharge event was observed in 2013 as a result of an anomalous heavy rainfall event. These results indicate that climatic factors largely control groundwater recharge in the Como Creek catchment and suggest that climatic changes could transition the currently snowmelt-dominated, recharge-driven aquifer-stream system to a
hybrid hydroclimatic regime (mix of rain and snow) (Allen et al., 2010).

While the observed recharge rates and water table fluctuations are only representative of the C-1 subalpine area near the groundwater wells, these results presented are the first approximation of groundwater recharge in the subalpine area of the Como Creek catchment and the Niwot Ridge study area. Uncertainty in recharge estimates, however, reflects limitations and assumptions of the WTF method, and future work should refine the estimates for $S_y$ in the subalpine through laboratory and field methods. Clearly, precipitation variability throughout the year influences groundwater recharge resulting from the size of the annual snowpack in complex ways, highlighting the importance of interannual sensitivity in hydrologic analysis of snow-dominated mountainous catchments. With changes in the snow to rain fraction of precipitation predicted at higher elevations of the western US, groundwater recharge that mainly occurs during snowmelt runoff may instead occur with rain spread across the winter months. Higher intensity precipitation could then result in high runoff and low infiltration and vice versa, depending on the current rate of snowpack melting, with the magnitude of snowmelt recharge likely to decrease regardless (Segal et al., 2014). Competing processes such as groundwater recharge and discharge to streamflow and changes in the timing of ET demands during periods of precipitation variability will determine the magnitude of annual actual groundwater recharge and subsurface storage change.

1.5.3 Changing Hydrologic Connectivity

The 2003-2014 record of $\delta^{18}$O, Ca$^{2+}$, DOC, and NO$_3^-$ for Como Creek provides a means of examining the nature of the waters exported from the catchment over time (Figure 1.4). Enrichment of stream $\delta^{18}$O from summer rains in 2006 and 2012 and autumn rains in 2013 was observed, indicating increased hydrologic connectivity between the subsurface and stream during
these events when normally it is decreased (Figure 1.4a). While DOC in Como Creek showed evidence of snowmelt-soil interactions and a flushing effect of snowmelt on soils, NO$_3^-$ remained minimal, highlighting its immobility and likely assimilation into the soil system. At all four Como Creek sites, influence on stream DOC from the 2012 summer rains and 2013 autumn rains was apparent (Figure 1.7), resulting in a second peak for the year and increased hydrologic connectivity between soils and surface waters. Relative droughts and floods have influenced the build up and subsequent transport of nutrients from subalpine soils, altering the fate and delivery of nutrients to forest and stream ecosystems. Additionally, alpine ecosystems have become subject to increased atmospheric nitrogen deposition derived from the combustion of fossil fuels in adjacent metropolitan areas, ultimately transitioning them from nitrogen (N)-limited to N-saturated ecosystems, with implications for downstream water quality and environmental stability (Aber et al., 1989; Williams et al., 1996a; Hafich, 2014). Future years hold the possibility for increased air temperature and precipitation variability under a changing climate, which will impact surface water-groundwater interactions, specifically recharge and discharge dynamics, altering the chemistry and quantity of waters within and those exported out of the Como Creek catchment to the BCW.

Subalpine soil moisture variation and response to snowmelt provides insight on linkages with subsurface flow, climate, plant water use, forest health, and catchment-scale water fluxes that can be used for improving hydrologic predictions at the catchment scale (Bales et al., 2011). Previous findings within the Como Creek catchment indicated that peak soil moisture occurred with snow disappearance (Harpold et al., 2014b). For this study, surface infiltration of water in the subalpine is apparent during both snowmelt and subsequent summer rain events (Figure 1.10), similar to other studies that attributed the rapid initial drainage to both soil properties and
ET (Bales et al., 2011). Soil moisture upwelling during snowmelt, which was often observed but did not commonly connect to surface infiltration from above, could be brought about by snowmelt infiltration at a higher elevation, causing the water table at lower elevations to rise and infiltrate into subsurface soils. This upwelling can provide valuable soil moisture content to vegetation around snowmelt when peak photosynthetic uptake of CO$_2$ occurs (Monson et al., 2002). Bales et al. (2011) found that around one third of annual ET came from water stored deeper than 1 m below the surface for a Sierra Nevada forested headwater catchment, and soils dried out faster after rain events compared to snowmelt. Changes in climate, vegetation structure, and the timing and magnitude of snowmelt could increase atmospheric water loss at Niwot Ridge, leading to a decrease in groundwater recharge and streamflow (Molotch et al., 2009). Changes in water availability coupled with the increased atmospheric demand for water will govern forest responses to warming (Tague and Peng, 2013). The degree to which trees become water stressed depends not only on the magnitude of groundwater and soil recharge from snowmelt that remains into the summer, but also on the accessibility to those deeper water reserves (Molotch et al., 2009). Water deficits that cause forest disturbances further influence snow accumulation by changing forest canopy structure that acts as a control on the relative influences of radiative and turbulent fluxes of the snowpack energy balance (Harpold et al., 2014a). Studies on forest disturbance in high elevation areas of the western US have reported varying results regarding both the magnitude and direction of change in snow accumulation, (Harpold et al., 2014ab; Gleason et al., 2013; Biederman et al., 2014; Bearup et al., 2014) highlighting additional uncertainties present within these complex and changing systems.

Results from this study indicate that precipitation variability can radically influence the surface water-groundwater interactions of the Como Creek catchment on an intra-annual
timescale. Our results suggest that reductions and enhancements of catchment hydrologic connectivity, or the water-mediated transfer of matter, energy, and organisms across the hydrologic cycle, will both occur within mountainous headwater catchments of the western US subject to increased precipitation variability (Pringle, 2001). However, less overall snowpack and snowmelt-derived groundwater recharge will likely result in a net decrease of sustained hydrologic connectivity over time. Remaining questions for further research on groundwater dynamics in the catchment include constraining the tradeoffs between forest ET, groundwater recharge, and streamflow in order to forecast future water yield from the catchment.

1.6 Conclusion

This study presents the first estimates of groundwater residence time and recharge in the subalpine portion of the Como Creek catchment and the Niwot Ridge study area in the Colorado Rocky Mountains. The strength of this study lies in the extensive temporal context over which the analysis took place, specifically including years of both above and below average snowfall. Particularly, a large and rare rain event in the autumn of 2013 and the anomalous snow year preceding it were used as a proxy to evaluate the response of surface water-groundwater interactions to precipitation variability in a mountainous headwater catchment. Groundwater residence times were on the order of 2-6 years and were greater with depth, with an estimated mean catchment water residence time of 1.13 years. Net subalpine groundwater recharge was estimated to account for an average of 36% of event precipitation, with slower recharge rates and less recharge observed during a year with below average snowfall. Two major recharge events were observed in 2013 followed by extremely high surface water discharge upon snowmelt in 2014, providing major implications for future flooding following precipitation variability. Results suggest that the subalpine aquifer-stream system is recharge-driven and snowmelt-
dominated, but has the possibility of transitioning to a hybrid hydroclimatic system with increased recharge from seasonal rains. Observed changes in hydrologic connectivity, including multiple major groundwater recharge events for one year, a drying out of the subsurface following snow drought, and decreased catchment water residence time due to large rain inputs, provide insight into future catchment response under a changing climate. More robust analyses of source waters and flowpaths influencing Como Creek streamflow during this variable period are needed to place the implications of the above results in the full context of hydrologic connectivity. These components will be addressed in Chapter 2 by utilizing hydrologic mixing models to determine the timing and magnitude of source water contributions to streamflow.
CHAPTER 2
Interannual variation of streamflow hydrochemistry and source waters in a subalpine, headwater catchment, Colorado Rocky Mountains, USA

Abstract

Geochemical ($\text{Na}^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, Si, ANC) and isotopic ($\delta^{18}\text{O}$) tracers were used to identify source water contributions to streamflow in the mixed alpine-subalpine Como Creek headwater catchment of the Boulder Creek Watershed across years marked with precipitation variability. Using diagnostic tools of mixing models and end-member mixing analysis (EMMA), conservative tracers in streamflow were identified and used to evaluate potential end-members on an annual basis so as not to mask interannual variations in end-member chemistry. The Como Creek catchment was identified as a three-component system for each water year from 2011-2014, with mean contributions of 29% subalpine groundwater, 35% snowmelt, and 36% soil water from near treeline, signifying the equally important roles each source plays in streamflow generation. Stream samples plotted with groundwater wells in EMMA, indicating high surface water-groundwater interactions in the catchment, while overall, precipitation sources did not represent appropriate end-members for streamflow. Hydrograph separation for the low snow year of 2012 indicated that the subalpine groundwater reservoir has a limited capacity to sustain streamflow following a low snow year and suggests that were it not for heavy summer rain inputs, Como Creek could have run dry. High soil water contributions to 2014 streamflow suggested that groundwater recharge observed from the September 2013 heavy rains carried over substantial soil moisture storage, resulting in a legacy effect for soil water that contributed to the highest peak discharge observed for Como Creek in 2014. This study emphasizes the utility of geochemistry and stable isotopes in addressing hydrologic questions in physically and spatially complex mountainous systems, particularly those regarding precipitation variability.
2.1 Introduction

Water on the earth’s surface is uniquely both ubiquitous and fleeting in nature, with all three phases of solid, liquid, and gas existing at temperatures and pressures commonly experienced on this planet. As a result, small changes in air temperature and precipitation can result in large changes in the amount and timing of snow cover in seasonally snow-covered regions, making them particularly vulnerable to climate change (Mote et al., 2005). At the same time, seasonally-snow covered mountainous areas provide indispensable and globally significant freshwater resources to downstream populations, highlighting the need to delineate climate change consequences on resulting water availability in these regions (Viviroli et al., 2011). Seasonal snowpack in mountainous areas acts as a vitally important natural freshwater reservoir, often constituting a large portion of streamflow leaving these areas and playing a crucial role in sustaining vegetation and replenishing groundwater and soil water reserves (Sueker et al., 2000; Hinckley et al., 2014). By slowly releasing water from storage through melting or groundwater discharge, both snowmelt and groundwater are often important contributors to streamflow in mountainous areas (Mote et al., 2005; Tague and Grant, 2009). In the western United States (US), more precipitation falling as rain (Knowles et al., 2006), reduced mountain snowpack (Mote et al., 2005), and earlier snowmelt and peak streamflow timing (Clow, 2010; Barnett et al., 2005) suggest a decrease in the extent of groundwater infiltration and recharge areas, and thus a decrease in groundwater recharge in mountainous areas (Taniguchi and Hiyama, 2014). While the magnitude and direction of predicted changes in precipitation resulting from higher air temperatures varies across the western US (Hamlet et al., 2005; Knowles et al., 2006), increased precipitation variability will nonetheless increase the challenges associated with water resource management in mountainous areas (Viviroli et al., 2011).
Since the vast physical and spatial complexities of mountainous areas often make hydrological assessment difficult, geochemical and isotopic data can provide powerful insight into otherwise uncharted hydrologic systems. Natural water has a hydrochemical composition that is heavily influenced by the medium through which it flows through, with rock or soil contact times often highly correlated with solute concentrations in the water (Baraer et al., 2015). Waters from different sources in a catchment, including precipitation, surface runoff, soil reserves, and subsurface reservoirs, are often characterized by different hydrologic flowpaths and residence times, resulting in distinct chemical and isotopic signatures for each water type (Caine, 1989; McGuire et al., 2005). If known, these unique signatures can be used in conjunction with stream chemistry data to identify the various sources of water contributing to streamflow in a catchment, thus delineating hydrologic linkages between terrestrial and aquatic ecosystems (Christopherson et al., 1990). Nonreactive isotope tracers such as $\delta^{18}$O that are generally unaltered by geochemical rock-water weathering reactions aid in identifying the sources of water in streamflow, while chemical tracers such as Na$^+$ or Si provide information on the geochemical reactions and flowpaths that influence those source waters prior to becoming streamflow (Baraer et al., 2015; Sueker et al., 2000). Since streamflow is essentially a mixture of source waters from various flowpaths across the landscape, known tracer levels of identified source waters, or end-members, can be used to calculate the mixing proportions of streamflow and build a conceptual understanding of streamflow generation through time (Christopherson and Hooper, 1992).

Several studies have employed chemical and isotopic tracers in hydrologic mixing model and hydrograph separation techniques for alpine and subalpine snow-dominated basins in the Rocky Mountains (Caine, 1989; Williams et al., 2006; Sueker et al., 2000; Liu et al., 2004; Campbell et al., 1995; Jin et al., 2012; Frisbee et al., 2011, Cowie, 2014). These studies have
shown that subsurface flow can account for more than half of streamflow during storms, the winter baseflow period, and even during snowmelt (Liu et al., 2004; Jin et al., 2012; Clow et al., 2003), highlighting groundwater’s ability to dictate catchment response to changes in precipitation inputs. Yet mountain groundwater systems are cryptic in nature, characterized by a wide range of hydrogeologic properties, flowpaths, and transport processes that impede widespread application of existing knowledge (Garfias, 2009). Attention has also been given to the role that soil water plays in streamflow generation (Christopherson et al., 1990; James and Roulet, 2006), particularly as subsurface stormflow (Bazemore et al., 1994; Liu et al., 2004), following recognition of its chemical distinction from both groundwater and precipitation (Kennedy et al., 1986). The significance of mountain water resources in the western US emphasizes the need to understand the interplay of groundwater, water in the unsaturated zone, and surface water runoff in alpine-subalpine areas subject to increased precipitation variability. Due to the predominant influence of an annual snowmelt event on the hydrographs of snow-dominated mountainous catchments, hydrologic research with interannual sensitivity is crucial for evaluating catchment response to precipitation variability and can provide valuable insight on the complex climate (i.e. temperature and precipitation) and landscape processes that govern the distribution of water across time and space.

Streamflow sources were determined for an alpine-subalpine, mountainous headwater catchment of Boulder Creek Watershed (BCW) in the Colorado Front Range across years characterized by precipitation variability. As most of the water in Boulder Creek is diverted for agricultural, domestic, and industrial use throughout the year, scientific understanding of the dynamic processes influencing streamflow generation in the watershed is needed for sustainable freshwater resource management and planning. Geochemical and isotopic signatures of
streamflow and potential source waters in the Como Creek catchment were evaluated using diagnostic tools of mixing models (Hooper, 2003) and End-Member Mixing Analysis (EMMA) between 2011 and 2014 (Christopherson and Hooper, 1992). This time period exhibited wide ranges in annual snowfall and stream discharge in the Como Creek catchment, as well as an anomalous week of heavy rains in September of 2013 (Figure 1.3). Groundwater recharge response in the subalpine portion of the Como Creek catchment reflected conditions on the surface over this time (Figure 1.8). While subsurface water was largely depleted following the low snow year of 2012, the heavy rains during autumn 2013 resulted in both substantial subalpine groundwater recharge and a decrease in mean residence time for water in the Como Creek catchment. These results indicated that projected changes in air temperature and precipitation variability have dynamic impacts on the hydrologic cycle in mountainous areas, inherently changing the hydrologic connectivity of both terrestrial and aquatic ecosystems and the resulting freshwater availability. Previous EMMA within the Como Creek catchment revealed that subalpine groundwater was a large contributor to annual streamflow, partially as a result of greater subsurface storage capacity in the subalpine relative to higher elevations (Cowie, 2014). From 2010-2012, average annual subalpine groundwater contribution to Como Creek was 36%, with snowmelt and rain contributing 54% and 10%, respectively (Cowie, 2014). However, EMMA was performed collectively over 2010-2012, potentially masking important interannual variations in end-member composition or contribution over the hydrologically variable time period. The purpose of this study is to investigate interannual variations in source waters and flowpaths contributing to Como Creek streamflow by performing EMMA on a yearly basis; that is, utilizing different end-member and stream chemistry datasets corresponding to each individual water year between 2011 and 2014. Assessing the flowpath evolution and
sources of streamflow over a period of time including both a drought and a flood will provide unique insight on how the Como Creek headwater catchment may respond to future precipitation variability predicted to accompany climate change.

The specific research questions for this study are:

1. How does the evolution of streamflow hydrochemistry differ between years with variable precipitation?
2. How do water sources and their relative contributions of water to streamflow change interannually given interannual variability in precipitation?
3. How important is the interannual variability of end-members to multi-year EMMA analyses?

2.2 Study Area

The Como Creek catchment is a subalpine, mountainous, headwater catchment in north central Colorado in the Front Range of the Rocky Mountains. The 5.36 km$^2$ catchment lies approximately 4-9 km east of the Continental Divide and ranges in elevation from 2900 to 3560 m a.s.l., with approximately 69% of catchment area below treeline and 31% above treeline (Figure 1.1; Knowles et al., 2015). The mean annual temperature and precipitation for the Como Creek catchment are near 4°C and 800 mm, with approximately 70 to 80% of the annual precipitation falling as snow from the base to the headwaters of the catchment, respectively (Monson et al., 2002; Williams et al., 2011). Climate data have been collected at the subalpine C-1 site (40° 02’ 09” N; 105° 32’ 09” W) in the catchment since the 1950s (Williams et al., 1996b), with additional climate programs operating in the vicinity including the Niwot Snowpack Telemetry (SNOTEL) Site (#663) and a National Atmospheric Deposition Program (NADP) site (CO90). In addition to operating the NADP CO90 site, the Niwot Ridge Long-
Term Ecological Research (NWT LTER) program also operates an unofficial NADP wet chemistry collector at the Soddie site (40º 02’ 52” N; 105º 34’ 15” W) near treeline in the catchment. Research in the Como Creek catchment dates back to the mid-1970s (Lewis and Grant, 1979; Hood et al., 2003ab; Darrouzet-Nardi et al., 2012; Williams et al., 2009; Cowie, 2014, Knowles et al., 2015). Residing above and adjacent to the Como Creek catchment is the extensively studied Saddle research site (40º 03’ 17” N; 105º 35’ 21” W) on the northern ridge of Green Lakes Valley. As a vitally important drinking water source to downstream populations, most of the 30 km² Green Lakes Valley watershed is closed to the public and protected by the City of Boulder. Data from the aforementioned programs pertaining to Como Creek and Niwot Ridge can be accessed via links in the Appendix.

The majority of the Como Creek catchment is forested and dominated by Engelmann spruce (Picea engelmannii), subalpine fir (Abies lasiocarpa), limber pine (Pinus flexilis) and lodgepole pine (Pinus contorta), with some aspen (Populus tremuloides) (Williams et al., 2011). Non-forested portions of the catchment including areas above treeline and some small seasonal wetlands are covered with grasses, forbs, sedges (Carex), and willows (Salix) (Lewis and Grant, 1979). Areas near treeline are characterized by ribbon forests and meadows comprised of moderately well-drained soils with loamy sand to gravel textures and little clay content (Williams et al., 2009). Having been glaciated during the Pleistocene, much of the area around and at C-1 resides on the Arapaho moraine, with a large portion underlain by Pinedale and Bull Lake glacial till (Williams et al., 2011). The USGS Ward quadrangle estimates a moraine thickness near 10m (Gable and Madole, 1976), yet a subalpine groundwater well installed in 2011 to a depth of 28 m was believed to only reach the bedrock-moraine interface. Soils overlying the Precambrian siliceous metamorphic and granitic bedrock are relatively thin,
ranging from 60-200 cm, and are deeper in areas with glacial till (Lewis and Grant, 1979; Murphy et al., 2003). In contrast with the nearby alpine Green Lakes Valley watershed, there are no lakes, rock glaciers, talus, exposed bedrock, or steep cliffs in the Como Creek catchment (Williams et al., 2011). Como Creek flows into North Boulder Creek, the source of 40% of the City of Boulder’s water supply (City of Boulder, 2016).

2.3 Data and Methods

2.3.1 Precipitation

Precipitation was sampled weekly at both the NADP CO90 site at C-1 between 2011 and 2014 and the unofficial NADP Soddie site between 2011 and 2013. For EMMA analysis, NADP precipitation data from both the C-1 and Soddie sites were split up by season, with June-September data regarded as rain and October-May data as snow. Individual samples in the spring and autumn months were further examined based on their $\delta^{18}O$ values and were grouped appropriately as rain or snow, generally with $\delta^{18}O$ values $>-12\%o$ classified as rain. Since ANC is typically very low in precipitation, NADP does not analyze precipitation for ANC. Therefore, an ANC value of 5 µeq/L was applied to all precipitation samples for EMMA purposes only (R. Cowie, pers. comm.).

2.3.2 Surface Water and Groundwater

Surface water samples were collected as grab samples approximately weekly since 2004 from Como Creek at the catchment outlet (Weir) according to the protocols in Williams et al. (2009) (Figure 1.1). Groundwater wells were sampled approximately weekly during the spring and summer months and monthly during the winter since 2010 when they were installed. The four wells near C-1 utilized for this portion of this study include three shallow wells south of C-1 (SO1, SO2, SO4), and one deeper well southwest of C-1 (SW2) (Figure 1.2; Appendix).
Groundwater wells consisted of piezometers made of PVC pipes screened at the bottom 1.5 m. Well depths generally range from 7-8 m, with the deeper well at 28 m. All groundwater wells at C-1 reside within unconsolidated glacial deposits, mainly sand, gravel, and cobbles, and were not known to have penetrated bedrock upon installation. Groundwater well sampling was performed using a 1 m teflon bailer after purging one full well volume and subsequently followed the protocol for surface water collection. Two alpine groundwater wells (SD3, SD4), located at the Saddle site just outside the Como Creek catchment, were also sampled and data are included in this study. The alpine wells were installed in 2005, drilled to a depth of 9 m, cased, and screened at the bottom 1.6 m in the underlying bedrock composed of Tertiary quartz monzonite (King, 2012).

2.3.3 Snowpack and Snowmelt

Snowpack was sampled approximately weekly from January until snowmelt at the C-1 and Soddie sites following the procedures in Williams et al. (1996b). Snowmelt was collected at the Soddie site in 1 m² snow lysimeters accessed via an underground laboratory. Melt samples flowed directly into bottles as grab samples before coming into contact with the ground and were collected approximately daily for the duration of the melt season (Williams et al., 1996b).

2.3.4 Soil Water

When available, soil water was collected at the Soddie site using zero-tension soil lysimeters accessed via an underground laboratory (Williams et al., 1996b). Soil water at C-1 was sampled via tension lysimeters co-located with the three pods of groundwater wells at C-1 (Figure 1.2; Appendix). The three pods of soil lysimeters at C-1 sample water from four different depths down to 1.5 m below the ground surface and were installed in 2011.
2.3.5 Laboratory Analyses

All precipitation and water samples were analyzed for $H^+$, $NH_4^+$, $Ca^{2+}$, $Na^+$, $Mg^{2+}$, $K^+$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $Si$, $δD$, $δ^{18}O$, pH, acid-neutralizing capacity (ANC), specific conductance, dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and total dissolved nitrogen (TDN) at the Kiowa Environmental Chemistry Laboratory in Boulder, CO, as part of the NWT LTER Program. Laboratory methods, detection limits, and instrumentation for chemical and nutrient analyses are as presented in Williams et al. (2009). Generally, detection limits for all solutes were less than 1 $µ$eq/L. Samples for stable water isotopes were analyzed via a Picarro L1102-i Isotopic Liquid Water Analyzer. The precision for $δ^{18}O$ and $δD$ were ± 0.05‰ and ± 0.1‰, respectively. Prior to 2009, water isotopes were analyzed at the Institute of Arctic and Alpine Research Stable Isotope Laboratory in Boulder, CO.

2.3.6 Diagnostic Tools of Mixing Models

Diagnostic tools of mixing models (Hooper, 2003) were used to determine the number of end-members contributing to streamflow and select conservative tracers to use for EMMA for each water year (1 October – 30 September) between 2011 and 2014. A principal component analysis (PCA) was performed for each year to extract eigenvectors ($V$, $n \times n$, where $n$ is the number of solutes) from the correlation coefficients of annual streamflow chemistry data ($X^*$). Eigenvectors and the transpose of the data matrix $V$ ($V^T$) were used to re-project streamflow chemistry ($\hat{X}^*$) given by:

$$\hat{X}^* = X^*V^T(VV^T)^{-1}V$$

Streamflow chemistry was re-projected into one- and two-dimensional subspaces defined by the first one or first two rows of the eigenvector matrix, respectively (Equation 2.1). Residuals, or the difference between the observed and projected concentrations for each solute,
were plotted against the observed solute concentrations to determine conservative tracers for EMMA. If the residuals vs. observed values displayed a random relationship, indicated by a linear model with a low $R^2$ ($\leq 0.2$), the solute was considered conservative. Higher $R^2$ values indicate a lack of fit in the model and a violation of the assumption of mixing models, and thus were not selected as appropriate tracers for EMMA (Hooper, 2003).

Additionally, the relative root mean square error (RRMSE) for each solute $j$ was calculated using the absolute values of the residuals:

$$RRMSE_j = \frac{\sum_{i=1}^{n} (\hat{x}_{ij} - \bar{x}_j)^2}{n \cdot \bar{x}_j}$$  \hspace{1cm} (2.2)$$

where $i$ is the sample number, $\hat{x}_{ij}$ is the projected solute concentration, $x_{ij}$ is the observed solute concentration, and $\bar{x}_j$ is the mean observed solute concentration. The RRMSE indicates the “thickness” of the data outside the lower dimensional subspace and thus gives a measure of the fit between modeled and observed values by aggregating the residuals into a single measure of predictive power (Hooper, 2003). Thus, solutes with low RRMSE ($<5\%$) are more acceptable as conservative tracers (Ali et al., 2010). No data on end-members were used in these initial diagnostic procedures (Liu et al., 2008b). The main purpose of a PCA is to create a lower dimensional mixing space, $U$, where most data observations can be assumed to lie for a given accuracy (Christopherson and Hooper, 1992). One-dimensional mixing spaces correspond to two end-members, while two-dimensional mixing spaces correspond to three end-members. Therefore, if the distribution between residuals and observed values are considered random for conservative tracers in the two-dimensional subspace, then three end-members are needed for EMMA performed using selected conservative tracers.
2.3.7  End-Member Mixing Analysis

End-Member Mixing Analysis (EMMA) (Christopherson et al., 1990; Christopherson and Hooper, 1992) reduces hydrochemical datasets of streamflow samples to identify the end-members, or chemically distinct water sources, that are significantly contributing to a stream in terms of quantity. Using the conservative tracers determined previously, EMMA was performed to identify end-members for each year and calculate their relative contributions to streamflow (Christopherson and Hooper, 1992; Hooper, 2001; James and Roulet, 2006; Ali et al., 2010; Liu et al., 2004, 2008a; Williams et al., 2006). A PCA was performed for each year to extract eigenvectors from the correlation matrix of conservative tracers in annual streamflow data ($X^*$, $n \times p$, where $n$ is the number of samples and $p$ is the number of conservative tracers) in order to re-project the streamflow chemistry, with:

$$ U = X^*V^T $$

(2.3)

where $U$ ($n \times m$, where $m$ is one less than the number of end-members) is the transformed data matrix in $U$-space and $V$ ($m \times p$) is the matrix of eigenvectors, where each eigenvector is a row (Christopherson and Hooper, 1992). Conservative tracer data from end-members are also projected into $U$-space using median tracer concentrations as the representative concentrations for the mixing model (Hooper, 2001). The eigenvalues that form the geometrical coordinates of projected end-members have corresponding eigenvalues that equate to the variance in the data explained by each projected end-member. If the first two of these principal component scores explained ≥90% of the variance of the data, then three end-members are needed, or one more than the number of components retained (Christopherson and Hooper, 1992).

An appropriate set of end-members will have more extreme concentrations than the stream samples, enclose most stream samples in $U$-space, be chemically distinct from other end-
members, and have lower temporal variability than the observed stream chemistry (Hooper, 2001). Proper end-members will also have a relatively small spatial distance between their actual and projected values in $U$-space for each of the conservative solutes. End-member eligibility is evaluated using the distance between the projected and original end-member compositions, or Euclidean distance:

$$d_j = \| b_j - b_j^* \| \quad (2.4)$$

$$b_j^* = b_j V^T (VV^T)^{-1} V \quad (2.5)$$

where $j$ is the tracer, $b_j$ is the original end-member tracer concentration, $b_j^*$ is the projected end-member tracer concentration in $U$-space, and $V$ is the matrix of eigenvectors extracted from the conservation tracers in stream samples (Christopherson and Hooper, 1992; Liu et al., 2008b). The Euclidean distance can be divided by the original median tracer concentration of the end-member and expressed as a percentage that represents the distance between the observed and projected end-member concentrations, with shorter distances indicative of a better fit of the end-member in EMMA (Liu et al., 2008b). Chosen end-members and their $U$-space projections were used to perform a three-component hydrologic mixing model to determine their relative contributions to Como Creek on the stream sampling dates for each year between 2011 and 2014. The tracer concentrations of the stream samples were then twice reconstructed using the original and then the projected median tracer concentrations of the eligible end-members and their percentage contribution for that sample. Corresponding reconstructed tracer concentrations in stream samples were plotted against original tracer concentrations to ascertain the mixing model precision for each year, with $R^2$ values $>0.70$ indicative of a well-posed model (Liu et al., 2008a). Corresponding slopes closer to 1 and intercepts closer to zero also indicate better model performance. If an annual hydrograph from Como Creek was available, a separated hydrograph
was created by linearly interpolating end-member contributions between sample dates. All EMMA and diagnostics were performed using R (3.1.3, 2014).

2.4 Results

2.4.1 Mixing Model Diagnostics

Solutes in Como Creek (Ca$^{2+}$, Na$^{+}$, Mg$^{2+}$, K$^{+}$, Cl$^{-}$, SO$_4^{2-}$, Si, δD, δ$^{18}$O, pH, ANC, d-excess) were evaluated as conservative tracers in both 1-D and 2-D mixing spaces using the stream chemistry datasets for the individual water years between 2011 and 2014. The $R^2$ values for each solute either decreased or did not change from 1-D to 2-D mixing spaces every year, indicating that solutes were relatively more conservative in 2-D. Additionally, the RRMSE changed minimally for most solutes between mixing spaces (<0.2%) but was relatively lower for all solutes in 2-D mixing space every year, indicating that the reference mixing model better explained and fit the variability observed in the stream data in 2-D. Therefore, a 2-D mixing space was needed and three end-members were needed to explain the Como Creek catchment stream chemistry. Diagnostics are not reported for solutes in 1-D mixing space.

In 2-D mixing space for every year, distributions of residuals for Ca$^{2+}$, Na$^{+}$, Mg$^{2+}$, ANC, Si, and δD displayed $R^2$ values <0.23 (Figure 2.1), indicating near random and conservative behavior. Only in 2014 did δ$^{18}$O have a slightly larger $R^2$ value of 0.38. Nevertheless, it is necessary to include δ$^{18}$O as a conservative tracer for this study in order to distinguish between the different precipitation end-members that are relatively dilute in other solutes (e.g. NADP Soddie, Rain Soddie, Snow C-1). Values of $R^2$ for pH were also low, with the highest value of 0.35 observed in 2013. For K$^{+}$, Cl$^{-}$, SO$_4^{2-}$, and d-excess, $R^2$ values >0.4 were generally observed, indicating that they should not be used as conservative tracers in EMMA for Como Creek. The RRMSE was <3% for all solutes in all years with the exception of SO$_4^{2-}$ for 2013 (~3.3%)
The same six conservative tracers were chosen for use in EMMA for each of the four years of analysis for Como Creek (Ca\(^{2+}\), Na\(^+\), Mg\(^{2+}\), Si, \(\delta^{18}\)O, and ANC). This set of tracers was proven conservative for each year via the diagnostic tools of mixing models discussed above.

**Figure 2.1.** Distribution of residuals against observed solute concentrations in 2-D mixing space for 2011-2014 Como Creek stream chemistry. \(R^2\) values are shown for fitted lines.
Figure 2.2. Relative Root Mean Square Error (RRMSE, %) for all potential tracers for 2011-2014 Como Creek stream chemistry.

2.4.2 End-Member Mixing Analysis

Using the previously determined conservative tracers (Ca\(^{2+}\), Na\(^{+}\), Mg\(^{2+}\), Si, \(\delta^{18}O\), and ANC), a PCA was performed on the Como Creek stream chemistry for each water year between 2011 and 2014. The first two principal components explained 96%, 92%, 90%, and 95% of the total variance in the stream chemistry data for 2011, 2012, 2013, and 2014, respectively. This
confirms that three end-members were needed for each year when using this set of conservative tracers, or one more than the number of components retained to explain 90% of the variance.

A total of seventeen distinct waters were evaluated as potential end-members for Como Creek between 2011 and 2014, including six precipitation groups (NADP Soddie, Rain Soddie, Snow Soddie, NADP C-1, Rain C-1, Snow C-1), three shallow subalpine groundwater wells (SO1, SO2, SO4, in moraine), one deep subalpine groundwater well (SW2, in moraine), two alpine groundwater wells (SD3, SD4, in fractured rock), two soil lysimeter datasets (Soil Soddie, treeline; Soil C-1, subalpine), two snowpack datasets (Snowpack Soddie, Snowpack C-1) and one snowmelt dataset (Snowmelt Soddie). Only fourteen waters were evaluated for Como Creek in 2014 since a complete precipitation chemistry dataset was not available for the NADP Soddie site that year. To evaluate end-members in 2-D mixing space using the conservative tracers, the first 2 $U$-space projections of each end-member were used to construct mixing diagrams for each year (Figures 2.3-2.6). End-members are shown by their projected medians and have lines drawn to 25% and 75% quartiles to show their temporal variability in $U$-space. Diagnostics from stream tracer chemistry indicated that for the $U$-space projections across all years, axis $U2$ roughly depicted the relative distribution of $\delta^{18}O$ for the potential end-members, while axis $U1$ depicted the relative distribution of the other tracers ($Ca^{2+}, Na^+, Mg^{2+}, Si$, ANC). This is apparent when considering the distribution of precipitation end-members for all years in the $U$-space projections, with rain plotted furthest away from snow and snowpack and the cumulative NADP end-members in between.
Figure 2.3. Orthogonal projection of end-members onto $U$-space defined by 2011 streamflow chemistry at Como Creek. End-members are shown by their medians and 25% and 75% quartiles. Triangles of dashed lines show end-members that enclose stream samples. Ca$^{2+}$, Na$^+$, Mg$^{2+}$, Si, $\delta^{18}$O, and ANC explained 96% of the total variance in the 2011 Como Creek stream chemistry.
Figure 2.4. Orthogonal projection of end-members onto U-space defined by 2012 streamflow chemistry at Como Creek. End-members are shown by their medians and 25% and 75% quartiles. Triangle of dashed lines shows end-members that enclose stream samples. Ca$^{2+}$, Na$^{+}$, Mg$^{2+}$, Si, $\delta^{18}$O, and ANC explained 92% of the total variance in the 2012 Como Creek stream chemistry.
Figure 2.5. Orthogonal projection of end-members onto $U$-space defined by 2013 streamflow chemistry at Como Creek. End-members are shown by their medians and 25% and 75% quartiles. Triangles of dashed lines show end-members that enclose stream samples. Ca$^{2+}$, Na$^+$, Mg$^{2+}$, Si, $\delta^{18}$O, and ANC explained 90% of the total variance in the 2013 Como Creek stream chemistry.
Figure 2.6. Orthogonal projection of end-members onto $U$-space defined by 2014 streamflow chemistry at Como Creek. End-members are shown by their medians and 25% and 75% quartiles. Triangles of dashed lines show end-members that enclose stream samples. Ca$^{2+}$, Na$^+$, Mg$^{2+}$, Si, $\delta^{18}$O, and ANC explained 95% of the total variance in the 2014 Como Creek stream chemistry.

Eligible end-members should form vertices of a triangle, constraining the majority, if not all, of the stream samples. In general, waters from the shallow groundwater wells at C-1 and the Saddle (<10 m depth) tended to plot with the Como Creek stream samples between 2011 and 2014, indicating a well-mixed surface water-groundwater system but also their inability to represent unique source waters to streamflow (Figures 2.3-2.6). The one deep groundwater end-member from the subalpine (SW2) plotted consistently independent of the stream samples, suggesting it may be a suitable end-member and that the most important source of groundwater to Como Creek is from water stored in the moraine deposits. Based on the differences in $\delta^{18}$O and water table depth between the deep and shallow subalpine groundwater wells (Figures 1.8,
1.9), it is reasonable to assume that unique flowpaths are influencing each water source. Snow, snowpack, and snowmelt end-members generally plotted in the same area of the mixing spaces. Soil water from the Soddie site consistently plotted in the same direction as rain while soil water from C-1 plotted closer to deep subalpine groundwater (SW2). Both soil water from the Soddie site and a rain end-member appear to be appropriate bounding end-members in $U$-space for most of the study period, along with deep subalpine groundwater (SW2) and snowmelt from the Soddie site (Figures 2.3-2.6). The high variance of the Soddie soil water in 2012 over the $U_2$ axis can be attributed to $\delta^{18}O$ enrichment of Soddie soil water observed between July and September consistent with high summer rainfall, suggesting that the July-September Como Creek samples were still heavily influenced by soil water regardless of their position outside the end-member triangle (Figure 2.4).

Mixing diagrams provide insight into significant end-member contributions to streamflow, however, they do not indicate the fit of end-members in the 2-D mixing space, and thus lack the ability to convey the appropriateness of end-member selection. To test the ability of the end-members to fit in the Como Creek mixing space, percent differences representing the distance between the observed and projected end-member tracer concentrations (i.e. Euclidean distance) between 2011 and 2014 were calculated using Equations 2.4 and 2.5 (Table 2.1). It is important to understand that Euclidean distance is not how far the end-member is from the stream samples in the Como Creek mixing space and thus cannot be inferred from the mixing diagrams in Figures 2.3-2.6. Overall, precipitation and snowpack end-members fit poorly in the EMMA mixing space for all conservative tracers except $\delta^{18}O$, as indicated by very high percent differences, due to the low concentration of solutes present in the samples. James and Roulet (2006) suggested a value $\leq 15\%$ as indicative of a good fit in the mixing space; thus, the
consistently low end-member distances for $\delta^{18}O$ across all years suggests that the assumption of conservative behavior is most appropriate for $\delta^{18}O$ in the Como Creek catchment. The C-1 groundwater wells (SW2, SO1, SO2, SO4) fit best in the 2-D mixing space across all tracers and years. End-member distances were relatively much lower for soil water than for precipitation across all years, demonstrating that soil water fits better in the Como Creek 2-D mixing-space and is superior to precipitation in EMMA. In addition to bounding stream samples, deep subalpine groundwater (SW2) and snowmelt from the Soddie site also displayed a better fit in EMMA across all years relative to other potential end-members. Thus, snowmelt and soil water from near treeline (Soddie) and deep subalpine groundwater (SW2) were identified as the end-members of Como Creek streamflow for each year between 2011 and 2014 based on their fit in the Como Creek mixing space and bounding of stream samples in $U$-space (Table 2.1; Figures 2.3-2.6).
Table 2.1. Percent differences between $U$-space projections and original values (medians) of end-members in the Como Creek catchment, 2011-2014. Differences $\leq 15\%$ are bolded, indicating a good fit in the mixing space.

<table>
<thead>
<tr>
<th>End-Member</th>
<th>ANC</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Na$^+$</th>
<th>Si</th>
<th>$\delta^{18}O$</th>
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2.4.3 Relative Contributions of End-Members

The three end-members that were determined to be most suitable for each year’s streamflow were used to perform a three-component mixing model and calculate the relative contribution of each end-member to streamflow for each stream sample. When determining the relative contribution of each chosen end-member to streamflow, stream samples falling outside the end-member triangle were geometrically forced to zero for one component and became a two-component sample of the two geometrically closest end-members in $U$-space (Liu et al., 2004). This occurred in 2012 for three stream samples from the end of March falling just outside the end-member triangle near the mixing line between snowmelt and deep subalpine groundwater, with soil water contribution quantified as zero (Figure 2.4). All fourteen stream samples taken after peak Como Creek discharge in 2012 ($n = 60$ for 2012), which occurred with summer rains and not annual spring snowmelt, fell outside of the triangle formed by the projected medians of the end-members, showing indication of a heavy rain influence (Figure 2.4). The Soddie soil water end-member varied in the direction of rain over the $U_2$ axis, corresponding with soil water samples from July-September and supporting the notion that soil
water is still an important flowpath contributing to streamflow during 2012. Additionally, the stream sample corresponding to the week of the September 2013 heavy rains showed a rain influence but was still within the range of Soddie soil water in the Como Creek mixing space (Figure 2.5). Thus, the snowmelt contributions for the fourteen July-September 2012 samples and the one September 2013 sample were quantified as zero.

Using the geometric mixing proportions of each end-member and their respective observed and projected median tracer concentrations, tracer concentrations of Como Creek stream samples were reconstructed and compared to original values to ascertain the mixing model precision and goodness of fit for each year (Table 2.2). The $R^2$ values corresponding to the relationship between the reconstructed and original solute concentrations of stream samples were greater than $>0.7$ for all tracers in all years except 2012, indicating that the mixing models employed for those years were well-posed and reasonably successful (Liu et al., 2008a). Use of the projected end-member concentrations for reconstructing stream sample concentrations improved the fit for some tracers in 2012, including ANC and $\delta^{18}O$, and mainly decreased the intercept value for each tracer, yet had varying influence on slope. Regardless, $R^2$ values were above 0.5, indicating reasonably good reproduction of stream samples by the selected end-members for 2012. It is key to remember that stream samples were reconstructed using the end-member tracer concentration medians, representing a source of uncertainty in the validation of EMMA results. Soil water samples taken during the same time period as the outlying July-September stream samples in the 2012 Como Creek mixing diagram (Figure 2.4) show a similar variation in chemistry. Thus, those stream samples could be reconstructed using a different percentile of Soddie soil water chemistry to further improve model performance. For the sake of consistency, median tracer concentrations were used for all mixing models across all years.
Overall, goodness of fit results in 2.2 justified end-member selections and EMMA solutions. Separated hydrographs for 2011, 2012, and 2014 are shown in Figure 2.7. Results from the three-component hydrologic mixing models showed that between 2011 and 2014, mean relative contributions to Como Creek streamflow were 36% soil water from near treeline, 35% snowmelt, and 29% deep subalpine groundwater. Increases in total groundwater and soil water contributions during snowmelt corresponded with increases in subalpine water table level and the overall response of the hydrologic system at this time, supporting the mixing model results (Figures 1.3, 1.8, 1.10).
Table 2.2. Goodness of fit for three-component mixing models as measured by a regression of EMMA predictions against observations of Como Creek streamflow for the original and projected median concentrations of selected end-members for Como Creek, 2011-2014 (groundwater, snowmelt, and soil water).

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<th>Tracer</th>
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Figure 2.7. Results of three-component mixing models using EMMA for Como Creek from 10 April – 30 September of 2011, 2012, and 2014. Contributions are shown in red for deep subalpine groundwater, green for soil water from the Soddie site, and blue for snowmelt from the Soddie site. Daily source-water contributions were linearly interpolated from the contributions estimated for the observed samples.
In 2011, Como Creek streamflow was composed of on average 33% deep subalpine groundwater (SW2), 42% snowmelt from the Soddie site, and 25% soil water from the Soddie site (Figure 2.7). Relative contributions from groundwater were highest during baseflow in the autumn and spring and prior to snowmelt. Snowmelt contributions remained lowest during the onset of baseflow in October but still characterized ~25% of streamflow during the winter months, increasing into summer and remaining elevated until autumn. Maximum snowmelt contributions of 79% were observed on 27 June 2011, while peak SWE corresponded to 22 May 2011 and peak Como Creek discharge occurred on 20 June 2011 (Figure 1.3bc). Soil water had peak total contributions during snowmelt and through the summer, with relative contributions peaking in the autumn at 70% on 7 September 2011.

In 2012, Como Creek streamflow consisted of on average 30% deep subalpine groundwater (SW2), 32% snowmelt from the Soddie site, and 38% soil water from the Soddie site (Figure 2.7). While groundwater constituted roughly a third to half of Como Creek streamflow through April 2012, total groundwater contributions peaked in the spring with snowmelt, with contributions more variable during the remainder of the year. Snowmelt contributions peaked at 68% on 8 June 2012, nearly three months after peak SWE on 11 March 2012. Soil water characterized the majority of streamflow between July to September (>60%), corresponding with the heavy rain influence observed for the Como Creek hydrograph at this time period (Figure 1.3c). By the time peak flow occurred in 2012 due to summer rains, snowmelt contributions to Como Creek were quantified as zero, reflecting the small size and short duration of the 2012 snowpack. Around 24 July 2012, streamflow was estimated to be 100% soil water, with near zero contributions from groundwater.
In 2013, Como Creek stream samples were comprised of an average 29% deep subalpine groundwater (SW2), 41% snowmelt from the Soddie site, and 30% soil water from the Soddie site. Groundwater contributions peaked on 19 April 2013 at 58%, followed by peak SWE on 11 May 2013 and peak Como Creek discharge around the first week of June. Snowmelt contributions peaked after peak discharge at 76% of streamflow on 13 June 2013. Soil water contributions constituted half of streamflow in mid-May at peak SWE, decreasing after snowmelt and increasing into the late summer and autumn. The 10 September 2013 stream sample corresponding to the heavy rains was estimated to be >90% soil water, with the remainder explained by groundwater and contributions from snowmelt quantified as zero. It is notable to recognize that in both 2012 and 2013 at some point during the late summer and early autumn, snowmelt contributions to streamflow were quantified as zero, with the majority of streamflow composed of soil water and a small fraction by deep subalpine groundwater.

Como Creek streamflow during the 2014 water year was characterized by an average of 24% deep subalpine groundwater, 28% snowmelt from the Soddie site, and 49% soil water from the Soddie site (Figure 2.7). Peak SWE on 18 April 2014 was followed by peak snowmelt contributions to streamflow of 51% on 6 May 2014 and peak groundwater contributions of 48% on 15 May 2014. Peak Como Creek discharge occurred afterward on 2 June 2014 and was characterized mainly by soil water and snowmelt. Soil water contributions remained high (>50%) during the months following the September 2013 heavy rains and increased relatively again in August 2014. Soil water remained high on the falling limb of the hydrograph, suggesting consistent streamflow contribution from soil water flowpaths following snowmelt. Although 2014 had the highest peak flows out of Como Creek, the highest peak SWE, and the
second longest snowpack duration of the years analyzed (Figure 1.3bc), average relative snowmelt contributions to streamflow were lowest during this year.

2.5 Discussion

Water derived from snowmelt, deep subalpine groundwater (>15 m depth), and soil water from near treeline were important contributors to streamflow across all years. However, precipitation was not, indicating that most rain or snow infiltrates the subsurface before entering the stream. One late September 2011 stream sample shows more influence from rain but is still within the triangle using soil water as an end-member, suggesting that rains received during this time period somewhat interacted with surface soils before leaving the catchment via streamflow (Figure 2.3). Only in 2012 did stream samples after peak discharge deviate away from snowmelt instead of towards it in the mixing space, indicating summer streamflow had a stronger influence from rain and soil water and a weaker influence from snowmelt relative to other years, which was corroborated by the annual hydrograph (Figures 1.3c, 2.4). For 2013, one stream sample corresponding to the week of the heavy September 2013 rains did not fall within the triangle formed by soil water, deep subalpine groundwater, and snowmelt (Figure 2.5), suggesting a shorter interaction of rain with surface and soils before discharge during the event. This was confirmed via the residence time analysis for Como Creek catchment in Chapter 1 that yielded a much smaller value for 2013 due to the event.

The 2012 separated hydrograph supports the notion that the subsurface dried out substantially during this low snow year (Figure 2.7), and the absence of snowmelt in 2012 and 2013 streamflow momentarily during the autumn indicates the high demand for snowmelt water in the Como Creek catchment. The presence of groundwater from July-September 2012, supplying the remaining ≤40% of streamflow not characterized by soil water, signifies the
importance of groundwater in sustaining streamflow in mountainous areas during years with fragmented precipitation inputs. Huntington and Niswonger (2012) modeled projected climate impacts on surface water-groundwater interactions in snow-dominated regions and found that groundwater discharge to streams was depleted during the summer with earlier snowmelt due to earlier drainage of shallow aquifers, regardless of increased precipitation or groundwater. They estimated that these processes resulted in a 30% reduction in annual summer flow, suggesting that dry season water stress may become more severe even if annual precipitation increases (Huntington and Niswonger, 2012). Similarly, total groundwater contributions in Como Creek showed signs of depletion following the low snow year of 2012, corresponding with the general drying out of the subsurface via water table levels and recharge estimates reported in Chapter 1. Were it not for heavy summer rains in 2012, Como Creek could have run dry. Relatively short residence times (2-6 years) for subalpine groundwater in Como Creek, which inherently represent average times and thus could be shorter, suggest that if multiple low snow years were to occur simultaneously, groundwater’s ability to compensate for decreased or earlier snowmelt inputs may be exhausted. Low flows during summers have resulted in heightened competitive demands for limited resources (Tague and Grant, 2009), a critical implication for water rights and water availability in the western US.

It is notable that soil water was the largest component of streamflow in 2014, compared to only 25% over 2011. Snowmelt in 2011 was later and faster, potentially decreasing infiltration of snowmelt and resulting in more overland flow, while also corresponding with increased summer ET influences on soil water availability. Increases in soil water contribution in 2014 peak streamflow could indicate that the subsurface was at saturation following 2013 recharge from heavy autumn rains and snowmelt had primarily infiltrated and displaced existing
soil water to streamflow via shallow subsurface stormflow. The very high 2014 discharge did not correspond with a substantial increase in groundwater inputs to streamflow despite the large magnitude of recharge observed in both the autumn of 2013 and upon snowmelt in 2014. While soils are typically very dry in the autumn, the heavy 2013 rains provided additional soil water storage that contributed to high 2014 streamflow. Overall, soil water in Como Creek resembles that near the Soddie site and not C-1, indicating greater soil water contributions to streamflow from treeline than from the subalpine.

Previous EMMA for Como Creek (Cowie, 2014) determined that a 2-D mixing space (i.e. three end-members) was needed and conservative tracers Ca$^{2+}$, Na$^+$, Mg$^{2+}$, Si, $\delta^{18}$O, and ANC should be used for EMMA, similar to this study. This similarity in mixing model parameterization allows for an easy comparison of results between the two studies. Cowie (2014) primarily differed from this study in that he used a single dataset containing 2010-2012 Como Creek stream and end-member chemistry. Composite soil water end-members were considered too temporally variable in the single 2010-2012 mixing space relative to Como Creek stream samples, so rain was chosen as the third end-member along with deep subalpine groundwater and snowmelt. However, Cowie (2014) did not quantify end-member distances between projected and observed tracer concentrations, and thus did not identify the lack of fit between precipitation end-members with very low solute concentrations and the Como Creek mixing space. Although soil water end-members for this study also exhibited higher temporal variability, all end-member projections still plotted consistently for each individual year relative to other end-members and stream samples. Soil water’s temporal variability in the mixing space over the four years of analysis is likely due to its intermittent nature and reliance on precipitation or snowmelt. Thus, the composition of this end-member and contribution to streamflow may be
even more heavily reliant on the hydrologic connectivity of an area. These observations suggest that multi-year EMMA analyses have the potential to mask interannual variations in end-member composition that are heavily reliant on the hydrologic connectivity of an area that is often governed by unique annual precipitation inputs. Ali et al. (2010) conducted a similar EMMA analysis by breaking down multi-year stream chemistry datasets from a forested headwater catchment into different hydrologic scenarios based stream discharge and antecedent wetness of the catchment, reporting high temporal variation in the relative contributions of end-members to streamflow. Low stream discharge and dry conditions were associated with baseflow while high discharge and wet conditions were associated with soil water, similar to the findings in this study. Echoing the results of Ali et al. (2010), this study suggests caution in utilizing a single mixing space for evaluating streamflow sources across hydrologic conditions.

2.6 Conclusion

This study emphasizes the utility of geochemistry and stable isotopes in addressing hydrologic questions in physically and spatially complex mountainous systems. The Como Creek catchment was identified as a three-end member system, with dominant contributions from deep subalpine groundwater (>15 m depth) residing in moraine deposits, snowmelt, and soil water from near treeline. Overall, rain did not contribute much to streamflow but was instead assimilated into the soil system and stored there. Between 2011 and 2014, average relative contributions from end-members were 36% soil water, 35% snowmelt, and 29% groundwater, signifying the important roles each source plays in streamflow generation. While soil water characterized the majority of 2012 and 2014 streamflow, snowmelt was the largest contributor in 2011 and 2013. Hydrograph separation for 2012 revealed that soil water influenced by heavy summer rains constituted the majority of summer streamflow and indicated
that the subalpine groundwater reservoir has a limited capacity to sustain streamflow following a low snow year. Regardless of similar snowpack, 2014 streamflow witnessed nearly two times the mass of water as 2011, suggesting a legacy effect from increased soil water storage on streamflow as a result of heavy 2013 autumn rains. These variations in source waters suggest that the Como Creek system will likely transition to a more hybrid hydroclimatic regime (snow-rain) given further precipitation variability. The utilization of both diagnostic tools from mixing models and EMMA reduces uncertainties associated with choosing the proper end-members and conservative tracers for streamflow in a catchment. All EMMA and mixing model analyses were done on an individual year basis between 2011 and 2014 in order to represent interannual variations of end-members, particularly soil water. Caution should be taken when performing multi-year EMMA analyses with composite end-member datasets so as not to mask the true behavior and composition of a source water in the hydrologic system for a given year. End-member distance (i.e. Euclidean distance) cannot be inferred from EMMA mixing diagrams alone and should be addressed when selecting the proper end-members for a catchment via EMMA.
BIBLIOGRAPHY


Lewis, W.M., and M.C. Grant, Changes in the output of ions from a watershed as a result of the acidification of precipitation, Ecology, 60, pp 1093–1097, 1979.


Uccellini, L.W., The Record Front Range and Eastern Colorado Floods of September 11-17, 2013, NOAA Service Assessment, June 2014.


overview and recommendations for research, management, and policy, Hydrology and Earth System Sciences, 15, pp 471-504, 2011.


## APPENDIX

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Links for Niwot Ridge Climate Programs

Niwot SNOTEL: http://wcc.sc.egov.usda.gov/nwcc/site?sitenum=663
Niwot Ridge LTER: http://niwot.colorado.edu/
NADP CO90: http://nadp.isws.illinois.edu/data/sites/sitedetails.aspx?id=CO90&net=NTN