Surface and subsurface water contributions to streamflow from a mesoscale watershed in complex mountain terrain

Qinghuan Zhang[1,2], John F. Knowles[1,3], Rebecca T. Barnes[4], Rory M. Cowie[5], Nathan Rock[1], Mark W. Williams[1,2]

[1]Institute of Arctic and Alpine Research, University of Colorado Boulder, Boulder, CO, USA

[2]Department of Geography, University of Colorado Boulder, Boulder, CO, USA

[3]School of Geography and Development, University of Arizona, Tucson, AZ, USA

[4]Environmental Program, Colorado College, Colorado Springs, CO, USA

[5]Mountain Studies Institute, Durango, CO, USA

Corresponding author:
Qinghuan Zhang
Institute of Arctic and Alpine Research
University of Colorado
UCB 450
Boulder, CO 80309-0450
Email: Qinghuan.Zhang@Colorado.edu
Tel: (720) 625-1606
Fax: (303) 492-6388

Abstract

An understanding of surface and subsurface water contributions to streamflow is essential for accurate predictions of water supply from mountain watersheds that often serve as water towers for downstream communities. As such, this study used the end-member mixing analysis (EMMA) technique to investigate source water contributions and hydrologic flow paths of the 264 km^2 Boulder Creek Watershed, which drains the Colorado Front Range, USA. Four conservative hydrochemical tracers were used to describe this watershed as a three end-member system, and tracer concentration reconstruction suggested that the application of EMMA was robust. On average from 2009 to 2011, snowmelt and rain water from the subalpine zone and groundwater sampled from the upper montane zone contributed 54%, 22%, and 24% of the annual streamflow, respectively. These values demonstrate increased rain water and decreased snow water contributions to streamflow relative to area-weighted mean values derived from previous work at the headwater scale. Young water (2.3 ± 0.8 months) fractions of streamflow decreased from 18-22% in the alpine catchment to 8-10% in the lower elevation catchments and the watershed outlet with implications for subsurface storage and hydrological connectivity. These results contribute to a process-based understanding of the seasonal source water composition of a mesoscale watershed that can be used to extrapolate headwater streamflow generation predictions to larger spatial scales.

Keywords: End-member mixing analysis, streamflow generation, young water fraction, hydrological connectivity, nested catchments, hysteresis, Colorado Front Range

1. Introduction

Snow inputs support both ecosystems and human populations downstream, through the combination of surface water runoff and subsurface recharge (Jin et al., 2012; Viviroli et al., 2007; Mankin et al., 2015). Snowmelt water delivery to streams is modified by spatio-temporal variations in hydrological connectivity that affect the residence time of water on the landscape (Hrachowitz et al., 2016). Moreover, the surface- and subsurface-water contributions to streamflow and the inherent flow paths are affected by variations in climate and disturbance. For example, subsurface water sources are important to sustaining streamflow in high-elevation mountainous catchments throughout the year (Liu et al., 2004; Miller et al., 2016), and these sources are influenced by the timing, magnitude, and type of recharge, as well as the storage capabilities of the subsurface (Cowie et al., 2017). Consequently, effective water management and regulation of water resources in mountainous watersheds requires a thorough understanding of the seasonal mechanisms responsible for stream water recharge.

Mountain flowpaths are complicated by variable topography, bedrock permeability, soil depth, and forest cover that present challenges but also opportunities for the study of hydrologic connectivity in the context of water resources (Bales et al., 2006). Hydrochemical data, including ions and stable water isotopes, represent useful tracers with which we are able to gain understanding of source water and flow paths in complex terrain (Williams et al., 2006, 2011; Uchida et al., 2005; Robinson et al., 2009). In particular, End-Member Mixing Analysis (EMMA) is a hydrological mixing model that solves an over-determined set of equations by way of conservative hydrochemical or isotopic tracers to identify the various contributing source waters (Barthold et al., 2011). As a result, EMMA can be used to conceptualize streamflow generating processes and has been successfully applied to mountain catchments around the world (Hooper, 2003; Liu et al., 2004, 2008; Cras et al., 2007; Frisbee et al., 2011, 2013; Maurya et al., 2011; Baraer et al., 2015). The seasonal cycles of hydrological tracers such as $\delta^{18}O$ can also estimate the young water (2.3 ± 0.8 months) fraction of streamflow from highly heterogeneous sub-catchments with contrasting transit-time distributions (Kirchner, 2016a). The young water fraction of streamflow provides an indication of surface-subsurface water interactions and subsurface storage capacity, both of which influence hydrological pathways and their response to climate change. An understanding of how and whether these pathways vary as a function of elevation, precipitation type, and catchment size is therefore critical to a process-based understanding of mountain hydrology.

Mountains along the Front Range in Colorado, USA provide essential water resources for the Denver metropolitan area. Previous studies used EMMA to investigate streamflow components in first and second order catchments of the Boulder Creek watershed, and found that snowmelt contributions decreased with decreasing elevation, while rain water contributions concomitantly increased (Cowie et al., 2017). However, the manner in which these headwater stream components integrate to larger catchments characterized by geological, ecological, and climatic gradients is not well constrained. For example, a recent summary of source water studies in complex mountain terrain contained only three of fourteen studies from catchments comparable in size (within an order of magnitude) to the Boulder Creek watershed at Orodell, and two of those catchments were dominated by warm season glacial meltwater inputs that are only nominally important to Boulder Creek at this scale (Cowie et al., 2017; Table 1). In addition, source waters can also vary within a single ecosystem type, as evidenced by Liu et al. (2004) where differences in cryospheric features and snow depth explained the variation in streamflow source waters from two adjacent alpine catchments.

Scaling source water contributions to streamflow at larger spatial scales represents an outstanding problem in catchment hydrology. To address this problem, this study utilized hydrochemical tracers within a nested catchment sampling design to statistically model streamflow sources (i.e. use EMMA) within a mesoscale (264 km^2) watershed that is widely representative of semi-arid mountain terrain globally. In addition, we investigated whether certain elevation zones may disproportionately control streamflow chemical characteristics and subsequent streamflow generation at the watershed outlet by coupling results from EMMA to the fraction of young water calculated from water isotopes. Specifically, using weekly stream and source water (e.g. precipitation, groundwater) chemistry measurements from 2009 to 2011, we addressed the following research questions: (1) What are the constituent source water regions to Boulder Creek's main stem and how do they vary inter-annually? And, (2) how do these source waters relate to previously characterized headwater catchments in this spatially heterogeneous watershed? This information can be used to infer potential changes in streamflow recharge sources and/or hydrologic connectivity associated with future climate variability.

2. Site description

The Boulder Creek watershed ranges in elevation from 1779 m above sea level (asl) at the Orodell stream gauge (40.006°N; 105.33°W) to 4117 m asl at the summit of

North Arapahoe peak. The mean annual precipitation is 840 mm. There are four instrumented headwater catchments up-gradient from the Orodell stream gauge on Boulder Creek: Green Lakes Valley (GLV) in the alpine zone, Como Creek (CC) in the subalpine, Gordon Gulch (GG) in the montane, and Betasso (BET) in the foothill zone. Since the foothill catchment is characterized by intermittent streamflow, it was not included in this study. Streams in GLV, CC and GG all flow to North Boulder Creek, which joins Middle Boulder Creek 8 km above the Boulder Canyon Hydroelectric Plant near the Orodell stream gauge (Murphy et al., 2003). The Middle and North Boulder Creek sub-watersheds are very similar in land use and land cover, geology, elevation range, and size (Kinner, 2003; Williams et al., 2011). In general, low-flow in Boulder Creek occurs from October to March, while high-flow occurs from May to July and peaks in June, depending on snowpack depth and air temperature (Murphy et al., 2003).

The instrumented headwater catchments within Boulder Creek have distinct geologic and climatic features, soil types, and land cover patterns due to their elevation and landscape location (Table 1). The GLV watershed consists of distinct upper and lower basins separated by a 90-m glaciated valley-step. The upper GLV is in an alpine environment that contains steep rock walls, talus slopes, rock and cirque glaciers, permanent snowfields, and is characterized by poorly developed soils. The lower GLV has less exposed bedrock, fewer talus slopes, and more extensive soil and vegetation cover. It was last scoured by glaciers about 18,000 years ago and subsequently has an immature and truncated Critical Zone (CZO Boulder, 2015). The CC watershed slopes from west to east approximately 8 km east of the Continental Divide. This catchment has no lakes, talus, steep cliffs, or glaciers. It contains both subalpine forest and alpine tundra ecosystems with about 69% forest coverage (Knowles et al., 2015), and has experienced minimal human impact over the last 100 years (Williams et al., 2011). The forested GG catchment is located within the Arapahoe National Forest and is divided into the upper GG (GGU) and lower GG (GGL) basins. Both the GGU and GGL basins are located in the montane climatic zone and are underlain by biotite gneiss. Here, northerly and southerly exposures produce contrasting environments as a result of differences in solar radiation and soil moisture dynamics (Hinckley et al., 2014). Within the montane environment, thinner soils, less-weathered rock, grasses, and Ponderosa pine (*P.*

ponderosa) are found on south-facing slopes, while more weathered rock, thicker soils, and dense Lodgepole pine stands (*P. cortorta*) are found on north-facing slopes.

3. Data and Methods

3.1 Data acquisition

3.1.1 Discharge and streamflow sampling

Daily discharge data at Orodell were recorded by the United States Geological Survey at station number 6727000 from 1920 to 1995. Recent discharge data, from the year 2000 to present, were collected by the Colorado Division Support System at gage BOCOROCO, which is the same gauge as Orodell (http://www.dwr.state.co.us/SurfaceWater/data/detail_graph.aspx?ID=BOCOROCO). Missing values in the low flow season (20 November to 20 March) were set to 0.34 m^3 s^{-1} (0.107 mm day^{-1}), according to measured low flow data in this area (Mark Williams, unpublished data); there were no missing values during the rest of the year. At Orodell, streamflow samples for hydrochemical analysis were collected weekly as grab samples between 2009 to 2011 (http://criticalzone.org/boulder/data/dataset/2783/). At the outlets of the GG, CC, and GLV catchments, streamflow samples were collected weekly during the ice-free season and approximately monthly during the remainder of the year following protocols discussed in Williams et al. (2009).

3.1.2 Soil water

Monthly soil water samples were taken from tension lysimeters during May to July 2011 from the montane lower GG catchment. Tension lysimeters were also located in the subalpine CC catchment near the Niwot SNOwpack TELemetry (SNOTEL; Site 663) station, and to the southwest and south of the C1 Long Term Ecological Research (LTER) meteorological site from 1 to 4 feet beneath the soil surface (Figure 1c). In the CC catchment, zero-tension lysimeters were located at the Soddie site between 30-50 cm depth, and at four locations in the alpine GLV catchment (Figure 1). Soil water sampling at CC and GLV catchments was conducted on a weekly basis.

3.1.3 Groundwater

Groundwater samples were collected from wells at six locations in the montane GG catchment, numbered from wells 1 to 6. Wells 1 and 6 were deepest (17-18 m below the surface) and were located on north- and south-facing slopes, respectively, while wells 2 to 5 were shallow (4-6 m below the surface) and were located on the valley floor between the north- and south-facing slopes. The samples were collected using a 1-m Teflon bailer to minimize chemical contamination after purging three well volumes (Cowie, 2014). Groundwater samples from the montane zone were collected bi-weekly during low flow season, and weekly during other seasons. Groundwater wells in the subalpine CC catchment were co-located with the tension lysimeters near the Niwot SNOTEL site numbered 1 to 4 from south to north. The average water depth at these wells ranged from 5.6 m to 18.7 m below the surface. In the alpine GLV catchment there were seven shallow and seven deep groundwater wells (four each at the Saddle and three each at Martinelli; piezometers screened at the bottom 1.5 m; Figure 1) with total depths of 6.3 to 8.4 m (Cowie, 2014) and mean water depths ranging from 1.0 m to 7.1 m below the surface. Groundwater samples at CC and GLV were taken weekly during ice-free months and monthly during the winter at the alpine Saddle site.

3.1.4 Precipitation, snowmelt and snowpack samples

The National Atmospheric Deposition Program (NADP) collects precipitation chemistry samples within the GG (Site CO94), CC (Site CO90), and GLV (Site CO02) catchments using shielded Belfort 5-780 type collectors mounted 2 m above the ground (Cowie, 2014). An additional site located near treeline in the CC catchment (Soddie) also collects precipitation samples on a weekly basis, following the same protocols as the NADP program (Table 2). Snowpack samples were collected from snowpits during annual snow surveys conducted in May. Snow samples were collected for chemical and oxygen isotopic analyses using beveled polyvinyl chloride (PVC) tubes (50 mm diameter, 500 mm long), which had been soaked in 10% HCl and then rinsed at least five times with deionized water. Duplicate, vertical, contiguous cores in increments of 40 cm were collected from the snow-air interface to the ground. Snow was transferred from the cores into new polyethylene bags (Williams et al., 2009). Snowmelt samples were collected using snow lysimeters located at two locations within the CC catchment (Cowie et al., 2017).

3.2 Laboratory analyses

All water samples were analyzed in the Kiowa/Arikaree Laboratory at the Institute of Arctic and Alpine Research (INSTAAR), University of Colorado at Boulder; analytes included: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), chloride (Cl^{-}), nitrate (NO_3^{-}), sulfate (SO_4^{2-}), acid neutralizing capacity (ANC) μeq L^{-1}, and silica (Si) μmol L^{-1}. The detection limits were 0.26 μeq L^{-1} for Ca^{2+}, 0.23 μmol L^{-1} for Si, and less than 0.2 μeq L^{-1} for all other solutes (Williams et al., 2009). Stable water isotopes were analyzed using an L1102-I Isotopic Liquid Water Analyzer (Picarro Inc., Santa Clara, CA, USA). Isotopic compositions are expressed as a δ (‰) ratio of the sample to the Vienna Standard Mean Ocean Water (VSMOW), where *R* is the ratio of $^{18}O/^{16}O$ or $^{2}H/^{1}H$. The $\delta^{18}O$ and $\delta^{2}H$ of VSMOW are both 0‰ (Cook & Herczeg, 2000). The precision of $\delta^{18}O$ and $\delta^{2}H$ were 0.02‰ and 0.08‰, respectively, where *R* is calculated by:

$$(\delta^{18}O, \delta^{2}H)_{sample} = [(\frac{R_{sample}}{R_{VSMOW}}) - 1] \times 10^{3} \quad (1)$$

3.3 Young water fraction in streamflow

The $\delta^{18}O$ values in precipitation generally follow a sinusoidal function with a period of one year:

$$\delta_{in}(t) = A\sin(wt) + M_1 \quad (2)$$

where A and M_1 represent the variation in the amplitude and mean value of $\delta^{18}O$, w is the radial frequency of annual fluctuations or 0.017214 rad d^{-1} (DeWalle et al., 1997), and *t* is time in days after 1 January of each year. For measurements in one year, *t* represents day of year. For more than one year, *t* is the cumulative day since day 1 of year 1. Assuming a steady state (i.e., the flow rate and volume of water in the system are constant), a convolution integral is applied to produce the output function, which is also a sinusoidal function with a phase shift (ϕ), a mean value of $\delta^{18}O$ (M_2), but a smaller amplitude (*B*):

$$\delta_{out}(t) = B\sin(wt + \phi) + M_2 \quad (3)$$

In heterogeneous systems, seasonal cycles of conservative tracers can be unreliable estimators of catchment mean transit times (the average time that elapses between a given parcel of water entering a catchment as precipitation and leaving as streamflow) since tributary cycles will be out of phase with each other and their amplitudes may not average linearly (Kirchner, 2016a). Under this condition, the young water fraction (F_{yw}) is a more robust measure of hydrologic cycling than the mean transit time since the young water fraction does not assume that the catchment is homogeneous or that the transit time distribution has any particular shape (Kirchner, 2016b). The young water fraction is defined as the fraction of discharge that is younger than a threshold age of 2.3 ± 0.8 months (Kirchner, 2016a). In this study, the young water fraction is surface runoff that has not infiltrated to the subsurface, and is calculated using the $\delta^{18}O$ amplitude of precipitation and streamflow as:

$$F_{yw} = \frac{B}{A} \times 100\% \quad (4)$$

3.4 End-member mixing analysis

End member mixing analysis (EMMA) utilizes conservative chemical tracers to partition source water contributions within a catchment (Hooper, 2003). EMMA assumes that stream water chemistry is controlled by physical mixing of end-members, rather than by equilibrium chemical processes. Potential flow components or end-members include precipitation, tributaries, and groundwater in various aquifers. For a three end-member system, the hydrograph separation is calculated as:

$$Q_s C_s = Q_1 C_1 + Q_2 C_2 + Q_3 C_3 \quad (5)$$

where Q represents flow rate, C represents tracer concentration, and the subscript represents the water source (s is streamflow, and 1, 2, and 3 represent sources 1, 2, and 3). In the current study, orthogonal projections of streamflow samples and end-members were used to solve for proportions of end-member contributions to streamflow (e.g. Liu et al., 2008). In order to apply Equation (5), three additional assumptions must be satisfied: (1) the tracer concentration of each component is distinct from the other two components for one or more of the tracers; (2) the tracer concentrations of the three components are not collinear; and (3) only three components contribute to streamflow.

Tracer selection criteria specifically included (1) there was no evidence of a pattern between residual and measured solute concentrations (e.g. $p > 0.05$ and $R^2 < 0.1$), (2) the root-mean-square error (RMSE) was less than 40% (Hooper, 2003), (3) the relative RMSE decreased from the 1-D (two end-members) mixing subspace to higher-dimensional subspaces (e.g. 2-D subspace) (Frisbee et al., 2011), and (4) the quantitative Euclidean distance between potential end-members and projected stream water samples was less than 15% (James & Roulet, 2006). Larger catchments and longer time periods often exhibit increased spatio-temporal variability of tracer concentrations and may require the determination of more end-members. Although with an increased number of tracers, the probability that three or more end-members are identified increases, more tracers do not necessarily mean that more end-members can be identified (Barthold et al., 2010).

3.5 Data processing for EMMA

Median values for snowmelt and snowpack at maximum snow water equivalent and volume-weighted mean solute concentrations from the NADP collectors at the montane, subalpine, and alpine catchments were selected to represent snow and rain samples, respectively (Cowie et al., 2017). If the precipitation type was rain, the data were used to calculate volume-weighted mean concentrations of each solute. If the precipitation type was a rain/snow mix, then $\delta^{18}O$ values were used to determine rain versus snow samples. For example, a $\delta^{18}O$ value more depleted than -15‰ was assumed to be a snow event and a $\delta^{18}O$ value more enriched than -15‰ was assumed to be a rain event. In general, rain samples from the alpine and subalpine catchments exhibited similar solute concentrations and stable water isotope values, whereas rain samples collected from the montane catchment were relatively more concentrated than those from the higher elevation catchments. All solutes in the rain samples were relatively dilute and showed little correlation with elevation ($R^2 = 0.02$ for NO_3^- and Ca^{2+}; $R^2 = 0.05$ for SO_4^{2-}; $R^2 < 0.01$ for all other solutes). For subsurface samples, median values of soil water samples from the tension and zero-tension lysimeters were applied to the alpine and subalpine catchments, and median values of groundwater samples were applied to each groundwater well. Uncertainty analysis was performed whereby tracer concentrations in two end-members were held constant at the median value while the third end-member was allowed to vary across the interquartile range (25%-75%). The same process was repeated for all three end-members and uncertainty is reported as the range of the relative contributions of each particular source water (Cowie et al., 2017).

4. Results

4.1 Discharge and stream water chemistry

May to July discharge accounted for 72-78% of annual total discharge in Boulder Creek at Orodell. The average daily streamflow during 2009 (2.4 $m^3 s^{-1}$) and 2010 (2.4 $m^3 s^{-1}$) were identical to the historical average (2.4 $m^3 s^{-1}$ between 1920 and 1995), while the average daily streamflow in 2011 (3.6 $m^3 s^{-1}$) was 50% higher. Solute concentrations peaked (were most enriched) in April of each year, then decreased (were depleted) throughout the summer, before increasing (becoming enriched) again during low flows in the fall (Figure 2). During peak discharge in June, solute concentrations were lowest, $\delta^{18}O$ values were most depleted, and all of the solute concentrations except NO_3^- showed a clockwise hysteretic loop (Figure 3) indicative of a snowmelt-dominated recharge source.

4.2 Stable water isotopes in end-members and stream water

Although δ^2H and $\delta^{18}O$ relationships in precipitation generally follow the Global Meteoric Water Line (GMWL): $\delta^2 H = 8\delta^{18} O + 10$ (Craig, 1961), a local meteoric water line (LMWL) can be formed with stable water isotopes in local precipitation. The LMWL ($R^2 = 0.99$; $p < 0.05$, $n = 288$) includes precipitation samples from the montane, subalpine, and alpine catchments, and is shown in Figure 4a. The $\delta^{18}O$ and δ^2H values in stream water from the alpine catchment (GL4) were close to the LMWL, but the $\delta^{18}O$ and δ^2H values in stream water from the montane (GG) catchment were shifted to the right of the LMWL, indicating more evaporative losses (Figure 4b). With respect to specific source waters, snow samples were generally located above the LMWL indicating sublimation loss (St Amour et al., 2005). In contrast, stable isotopes of soil water were located on the LMWL in the subalpine and alpine catchments, suggesting direct precipitation recharge, i.e. the water was not subject to secondary processes such as evaporation prior to export (Laudon & Slaymaker, 1997). In the montane zone, both stream water and groundwater were isotopically located below the LMWL, suggesting evaporation of the groundwater/soil water recharge source, either from the snowpack or from within the unsaturated zone (Cecil et al., 2005).

4.3 Young water fractions in headwater catchments and the lower main stem

Young water fractions (F_{yw}) were calculated for each year separately, and as an average using data over the three years (2009-2011) (Table 3). The results show that F_{yw} was highest in alpine streamflow (12-22%), and was generally lower but of similar magnitude in subalpine streamflow (8-10%), montane streamflow (7-12%) and at the watershed outlet (6-11%). Not surprisingly, in the high-flow year of 2011, F_{yw} values were greater than the other years in all streamflow samples due to relatively greater precipitation inputs. In general, young water fractions below 22% throughout the Boulder Creek Watershed were consistent with the assumption that steeper watersheds contain less young water as a result of increasingly complicated flowpaths (Jasechko et al., 2016).

4.4 Reservoir effects on stream water chemistry

There are three major reservoirs in the Boulder Creek Watershed above Orodell. In order to constrain the potential impact of reservoirs in this watershed on stream water chemistry, paired t-tests were performed on water chemistry upstream and downstream of the Barker reservoir near Nederland, Colorado. Between the two sites, solute concentrations generally increased, base cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) and Cl^- all increased ($p < 0.05$); however, DOC, $\delta^{18}O$, NO_3^- and SO_4^{2-} concentrations were not significantly altered by the reservoir (upstream-downstream comparison, $p > 0.05$).

4.5 Tracer and end-member selections at Orodell

Stream water samples at Orodell were used to determine appropriate tracers for EMMA. The randomness of solute concentration residuals improved from the 1-D to the 2-D mixing spaces as evidenced by decreased R^2 and increased p-values. Using the criteria $R^2 < 0.1$, and $p \geq 0.01$, five tracers were initially selected from the 2-D mixing space: Ca^{2+}, Mg^{2+}, SO_4^{2-}, Na^+, and ANC. However, potential streamflow end-members (e.g. snow, groundwater) on bi-plots of Na^+ and SO_4^{2-} were not distinctly located, so these solutes were ultimately not selected as tracers. In contrast, $\delta^{18}O$ was included as a tracer since it can distinguish between rain and snow and does not experience chemical or biological transformations. Thus, the four tracers selected were: Ca^{2+}, Mg^{2+}, ANC, and $\delta^{18}O$. When these tracers were applied in a PCA analysis to extract eigenvalues and eigenvectors from the correlation matrix of streamflow chemistry, the first two principal components explained 99% of the total variance of stream water chemistry. Potential end-members were orthogonally projected to the mixing U-space defined by stream water at Orodell (Figure 5a) where dashed lines represent the 25th and 75th percentile of solute concentrations for selected end-members. The end-members that were ultimately recognized as streamflow recharge sources at Orodell from 2009 to 2011 were: (1) snowmelt sampled from the subalpine zone near treeline, (2) rain water sampled from the subalpine zone, and (3) groundwater sampled from the upper montane zone (Table 4). Rain water was selected in lieu of soil water, despite a relatively longer Euclidean distance, given that the rain water samples clustered together in orthogonal space while the soil water samples did not (Figure 5a).

4.6 Validation of the EMMA results and hydrograph separation

The re-creation of tracer concentrations in stream water provides a quantitative assessment of model results and ensures that the results are physically meaningful (Liu et al., 2008). Tracer concentrations were re-created using the EMMA results and chemical compositions in end-members (Table 5). In general, the points had significant R^2 ($p < 0.05$) values higher than 0.97. Specifically, Mg^{2+} and $\delta^{18}O$ were always well predicted, Ca^{2+} was under-predicted at values above approximately 200 μeq L^{-1} with an overall slope of 0.65, and ANC was over-predicted at values above approximately 500 μeq L^{-1} with an overall slope of 1.40. Calculated annual source water contributions were not significantly different from the three year average. Overall, snowmelt from the subalpine zone near treeline contributed 54% (42-72%) of streamflow, groundwater from the upper montane zone contributed 24% (18-30%) of streamflow, and rain water from the subalpine zone contributed 22% (9-35%) of the annual streamflow at Orodell. Intraannually, contributions of snowmelt water dominated at peak flow, while contributions of groundwater increased during the recession limb of the hydrograph.

5. Discussion

Previous studies have investigated streamflow sources among headwater catchments in the Colorado Front Range (Liu et al., 2004; Williams et al., 2009; Cowie et al., 2017), but it remains unclear how or if these results and the EMMA method scale to larger order watersheds. In this study, we illustrate that annual mixing model results from representative headwater systems linearly scale to approximate downstream sources of water as determined by EMMA. Further, these results highlight the importance of subalpine ecosystems near treeline as “water towers” within mountain catchments (e.g. Viviroli et al., 2007).

5.1 Applying EMMA to a mesoscale watershed in complex terrain

Reconstruction of tracer concentrations (Table 5) showed that Mg^{2+} and $\delta^{18}O$ were well-predicted, while ANC was over-predicted and Ca^{2+} was under-predicted at higher concentrations. The under-prediction of Ca^{2+} could have resulted from the presence of carbonate dust (Clow et al., 2002); dry deposition can contribute a significant portion (44% in winter; Clow et al., 1997) to total atmospheric Ca^{2+} deposition in alpine ecosystems. Throughfall can also accumulate Ca^{2+} as it comes in contact with the leaves and branches of trees (de la Crétaz & Barten, 2007); however, the quantity of throughfall water was small relative to other end-members. Over-prediction of ANC suggests that there may have been additional acid input to the system sufficient to reduce ANC beyond the organic acids in the montane water source, or that statistical correlation ($R^2 = 0.92$) between Ca^{2+} and ANC may have confounded the attribution of model errors. The uncertainty of the snowmelt end-member was highest in 2011, potentially due to a long-duration snowmelt season compounding the inherent spatio-temporal variability of infiltrating snowmelt. For example, snowmelt at the beginning of the season may be more enriched than later in the snowmelt season, due to evaporation of light water isotopes in the snow accumulation period, and a longer transit time (Tetzlaff et al., 2015). Notwithstanding, Euclidean distances and tracer re-constructions in the context of our uncertainty and young water fraction analyses suggest that the tracer-based results were not obviously subject to deleterious effects from hydrodynamic mixing and/or molecular diffusion at this spatial scale (e.g. Jones et al., 2006; Park et al., 2011).

Previous work at the headwater catchment scale demonstrates that streamflow is comprised of decreasing snowmelt water but increasing groundwater and rainfall with decreasing elevation due to longer flow paths/contact times and a higher rain/snow precipitation ratio (Cowie et al., 2017). As a result, the degree to which source water contributions at Orodell can be recreated by scaling these headwater (representative of 71% of the watershed, as defined by elevation) contributions constrains the function and composition of the main stem relative to its nested headwaters (Figure 6). Given the land cover/ecosystem gradient with elevation, we tested this using area-weighted elevation ranges defined in Murphy et al. (2003) to delineate the Boulder Creek watershed into discrete ecosystems. The watershed was made up of 11.7% alpine tundra (above 3500 m), 47.2% subalpine (2700-3500 m), 27.3% montane (2400- 2700 m), and 13.8% foothills (1800-2400 m) ecosystems, and the results: 62% snowmelt, 25% groundwater, 11% rain, and 2% talus water were not statistically different than what was calculated using solute concentrations at Orodell and EMMA (Table 6). Similar results from the two methods indicate that source waters in small headwater catchments can be used to calculate the annual variability of source waters throughout the watershed, and that streamflow recharge processes can be accurately predicted from the aggregation of headwater systems as a result. This exercise also highlights the importance of nutrient cycling in headwater systems, as opposed to the relatively unreactive main stem.

5.2 Snowpack variability drives hydrological cycling within and among years

Hydrograph separation illustrates that montane groundwater was a significant source of streamflow to the main stem of Boulder Creek during the rising limb of the hydrograph (Figure 7). At the onset of the snowmelt season, however, solute concentrations decreased, indicative of snow's dilution effect on stream chemistry. Over the course of the year, solute concentrations increased again concurrently with groundwater (or baseflow) contributions. This seasonal shift in source waters was also reflected by the generally clockwise seasonal hysteretic behavior of various solutes

(Figure 3); recharge at Orodell followed a counter-clockwise loop, from rain, to groundwater, to snowmelt, and then back to rain water before returning to the starting point again (Figure 5). Streamflow from the alpine and subalpine catchments also showed a counter-clockwise hysteretic behavior, but streamflow from the montane zone was disorganized (Figure S1). We attribute this phenomenon to greater evapotranspiration and better soil development in the montane zone that make streamflow recharge more divergent and less easy to define. Similar hysteretic patterns and EMMA results suggest that streamflow recharge sources were similar amongst Orodell, GLV, and CC. This likely resulted from the dominance of alpine and subalpine landscapes within the larger watershed as well the overall trend toward greater precipitation and thus greater contributing volumes at higher elevations.

There was evidence of chemostatic behavior at flows greater than 10 $m^3 s^{-1}$ where solute concentrations remained relatively constant with respect to streamflow variations (Godsey et al., 2009). Although chemostatic behavior can result from different phenomena including cation exchange, changes in reactive mineral surface area, and decreased weathering rates (Clow & Drever, 1996), hydrograph separations imply that chemostatic behavior resulted from seasonal flushing of snowmelt during the rising and recession limbs (Figure 7), which has subsequent implications for the potential displacement of stored subsurface water (Barnhart et al., 2016). Orthogonal projections of end-members into U-space specifically reveal a trend toward increasing groundwater contributions to streamflow in 2010 (Figure 5, where stream water points migrated closer to groundwater end-member), which mainly occurred prior to snowmelt, and could represent additional infiltration of displaced pre-event subsurface water. With earlier and slower snowmelt, higher rain to snow ratios, and increasing air temperatures that may cause higher evapotranspiration rates especially during the spring (e.g. Berghuijs et al., 2014; Musselman et al., 2017; Cayan et al., 2013), the strength of linked snowmelt-groundwater contributions to streamflow suggested by this work may decrease non-linearly as a function of changing hydrological connectivity in the future.

5.3 The importance of subalpine ecosystems to the "mountains as water towers" framework

Interpretation of young water fractions within the context of the EMMA results allows for elevation-specific inferences about surface-subsurface hydrologic connectivity in this mesoscale watershed. For example, the variation in calculated young water fractions in stream water and the fraction of water contributed by snowmelt (EMMA) demonstrates that while the alpine streams receive the greatest amount of direct precipitation, snow accumulation and the resulting snowmelt flux is greatest in the subalpine just below tree line, due to wind redistribution of the snow down gradient (Figure 6b; Freudiger et al., 2017). Although snowmelt contributions include both surface runoff and subsurface flow, only the surface runoff portion can be accredited to the young water fraction, which results in snowmelt contributions greater than the calculated young water fractions. Young water has a transit time of 2.3 ± 0.8 months, while subsurface flow has a transit time of three or more months, spanning the snowmelt season. The higher young water fraction in the alpine zone suggests that a greater fraction of snowmelt is routed directly to the stream, as compared to in the subalpine. This is further supported by comparing the isotopic composition of various source waters (Coplen et al., 2000; Rodgers et al., 2005; Uhlenbrook & Hoeg, 2003).

Within the "mountains as water towers" framework (e.g. Viviroli et al., 2007), we can thus infer the relative functions of alpine (water is delivered faster) compared to subalpine (more water is delivered) areas from the combination of EMMA results and young water fractions. The predominance of snow precipitation, shallow soils, and subsurface fracture flow promote considerable origination of young water from alpine areas within the Orodell catchment. Conversely, the subalpine zone accumulates more snow precipitation than the other elevation zones, and since this region also has more developed soils, it functions as the primary water storage zone in the catchment. Previous work in the subalpine CC catchment showed that a significant amount of streamflow was this year's snowmelt that had infiltrated the subsurface and undergone subsequent biological and geochemical reactions (Williams et al., 2009). This was supported by the $\delta^{18}O{\sim}\delta^{2}H$ relationship that we observed in CC streamflow (samples located on the lower part of the LMWL; Figure 4b). Although the dominant role of snowmelt as a source of streamflow is well known (e.g. Li et al., 2017), these results add context to previous work at the headwater scale by showing the degree to which snowmelt water may be translated into shallow subsurface flow at a larger spatial scale.

6. Conclusion

Hydrochemical tracers including stable water isotopes are useful tools with which to understand flow paths and source water contributions to streamflow in the context of water resources and climate change. End-Member Mixing Analysis was applied to the mesoscale Boulder Creek Watershed at Orodell, which provides water resources to the Denver metropolitan area downstream. The four-tracer model showed that snowmelt from the subalpine zone contributed approximately half of streamflow and was the dominant streamflow recharge source, while groundwater contributions from the upper montane zone and rain water contributions from the subalpine zone together composed approximately the other half of streamflow. In spite of complex mountain terrain characterized by elevational gradients in geological features, precipitation amount, type, and redistribution, we were able to predict streamflow generation in the main stem of the watershed from measurements in headwater catchments representative of the constituent ecosystem types throughout the watershed. These results contribute to a better understanding of streamflow source waters in complex mountain terrain that may be used to broadly inform water resources management with respect to allocation practices in the presence of climate variability and/or change.

Acknowledgements

This research was partially sponsored by an NSF grant (DEB 1115068) to Patrick Bourgeron. The authors also wish to thank the Niwot Ridge LTER program, the Boulder Critical Zone Observatory, Holly Miller at the Kiowa/Arikaree Environmental Laboratory at the University of Colorado Boulder, Fengjing Liu for help with the EMMA analysis, and Leanne Lestak for GIS support.

References

Bales, R. C., Molotch, N. P., Painter, T. H., Dettinger, M. D., Rice, R., & Dozier, J. (2006). Mountain hydrology of the western United States. *Water Resources*

Research, *42*, W08432. https://doi.org/10.1029/2005WR004387

Baraer, M., McKenzie, J., Mark, B. G., Gordon, R., Bury, J., Condom, T., et al. (2015). Contribution of groundwater to the outflow from ungauged glacierized catchments: a multi-site study in the tropical Cordillera Blanca, Peru. *Hydrological Processes*, *29*(11), 2561–2581. https://doi.org/10.1002/hyp.10386

Barnhart, T. B., Molotch, N. P., Livneh, B., Harpold, A. A., Knowles, J. F., & Schneider, D. (2016). Snowmelt rate dictates streamflow. *Geophysical Research Letters*, *43*, 8006–8016. https://doi.org/10.1002/2016GL069690

Barthold, F. K., Tyralla, C., Schneider, K., Vaché, K. B., Frede, H.-G., & Breuer, L. (2011). How many tracers do we need for end member mixing analysis (EMMA)? A sensitivity analysis. *Water Resources Research*, *47*, W08519. https://doi.org/10.1029/2011WR010604

Barthold, F. K., Wu, J., Vaché, K. B., Schneider, K., Frede, H.-G., & Breuer, L. (2010). Identification of geographic runoff sources in a data sparse region: hydrological processes and the limitations of tracer-based approaches. *Hydrological Processes*, *24*, 2313–2327. https://doi.org/10.1002/hyp.7678

Berghuijs, W. R., Woods, R. A., & Hrachowitz, M. (2014). A precipitation shift from snow towards rain leads to a decrease in streamflow. *Nature Climate Change*, *4*, 583–586. https://doi.org/10.1038/nclimate2246

Cayan, D. R., Tyree, M., Kunkel, K. E., Castro, C., Gershunov, A., Barsugli, J., et al. (2013). Future Climate: Projected Average. In G. Garfin, A. Jardine, R. Merideth, M. Black, S. LeRoy (Eds.), *Assessment of Climate Change in the Southeast United States: A Report Prepared for the National Climate Assessment* (pp. 101–125). A report by the Southwest Climate Alliance. Washington, DC: Island Press.

Cecil, L. D., Hall, L. F., Benjamin, L., Knobel, L. L., & Green, J. R. (2005). Comparison of local meteoric water lines in southeastern Idaho, Western Wyoming, and South-Central Montana and the associated hydrologic implications. *Journal of the Idaho Academy of Science*, *41*(2), 13–28.

Clow, D. W., & Drever, J. I. (1996). Weathering rates as a function of flow through an alpine soil. *Chemical Geology*, *132*, 131–141. https://doi.org/10.1016/S0009-2541(96)00048-4

Clow, D. W., Ingersoll, G. P., Mast, M. A., Turk, J. T., & Campbell, D. H. (2002). Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: Implications for winter dry deposition. *Atmospheric Environment*, *36*, 2337–2348. https://doi.org/10.1016/S1352-2310(02)00181-4

Clow, D. W., Mast, M. A., Bullen, T. D., & Turk, J. T. (1997). Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado. *Water Resources Research*, *33*(6), 1335–1351. https://doi.org/10.1029/97WR00856

Cook, P. G., & Herczeg, A. L. (Eds.). (2000). *Environmental tracers in subsurface hydrology*. Boston, MA: Springer.

Coplen, T. B., Herczeg, A. L., & Barnes, C. (2000). Isotope Engineering-Using Stable Isotopes of the Water Molecule to Solve Practical Problems. In: P. G. Cook, A. L. Herczeg (Eds.), *Environmental tracers in subsurface hydrology* (pp.79–110). Boston, MA: Springer.

Cowie, R. M. (2014). *Surface water and groundwater interactions in natural and mining impacted mountain catchments* (Doctoral dissertation). Retrieved from Proquest Dissertations Publishing. (UMI Number: 3672393). Boulder, CO: University of Colorado Boulder

Cowie, R. M., Knowles, J. F., Dailey, K. R., Williams, M. W., Mills, T. J., & Molotch, N. P. (2017). Sources of streamflow along a headwater catchment elevational gradient. *Journal of Hydrology*, *549*, 163–178. https://doi.org/10.1016/j.jhydrol.2017.03.044

Craig, H. (1961). Isotopic variations in meteoric waters. *Science*, *133*(3465), 1702–1703. https://doi.org/10.1126/science.133.3465.1702

Cras, A., Marc, V., & Travi, Y. (2007). Hydrological behavior of sub-Mediterranean alpine headwater streams in a badlands environment. *Journal of Hydrology*, *339*(3-4): 130–144. https://doi.org/10.1016/j.jhydrol.2007.03.004

CZO Boulder. (2015). Boulder Creek Critical Zone Observatory. (http://criticalzone.org/boulder/infrastructure/field-areas-boulder/)

de la Crétaz, A. L., & Barten, P. K. (2007). *Land Use Effects on Streamflow and Water Quality in the Northeastern United States*. Boca Raton, FL: CRC Press.

DeWalle, D. R., Edwards, P. J., Swistock, B. R., Aravena, R., & Drimmie, R. J. (1997). Seasonal isotope hydrology of three Appalachian forest catchments. *Hydrological Processes*, *11*(15), 1895–1906. https://doi.org/10.1002/(SICI)1099-1085(199712)11:15<1895::AID-HYP538> 3.0.CO;2-#

Freudiger, D., Kohn, I., Seibert, J., Stahl, K., & Weiler, M. (2017). Snow redistribution for the hydrological modeling of alpine catchments. *Wiley Interdisciplinary Reviews-Water*, *4*(5), e1232. https://doi.org/10.1002/wat2.1232

Frisbee, M. D., Phillips, F. M., Campbell, A. R., Liu, J., & Sanchez, S. A. (2011). Streamflow generation in a large, alpine watershed in the southern Rocky Mountains of Colorado: Is streamflow generation simply the aggregation of hillslope runoff responses? *Water Resources Research*, *47*, W06512. https://doi.org/10.1029/2010WR009391

Frisbee, M. D., Phillips, F. M., White, A. F., Campbell, A. R., & Liu, F. (2013). Effect of source integration on the geochemical fluxes from springs. *Applied Geochemistry*, *28*, 32–54. https://doi.org/10.1016/j.apgeochem.2012.08.028

Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration-discharge relationships reflect chemostatic characteristics of US catchments. *Hydrological Processes*, *23*, 1844–1864. https://doi.org/10.1002/hyp.7315

Hinckley, E. S., Ebel, B. A., Barnes, R. T., Anderson, R. S., Williams, M. W., & Anderson, S. P. (2014). Aspect control of water movement on hillslopes near the rain-snow transition of the Colorado Front Range. *Hydrological Processes*, *28*, 74–85. https://doi.org/10.1002/hyp.9549

Hooper, R. P. (2003). Diagnostic tools for mixing models of stream water chemistry. *Water Resources Research*, *39*(3), 1055. https://doi.org/10.1029/2002WR001528

Hrachowitz, M., Benettin, P., van Breukelen, B. M., Fovet, O., Howden, N. J. K., Ruiz, L., et al. (2016). Transit times-the link between hydrology and water quality at the catchment scale. *Wiley Interdisciplinary Reviews-Water*, *3*, 629–657. https://doi.org/10.1002/wat2.1155

James, A. L., & Roulet, N. T. (2006). Investigating the applicability of end-member mixing analysis (EMMA) across scale: A study of eight small, nested catchments in a temperate forested watershed. *Water Resources Research*, *42*, W08434.

https://doi.org/10.1029/2005WR004419
Jasechko, S., Kirchner, J. W., Welker, J. M., & McDonnell, J. J. (2016). Substantial proportion of global streamflow less than three months old. *Nature Geoscience, 9*, 126–129. https://doi.org/10.1038/ngeo2636
Jin, L., Siegel, D. I., Lautz, L. K., & Lu, Z. (2012). Identifying streamflow sources during spring snowmelt using water chemistry and isotopic composition in semi-arid mountain streams. *Journal of Hydrology*, *470-471*, 289–301. https://doi.og/10.1016/j.jhydrol.2012.09.009
Jones, J. P., Sudicky, E. A., Brookfield, A. E., & Park, Y.-J. (2006). An assessment of the tracer-based approach to quantifying groundwater contributions to streamflow. *Water Resources Research, 42*, W02407. https://doi.org/10.1029/2005WR004130
Kinner, D. A. (2003). Delineation and characterization of the Boulder Creek Watershed and its sub-watersheds. In S. F. Murphy, P. L. Verplanck, L. B. Barber (Eds.), *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*. Water Resources Investigation Report 03-4045. Denver, CO: U.S. Geological Survey
Kirchner, J. W. (2016a). Aggregation in environmental systems – Part 1: Seasonal tracer cycles quantify young water fractions, but not mean transit times, in spatially heterogeneous catchments. *Hydrology and Earth System Sciences*, *20*, 279–297. https://doi.org/10.5194/hess-20-279-2016
Kirchner, J. W. (2016b). Aggregation in environmental systems – Part 2: Catchment mean transit times and young water fractions under hydrologic nonstationarity. *Hydrology and Earth System Sciences*, *20*, 299–328. https://doi.org/10.5194/hess-20-299-2016
Knowles, J. F., Harpold, A. A., Cowie, R., Zeliff, M., Barnard, H. R., Burns, et al. (2015). The relative contributions of alpine and subalpine ecosystems to the water balance of a mountainous, headwater catchment. *Hydrological Processes, 29*(22), 4794–4808. https://doi.org/10.1002/hyp.10526
Laudon, H., & Slaymaker, O. (1997). Hydrograph separation using stable isotopes, silica and electrical conductivity: an alpine example. *Journal of Hydrology*, *201*(1-4), 82–101. https://doi.org/10.1016/S0022-1694(97)00030-9

Li, D., Wrzesien, M. L., Durand, M., Adam, J., & Lettenmaier, D. P. (2017). How much runoff originates as snow in the western United States, and how will that change in the future? *Geophysical Research Letters*, *44*(12), 6163–6172. https://doi.org/10.1002/2017GL073551

Liu, F., Bales, R. C., Conklin, M. H., & Conrad, M. E. (2008). Streamflow generation from snowmelt in semi-arid, seasonally snow-covered, forested catchments, Valles Caldera, New Mexico. *Water Resources Research*, *44*(12), W12443. https://doi.org/10.1029/2007WR006728

Liu, F., Williams, M. W., & Caine, N. (2004). Source waters and flow paths in an alpine catchment, Colorado Front Range, United States. *Water Resources Research*, *40*(9), W09401. https://doi.org/10.1029/2004WR003076

Mankin, J. S., Viviroli, D., Singh, D., Hoekstra, A. Y., & Diffenbaugh, N. S. (2015). The potential for snow to supply human water demand in the present and future. *Environmental Research Letters*, *10*, 114016. https://doi.org/10.1088/1748-9326/10/11/114016

Maurya, A. S., Shah, M., Deshpande, R. D., Bhardwaj, R. M., Prasad, A., & Gupta, S. K. (2011). Hydrograph separation and precipitation source identification using stable water isotopes and conductivity: River Ganga at Himalayan foothills. *Hydrological Processes*, *25*(10), 1521–1530. https://doi.org/10.1002/hyp.7912

Miller, M. P., Buto, S. G., Susong, D. D., & Rumsey, C. A. (2016). The importance of base flow in sustaining surface water flow in the Upper Colorado River Basin. *Water Resources Research*, *52*, 3547–3562. https://doi.org/10.1002/2015WR017963

Murphy, S. F., Barber, L. B., Verplanck, P. L., & Kinner, D. A. (2003). Environmental setting and hydrology of the Boulder Creek Watershed, Colorado. In S. F. Murphy, P. L. Verplanck, L. B. Barber (Eds.), *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*. Water Resources Investigation Report 03-4045. Denver, CO: U.S. Geological Survey

Musselman, K. N., Clark, M. P., Liu, C., Ikeda, K., & Rasmussen, R. (2017). Slower snowmelt in a warmer world. *Nature Climate Change*, *7*, 214–220. https://doi.org/10.1038/NCLIMATE3225

NWT LTER. (2015). Niwot Ridge Long Term Ecological Research Program. (http://niwot.colorado.edu/data/landing/)

Park, Y.-J., Sudicky, E. A., Brookfield, A. E., & Jones, J. P. (2011). Hydrologic response of catchments to precipitation: Quantification of mechanical carriers and origins of water. *Water Resources Research*, *47*, W12515. https://doi.org/10.1029/2011WR010075

Robinson, Z. P., Fairchild, I. J., & Arrowsmith, C. (2009). Stable isotope tracers of shallow groundwater recharge dynamics and mixing within an Icelandic sandur, Skeiđarársandur. In D. Marks, R. Hock, M. Lehning, M. Hayashi, R. Gurney (Eds.), *Hydrology in Mountain Regions: Observations, Processes and Dynamics* (pp. 119–125). Perugia, Italy: International Association of Hydrological Sciences.

Rodgers, P., Soulsby, C., & Waldron, S. (2005). Stable isotope tracers as diagnostic tools in upscaling flow path understanding and residence time estimates in a mountainous mesoscale catchment. *Hydrological Processes*, *19*(11), 2291–2307. https://doi.org/10.1002/hyp.5677

St Amour, N. A., Gibson, J. J., Edwards, T. W. D., Prowse, T. D., & Pietroniro, A. (2005). Isotopic time-series partitioning of streamflow components in wetland-dominated catchments, lower Liard River basin, Northwest Territories, Canada. *Hydrological Processes*, *19*(17), 3357–3381. https://doi.org/10.1002/hyp.5975

Tetzlaff, D., Buttle, J., Carey, S. K., van Huijgevoort, M. H. J., Laudon, H., McNamara, J. P., et al. (2015). A preliminary assessment of water partitioning and ecohydrological coupling in northern headwaters using stable isotopes and conceptual runoff models. *Hydrological Processes*, *29*(25), 5153–5173. https://doi.org/10.1002/hyp.10515

Uchida, T., Asano, Y., Onda, Y., & Miyata, S. (2005). Are headwaters just the sum of hillslopes? *Hydrological Processes*, *19*, 3251–3261. https://doi.org/10.1002/hyp.6004

Uhlenbrook, S., & Hoeg, S. (2003). Quantifying uncertainties in tracer-based hydrograph separations: a case study for two-, three- and five-component hydrograph separations in a mountainous catchment. *Hydrological Processes*, *17*(2), 431–453. https://doi.org/10.1002/hyp.1134

Viviroli, D., Dürr, H. H., Messerli, B., Meybeck, M., & Weingartner, R. (2007). Mountains of the world, water towers for humanity: Typology, mapping, and global significance. *Water Resources Research*, *43*(7), W07447. https://doi.org/10.1029/2006WR005653

Williams, M. W., Barnes, R. T., Parman, J. N., Freppaz, M., & Hood, E. (2011). Stream Water Chemistry along an Elevational Gradient from the Continental Divide to the Foothills of the Rocky Mountains. *Vadose Zone Journal*, *10*, 900–914. https://doi.org/10.2136/vzj2010.0131

Williams, M. W., Knauf, M., Caine, N., Liu, F., & Verplanck, P. L. (2006). Geochemistry and source waters of rock glacier outflow, Colorado Front Range. *Permafrost and Periglacial Processes*, *17*, 13–33. https://doi.org/10.1002/ppp.535

Williams, M. W., Seibold, C., & Chowanski, K. (2009). Storage and release of solutes from a subalpine seasonal snowpack: soil and stream water response, Niwot Ridge, Colorado. *Biogeochemistry*, *95*, 77–94. https://doi.org/10.1007/s10533-009-9288-x

Table and Figure Captions

Table 1. Basic geographic and climatic characteristics of the constituent headwater catchments.

Table 2. Water samples collected from each sub-catchment (n represents the number of samples). Locations of the Martinelli, Saddle, Soddie, and Sugarloaf sites are shown in Figure 1. Abbreviations are Green Lakes Valley (GLV), Como Creek (CC), and Gordon Gulch (GG).

Table 3. Young water fractions (F_{yw}) in streamflow from headwater catchments to the watershed outlet. The amplitudes of $\delta^{18}O$ values are in per mil (‰) relative to Vienna

Standard Mean Ocean Water (VSMOW). Abbreviations are precipitation (P), streamflow (Q), and amplitude (Amp).

Table 4. End-member differences between U-space projections and their original values (medians). GW is groundwater, MART is Martinelli, and SDL is Saddle.

Table 5. Predicted versus measured concentrations for selected tracers of stream water at Orodell. Units are in µeq/L for solutes or ‰ for $\delta^{18}O$. Percent difference is the average difference between predicted and measured concentrations.

Table 6. Relative contributions and uncertainty (presented as a range of percent contributions as defined in Section 3.5) of each end-member to annual streamflow at Orodell (this study) and its headwater catchments (previous studies by Liu et al., 2004 and Cowie et al., 2017). MART is Martinelli, GLV is Green Lake 4, CC is Como Creek, GG is Gordon Gulch.

Figure 1. (a) Location map of headwater catchments and Orodell sampling sites in the upper Boulder Creek Watershed, (b) Green Lakes Valley (GLV), (c) Como Creek (CC), and (d) Upper (GGU) and Lower (GGL) Gordon Gulch. The relative location of the Boulder Creek Watershed in the Rocky Mountains, USA is provided in the panel (a) inset for reference. Locations of all sampling points are shown. Imagery for backdrop provided by ArcGIS, USDA FSA NAIP 2015 (Figure adapted from Cowie et al. 2017). See Table 2 for intra-catchment sampling information. Abbreviations are Martinelli (MART) and Green Lake 4 (GL4).

Figure 2. Time series of solute concentrations and streamflow. (a) shows selected cations and anions, (b) shows $\delta^{18}O$ values in stream water, and (c) shows daily specific streamflow at Orodell.

Figure 3. Solute concentrations in streamflow versus discharge at Orodell from 2009 to 2011. Red and blue lines denote the rising and falling limbs of the annual hydrograph, respectively.

Figure 4. Stable water isotopes in (a) precipitation and stream water samples from both headwater catchments and the main stem from 2009 to 2011. The solid line represents the GMWL, and the dashed blue line represents the LMWL, which is defined by the equation in blue. (b) is enlarged to show the behavior and variability of the stream water samples in (a).

Figure 5. Orthogonal projections of end-members into U-space defined by stream water chemistry at (a) Orodell as well as stream water in (b) 2009 (n=32), (c) 2010 (n=39), and (d) 2011 (n=17). The dashed lines represent the 25th and 75th percentiles. GW is groundwater and the SDL and MART labels correspond to the alpine Saddle and Martinelli wells.

Figure 6. (a) Conceptual diagram depicts the process by which headwater sources were scaled up to represent the hydrological constituents of the main stem of Boulder Creek at Orodell. (b) shows relative snow accumulation and young water fractions along the elevational gradient.

Figure 7. Hydrograph separations show the intra- and inter-annual variability of the source waters contributing to Boulder Creek discharge at Orodell from 2009 to 2011. In the top panel, line (a) represents the peak annual groundwater contribution, and line (b) represents the peak annual snowmelt contribution.

Figure S1. Orthogonal projections of end-members and headwater stream samples into U-space defined by stream water chemistry at Orodell during (a) 2009, (b) 2010, and (c) 2011.