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Research papers

Summer runoff generation in foothill catchments of the Colorado Front Range

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ABSTRACT

Climatic shifts, disturbances, and land-use change can alter hydrologic flowpaths, water quality, and water supply to downstream communities. Prior research investigating streamflow generation processes in mountainous areas has largely focused on high-elevation alpine and subalpine catchments; less is known about these processes in lower-elevation foothills and montane catchments. In these lower-elevation ecoregions, precipitation shifts seasonally from snow to rain, which can result in differing seasonal flowpaths. We analyzed stream water for electrical conductivity, SiO_2, Ca, Mg, Na, Cl, SO_4, K, and dissolved organic carbon on both a weekly and storm event basis from April to August 2018 in three small (<10 km^2) foothill catchments, and one larger (63.2 km^2) catchment extending from the foothills to the subalpine ecoregions, in the Colorado Front Range. Using two end-member hydrograph separations and concentration-runoff relationships, we inferred the dominant catchment-scale flowpaths of precipitation to the streams. We selected catchments with varying land use to investigate the relationship between these characteristics and hydrologic flowpaths. We observed that concentrations of lithogenic constituents generally increased and dissolved organic carbon decreased as seasonal runoff decreased in the three foothill catchments, reflecting a transition from shallow subsurface flowpaths to deeper subsurface flowpaths. Elevated SO_4 and Cl concentrations during low-flow periods in two of our catchments suggest that historical or current anthropogenic activities, such as mining, application of road salt, and/or near-stream septic systems, affect local stream and groundwater chemistry. In a foothill catchment with anthropogenic and geologic impervious surfaces, streamflow during storm responses was sourced from faster, surficial flowpaths compared to a less disturbed neighboring catchment, highlighting the influence of anthropogenic land-use on runoff generation. This study provides insight into the fundamental hydrology of foothill catchments and how they may function in the future with human development, precipitation shifts and disturbances.

1. Introduction

Understanding the paths by which water flows through a landscape (hydrologic flowpaths) is critical for the provisioning of fresh water for human use (Barnett et al., 2005; Berghuijs et al., 2014), maintaining ecosystem stability and functionality (Bunn and Arthington, 2002), and predicting how disturbances may impact both water quantity and water quality (Mirus et al., 2017; Murphy et al., 2018). Intermittent and ephemeral streams in lower elevation regions of mountains have been recognized as important vehicles for energy, water, material, and biota, as well as maintaining ecosystem health (Acuña et al., 2014; Buttle et al., 2012). Insight into hydrologic functioning in these areas is critical for understanding the impacts of climate and land use change on water supplies (Blöschl et al., 2019; Clow, 2010; Kampf and Lefsky, 2016; Leigh et al., 2016; Theobald and Romme, 2007). Within the Rocky Mountains of Colorado, USA, intermittent streams in foothill and montane ecoregions are understudied compared to perennial, snowmelt-dominated waterways in higher elevation regions (Cowie et al., 2017; Datry et al., 2014; Leigh et al., 2016).

Climatic change is predicted to affect the timing, magnitude and duration of active hydrologic flowpaths and streamflow generation processes in mountainous areas (Barnett et al., 2008; Diffenbaugh et al., 2005; Foks et al., 2018; Hinckley et al., 2014; Kampf and Lefsky, 2016) by accelerating atmospheric warming (Pepin et al., 2015; Rangwala and

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Miller, 2012), increasing the elevations of rain-snow transition points (Abatzoglou, 2011; Knowles et al., 2006; Stewart et al., 2005), and increasing rainfall intensity (Prein et al., 2017). Recent work in Colorado has shown that the dominant source of annual peak discharge is shifting from snowmelt to rainfall (Kampf and Lefsky, 2016). Increases in the rain-to-snow ratio (Knowles et al., 2006) will result in rain events contributing proportionally more to annual stream discharge. This shift from snowmelt to rainfall warrants an improved understanding of how water is delivered to streams during summer rain events, especially in lower elevation catchments.

In addition to climate change impacts, anthropogenic activities common to lower elevation catchments can alter hydrologic processes. The foothill and montane ecoregions in the western United States (US) commonly overlap with the wildland-urban interface (WUI)—the intersection of human development and wildlands—which is expected to double in land area by 2030 (Theobald and Romme, 2007). In this region, hydrologic flowpaths and runoff are altered by replacing vegetated areas with impermeable surfaces, leading to decreased infiltration capacity and increased surface runoff volumes during precipitation events (Bernhardt and Palmer, 2007; Gremillion et al., 2000; Pickett et al., 2011; Shuster et al., 2005). In addition, expansion of the WUI will likely increase wildfire frequency in the future (Balch et al., 2017) resulting in additional impacts to water quality, supply and treatment as well as runoff generation processes (Ice et al., 2004; Scott et al., 2013). In much of the western US, historical hard-rock mining has left legacy waste and underground workings that can degrade water quality (Coulthard and Macklin, 2003; Nordstrom, 2011; Rösner, 1998; Singer et al., 2008), especially when combined with vegetation removal by wildfires (Murphy et al., 2020).

Understanding how hydrologic flowpaths change across different time scales within foothill and montane catchments can improve our ability to predict how land use, disturbances, and climatic changes will affect water resources. The relationship between constituent (solute) concentrations (C) and runoff (R) provide insight into the magnitude and timing of hydrologic flowpaths contributing to streamflow across a range of flow regimes (Chorover et al., 2017; Evans and Davies, 1998; Godsey et al., 2009; Johnson et al., 1969; Murphy et al., 2018; Musolff et al., 2015; Rose et al., 2018; Stallard and Murphy, 2014). During low-flow conditions, lithogenic constituents associated with bedrock weathering and deeper subsurface flowpaths (e.g., SiO_2, Ca, Mg, Na and K) typically become enriched in the stream, whereas bioactive constituents associated with shallow subsurface flowpaths (e.g., dissolved organic carbon (DOC)) typically decrease (Chorover et al., 2017; Evans and Davies, 1998; Godsey et al., 2009; Rose et al., 2018). In turn, the spatiotemporal aspects of hydrologic flowpaths contributing to the stream can be inferred from stream chemistry (Dalzell et al., 2007; Murphy et al., 2018). In addition to C/R relationships, insight into streamflow generation processes can be gained from hydrometric and hydrograph separation methods using simple end-member mixing approaches (Birch et al., 2016; Buttle, 1994; Hooper and Shoemaker, 1986; Klaus and McDonnell, 2013; Martínez-Santos et al., 2014; Sklash et al., 1979).

The overarching goal of this study is to advance our limited knowledge of how lower elevation, mountainous catchments function in the semi-arid Colorado Front Range. Our approach examines catchments with and without anthropogenic impacts, such as mining and low-density housing, as well as catchments that vary in the proportion of annual precipitation inputs (i.e., snow vs. rain). Given that these ecoregions are experiencing trends towards greater rainfall contributions to peak flows (Kampf and Lefsky, 2016), we conducted our study in the summer to investigate rain-driven processes. We address the following research questions: what are the dominant flowpaths in lower elevation catchments with varying land use during summer storm events as inferred by hydrometrics and stream chemistry, and how do hydrologic flowpaths in these catchments change from early to late summer? We address these questions by performing hydrograph separations, investigating stream chemistry and runoff behavior during storm events, and analyzing the relationship between constituent concentrations and runoff.

2. Study area

We conducted our study in the Boulder Creek Watershed (1,160 km^2) located in the Colorado Front Range (Fig. 1). The watershed spans an elevation gradient from 1,480 to 4,120 m and can be divided into five major climatic zones/ecoregions: plains (1,450–1,800 m), foothill (1800–2400 m), montane (2400–2700 m), subalpine (2700–3500 m), and alpine (3500–4200 m) (Murphy, 2006). Excluding the plains ecoregion, which is downstream of our study area, the foothill and montane ecoregions comprise 58% of the watershed, and the subalpine and alpine regions comprise 42%. The foothill regions are underlain by Precambrian, metamorphic and granitic bedrock, predominately gneiss and schist; the subalpine regions contain those rock types and also minimal Tertiary volcanics and Quaternary alluvium deposits (see figure in Murphy, 2006, p. 4). Summer (mid-June through mid-September) precipitation is characterized by convective thunderstorms with substantial spatial variation in rainfall. The majority of precipitation in the subalpine and alpine regions is delivered as snow in the winter and spring, while in the montane and foothills ecoregions annual precipitation is ~ 30–60% snow, 25–40% rain and 15–30% mixed snow and rain (that is, air temperature crossed 2 °C during the event) (Cowie, 2010). Lower elevations in the Boulder Creek watershed receive a greater percentage of precipitation in April-September than do higher elevations (e.g., the plains receive about 65% of precipitation during that time, compared to the subalpine receiving about 53% during that time; Murphy et al., 2015, Table S5). Highest runoff in Boulder Creek typically occurs from April-June from snowmelt and mixed rain/snow events, and annual low flow occurs from September to March (Murphy, 2006).

We compared three catchments in the foothill and lower montane ecoregions of the watershed: Keystone Gulch, Hawkin Gulch and Lost Gulch (Fig. 1). These foothill catchments are small (3.6–5.3 km^2), north-flowing, steep (38.4–44.6% slope), and are 94.0–98.7% forested (Table 1). Satellite imagery of these catchments and visual identification shows that exposed rock outcrops of granodiorite are common. South- and west-facing slopes with more sun exposure are dominated by ponderosa pine (*Pinus ponderosa*) with interspersed Rocky Mountain juniper (*Juniperus scopulorum*), while north- and east-facing slopes are typically dominated by more shade-tolerant Rocky Mountain Douglas-fir (*Pseudotsuga menziesii* var. *glauca*) and Colorado blue spruce (*Picea pungens*) with few aspen (*Populus tremuloides*) (Kaufmann et al., 2006). Most of Hawkin Gulch and upper portions of Keystone Gulch are Boulder County-designated environmental conservation areas. Keystone Gulch has considerably more anthropogenic impacts than Hawkin or Lost Gulch, including low-density housing and a low-intensity trafficked paved road that extends the entire elevation range of the catchment. Keystone Gulch also contains 38 historical underground hard-rock mines, which are primarily located within a 3-km^2 radius and have tunnels that are typically <100 m long (Lovering and Goddard, 1950).

We compared the three foothills catchments to the larger (63.2 km^2) Fourmile Creek catchment, which extends from the foothills to subalpine ecosystems, to investigate the impact of prolonged snowmelt on stream chemistry and hydrologic flowpaths (Table 1). Climate in the lower portion of the Fourmile Creek catchment is similar to the foothills catchments (mean annual precipitation 500–600 mm; Murphy et al., 2015), but due to higher winter precipitation in in the headwaters, Fourmile Creek receives greater contributions from snowmelt. Land use is similar to Keystone Gulch, with roads, low-density housing, and underground mines, though the mines are more spatially extensive (Lovering and Goddard, 1950).

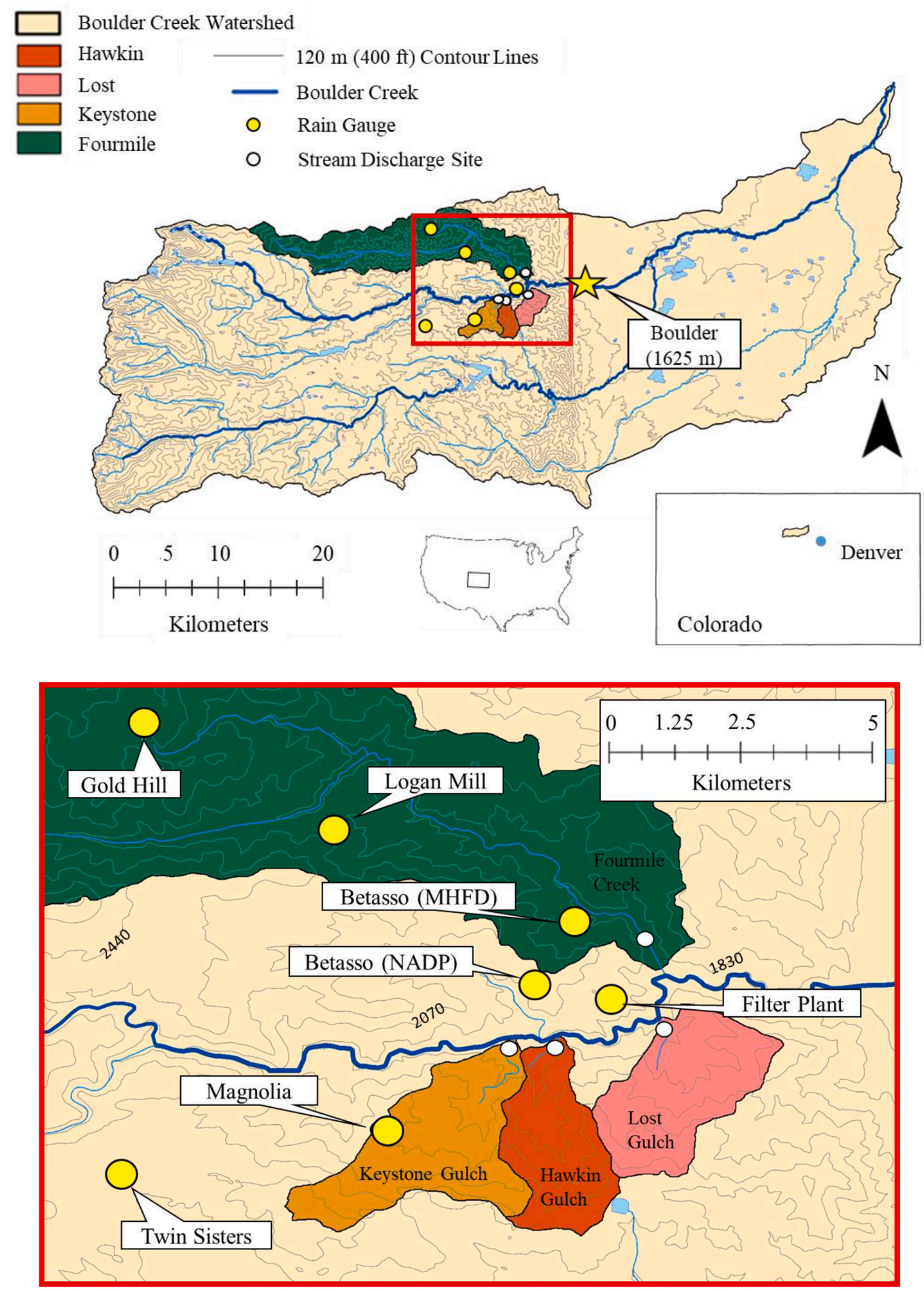

Fig. 1. Map of the Boulder Creek Watershed showing locations of each study catchment, locations of the Mile High Flood District rain gauges (Gold Hill, Logan Mill, Betasso, Filter Plant, Magnolia and Twin Sisters) as well as the National Atmospheric Deposition Precipitation site at Betasso.

3. Data collection and methods

3.1. Precipitation data and sampling

Local incremental rainfall data (from 1.0 mm tipping bucket rain gauges) were obtained from the Mile High Flood District (MHFD, 2019). The MHFD Magnolia site is the closest site to the foothill catchments and was primarily used to estimate rainfall in those catchments, and both the MHFD Betasso and Logan Mill sites were evaluated for Fourmile Creek (Fig. 1). Daily precipitation totals and maximum 30-min rainfall intensities (I_{30}) were calculated at all sites. We used I_{30} because in mountainous terrain in this region, most of the 1-hour rainfall falls in the first 30 min (Moody and Martin, 2001) and this metric has been used in evaluating flow response in this region (Murphy et al., 2015, 2018). Maximum I_{30} is calculated by summing tipping bucket rainfall data within a 30-minute period and doubling the value to obtain units of mm/hr (Moody and Martin, 2001).

We used data from the Betasso National Atmospheric Deposition Program (NADP) site for concentrations of Ca and Mg in precipitation (NADP, 2019; see Fig. 1 for location). At this site in an open canopy, we deployed a sequential sampler to measure rainfall and collect multiple precipitation samples during storms, but it malfunctioned. Subsequently, we collected bulk precipitation samples for electrical conductivity (EC) analysis at this site. The bulk precipitation sampler was washed using ultra-pure deionized water (DI water) three times before each sample collection.

3.2. Stream discharge and electrical conductivity

Continuous stream stage data were obtained at all sites except Lost

Table 1
Site characteristics and summary of water samples collected at each site in the study area. Site characteristics were derived from the U.S. Geological Survey program StreamStats (USGS, 2020) and a 10-m digital elevation model with ArcGIS.

	Hawkin Gulch	Lost Gulch	Keystone Gulch	Fourmile Creek
Area (km^2)	3.6	4.5	5.3	63.2
Avg. Elevation (m)	2158	2061	2240	2435
Min. Elevation (m)	1817	1768	1838	1746
Max. Elevation (m)	2457	2371	2633	3515
Ecoregion Type	foothills (96%) montane (4%)	foothills (100%)	foothills (78%) montane (22%)	foothills (45%) montane (36%) subalpine (19%)
Avg. Basin Slope	44.6	41.3	38.4	36.8
% Forest Cover	98.7	94	96.2	65.9
Avg. Annual Precip. (mm)	540	534	542	552 (up to 1000 in subalpine region)
Dominant Geology	Granodiorite	Granodiorite	Granodiorite	Granodiorite and some volcanics
Presence of Historical Mines	No	No	Yes	Yes
Presence of Roads and Houses	Few	Few	Yes	Yes
Grab Samples	20	20	18	30
Storm Samples	11	0	26	17
Total Samples	31	20	44	47
Date Flow Ended	7/24/2018	7/4/2018	7/12/2018	Perennial
Other notes	–	–	–	23% area burned in 2010

Gulch. For Keystone and Hawkin Gulch, we recorded stage every 5 min with a calibrated, submerged pressure transducer (model-CS451) and a CR1000 data logger (Campbell Scientific, Inc., Logan, UT, USA), measured discharge weekly using a flow meter (AquaCalc Pro, JBS Instruments, Columbus, OH, USA), and calculated a stage-discharge relationship. Fourmile Creek discharge data (5-min interval) were retrieved from the U.S. Geological Survey (USGS) stream-gaging station Fourmile Creek at Orodell, CO (06727500), located approximately 100 m upstream of its confluence with Boulder Creek (U.S. Geological Survey (USGS), 2019; see Fig. 1 for location). We did not install a pressure transducer at Lost Gulch due to resource constraints, but measured discharge when samples were collected. At all catchments, runoff (mm/hr) was calculated by dividing stream discharge by drainage area.

Temperature-corrected EC was recorded every 5 min using laboratory-calibrated conductivity loggers (model-U24-001, Onset Computer Corporation, Bourne, MA, USA) at all sites. To account for instrument data drift, we calibrated EC data to weekly measurements collected with a laboratory-calibrated, hand-held EC meter (model-2052, Amber Science Inc., Eugene, Oregon, USA). An instrument malfunction at Fourmile Creek resulted in the loss of 5-min EC data from that catchment. Additionally, we measured EC in every water sample and selected 3–6 samples per sampled storm event for complete water chemistry analysis based on variations in discharge and EC.

3.3. Water sampling

Stream samples were collected as grab samples at all sites across the season from April 18 to August 1 (Table 1) approximately every week (less in April and early May), or until the streams stopped flowing. We refer to “seasonal” changes throughout this paper to reflect this period of April 18 to August 1. Additional grab samples were collected before and after (typically within 24 hr before the start, and 24 hr after the end) storm events. During storm events, samples were collected at Keystone Gulch, Hawkin Gulch and Fourmile Creek using automatic samplers (model-6712, Teledyne ISCO, Lincoln, NE, USA) on a 15-min or 30-min interval, depending on storm forecast. Automatic samplers were programmed to begin sampling based on rising stream stage compared to current stage, previous stage behavior and future storm forecast. During some storm events, increases in stage were not large enough to activate the automatic samplers. Storm samples were not collected at Lost Gulch.

3.4. Laboratory analysis

We preserved water samples following standard techniques of cooling, filtering, and acidifying samples for laboratory analysis (McCleskey et al., 2012). Stream water samples were analyzed for major cations and anions, DOC, metals (Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Sr, U, V, W, Zn), EC, and pH. Precipitation samples were analyzed for EC. Refer to the SI for details on laboratory analytical methods, precision and accuracy (Table S1). All stream chemistry data are available from the Boulder Creek Critical Zone Observatory database (http://www.hydroshare.org).

3.5. Concentration-runoff relationships

To investigate how hydrologic flowpaths change from early to late summer, we developed linear regressions between concentration-runoff (C/R) at each site. For each site, C/R relationships for EC, SiO_2, Ca, Mg, Na, Cl, SO_4, DOC, and K were fitted using both grab and storm water samples combined with the formula:

$$log(C) = a + b^{*}(log(R)) \tag{1}$$

where a is the slope intercept, b is the slope, R is runoff (mm/hr), and C is a predicted constituent concentration expressed in mg/l. A negative slope ($b < 0$) indicates constituent dilution where the concentrations decrease with increased discharge, while a positive slope ($b > 0$) indicates enrichment where the concentrations increase with increased discharge (Godsey et al., 2009). All data analyses was run in the “R” statistical package (R Core Team, 2018).

3.6. Hydrograph separation

To infer dominant hydrologic flowpaths during storm events, we used a one-tracer, two end-member mixing model to perform hydrograph separations in Keystone Gulch and Hawkin Gulch, two adjacent catchments which are similar in elevation and precipitation but differ in anthropogenic impacts. For a two end-member system, the hydrograph separation is calculated as:

$$\text{Event Water Fraction} = \frac{(\text{Tracer}_{\text{mix}} - \text{Tracer}_{\text{pre-event}})}{(\text{Tracer}_{\text{event}} - \text{Tracer}_{\text{pre-event}})} \tag{2}$$

$$\text{Pre-event Fraction} = (1 - \text{Event Water Fraction}) \tag{3}$$

where pre-event water (baseflow) and event water (precipitation) are end-members and EC or constituents (Ca or Mg) are a tracer. Several conditions and assumptions must be met to perform the two end-member hydrograph separation: 1. Only two components are contributing to stormflow during the event (baseflow and event water); 2. Tracer values of each component are significantly different and remain constant during the event, or changes are known; and 3. Streamwater is completely mixed and there is minimal evaporation (Klaus and McDonnell, 2013; Wels et al., 1991). After confirming that the tracer values of each component are significantly different and assuming conditions (2) and (3) were met, we separated storm hydrographs into event water and pre-event water contributions using EC as a tracer.

While EC is frequently used as a tracer in hydrograph separation studies, it does not always behave conservatively in the environment (Laudon and Slaymaker, 1997), so we assessed its suitability as a conservative tracer by comparing hydrograph separation results derived using EC as a tracer to those derived using Ca and Mg as tracers. Because EC is largely controlled by major constituents such as Ca and Mg, hydrograph separations based on either EC, Ca, or Mg should yield similar results. Through a quantitative comparison using linear regression, we assumed that a high R^2 and near one-to-one slope between EC and primarily bedrock-derived solutes with minimal biological activity (Mg, Ca) would indicate the suitability of EC as a conservative tracer. If these conditions were met, hydrograph separation results were obtained using EC as a tracer due to the comparatively higher temporal resolution of collection in comparison to grab sampling for Ca and Mg. To estimate error in these hydrograph separations, results from two end-member hydrograph separations using EC, Ca, and Mg as tracers were compared (Fig. S3 and Table S2). We primarily used hydrograph separation results using EC as a tracer in the results and discussion.

We also evaluated error in the EC value of precipitation used for hydrograph separations. The sequential precipitation sampler malfunctioned during some storm events, and thus EC values for precipitation during individual storms were not available. In addition to comparing EC-derived hydrograph separations to those derived from Mg and Ca values, three different hydrograph separations for each storm event were calculated using the average EC value ±two standard deviations (18.2 μS/cm, 20.8 μS/cm, and 15.6 μS/cm, respectively) of all precipitation samples collected to investigate if the mean (18.2 μS/cm) is a representative precipitation EC tracer value. Using ±two standard deviations as the event EC tracer value minimally changed the results of component contributions (<2%) and 18.2 μS/cm was exclusively used as the tracer value for event water in final hydrograph separation analysis.

Uncertainty estimates for the final mixing model results utilizing EC as a tracer were obtained following the methodology derived by Genereux (1998). Following this method, the standard deviation of streamflow EC measurements 48 h prior to the start of each event, the standard deviation of EC in precipitation, and the manufacturer's reported instrument error were propagated to estimate uncertainty for each individual sample's mixing model calculation. These uncertainty estimates were then characterized by the mean, median, and range of uncertainty estimates for the event and pre-event fractions calculated using Eqs. (2) and (3).

4. Results

4.1. Precipitation

During the 2018 water year (October 1, 2017 to September 30, 2018), 57% of annual precipitation fell from April through July near our field catchments at the Betasso NADP site (Fig. 1), with the highest monthly precipitation totals occurring in May (129 mm) and June (60 mm) (Fig. S1). In May and June, there were ten storms with > 10 mm precipitation, with the two largest events occurring on June 18 (27 mm) and May 2 (24 mm). A prolonged dry period occurred from June 20 to July 15, when <7 mm of precipitation fell in 24 days. Similar to previous studies in this area, we observed substantial spatial variation in rainfall during summer convective storms (Murphy et al., 2015) (Table S3). For example, on June 18, all gages recorded > 20 mm except two sites within the Fourmile Creek catchment (Logan Mill and Gold Hill) which recorded < 4 mm.

4.2. Stream runoff

Runoff in all the catchments varied by several orders of magnitude during the study period, with runoff generally decreasing from mid-May to August (Fig. 2). Runoff values from the foothill catchments were similar to each other throughout the season (ranging from 0.0005 mm/hr to 0.08 mm/hr) and were lower than runoff of Fourmile Creek. Keystone, Hawkin and Lost Gulch had intermittent flow which ceased on July 12, July 24, and July 4, respectively, and did not flow again, except intermittently in response to storms, during the study period.

Runoff increased in response to storm events in all catchments. The largest storm of the season (June 18) caused runoff to peak at 0.08 mm/hr and 0.03 mm/hr at Keystone Gulch and Hawkin Gulch, respectively (Fig. 2). Seasonal peak runoff at Fourmile Creek (0.14 mm/hr) occurred in response to an early season storm on May 18.

4.3. Seasonal times series of electrical conductivity and constituents

4.3.1. Electrical conductivity

EC was related to runoff and responded to storm events in all study catchments, but the response differed among the catchments (Fig. 2). In general, EC was inversely related to runoff across the season, being lowest in mid-May during high runoff and highest in July during low runoff. EC values in the three foothill catchments were similar to each other throughout the season (range: 126–403 μS/cm, mean: 267 μS/cm± 62 SD), but EC was typically lower in Fourmile Creek (range: 144–285 μS/cm) during the first half of the study period, which coincided with snowmelt in the headwaters of Fourmile Creek. Natural Resources Conservation Service records indicated snowmelt in upper Fourmile Creek began on approximately May 4, and was snow-free by May 23 (United States Department of Agriculture (USDA) National Resources Conservation Service (NRCS), 2019). Fourmile Creek EC increased from 187 μS/cm on June 15 to 305 μS/cm on July 4, approaching values of the foothill catchments. After early July, EC at Fourmile Creek increased similarly to EC at the foothill catchments for the rest of the season (Fig. 2). During storms, EC of Hawkin Gulch always decreased, but EC in Fourmile Creek increased above pre-storm values. EC at Keystone Gulch decreased during all storms except during the storm runoff response on May 22, in which EC increased above pre-storm EC levels.

4.3.2. Major cations, anions and silica

We observed seasonal variations in lithogenic constituent (SiO_2, Ca, Cl, Mg, Na, SO_4, and K) concentrations, with the lowest concentrations during the spring runoff period (May) and the highest concentrations in June and July during low flow (Fig. 2). The three foothill catchments had similar concentrations of SiO_2, Ca, Mg, and K, but Keystone Gulch had higher concentrations of Cl and Na. Fourmile Creek usually had lower concentrations of most lithogenic constituents than the foothill catchments during spring runoff, but similar or higher concentrations during the low-flow period of late June and July (Fig. 2). In comparison to the foothill catchments, Fourmile Creek always had lower SiO_2 concentrations, and higher SO_4 concentrations. Concentrations of Cl and Na in Keystone Gulch (7.2–21.2 mg/l Cl, 6.6–12.5 mg/l Na) were more similar to Fourmile Creek (4.1–30.6 mg/l Cl, 6.1–12.5 mg/l Na) than to the other foothill catchments (2.2–11.3 mg/l Cl, 5.0–8.8 mg/l Na). At all sites, NO_3 concentrations were typically below detection limit (105 out of 158 samples were < 0.01 mg/l) with a maximum value of 2.2 mg/l.

4.3.3. Dissolved organic carbon

Keystone Gulch generally had the highest DOC concentrations (3.6–14.0 mg/l, median: 7.2 mg/l ± 2.1 SD) of all the study sites, while Fourmile Creek had the lowest concentrations (2.5–7.0 mg/l, median:

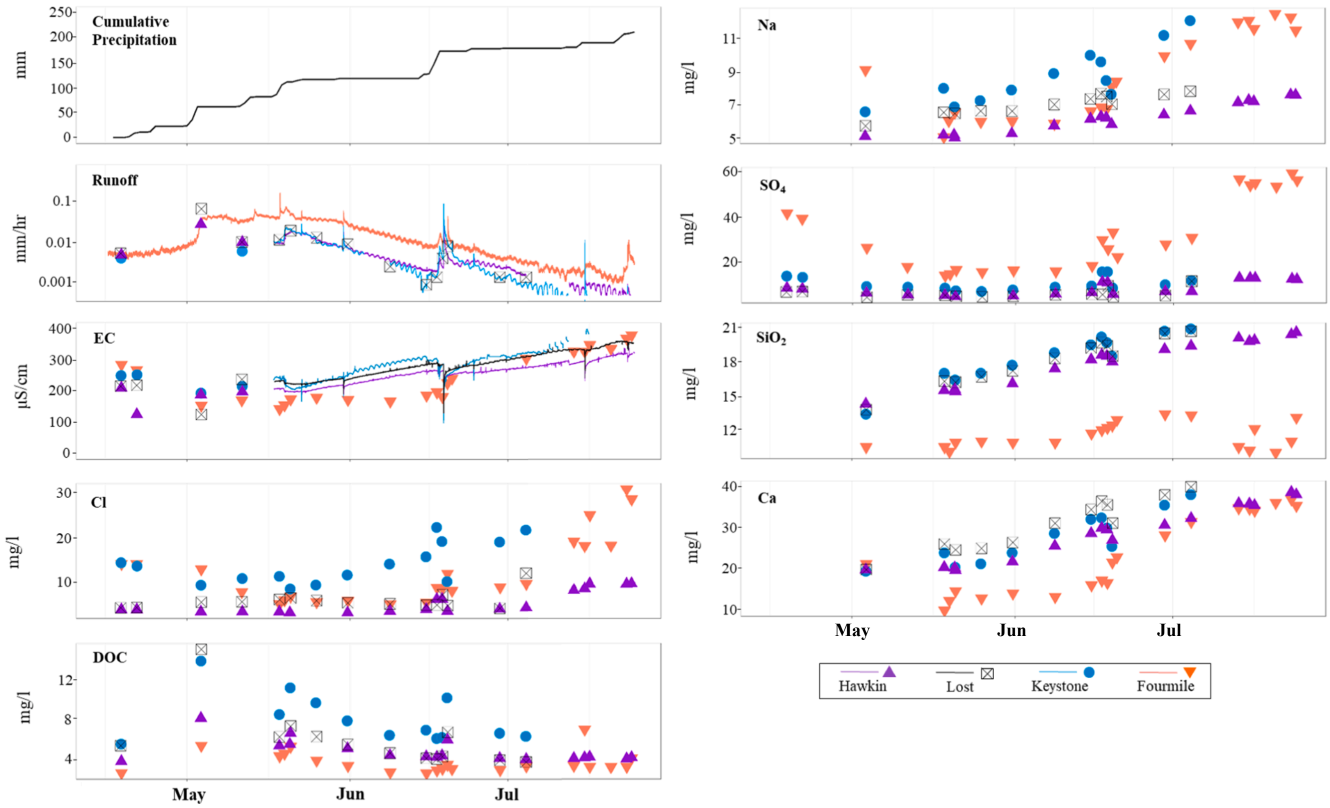

Fig. 2. Times series of weekly grab samples from April 18 to August 1. Concentrations/values of precipitation (mm), runoff (mm/hr), EC, Cl, DOC, Na, SO_4, SiO_2, and Ca at all sites. Cumulative precipitation data (mm) is from the Mile High Flood District Magnolia precipitation site, the closest site to the headwaters of the foothill catchments (see Fig. 1 for locations). Mg and K concentrations are not shown but have similar concentration behavior to Ca. The approximate end of snowmelt is mid- to late-May at the foothill catchments and early- to mid-June for Fourmile Creek. All EC units are µS/cm, all constituents are in mg/l. Runoff values < 0.0005 mm/hr (only observed in Keystone Gulch and Hawkin Gulch) are not plotted.

3.3 mg/l ± 1.3 SD) (Figs. 2 and 3). Hawkin Gulch and Lost Gulch usually had similar DOC concentrations throughout the season (1.9–8.1 mg/l, median: 4.2 mg/l ± 2.1 SD). Seasonal variations in DOC were similar across all sites and DOC concentrations were highest in the high runoff period (early May to June). During the low runoff period (June to August), DOC concentrations generally remained constant at each catchment (~6.5 mg/l at Keystone Gulch and ~3.5 mg/l at the other sites).

4.3.4. Metals

Metal concentrations in all watersheds were generally low; concentrations of As, Be, Cd, Co, Cr, Mo, Ni, P, Pb, Sb, Se, and W were nearly always below detection limits. At all sites, concentrations of Fe ranged from < 0.002 mg/l (below detection limit) to 0.07 mg/l. In the foothill catchments, Fe concentrations were highest in Keystone Gulch (mean concentration = 0.021 mg/l) and lowest in Hawkin Gulch (mean concentration = 0.006 mg/l). Across all sites, concentrations of Zn were typically low and ranged from < 0.001 to 0.08 mg/l. Mn concentrations at Fourmile Creek and Keystone Gulch were always higher (ranged from < 0.001 to 0.132 mg/l) than in Lost Gulch and Hawkin Gulch (ranged from < 0.001 mg/l to 0.002 mg/l).

4.4. Concentration-runoff relationships

C/R relationships were strong ($R^2 > 0.50$, $p < 0.01$) for Ca, Mg, Na, Cl, and SO_4 in all catchments, except for Cl and SO_4 in Lost Gulch (Fig. 3, Table 2). Log SiO_2/R relationships were strong in Hawkin and Lost Gulch ($R^2 > 0.65$, $p < 0.01$) but weaker in Keystone Gulch and Fourmile Creek ($R^2 < 0.35$, $p < 0.01$). Relationships between runoff and K or DOC were generally weaker and more variable (Table 2).

C/R relationships exhibited different slope characteristics among constituents (Fig. 3, Table 2). At all catchments, the relationships between runoff and EC, SiO_2, Ca, Mg, Na, Cl, SO_4 and K concentrations had negative slopes (except for Cl at Lost Gulch). DOC/R exhibited positive slopes at all catchments except at Keystone Gulch, where the slope was approximately zero (Fig. 3).

4.5. Storm event response and hydrograph separations at the foothill catchments

Streamflow dynamics during storm events differed between the Keystone and Hawkin Gulch catchments. Across the five sampled storm events, total precipitation ranged from 3 to 38 mm. Maximum I_{30} ranged from 3 to 33 mm/hr; during a storm on June 18, gages in all catchments recorded an $I_{30} > 15$ mm/hr. During three of four sampled storm events, Keystone Gulch exhibited a rapid runoff response to rainfall with a rapid (10 to 30 min) time-to-peak and a subsequent steep recession, while Hawkin Gulch exhibited a longer (45–65 min) response (Table 3, Figs. 4 and 5). During the low-intensity storm event on June 17 (max. I_{30}: 6 mm/hr), however, Keystone Gulch and Hawkin Gulch both had very small and slow runoff responses. During all storms, Keystone Gulch had higher runoff peaks than Hawkin Gulch (Table 3). For example, during the largest storm of the season on June 18 (Fig. 2), runoff rates at Keystone Gulch and Hawkin Gulch peaked at 0.08 mm/hr and 0.03 mm/hr, respectively (Fig. 4).

Concentrations of SiO_2, Ca, Cl and SO_4 in Hawkin and Keystone Gulch generally decreased during storm events. The greatest decrease occurred on June 18; within ten minutes, concentrations of SiO_2, Ca, Cl and SO_4 decreased 60 to 80% in Keystone Gulch and 15–30% in Hawkin Gulch (Fig. 4). Concentrations of DOC peaked on the falling limb at 12.7

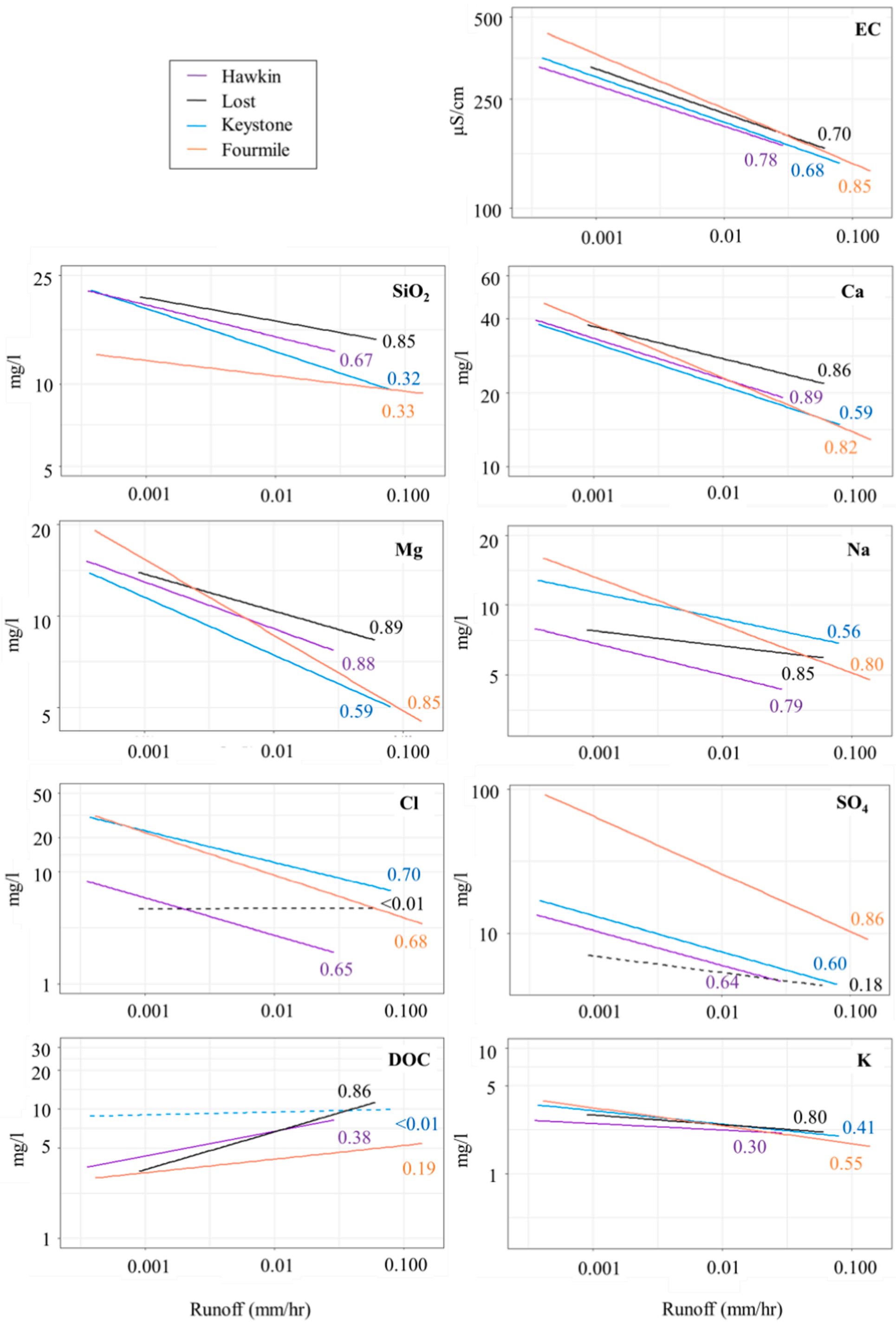

Fig. 3. C/R relationships (log transformed) for EC, SiO_2, Ca, Mg, Na, Cl, SO_4, DOC, and K at all catchments using all storm and grab samples with R^2 values displayed. All C/R relationships have p-values < 0.01, except where the dashed lines indicate p-values > 0.05.

mg/l in Keystone Gulch and 16.6 mg/l in Hawkin Gulch. Lithogenic constituent concentrations increased with increased runoff during the storm events on May 22 (Fig. S2) at Keystone Gulch.

For all storm events, Hawkin Gulch's runoff response to rainfall was dominated by pre-event water contributions (event water estimates < 50%; Table 3). In contrast, event water estimates at Keystone Gulch peaked above 50% during three out of the four storm events and ranged from 21% on June 17 to 70% during the largest runoff event of the season on June 18 (Fig. 5); and the timing of peak event water generally coincided with peak runoff. This large dilution on June 18 coincided with the highest event water fraction (70%) calculated at Keystone Gulch. During this storm, peak DOC at Keystone Gulch occurred 80 min after peak event water contributions to streamflow, while in Hawkin Gulch, DOC concentrations peaked 30 min after peak event water contributions. Keystone Gulch had much higher DOC concentrations (20.7 mg/l) in response to the storm on July 15 than during the larger June 18 storm (12.7 mg/l); this may be related to Keystone Gulch being completely dry before the July 15 storm.

Calculated event water estimates using Ca and Mg as tracers are similar to using EC as a tracer (for Ca and Mg, linear regression R^2 is 0.97

Table 2
R^2, slope and p-values from Log(Constituent) – Log(Runoff) analysis of EC, SiO_2, Ca, Mg, Na, Cl, SO_4, DOC, and K for Keystone Gulch, Hawkin Gulch, Fourmile Creek and Lost Gulch using storm and grab samples. Notes: * indicate $R^2 < 0.2$ and *italics* indicate p-value > 0.05.

R^2	**EC**	**SiO_2**	**Ca**	**Mg**	**Na**	**Cl**	**SO_4**	**DOC**	**K**
Keystone Gulch	0.68	0.32	0.59	0.59	0.56	0.70	0.60	*< 0.01*	0.41
Hawkin Gulch	0.78	0.67	0.89	0.88	0.79	0.65	0.64	0.38	0.30
Lost Gulch	0.70	0.85	0.86	0.89	0.85	*< 0.01*	*0.18*	0.86	0.80
Fourmile Creek	0.85	0.33	0.82	0.85	0.80	0.68	0.86	0.19	0.55
Slope	**EC**	**SiO_2**	**Ca**	**Mg**	**Na**	**Cl**	**SO_4**	**DOC**	**K**
Keystone Gulch	−0.15	−0.14	−0.18	−0.18	−0.11	−0.27	−0.23	*0.02**	−0.11
Hawkin Gulch	−0.15	−0.11	−0.16	−0.15	−0.13	−0.33	−0.24	0.19	−0.05
Lost Gulch	−0.16	−0.04	−0.13	−0.12	−0.06	*0.00**	*−0.11**	0.29	−0.08
Fourmile Creek	−0.22	−0.06	−0.22	−0.25	−0.21	−0.39	−0.40	0.09	−0.15
p-value	**EC**	**SiO_2**	**Ca**	**Mg**	**Na**	**Cl**	**SO_4**	**DOC**	**K**
Keystone Gulch	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	*0.69*	<0.01
Hawkin Gulch	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Lost Gulch	<0.01	<0.01	<0.01	<0.01	<0.01	*0.96*	*0.07*	<0.01	<0.01
Fourmile Creek	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table 3
Summary of all storms sampled at all sites with date (all storms are in 2018) sampled, maximum 30 min intensity, total precipitation, peak runoff, time to peak runoff, maximum event water and timing of maximum event water (using EC as a tracer), average high and low temperatures the week before the storm event, and the total precipitation the week before the storm event. All precipitation data is from the Mile High Flood District Magnolia site, except where $^{-}$ is precipitation data from the Logan Mill site and * is from the Mile High Flood District Betasso site (Mile High Flood District (MHFD), 2019). Temperature data are from the Betasso NADP site (National Atmospheric Deposition Program (NADP), 2019; see Fig. 1 for location).

Site	Hawkin Gulch			Keystone Gulch				Fourmile Creek			
Storm Date	June 17	June 18	July 15	May 22	June 17	June 18	July 15	May 18	June 17	June 18	June 19
Max. I_{30}	3	19	6	3	3	19	6	33*	3^{-}	15*	13^{-}
Total Precip (mm)	21	24	9	3	21	24	9	38*	15^{-}	16*	12^{-}
Peak Runoff (mm*hr^{-1})	< 0.01	0.03	< 0.01	0.03	0.01	0.08	0.01	0.14	0.01	0.04	0.04
Time to Peak (min)	>180	45	65	15	>180	30	10	50	>180	35	5
Max. Event Water (%)	5	46	22	–	21	70	63	–	–	–	–
Timing of Max. Event Water	peak	falling	rising	–	peak	rising	peak	–	–	–	–
Avg. High/Low Temp. (C) Week Before	31/11	28/11	34/14	19/5	31/11	28/11	34/14	20/3	31/11	28/11	27/11
Total Precip (mm) Week Before	9	30	2	30	9	30	2	8*	0^{-}	15*	31^{-}

and 0.95, and slope is 0.84 and 0.86, respectively; Fig. S3). Average percent differences between using EC as a tracer versus using Ca and Mg were lower at Hawkin Gulch (14.8%) than at Keystone Gulch (26.9%). The time to peak event water was the same regardless of which tracer was used in the hydrograph separation. For one storm event (on May 22) at Keystone Gulch, using EC, Mg, or Ca as tracers violated the assumption that tracer values of each component are significantly different and remain constant during the event, or changes are known. During all other events, calculated uncertainty estimates for mixing model results utilizing EC as a tracer were relatively small, with a mean uncertainty for event fractions at both catchments ranging from ± 0.02 to ± 0.06 with a mean of ± 0.03. Uncertainty calculations for individual mixing model results, and summary statistics of these calculations can be found in Tables S4 and S5.

5. Discussion

5.1. How do hydrologic flowpaths change from early to late summer in lower elevation catchments with varying land use?

Relations between stream runoff and water chemistry in our catchments suggest a transition in dominant flowpaths from the shallow subsurface during high flow to deeper groundwater during low flow. Concentrations of lithogenic (e.g., SiO_2, Ca, Mg, and Na) constituents increased with decreasing runoff during the season, while the bioactive constituent DOC decreased (Figs. 2 and 3); many studies have shown this same pattern, and attributed it to a shift of flowpaths from the DOC-rich, weathering-product-poor shallow subsurface to deeper flowpaths moving through bedrock or deep soil (Boyer et al., 1997; Burns et al., 2016; Hornberger et al., 1994; Chorover et al., 2017; Godsey et al., 2009; Murphy et al., 2018; Stallard and Murphy, 2014). Slopes of C/R relationships for SiO_2, Ca, Mg, and Na in our catchments are shallow (range: −0.25 to −0.04; Table 3) and similar to the near-chemostatic slopes found by Godsey et al. (2009) in a study of 59 geochemically diverse US catchments. Our results differ from C/R relationships of alpine and subalpine catchments in Colorado, which are strongly dependent on the magnitude of runoff: there, low-flow periods tend toward chemostatic behavior, while high-flow periods are chemodynamic, with substantial dilution of lithogenic solutes (Stottlemyer and Troendle, 1992; Podzorski, 2018). These higher-elevation systems experience dilution of lithogenic constituents that persists into late summer/early fall due to prolonged snowmelt. Lithogenic constituents in our catchments, however, were lowest in late May/early June and were higher during the remainder of the summer, when streamflow was low.

The differences between stream water chemistry and C/R relationships in foothill/ montane catchments and subalpine/alpine catchments in the Colorado Front Range likely result from the greater contribution of seasonal snowmelt to streamflow and a longer snowmelt season at higher elevations (Cowie et al., 2017; Williams et al., 2011). The average date of complete snowpack melt from water years 2008–2017 was May 31 at the subalpine Niwot Ridge SNOTEL site (elevation: 3321 m), but nearly a month earlier (April 28) at montane (elevation: 2734 m) Gordon Gulch (United States Department of Agriculture (USDA) National Resources Conservation Service (NRCS), 2019; Anderson and Ragar, 2019). In Fourmile Creek, which extends from the foothills to the subalpine, lithogenic constituent concentrations were lower from May to mid-June, when snowmelt derived from the subalpine region controlled stream discharge (Fig. 2). After snowmelt waned, EC and concentrations of Ca and Na increased, approaching levels similar to those of the

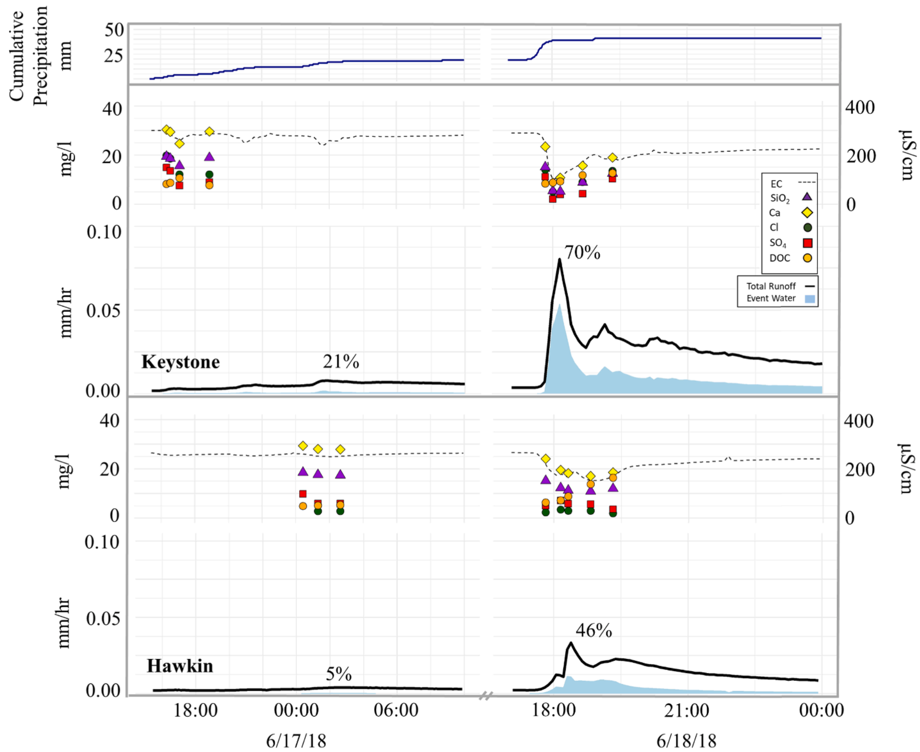

Fig. 4. Precipitation, total runoff, event water fraction using EC as a tracer (with % peak event water estimate indicated), EC, and concentrations of SiO_2, Ca, Cl, SO_4 and DOC on June 17, June 18, and June 19 at Keystone Gulch and Hawkin Gulch. Precipitation data are from the Mile High Flood District Magnolia precipitation site (see Fig. 1 for locations).

foothill catchments (Fig. 2). Zhang et al. (2018) estimated that ~24% of annual discharge in Boulder Creek was sourced from groundwater flow from the montane ecoregions. However, this estimate did not include foothills catchments, and our results suggest that 24% may be an underestimate of groundwater contributions from low to mid-elevation catchments. Williams et al. (2011) observed an increase in base cation concentrations in stream water with decreasing elevation in headwater catchments in the Boulder Creek Watershed, which may also indicate greater groundwater contributions at lower elevations. Recent work by Kampf and Lefsky (2016) demonstrated that peak snow water equivalents have declined over the past three decades throughout the Colorado Front Range. If snowpack depth and snow water equivalent continue to decrease with increasing temperatures in high elevation areas, catchments in the foothills and montane ecoregions may contribute not only a greater proportion of annual flow but also impact water quality with higher concentrations of lithogenic constituents.

Water chemistry suggests that anthropogenic activities such as housing, roads, and historical mining affect Keystone Gulch and Fourmile Creek, to a varying seasonal degree. We observed high concentrations of Cl in these catchments, particularly during low-flow conditions in the later season. Chloride concentration is low in the Boulder Creek Granodiorite, which underlies our study sites (Gable, 1980), so bedrock is not a likely source. In urbanized catchments, high Cl concentrations in streamwater are typically linked to a combination of both effluent from local septic systems, and long-term road salt application (Sherwood, 1989; Gutchess et al., 2016; Kelly et al., 2008; Stets et al., 2018). Several residences with domestic sewage systems are located adjacent to the stream channel in both Keystone Gulch and Fourmile Creek and may contribute Cl to the groundwater system. The U.S. Natural Resource Conservation Service (NRCS) assessed the soils in these areas to be “very limited” for septic use, which suggests that less effective performance of septic systems may be expected (Soil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture (USDA), 2020); thus, it is possible that wastewater, which can be elevated in chloride (Gutchess et al., 2016), may be contributing to nearby streams. In addition, Boulder County applies a mixture of sand and 5–10% rock salt (NaCl) to roads that parallel Keystone Gulch and Fourmile Creek (Boulder County, 2019), and it is possible that Cl enters local groundwater and is transported to streams (Kelly et al., 2008; Ledford et al., 2016; Perera et al., 2013; Sherwood, 1989). Residence times of Cl in altered groundwater systems has been estimated to range from 20 to 30 years (Gutchess et al., 2016) to hundreds and thousands of years (Novotny et al., 2009), highlighting a potential long-term impact of land-use change on stream chemistry in the Colorado Front Range.

Elevated SO_4 concentrations in Fourmile Creek may be related to the presence of widespread historical underground mines in this catchment. Minimal SO_4 is present in Boulder Creek Granodiorite, which underlies most of our study area (Gable, 1980), but pyrite is present in ore deposits in the Fourmile Creek catchment (Lovering and Goddard, 1950; Plumlee et al., 1995), and oxidation of pyrite can lead to elevated SO_4 in waters downstream of mines (Nordstrom, 2011, 2009). Indeed, mine discharge in the Fourmile Creek catchment, which is derived from deeper flowpaths through abandoned subsurface mine workings (Murphy et al., 2020), contains elevated SO_4 (McCleskey et al., 2012; Murphy et al., 2020b). During spring, snowmelt runoff derived from the upstream subalpine region provides dilution of the stream. Keystone Gulch also contains historical underground mines, but we did not observe high concentrations of SO_4 in that catchment. In contrast to the ore in Fourmile Creek, the telluride ore mined in Keystone Gulch has limited pyrite (Plumlee et al., 1995), and the mines are less spatially extensive. While flowpaths in Keystone Gulch may also intersect historical mines, the resultant mine discharge would likely have low SO_4 concentrations. Limitations on property access prevented us from sampling of mine discharge in Keystone Gulch. Despite the presence of mines in both of these watersheds, metal concentrations were generally low and can be attributed to the type of ore deposit in both (Plumlee et al., 1995).

Other studies have suggested that atmospheric deposition is a considerable source of both Cl and SO_4 to montane and foothills

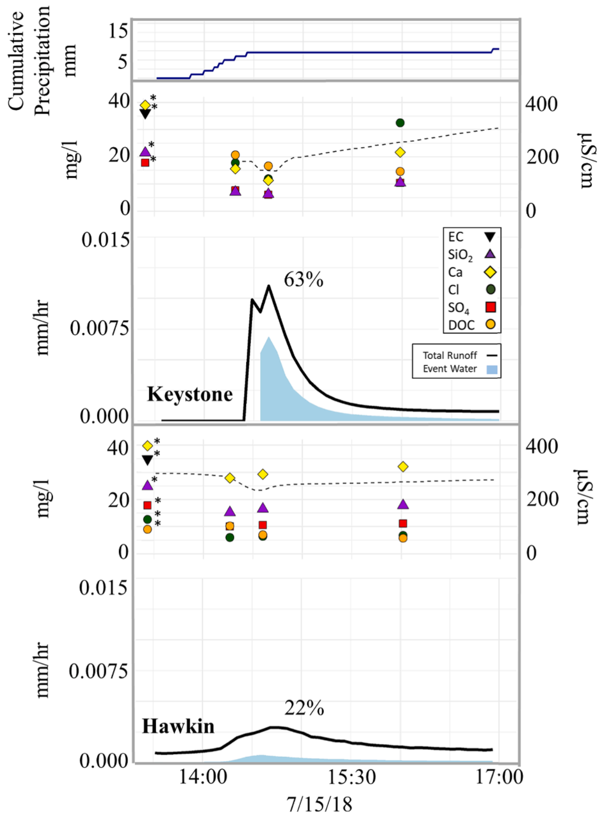

Fig. 5. Precipitation, total runoff, event water fraction using EC as a tracer (with % peak event water estimate indicated), EC, and concentrations of SiO_2, Ca, Cl, SO_4 and DOC on July 15 at Keystone and Hawkin Gulch. Precipitation data are from the Mile High Flood District Magnolia precipitation site (see Fig. 1 for location). Constituent concentrations with * are from samples collected from Hawkin Gulch at 12:55 on July 15 and from Keystone Gulch at 16:54 on July 12.

catchments in the Boulder Creek Watershed (Aguirre et al., 2017; Mills, 2016), but the reported deposition and stream fluxes do not fully explain the patterns we observed in our catchments. Dust deposition in the montane/foothills region is greatest during the early summer months with the highest rates being between the months of May and July (Aguirre et al., 2017; Heindel et al., 2020); however, Cl and SO_4 concentrations in our streams became more dilute during these months and only increased late in the summer—out of phase with seasonal deposition patterns. In nearby montane Gordon Gulch, Cl and SO_4 concentrations were variable, yet consistently higher in streamwater than in groundwater. Concentrations in groundwater remained relatively constant throughout the year, but stream concentrations became more enriched in response to summer rain events, especially in the late fall following prolonged dry periods (Mills 2016). Concentrations of SO_4 and Cl in streamwater increased in response to a large rain event in late June in Fourmile Creek and Keystone Gulch, respectively (Fig. 2), but this response was not consistent among all catchments, or across all rain events, as would be expected if atmospheric deposition was the primary driver for SO_4 and Cl enrichment in streams. In addition, peak SO_4 and Cl concentrations in Fourmile Creek and Keystone Gulch stream water during our study were >10 times greater than those observed in Gordon Gulch over a three-year period (Mills 2016). Therefore, while atmospheric deposition may contribute to SO_4 and Cl to some degree in our catchments, it is likely a small fraction.

5.2. What are the dominant flowpaths during summer storm events in foothill catchments?

Comparing the timing and magnitude of peak event water fractions, hydrograph and constituent behavior indicated dominant flowpaths during storm events differed between Keystone Gulch and Hawkin Gulch. Peak event water estimates at Hawkin Gulch (Table 3), the largely undisturbed foothills catchment, were consistent with past studies where storm hydrographs are dominated by pre-event water contributions (Brown et al., 1999; Buttle, 1994; Buttle and Peters, 1997; Marc et al., 2001; Genereux and Hooper, 2012; Gibson et al., 2005; Hoeg et al., 2000; Hooper and Shoemaker, 1986; Klaus and McDonnell, 2013; Sklash et al., 1979). Event water contributions typically peaked on the falling limb, indicating that substantial volumes of event water were delivered to Hawkin Gulch after peak runoff. Concentrations of DOC and lithogenic constituents were highest and lowest, respectively, on the falling limb, suggesting that this event water traveled through shallow subsurface flowpaths intersecting DOC-rich soils (Boyer et al., 1997; Hornberger et al., 1994; McDowell and Likens, 1988; McGlynn et al., 1999; Mills, 2016). In contrast, Keystone Gulch, the foothill catchment with anthropogenic disturbances, had peak event water contributions > 50% that coincided with peak or near peak runoff, and low DOC and lithogenic constituent concentrations. This suggests the rapid pulse of event water at Keystone Gulch is likely not delivered through shallow subsurface flowpaths (Klaus et al., 2013; McDonnell, 1990) or overland flowpaths over soils, both of which are typically rich in DOC (Gremillion et al., 2000; Pearce, 1990).

We posit that overland flow that bypasses both DOC and lithogenic constituents is the primary contributor of event water contributions at Keystone Gulch. Although overland flow across impervious surfaces has been shown to flush accumulated DOC on roads and pavement into streams during storm events (Aitkenhead-Peterson et al., 2009; Hook and Yeakley, 2005; Wise et al., 2019), these studies were in highly urbanized watersheds with more traffic-intensive roads relative to Keystone Gulch. Keystone Gulch has low-density, low-intensity trafficked roads and it is possible that flowpaths across impervious surfaces in Keystone Gulch have low DOC concentrations. Another possible explanation for the large pulse of event water at Keystone Gulch is overland flow across several near-stream, rock outcrops upstream of our sampling point. Rock outcrop complexes make up approximately 14% of the area of Keystone Gulch, and are concentrated near the stream outlet and along an ephemeral tributary in the upper portion of the catchment (U.S. Geological Survey (USGS), 2020). At the Panola Mountain Research Watershed in Georgia, Burns et al. (2001) showed constituent-dilute water was sourced from upstream rock outcrops and dominated peak runoff during storm responses. However, with our current data set, the precise mechanism for the quick delivery of event water at Keystone Gulch cannot be definitively determined.

6. Conclusion

This research contributes to a broader understanding of current streamflow-generating processes in foothill catchments of the western US and provides a baseline from which future climatic variability and disturbances to such catchments may be assessed. We found that lithogenic constituent concentrations in foothill catchments increased throughout the summer and showed less seasonal variation than higher elevation catchments due to relatively lower snowmelt contribution. Event water contributions in a disturbed catchment (e.g., housing and road development) were higher than event water contributions in a neighboring catchment with no disturbances. The presence of higher Cl concentrations in the disturbed catchments suggest that road salt or septic systems may be affecting stream chemistry, while the presence of higher SO_4 in one of the mined catchments, but not the other, may be related to ore type and/or spatial extent of mines. Our results highlight the importance of considering different components of land-use in the wildland-urban interface when investigating stream chemistry and runoff generation processes. In the context of future development, our findings have implications for predicting future changes in stream chemistry and hydrology in this rapidly developing region.

CRediT authorship contribution statement

Isaac S. Bukoski: Writing - original draft, Investigation, Formal analysis, Visualization, Funding acquisition. **Sheila F. Murphy:** Writing - review & editing, Conceptualization, Resources, Supervision, Funding acquisition. **Andrew L. Birch:** Writing - review & editing, Formal analysis. **Holly R. Barnard:** Writing - review & editing, Conceptualization, Resources, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements and Data availability

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2020.125672.

References

Abatzoglou, J.T., 2011. Influence of the PNA on declining mountain snowpack in the western United States. Int. J. Climatol. 31, 1135–1142. https://doi.org/10.1002/joc.2137.

Acuña, V., Datry, T., Marshall, J., Barceló, D., Dahm, C.N., Ginebreda, A., Mcgregor, G., Sabater, S., Tockner, K., Palmer, M.A., 2014. Why should we care about temporary waterways? Science 343, 1080–1081. https://doi.org/10.1126/science.1246666.

Aguirre, A.A., Derry, L.A., Mills, T.J., Anderson, S.P., 2017. Colloidal transport in the Gordon Gulch catchment of the Boulder Creek CZO and its effect on C-Q relationships for silicon. Water Resour. Res. 53, 2368–2383. https://doi.org/10.1002/2016WR019730.

Aitkenhead-Peterson, J.A., Steele, M.K., Nahar, N., Santhy, K., 2009. Dissolved organic carbon and nitrogen in urban and rural watersheds of south-central Texas: Land use and land management influences. Biogeochemistry 96, 119–129. https://doi.org/10.1007/s10533-009-9348-2.

Anderson, S.; Ragar, D. (2019). CZO dataset: Gordon Gulch: upper - snow depth (2008-2017) - snow pole transects (manual) (GGU_SP_1-10_Tran). Boulder Creek Critical Zone Observatory. 2019. http://criticalzone.org/boulder/data/dataset/2430/.

Balch, J.K., Bradley, B.A., Abatzoglou, J.T., Nagy, R.C., Fusco, E.J., 2017. Human-started wildfires expand the fire niche across the United States. Proceed. Nat. Acad. Sci. 114 (11), 2946–2951. https://doi.org/10.1073/pnas.1617394114.

Barnett, T.P., Adam, J.C., Lettenmaier, D.P., 2005. Potential impacts of a warming climate on water availability in snow-dominated regions. Nature 438, 303–309. https://doi.org/10.1038/nature04141.

Barnett, T.P., Pierce, D.W., Hidalgo, H.G., Bonfils, C., Santer, B.D., Das, T., Bala, G., Wood, A.W., Nozawa, T., Mirin, A. a, Cayan, D.R., Dettinger, M.D. (2008). Human-induced changes in the hydrology of the western United States. Science. 319 (80), 1080–1083. https://doi.org/10.1126/science.1152538.

Berghuijs, W.R., Woods, R.A., Hrachowitz, M., 2014. A precipitation shift from snow towards rain leads to a decrease in streamflow. Nat. Clim. Chang 4, 583–586. https://doi.org/10.1038/nclimate2246.

Bernhardt, E.S., Palmer, M.A., 2007. Restoring streams in an urbanizing world. Freshw. Biol. 52, 738–751. https://doi.org/10.1111/j.1365-2427.2006.01718.x.

Birch, A.L., Emanuel, R.E., James, A.L., Nichols, E.G., 2016. Hydrologic impacts of municipal wastewater irrigation to a temperate forest watershed. J. Environ. Qual. 45, 1303. https://doi.org/10.2134/jeq2015.11.0577.

Blöschl, G., Bierkens, M.F.P., Chambel, A., Cudennec, C., Destouni, G., Fiori, A., et al., 2019. Twenty-three unsolved problems in hydrology (UPH) – a community perspective. Hydrol. Sci. J. 6667, 1–18. https://doi.org/10.1080/02626667.2019.1620507.

Boulder County (2019). Road maintenance snow removal. Road Maintenance Division. https://www.bouldercounty.org/transportation/road-maintenance/snow-removal/.

Boyer, E.W., Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1997. Response characteristics of DOC flushing in an alpine catchment. Hydrol. Process. 11, 1635–1647. https://doi.org/10.1002/(SICI)1099-1085(19971015)11:12<1635::AID-HYP494>3.0.CO;2-H.

Brown, V.A., McDonnell, J.J., Burns, D.A., Kendall, C., 1999. The role of event water, a rapid shallow flow component, and catchment size in summer stormflow. J. Hydrol. 217, 171–190. https://doi.org/10.1016/S0022-1694(98)00247-9.

Bunn, S.E., Arthington, A.H., 2002. Basic principles and ecological consequences of altered flow regimes for aquatic biodiversity. Environ. Manage. 30, 492–507. https://doi.org/10.1007/s00267-002-2737-0.

Burns, D.A., McDonnell, J.J., Hooper, R.P., Peters, N.E., Freer, J.E., Kendall, C., Beven, K., 2001. Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain research watershed (Georgia, USA). Hydrol. Process. 15, 1903–1924. https://doi.org/10.1002/hyp.246.

Burns, M.A., Barnard, H.R., Gabor, R.S., McKnight, D.M., Brooks, P.D., 2016. Dissolved organic matter transport reflects hillslope to stream connectivity during snowmelt in a montane catchment. Water Resour. Res. 52, 4905–4923. https://doi.org/10.1002/2015WR017878.

Buttle, J.M., 1994. Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. Prog. Phys. Geogr. 18, 16–41. https://doi.org/10.1177/030913339401800102.

Buttle, J.M., Boon, S., Peters, D.L., Spence, C., (Ilja) van Meerveld, H.J., Whitfield, P.H. (2012). An overview of temporary stream hydrology in Canada. Can. Water Resour. J. / Rev. Can. des ressources hydriques. 37, 279–310. https://doi.org/10.4296/cwrj2011-903.

Buttle, J.M., Peters, D.L., 1997. Inferring hydrological processes in a temperate basin using isotopic and geochemical hydrograph separation: a re-evaluation. Hydrol. Process. 11, 557–573. https://doi.org/10.1002/(SICI)1099-1085(199705)11:6<557::AID-HYP477>3.0.CO;2-Y.

Chorover, J., Derry, L.A., McDowell, W.H., 2017. Concentration-discharge relations in the critical zone: implications for resolving critical zone structure, function, and evolution. Water Resour. Res. 53, 8654–8659. https://doi.org/10.1002/2017WR021111.

Clow, D.W., 2010. Changes in the timing of snowmelt and streamflow in Colorado: A response to recent warming. J. Clim. 23, 2293–2306. https://doi.org/10.1175/2009JCLI2951.1.

Coulthard, T.J., Macklin, M.G., 2003. Modeling long-term contamination in river systems from historical metal mining. Geology 31, 451–454. https://doi.org/10.1130/0091-7613(2003)031<0451:MLCIRS>2.0.CO;2.

Cowie, R.M., 2010. The hydrology of headwater catchments from the plains to the continental divide, Boulder Creek watershed, Colorado. Geol. Sci. Grad. Theses & Diss. 13.

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. J. Hydrol. 549, 163–178. https://doi.org/10.1016/j.jhydrol.2017.03.044.

Dalzell, B.J., Filley, T.R., Harbor, J.M., 2007. The role of hydrology in annual organic carbon loads and terrestrial organic matter export from a midwestern agricultural watershed. Geochim. Cosmochim. Acta 71, 1448–1462. https://doi.org/10.1016/j.gca.2006.12.009.

Datry, T., Larned, S.T., Tockner, K., 2014. Intermittent rivers: a challenge for freshwater ecology. Bioscience 64, 229–235. https://doi.org/10.1093/biosci/bit027.

Diffenbaugh, N.S., Pal, J.S., Trapp, R.J., Giorgi, F., 2005. Fine-scale processes regulate the response of extreme events to global climate change. Proc. Natl. Acad. Sci. 102, 15774–15778. https://doi.org/10.1073/pnas.0506042102.

Evans, C., Davies, T.D., 1998. Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry. Water Resour. Res. 34, 129–137. https://doi.org/10.1029/97WR01881.

Foks, S.S., Stets, E.G., Singha, K., Clow, D.W., 2018. Influence of climate on alpine stream chemistry and water sources. Hydrol. Process. 32 (13), 1993–2008. https://doi.org/10.1002/hyp.13124.

Gable, D.J., 1980. The Boulder Creek batholith, Front Range, Colorado, 1101. U.S. Geological Survey Professional Paper, pp. 1–88.

Genereux, D.P., 1998. Quantifying uncertainty in tracer-based hydrograph separations. Water Resour. Res. 34 (4) https://doi.org/10.1029/98WR00010.

Genereux, D.P., Hooper, R.P. (2012). Oxygen and hydrogen isotopes in rainfall-runoff studies, isotope tracers in catchment hydrology. 319-346. Elsevier B.V. https://doi.org/10.1016/b978-0-444-81546-0.50017-3.

Gibson, J.J., Edwards, T.W.D., Birks, S.J., St Amour, N.A., Buhay, W.M., McEachern, P., Wolfe, B.B., Peters, D.L., 2005. Prog. in Iso Tra. Hydro. in Canada. Hydrol. Process. 19, 303–327. https://doi.org/10.1002/hyp.5766.

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

Gremillion, P., Gonyeau, A., Wanielista, M., 2000. Application of alternative hydrograph separation models to detect changes in flow paths in a watershed undergoing urban development. Hydrol. Process. 14, 1485–1501. https://doi.org/10.1002/1099-1085(20000615)14:8<1485::AID-HYP988>3.0.CO;2-1.

Gutchess, K., Jin, L., Lautz, L., Shaw, S.B., Zhou, X., Lu, Z., 2016. Chloride sources in urban and rural headwater catchments, central New York. Sci. Total Environ. 565 (2016), 462–472.

Heindel, R.C., Putman, A.L., Murphy, S.F., Repert, D.A., Hinckley, E.-L.S., 2020. Atmospheric dust deposition varies by season and elevation in the Colorado Front Range, USA. J. Geophy. Res. Earth Surface 125. https://doi.org/10.1029/2019JF005436.

Hinckley, E.L.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. Hydrol. Process. 28, 74–85. https://doi.org/10.1002/hyp.9549.

Hoeg, S., Uhlenbrook, S., Leibundgut, C., 2000. Hydrograph separation in a mountainous catchment - combining hydrochemical and isotopic tracers. Hydrol. Process. 14 (7), 1199–1216. https://doi.org/10.1002/(SICI)1099-1085(200005)14:7<1199::AID-HYP35>3.0.CO;2-K.

Hook, A.M., Yeakley, J.A., 2005. Stormflow dynamics of dissolved organic carbon and total dissolved nitrogen in a small urban watershed. Biogeochemistry 75, 409–431. https://doi.org/10.1007/s10533-005-1860-4.

Hooper, R.P., Shoemaker, C.A., 1986. A comparison of chemical and isotopic hydrograph separation. Water Resour. Res. 22, 1444–1454. https://doi.org/10.1029/WR022i010p01444.

Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma. Colorado. Biogeochem. 25, 147–165. https://doi.org/10.1007/BF00024390.

Ice, G.G., Neary, D.G., Adams, P.W., 2004. Effects of Wildfire on Soils and Watershed Processes. J. For. 102 (6), 16–20. https://doi.org/10.1093/jof/102.6.16.

Johnson, N.M., Likens, G.E., Bormann, F.H., Fisher, D.W., Pierce, R.S., 1969. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resour. Res. 5, 1353–1363. https://doi.org/10.1029/WR005i006p01353.

Kampf, S.K., Lefsky, M.A., 2016. Transition of dominant peak flow source from snowmelt to rainfall along the Colorado Front Range: historical patterns, trends, and lessons from the 2013 colorado front range floods. Water Resour. Res. 52, 407–422. https://doi.org/10.1002/2015WR017784.

Kaufmann, M.R., Veblen, T., Romme, W.H. (2006). Historical fire regimes in ponderosa pine forests of the Colorado Front Range and recommendations for ecological restoration and fuels management. Front Range Fuels Treat. Partnersh. Round Table 1–19. https://doi.org/10.13140/RG.2.1.3834.1521.

Kelly, V.R., Lovett, G.M., Weathers, K.C., Findlay, S.E.G., Strayer, D.L., Burns, D.J., Likens, G.E., 2008. Long-term sodium chloride retention in a rural watershed: Legacy effects of road salt on streamwater concentration. Environ. Sci. Technol. 42, 410–415. https://doi.org/10.1021/es071391l.

Klaus, J., McDonnell, J.J., 2013. Hydrograph separation using stable isotopes: Review and evaluation. J. Hydrol. 505, 47–64. https://doi.org/10.1016/j.jhydrol.2013.09.006.

Klaus, J., Zehe, E., Elsner, M., Külls, C., McDonnell, J.J., 2013. Macropore flow of old water revisited: Experimental insights from a tile-drained hillslope. Hydrol. Earth Syst. Sci. 17, 103–118. https://doi.org/10.5194/hess-17-103-2013.

Knowles, N., Dettinger, M.D., Cayan, D.R., 2006. Trends in snowfall versus rainfall in the western United States. J. Clim. 19, 4545–4559. https://doi.org/10.1175/JCLI3850.1.

Laudon, H., Slaymaker, O., 1997. Hydrograph separation using stable isotopes, silica and electrical conductivity: an alpine example. J. Hydrol. 201 (1–4), 82–103. https://doi.org/10.1016/S0022-1694(97)00030-9.

Ledford, S.H., Lautz, L.K., Stella, J.C., 2016. Hydrogeologic processes impacting storage, fate, and transport of chloride from road salt in urban riparian aquifers. Environ. Sci. Technol. 50, 4979–4988. https://doi.org/10.1021/acs.est.6b00402.

Leigh, C., Boulton, A.J., Courtwright, J.L., Fritz, K., May, C.L., Walker, R.H., Datry, T., 2016. Ecological research and management of intermittent rivers: an historical review and future directions. Freshw. Biol. 61, 1181–1199. https://doi.org/10.1111/fwb.12646.

Lovering, T.S., Goddard, E.N. (1950). Geology and ore deposits of the Front Range, Colorado. U.S. Geological Survey Professional Paper. 223, 319. https://doi.org/10.3133/pp223.

Martínez-Santos, M., Antigüedad, I., Ruiz-Romera, E., 2014. Hydrochemical variability during flood events within a small forested catchment in Basque Country (Northern Spain). Hydrol. Process. 28 (21), 5367–5381. https://doi.org/10.1002/hyp.10011.

Marc, V., Didon-Lescot, J.F., Michael, C., 2001. Investigation of the hydrological processes using chemical and isotopic tracers in a small Mediterranean forested catchment during autumn recharge. J. Hydrol. 247 (3–4), 215–229. https://doi.org/10.1016/S0022-1694(01)00386-9.

McCleskey, R. B., Writer, J. H., & Murphy, S. F. (2012). Water chemistry data for surface waters impacted by the Fourmile Canyon Wildfire, Colorado, 2010-2011. U.S. Geological Survey Open-File Report. 2012–1104. Reston, Virginia: U.S. Geological Survey. https://doi.org/10.3133/ofr20121104.

McDonnell, J.J., 1990. A rationale for old water discharge through macropores in a steep, humid catchment. Water Resour. Res. 26, 2821–2832. https://doi.org/10.1029/WR026i011p02821.

McDowell, W.H., Likens, G.E., 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecol. Monogr. 58, 177–195. https://doi.org/10.2307/2937024.

McGlynn, B.L., McDonnell, J.J., Shanley, J.B., Kendall, C., 1999. Riparian zone flowpath dynamics during snowmelt in a small headwater catchment. J. Hydrol. 222, 75–92. https://doi.org/10.1016/S0022-1694(99)00102-X.

Mile High Flood District (MHFD). (2019). MHFD's ALERT system real-time data. https://mhfd.onerain.com. Accessed on 6/1/2019.

Mills, T.J. (2016). Water chemistry under a changing hydrologic regime: investigations into the interplay between hydrology and water-quality in arid and semi-arid watersheds in Colorado, USA. Dep. Geog. Grad. Theses Diss. 101. 101.https://scholar.colorado.edu/geog_gradetds/101.

Mirus, B.B., Ebel, B.A., Mohr, C.H., Zegre, N., 2017. Disturbance hydrology: preparing for an increasingly disturbed future. Water Resour. Res. 53, 10007–10016. https://doi.org/10.1002/2017WR021084.

Moody, J.A., Martin, D.A. (2001). Post-fire, rainfall intensity-peak discharge relations for three mountainous watersheds in the western USA. Hydrol. Process. 15, 2981–2993. https://doi.org/10.1002/hyp.386.

Murphy, S. F. (2006). State of the watershed: Water quality of Boulder Creek, Colorado. U.S. Geological Survey Circular. 1284. Reston, Virginia: U.S. Geological Survey. https://doi.org/10.3133/cir1284.

Murphy, S.F., McCleskey, R.B., Martin, D.A., Holloway, J.M., Writer, J.W., 2020a. Wildfire-driven changes in hydrology mobilize arsenic and metals from legacy mine waste. Sci. Total Environ. 743, 140635 https://doi.org/10.1016/j.scitotenv.2020.140635.

Murphy, S.F., McCleskey, R.B., D.A., Holloway, J.M., Writer, J.W., Martin, D.A., and Stricker, C.A. (2020b). Chemistry of water, stream sediment, wildfire ash, soil, dust, and mine waste for Fourmile Creek Watershed, Colorado, 2010-2019: U.S. Geological Survey Data Release. https://doi.org/10.5066/P941BIYS.

Murphy, S.F., McCleskey, R.B., Martin, D.A., Writer, J.H., Ebel, B.A., 2018. Fire, flood, and drought: extreme climate events alter flow paths and stream chemistry. J. Geophys. Res. Biogeosci. 123, 2513–2526. https://doi.org/10.1029/2017JG004349.

Murphy, S.F., Writer, J.H., Mccleskey, B.R., Martin, D.A., 2015. The role of precipitation type, intensity, and spatial distribution in source water quality after wildfire. Environ. Res. Lett. 10, 84007. https://doi.org/10.1088/1748-9326/10/8/084007.

Musolff, A., Schmidt, C., Selle, B., Fleckenstein, J.H., 2015. Catchment controls on solute export. Adv. Water Resour. 86, 133–146. https://doi.org/10.1016/j.advwatres.2015.09.026.

National Atmospheric Deposition Program (NADP). (2019). Site ID: CO84, 15 min data from 10/1/2017 to 00:00 to 10/1/2018 00:00. http://nadp.slh.wisc.edu/siteOps/ppt/default.aspx.

Nordstrom, D.K., 2011. Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. Appl. Geochem. 26, 1777–1791. https://doi.org/10.1016/j.apgeochem.2011.06.002.

Novotny, E.V., Sander, A.R., Mohseni, O., Stefan, H.G., 2009. Chloride ion transport and mass balance in a metropolitan area using road salt. Water Resour. Res. 45, 1–13.

Pearce, A.J., 1990. Streamflow generation processes: an austral view. Water Resour. Res. 26 (12), 3037–3047. https://doi.org/10.1029/WR026i012p03037.

Pepin, N., Bradley, R.S., Diaz, H.F., Baraer, M., Caceres, E.B., Forsythe, N., Fowler, H., Greenwood, G., Hashmi, M.Z., Liu, X.D., Miller, J.R., Ning, L., Ohmura, A., Palazzi, E., Rangwala, I., Schöner, W., Severskiy, I., Shahgedanova, M., Wang, M.B., Williamson, S.N., Yang, D.Q., 2015. Elevation-dependent warming in mountain regions of the world. Nat. Clim. Chan. 5, 424–430. https://doi.org/10.1038/nclimate2563.

Perera, N., Gharabaghi, B., Howard, K., 2013. Groundwater chloride response in the Highland Creek watershed due to road salt application: a re-assessment after 20 years. J. Hydrol. 479, 159–168. https://doi.org/10.1016/j.jhydrol.2012.11.057.

Pickett, S.T.A., Cadenasso, M.L., Grove, J.M., Boone, C.G., Groffman, P.M., Irwin, E., Kaushal, S.S., Marshall, V., McGrath, B.P., Nilon, C.H., Pouyat, R.V., Szlavecz, K., Troy, A., Warren, P., 2011. Urban ecological systems: scientific foundations and a decade of progress. J. Environ. Manage. 92, 331–362. https://doi.org/10.1016/j.jenvman.2010.08.022.

Plumlee, G. S., Streufert, R. K., Smith, K. S., Smith, S. M., Wallace, A. R., Toth, M. I., K. Lee, G. (1995). Map showing potential metal-mine drainage hazards in Colorado, based on mineral-deposit geology. Open-File Report. 95–26, 11 p.; 1 over-size sheet. https://doi.org/doi.org/10.3133/ofr9526.

Podzorski, L.H. (2018). Expression of geochemical controls on water quality in Loch Vale, Rocky Mountain National Park. Colorado School of Mines Sci. Grad. Theses. https://hdl.handle.net/11124/172402.

Prein, A.F., Rasmussen, R.M., Ikeda, K., Liu, C., Clark, M.P., Holland, G.J., 2017. The future intensification of hourly precipitation extremes. Nat. Clim. Chan. 7, 48–52. https://doi.org/10.1038/nclimate3168.

Rangwala, I., Miller, J.R., 2012. Climate change in mountains: a review of elevation-dependent warming and its possible causes. Clim. Change 114, 527–547. https://doi.org/10.1007/s10584-012-0419-3.

R Core Team (2018). R: A language and environmental for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-Project.org/.

Rose, L.A., Karwan, D.L., Godsey, S.E., 2018. Concentration–discharge relationships describe solute and sediment mobilization, reaction, and transport at event and longer timescales. Hydrol. Process. 32, 2829–2844. https://doi.org/10.1002/hyp.13235.

Rösner, U., 1998. Effects of historical mining activities on surface water and groundwater - An example from northwest Arizona. Environ. Geol. 33, 224–230. https://doi.org/10.1007/s002540050241.

Scott, Joe H.; Thompson, Matthew P.; Calkin, David E. 2013. A wildfire risk assessment framework for land and resource management. Gen. Tech. Rep. RMRS-GTR-315. U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station. 83 p.

Sherwood, W.C., 1989. Chloride loading in the south fork of the shenandoah river, Virginia, U.S.A. Environ. Geol. Water Sci. 14, 99–106. https://doi.org/10.1007/BF01728501.

Shuster, W.D., Bonta, J., Thurston, H., Warnemuende, E., Smith, D.R., 2005. Impacts of impervious surface on watershed hydrology: a review. Urban Water J. 2, 263–275. https://doi.org/10.1080/15730620500386529.

Singer, M.B., Aalto, R., James, L.A., 2008. Status of the lower sacramento valley flood-control system within the context of its natural geomorphic setting. Nat. Hazards Rev. 9, 104–115. https://doi.org/10.1061/(asce)1527-6988(2008)9:3(104).

Sklash, M.G., Farvolden, R.N., Farvolden, R.N., 1979. The role of groundwater in storm runoff. Dev. Water Sci. 12, 45–65. https://doi.org/10.1016/S0167-5648(09)70009-7.

Soil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture (USDA). (2020) Web Soil Survey. Available online at the following link: http://websoilsurvey.sc.egov.usda.gov/. Accessed on 5/1/2020.

Stallard, R.F., Murphy, S.F., 2014. A unified assessment of hydrologic and biogeochemical responses in research watersheds in eastern Puerto Rico using runoff-concentration relations. Aquat. Geochem. 20, 115–139. https://doi.org/10.1007/s10498-013-9216-5.

Stets, E.G., Lee, C.J., Lytle, D.A., Schock, M.R., 2018. Increasing chloride in rivers of the conterminous U.S. and linkages to potential corrosivity and lead action level exceedances in drinking water. Sci. Total Environ. 613–614, 1498–1509. https://doi.org/10.1016/j.scitotenv.2017.07.119.

Stewart, I.T., Cayan, D.R., Dettinger, M.D. (2005). Changes toward earlier streamflow timing across western North America. J. Clim. 18, 1136–1155. https://doi.org/10.1175/JCLI3321.1.

Stottlemyer, R., Troendle, C.A., 1992. Nutrient concentration patterns in streams draining alpine and subalpine catchments, Fraser Experimental Forest, Colorado. J. Hydrol. 140, 1–4. https://doi.org/10.1016/0022-1694(92)90240-V.

Theobald, D.M., Romme, W.H., 2007. Expansion of the US wildland-urban interface. Landsc. Urban Plan. 83, 340–354. https://doi.org/10.1016/j.landurbplan.2007.06.002.

United States Department of Agriculture (USDA) National Resources Conservation Service (NRCS). (2019). SNOTEL Site Number 663, Niwot, Boulder, CO. https://wcc.sc.egov.usda.gov/nwcc/site?sitenum=663. Accessed on 6/1/2019.

U.S. Geological Survey (USGS). (2020). The StreamStats program. http://streamstats.usgs.gov. Accessed on 1/15/2020.

U.S. Geological Survey (USGS). (2019). USGS 06727500 Fourmile Creek at Orodell, CO. https://waterdata.usgs.gov/nwis/uv?06727500. Accessed on 6/1/2019.

Wels, C., Cornett, R.J., Lazerte, B.D., 1991. Hydrograph separation: a comparison of geochemical and isotopic tracers. J. Hydrol. https://doi.org/10.1016/0022-1694(91)90181-G.

Williams, M.W., Barnes, R.T., Parman, J.N., Freppez, M., Hood, E.W., 2011. Stream water chemistry along an elevation gradient from the Continental Divide to the Foothills of the Rocky Mountains. Vadose Zone J. 10, 900–919. https://doi.org/10.2136/vzj2010.0131.

Wise, J.L., Van Horn, D.J., Diefendorf, A.F., Regier, P.J., Lowell, T.V., Dahm, C.N., 2019. Dissolved organic matter dynamics in storm water runoff in a dryland urban region. J. Arid Environ. 165, 55–63. https://doi.org/10.1016/j.jaridenv.2019.03.003.

Zhang, Q., Knowles, J.F., Barnes, R.T., Cowie, R.M., Rock, N., Williams, M.W., 2018. Surface and subsurface water contributions to streamflow from a mesoscale watershed in complex mountain terrain. Hydrol. Process. 32 (7), 954–967. https://doi.org/10.1002/hyp.11469.