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Shifting groundwater fluxes in bedrock fractures: Evidence from stream water radon and water isotopes

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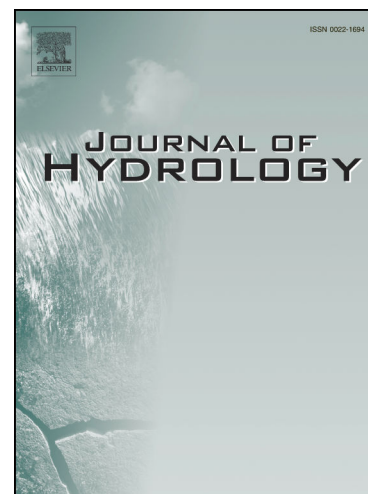
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1 **Shifting groundwater fluxes in bedrock fractures: Evidence from stream water radon and**  
2 **water isotopes**

3

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49 **Keywords:** groundwater surface water interactions, tracer hydrology, groundwater modeling,  
50 groundwater discharge, montane catchment

51

## 52 **1.0 Introduction:**

53 Streamflow derived from montane environments is important for downstream  
54 communities and ecosystem services but is vulnerable due to decreasing snowpack resulting  
55 from climate change (Viviroli et al., 2007; Mote et al., 2018; Viviroli et al., 2020). Earlier peak  
56 flows, smaller snowpacks, and higher evapotranspiration rates are predicted to decrease summer

57 flows (Stewart et al., 2005; Bavay et al., 2009; Ficklin et al., 2013; Azmat et al., 2016) leading to  
58 an increased reliance on groundwater (Kapnick and Hall, 2012; Somers et al., 2019). The  
59 relationship between groundwater and surface water (termed GW-SW interactions) is dominantly  
60 influenced by precipitation regime, vegetation, and geologic setting (Banks et al., 2011;  
61 Andermann et al., 2012; Safeeq et al., 2013; Carroll et al., 2018; Brooks et al., 2021). Especially  
62 of interest is summer precipitation (e.g., monsoon rains) which can contribute large amounts of  
63 water in the summer months (Shepard et al., 2002) and have the potential to buffer summer flows  
64 during low snowpack years (Carroll et al., 2020). Few studies have documented the impacts of  
65 monsoon rains on groundwater contribution in montane, snow dominated watersheds due to the  
66 remote nature of these catchments (Somers and McKenzie, 2020). Our understanding of GW-SW  
67 interactions can be enhanced with an improved understanding of the impacts of monsoon rains  
68 on groundwater contributions to summer flow, which is imperative for the future of water  
69 resources in montane environments.

70 GW-SW interactions are often difficult to quantify given the complex controls that  
71 geology exerts on spatial and temporal patterns of groundwater discharge (McClymont et al.,  
72 2012; Floriancic et al., 2018). Geologic features can play an important role in the locations and  
73 volume of groundwater discharge (Banks et al., 2009; Andermann et al., 2012). For example, in  
74 hard rock systems, groundwater predominantly flows through fractures due to their relatively  
75 higher permeability as compared to the surrounding matrix (Oxtobee and Novakowski, 2003).  
76 Groundwater in fractures can respond quickly to precipitation inputs (Flerchinger et al., 1993;  
77 Salve et al., 2012; Webb et al., 2017) rapidly recharging aquifers (Wittenberg et al., 2019) and  
78 discharging to streams (McDonnell et al., 1990). Alluvial deposits can also form in hard rock  
79 systems from long periods of sediment transport and deposition or glacial erosion. These  
80 deposits behave nearly opposite of fractured bedrock; they are characterized by high storage and  
81 have the potential to contribute large amounts of groundwater to summer stream flow over  
82 extended periods of time (Liu et al., 2004; Gordon et al., 2015; Käser and Hunkeler, 2016).

83 Hydrologic connectivity determines how different subsurface storage reservoirs  
84 contribute to surface water, and changes in hydrologic connectivity can be driven by changes in  
85 moisture conditions (Covino, 2017). Dynamic storage can be used as a proxy for hydrologic  
86 connectivity, where periods of higher dynamic storage indicate higher hydrologic connectivity  
87 (McIntosh et al., 2017; Dwivedi et al., 2018). Dynamic storage is part of overall catchment  
88 storage and defined as the variation in storage between wet and dry periods (Spence, 2007;  
89 Kirchner, 2009; Sayama et al., 2011; Dwivedi et al., 2018). Dynamic storage estimations have  
90 been leveraged to estimate subsurface storage (Sayama et al., 2011) and perform hydrograph  
91 separation (Dwivedi et al., 2018), and can be combined with other tracers leading to insights  
92 about flow path length and origin at the catchment scale. In montane environments, periods of  
93 high hydrologic connectivity typically occur during snowmelt, and recede throughout the  
94 summer (Jencso et al., 2010). However, in monsoon-impacted catchments, we expect that  
95 significant rainfall in the summer and fall months may temporarily increase hydrologic  
96 connectivity facilitating changes in GW-SW interactions. Additionally, we expect that the  
97 difference in storage capacity among geologic features in a catchment will cause them to respond  
98 variably to changes in moisture throughout the year, leading to shifts in dominant groundwater  
99 contributions throughout the summer (Käser and Hunkeler, 2016; Floriancic et al., 2018; Bush et  
100 al., 2023).

101 It is common to use geochemical and radioisotope tracers to quantify groundwater  
102 contribution to streamflow (Liu et al., 2004; Gardner et al., 2011; Gordon et al., 2015; Cowie et  
103 al., 2017; Beisner et al., 2018; Carroll et al., 2018). Radon ( $^{222}\text{Rn}$ ; half-life 3.8 days) is an  
104 effective tracer because of its elevated concentration in groundwater from the continuous decay  
105 of uranium in rocks and soils (Webb et al., 2017). Compared to other geochemical tracers,  $^{222}\text{Rn}$   
106 helps identify areas of high groundwater contribution because it degasses upon interaction with  
107 the atmosphere. Thus, areas of high  $^{222}\text{Rn}$  concentrations indicate localized groundwater flux into  
108 the stream. Radon has been used to assess groundwater contributions across a variety of  
109 environments including floodplains (Webb et al., 2017), urban rivers (Schubert et al., 2020),  
110 coastal streams (Peterson et al., 2010), mountain streams (Avery et al., 2018), and boreal lakes  
111 (Schmidt et al., 2010). Despite the wide range in geomorphic setting, few studies exist that use  
112  $^{222}\text{Rn}$  to identify groundwater contributions in montane environments (Gleeson et al., 2018).  
113 Radon can also be paired with non-degassing geochemical tracers to assess reach- or catchment-  
114 scale groundwater contribution (Genereux et al., 1993; Beisner et al., 2018; Gleeson et al., 2018;  
115 Cardenas et al., 2021). Stable water isotopes are a valuable tracer because they are conservative  
116 and are commonly used to assess groundwater contribution to montane streams (Fischer et al.,  
117 2015; Singh et al., 2016; Segura et al., 2019; Zuecco et al., 2018). Additionally, water isotopes  
118 vary with precipitation phase and season allowing for separation of streamflow into seasonal  
119 precipitation contributions (Allen et al., 2019a).

120 Significant advances in montane hydrodynamics could be achieved if the connectivity of  
121 geologic features to surface water could be more readily quantified. The aim of this paper is to  
122 understand how monsoon rains influence GW-SW interactions in bedrock fractures in a  
123 headwater stream of the Colorado River. We use  $^{222}\text{Rn}$  and stable water isotopes to explore the  
124 seasonal variation of groundwater discharge in a Colorado River headwater stream (Figure 1b).  
125 To capture the influence of summer precipitation on groundwater discharge we collected roughly  
126 weekly, synoptic stream  $^{222}\text{Rn}$  and water isotope samples across a stream reach of Coal Creek  
127 influenced by hillslope fractures. We focus on Coal Creek because the geologic setting gives rise  
128 to significant fracture networks (Figure 1c) and because of its potential for high monsoon  
129 efficiency (Carroll et al., 2020). Synoptic stream chemistry data were used to constrain a one-  
130 dimensional advective-dispersion model to estimate lateral groundwater discharge along the  
131 stream length throughout the summer.

## 132 **2.0 Methods**

### 133 *2.1 Study Site*

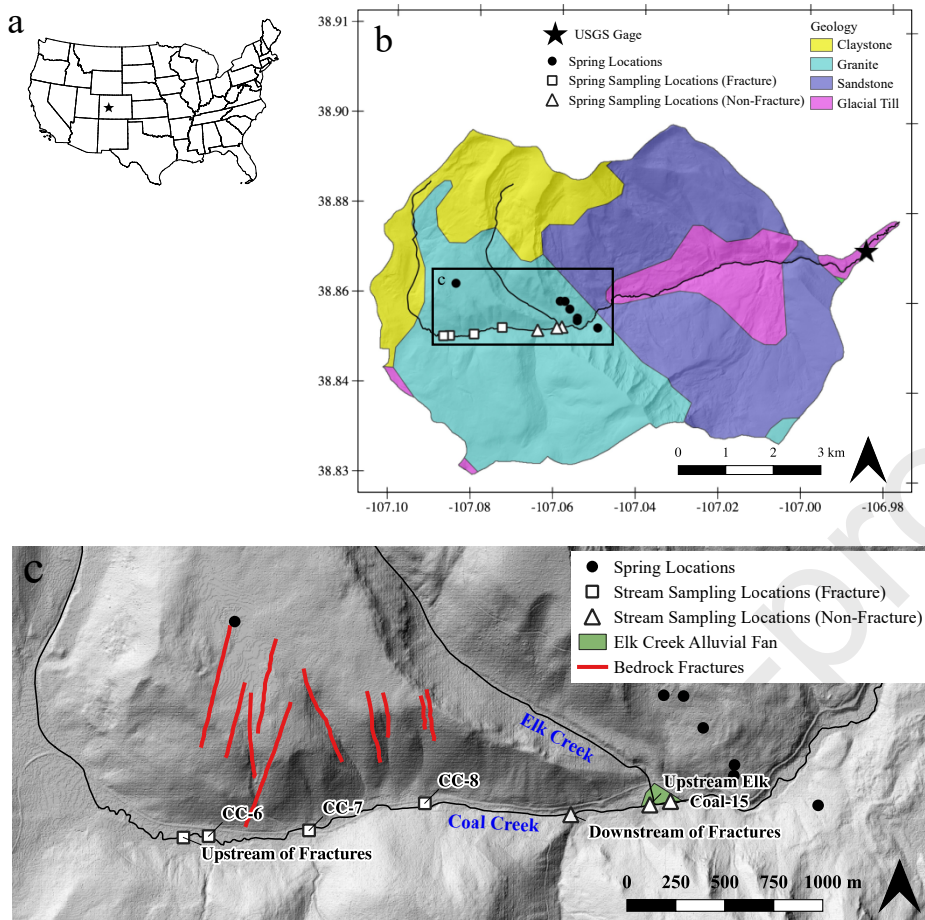
134 Coal Creek is a small (53 km<sup>2</sup>), high-elevation, headwater tributary to the Upper  
135 Colorado Basin located on the traditional homelands of the Nuu-*agha-tavá-pu* (Ute) peoples in  
136 the Ruby-Anthracite Range in the central Colorado Rocky Mountains. Coal Creek is located  
137 within the larger East River watershed (catchment area of 300 km<sup>2</sup>), which is a designated  
138 Science Focus Area (Hubbard et al., 2018) by the Department of Energy and a watershed  
139 observatory within the Critical Zone Collaborative Network (CZCN) supported by the National  
140 Science Foundation. As such, the East River, including Coal Creek, hosts a diverse collection of  
141 hydro-biogeochemical measurements that provide an ideal setting for examining the controls of  
142 groundwater inputs under summer monsoon conditions. The watershed and its key tributary

143 drainages, including Coal Creek, are broadly representative of snow-dominated basins in the  
144 Rocky Mountains.

145         The Coal Creek in elevation from 2712 to 3668 meters. Coal Creek originates near Lake  
146 Irwin and enters the Slate River near the town of Crested Butte before joining the East River and  
147 eventually the Gunnison River. The watershed is seasonally snow-covered from November  
148 through June. The average temperature is 0.9°C and it receives around 670 mm of precipitation  
149 each year, about 66% of which falls as snow (Carroll et al., 2018). The remaining precipitation  
150 falls during the summer monsoon season (July through September). Although monsoon rains  
151 comprise approximately 25% of the annual precipitation, they contribute only about 10% to the  
152 summer streamflow because the moisture is lost via evapotranspiration (Carroll et al., 2020;  
153 Sprenger et al., 2022). Vegetation in the basin is strongly aspect driven, with north facing aspects  
154 dominated by evergreen forest (65%) and south facing aspects dominated by deciduous (9%) and  
155 herbaceous (20%) vegetation. High elevation ridges are barren (3%) (Zhi et al., 2019). Discharge  
156 in Coal Creek is dominated by snowmelt, with average peak flow occurring in June. Flows  
157 recede throughout the summer and fall, with small peaks in flow due to monsoon events. Coal  
158 Creek reaches baseflow conditions by early September and they persist throughout the winter  
159 until the onset of snowmelt in April (Figure 2a).

160         The lower portion of the Coal Creek watershed is underlain predominately by sandstone  
161 (Upper Cretaceous Mesaverde Formation) with glacial till deposits occurring near the streambed.  
162 The upper portion of the watershed is underlain by mafic intrusive plutonic rock, emplaced  
163 during the Middle Paleocene. Areas of the upper north slope of the watershed are underlain by  
164 mudstone (Tertiary Wasatch Formation) (Figure 1b). Fractures have been mapped along the  
165 north hillslope in the upper watershed (Figure 1b). East of the mapped fractures is the contact  
166 between the upper basin intrusive plutonic rock and lower basin sandstone. This contact roughly  
167 bisects the Coal Creek watershed running northeast to southeast. Mapped along this contact  
168 zone, on either side of Coal Creek stream, is a dense spring network (Gaskill et al., 1991).  
169 Alluvial fans have been mapped at the confluence of tributaries with Coal Creek. These fans are  
170 Holocene age, poorly sorted material (Gaskill et al., 1991). Although many fans are present  
171 along the transect, our design only captures the alluvial fan associated with Elk Creek as our aim  
172 was primarily focused on the fracture zone compared to downstream behavior. Elk Creek is the  
173 only tributary that contributes significantly to streamflow generation along our study reach of  
174 Coal Creek throughout the summer.





175

176 Figure 1: (a) Location of Coal Creek watershed within the United States. (b) Geologic map of Coal Creek (Horton et  
 177 al., 2017) watershed showing stream sampling within fracture (white square) and non-fracture (white triangle) zone,  
 178 spring sampling (black circles) locations, and Coal Creek USGS gage (black star). (c) Inset of sampling sites  
 179 showing sampling locations relative to fractures (red lines) (Gaskill et al., 1991) and alluvial fan (green polygon).

## 180 2.2 Field Sample Collection

181 From June through October 2021 a total of 77 surface water samples and seven spring  
 182 samples were collected for  $^{222}\text{Rn}$  and water isotopes across eight stream sites and seven springs  
 183 (Table 1). Stream water sampling locations were collected along a 2842 m length reach in the  
 184 upper portion of Coal Creek watershed (Table S1). Sampling locations were selected to identify  
 185 the influence of mapped bedrock fractures on stream chemistry and discharge. All samples were  
 186 collected in the thalweg of the stream to ensure they were well mixed. Our study design focuses  
 187 on bookending the known fracture zone along Coal Creek, with one site located just above the  
 188 fractured hillslope (Upstream of Fractures, referred to as Upstream), three sampling locations  
 189 located along the transect of the stream that runs along the base of the hillslope with the mapped  
 190 fractures (CC-6, CC-7, CC-8; Figure 1B), and three samples below the fracture zone  
 191 (Downstream of Fractures, referred to as Downstream; Upstream of Elk Creek, referred to as  
 192 Upstream Elk; and Coal-15). We note that Upstream Elk and Coal-15 co-occur with the location  
 193 of the alluvial fan at Elk Creek. Elk Creek was sampled three times throughout the summer (late



194 May, late July, early October) at its confluence with Coal Creek, although only one sample (late  
195 July) was analyzed for  $^{222}\text{Rn}$ . To distinguish between the behavior of the bedrock fractures and  
196 non-fracture zones, the sites can be differentiated into fracture sites (< 2350 meters along reach,  
197  $n=5$ ) and non-fracture zone (> 2350 meters along reach,  $n=2$ ). Over 80% of surface water  
198 samples were analyzed for both  $^{222}\text{Rn}$  and water isotopes.

199 Of the seven springs, six were located on the south facing slope and one was located on  
200 the north facing slope. All but one of the springs were further east than the sampled stream reach.  
201 Each spring was sampled only once. Of the spring samples, four were analyzed for both  $^{222}\text{Rn}$   
202 and water isotopes.

### 203 2.2.1 Water Sampling

204 Locations in a stream with high  $^{222}\text{Rn}$  concentrations indicate localized areas of  
205 groundwater discharge.  $^{222}\text{Rn}$  is not affected by biological processes and is relatively inert,  
206 although is subject to physical loss and radioactive decay. Once groundwater enters the river,  
207  $^{222}\text{Rn}$  quickly dissipates due to degassing to the atmosphere (Schubert et al., 2020). Stream water  
208 was collected in 2L plastic bottles without headspace and spring water was collected in 500 mL  
209 plastic bottles ( $n=2$ ) or 250 mL glass bottles ( $n=4$ ) without headspace. Stream water was  
210 collected in large volume bottles to ensure accurate measurement and detection of  $^{222}\text{Rn}$  due to  
211 the relatively low concentration of  $^{222}\text{Rn}$  in stream water. Spring samples were collected in  
212 smaller bottles given the high concentration of  $^{222}\text{Rn}$  in groundwater and were collected in  
213 different bottle types due to bottle availability at the time of sampling. Each spring was sampled  
214 only once, and one duplicate stream water sample was collected with three of the six synoptic  
215 events. All samples were collected using a Grainger surface water pump (Model IL200P, RULE,  
216 Rye Brook, NY) powered by a 12V battery. Due to the large volume of water we needed to  
217 collect for  $^{222}\text{Rn}$  analysis, we designed a sampling scheme that pumped water from the thalweg to  
218 a 2L bottle onshore. The bottle was placed in a bucket with the tubing inside, filled, and capped  
219 underwater without headspace to minimize degassing of  $^{222}\text{Rn}$  and the cap was sealed with  
220 Parafilm<sup>TM</sup>. We sampled springs similarly by placing the pump in the pool at the spring head or  
221 as close to the spring head such that the pump was completely submerged. Samples were shipped  
222 in coolers overnight to Lawrence Berkeley National Lab for  $^{222}\text{Rn}$  analysis.

223 Stream and spring water were also collected for stable water isotope analysis. Water  
224 samples were filtered through a 0.45-micron Nylon filter into a 2 mL glass vial with Septa caps  
225 taking care to eliminate headspace and refrigerated until analysis. We relied on water isotopes of  
226 precipitation collected about 10 km north-east of Coal Creek during the 2021 water year as end  
227 members to compare stream and spring water isotopic composition. Samples were collected  
228 approximately weekly, and snow ( $n=23$ ) and rain ( $n=10$ ) samples were aggregated to assess  
229 seasonal variability in precipitation (Table S2). Rain gauges were made to U.S. Weather Bureau  
230 specifications with a capacity of 27.9 cm x 2 mm. Gauges were situated in areas sheltered from  
231 winds, attempting to maintain at least two lengths of surrounding tree height to avoid turbulence.  
232 Mineral oil was used to limit evaporative effects.

### 233 2.2.2 Stream Discharge

234 We measured stream discharge five times between June 25th and August 30th at the sites:  
235 Upstream of Fractures, Downstream of Fractures, and Coal-15 (Table S3). Starting August 3<sup>rd</sup>,  
236 discharge measurements were moved downstream from Upstream of Fractures to CC-6 because  
237 of beaver activity that dammed the Upstream site. Discharge was measured using a SonTek  
238 FlowTracker Handheld Acoustic Doppler Velocimeter. Cross sections were selected based on  
239 characteristics of straight channel, minimal boulders on stream bed, and evenly distributed flow  
240 across the channel. Due to changes in flow depth, cross section location varied throughout the  
241 summer to achieve the most accurate measurements.

### 242 *2.3 Isotope Sample Analysis*

243 Concentrations of <sup>222</sup>Rn in the water samples were measured using a RAD7 instrument  
244 (mfd. by DurrIDGE Co. Inc., Billerica MA). A closed loop system connected to the RAD7 (the  
245 RAD H20 for 2 L bottles - DurrIDGE Co.) was used to sparge <sup>222</sup>Rn for quantification within the  
246 instrument. After 15-minutes of sparging, counting began for 15-minute periods. After the first  
247 four counting periods (or one hour) the internal air pump of the RAD 7 was turned off, and  
248 counting continued for at least 10 counting periods, or a total counting time of at least 2.5 hours.  
249 The average temperature of the water sample during the sparging process was measured using a  
250 thermo-couple electronic thermometer (Thermopen MK4, ThermoWorks, USA) held to the  
251 bottle with a Velcro strap. This temperature was used to calculate the partitioning of <sup>222</sup>Rn  
252 between the air-loop and the water sample. Between sample analyses, the entire system was  
253 purged for 15 minutes with the atmosphere to remove <sup>222</sup>Rn from the system and reduce internal  
254 humidity. Statistical pooling of the counting periods for individual analyses was conducted using  
255 Isoplot (Ludwig, 2012). Measured <sup>222</sup>Rn concentrations were corrected for radioactive decay to  
256 the time of sample collection (typically measurements were analyzed < 48 hrs. post sample  
257 collection). Average analytical uncertainty was 1.2 pCi/L. <sup>222</sup>Rn concentrations are reported in  
258 Table 2 as pCi/L.

259 Hydrogen and oxygen isotope ratios of water were measured using an off-axis integrated  
260 cavity output spectrometer coupled to an autosampler interfaced with a heated injector block  
261 (Los Gatos Research, San Jose, USA). Average analytical uncertainty for hydrogen and oxygen  
262 isotopes are 0.05 and 0.14 per mil, respectively. Hydrogen and oxygen isotope ratios are reported  
263 in conventional  $\delta$  notation relative to the Vienna Standard Mean Ocean Water.

### 264 *2.4 Data Analysis*

#### 265 2.4.1 Discharge, Precipitation, and Evapotranspiration Metrics

266 Mean daily Coal Creek discharge was downloaded from the USGS gage 09111250. Daily  
267 precipitation and snow water equivalent (SWE) was downloaded from SNOTEL station 380  
268 located on Mt. Crested Butte. Potential evapotranspiration (PET) was calculated using the  
269 Penman-Monteith equation using temperature, wind, dew point, and radiation data from the  
270 KCOCREST52 WunderGround weather station in Mt Crested Butte, Colorado. Both the  
271 SNOTEL and WunderGround stations are located outside the watershed but located at the  
272 approximate elevation of the Coal Creek watershed of 3149 m (3097 m and 2913 m,  
273 respectively).

274 2.4.2 Seasonal Origin Index

275 The Seasonal Origin Index (SOI) is a metric that expresses the isotope signature of the  
 276 stream water relative to seasonal precipitation isotope cycles (Allen et al., 2019b). The SOI was  
 277 calculated for each stream water sample using the following equation:

$$278 \quad SOI = \begin{cases} \frac{\delta_x - \delta_{annP}}{\delta_{summerP} - \delta_{annP}} & \text{if } \delta_x > \delta_{annP} \\ \frac{\delta_x - \delta_{annP}}{\delta_{annP} - \delta_{winterP}} & \text{if } \delta_x < \delta_{annP} \end{cases}, \quad (\text{eq. 1})$$

279 where  $\delta_x$  is the  $\delta^{18}\text{O}$  isotopic signature of stream water, and  $\delta_{winterP}$ ,  $\delta_{summerP}$ , and  $\delta_{annP}$  are the  
 280  $\delta^{18}\text{O}$  isotopic signatures of volume-weighted winter, summer, annual precipitation at Coal Creek.  
 281 The SOI is -1 when all the stream water is comprised of winter precipitation ( $\delta_{winterP}$ ), +1 when  
 282 all the stream water is comprised of summer precipitation ( $\delta_{summerP}$ ), and 0 when the stream water  
 283 isotopic composition is equivalent to the weighted average of all water year precipitation ( $\delta_{annP}$ ).

284 2.4.3 Estimation of Groundwater Discharge Volume

285 Groundwater discharge volume along the fracture zone was estimated for six different  
 286 stream reaches throughout the summer (6/23-8/30) using StreamTran (Smerdon and Gardner,  
 287 2022), a Python-based, one-dimensional advective-dispersive transport model that uses coupled  
 288 mass balance equations of  $^{222}\text{Rn}$  concentration and discharge measurements along a transect to  
 289 estimate lateral groundwater discharge into the stream. StreamTran does not account for  
 290 increases in stream  $^{222}\text{Rn}$  concentration due to hyporheic exchange. The mass balance equation  
 291 representing discharge is given by:

$$292 \quad \frac{dQ}{dx} = Pw - Ew + \frac{Q_T}{dx} + q_{gi}w - q_{go}w \quad (\text{eq.2})$$

293 where  $Q$  ( $\text{m}^3 \text{s}^{-1}$ ) is stream discharge,  $x$  (m) is discretized distance downstream,  $P$  ( $\text{m s}^{-1}$ ) is the  
 294 precipitation rate,  $E$  ( $\text{m s}^{-1}$ ) is the evaporation rate,  $Q_T$  ( $\text{m}^3 \text{s}^{-1}$ ) is tributary discharge,  $q_{gi}$  ( $\text{m s}^{-1}$ ) is  
 295 the groundwater discharge gain flux,  $q_{go}$  ( $\text{m s}^{-1}$ ) is the groundwater loss flux, and  $w$  is the stream  
 296 width in meters.

297 For 1d advective-dispersive transport of  $^{222}\text{Rn}$  in the stream, including groundwater  
 298 inflow, atmospheric gas exchange, and solute decay, the mass balance equation is given by:

$$299 \quad \frac{dC}{dx} = \frac{d}{dx} \left( \frac{DA}{Q} \right) \left( \frac{dC}{dx} \right) + \frac{q_{gi}w}{Q} (C_{GW} - C) + \frac{Q_T}{dxQ} (C_T - C) - \frac{kw}{Q} (C - C_{ATM}) - \frac{A}{C} \lambda C \quad (\text{eq.3})$$

300 where  $C$  ( $\text{mol m}^{-3}$ ) is the stream concentration,  $D$  ( $\text{m}^2 \text{s}^{-1}$ ) is the longitudinal hydrodynamic  
 301 dispersivity,  $A$  ( $\text{m}^2$ ) is the stream cross-sectional area,  $C_{GW}$  ( $\text{mol m}^{-3}$ ) is the local groundwater  
 302 concentration,  $k$  ( $\text{m s}^{-1}$ ) is the gas exchange velocity,  $C_{ATM}$  ( $\text{mol m}^{-3}$ ) is the atmospheric  
 303 equilibrium concentration of the tracer,  $\lambda$  ( $\text{s}^{-1}$ ) is the decay coefficient, and  $C_T$  ( $\text{mol m}^{-3}$ ) is the  
 304 tributary concentration.

305 2.4.3.1 Solution technique and boundary conditions

306 Equations 2 and 3 are fully coupled and solved using a fully implicit, finite volume  
 307 method based using *FiPy* (Guyer et al., 2009), a python finite volume solver library. Equation 2  
 308 and 3 are solved simultaneously to estimate groundwater gain and loss along the stream reach  
 309 given measured discharge, stream geometry, tributary input, precipitation, evaporation, and  $^{222}\text{Rn}$   
 310 concentration along the stream reach. The groundwater concentration of  $^{222}\text{Rn}$ ,  $^{222}\text{Rn}$  gas  
 311 exchange velocity, and  $^{222}\text{Rn}$  decay coefficient are required estimated parameters. The coupled  
 312 equations are optimized using a Marquart-Levenberg optimization routine to minimize the chi  
 313 squared residual between the observed and modeled  $^{222}\text{Rn}$  and discharge stream measurements.  
 314 From these optimized equations, groundwater discharge is estimated along the transect at  $n$   
 315 equally spaced intervals, where  $n$  is equal to the number of samples.

316 The stream is discretized into 10000 equally spaced approximately  $\frac{1}{3}$  meter grids from  
 317 upstream to downstream. Model unit length varied between sampling date 08/30/21 and other  
 318 dates because samples from 08/30/21 began further downstream due to new construction of a  
 319 beaver dam at the Upstream sampling location. Constant discharge and concentration (Dirichlet)  
 320 boundary conditions are set at the upstream end of the model and set to the measured  
 321 concentration and discharge at the most upstream site for a given sampling event. Constant  
 322 discharge (Dirichlet) and constant concentration gradient (Neumann) boundary conditions are set  
 323 at the downstream end of the model.

#### 324 2.4.3.2 Parameterization

325 The model was parameterized to represent site conditions at the time of synoptic  
 326 sampling (Table 1). Atmospheric equilibrium concentration of  $^{222}\text{Rn}$  was set to zero. The  $^{222}\text{Rn}$   
 327 decay coefficient was set to  $3.82 \text{ d}^{-1}$  (Cook and Herczeg, 2000). The fully implicit finite volume  
 328 technique used controls the dispersive flux in the solution even when set to zero. Therefore,  
 329 longitudinal hydrodynamic dispersivity was set to zero, which means that numerical dispersion  
 330 of the grid cell spacing ( $\sim 1/3 \text{ m}$ ) controls the dispersive flux (Beisner et al., 2018). Stream width  
 331 and depth were measured each time discharge was measured (SI Table 1, SI Text 1) and linearly  
 332 interpolated along the stream reach.

333 Initial  $^{222}\text{Rn}$  gas exchange velocities were calculated for each sampling event using  
 334 estimated stream geometry and flow characteristics and were assumed to be constant for the  
 335 length of the reach (SI Table 2). Groundwater  $^{222}\text{Rn}$  concentration was measured from six  
 336 springs across the watershed. Calculated gas exchange velocities based on equations from  
 337 Raymond et al., (2012) and measured  $^{222}\text{Rn}$  concentrations lead to underestimation of discharge  
 338 and overestimation and ill-fitting of measured  $^{222}\text{Rn}$  concentrations (Text S3; Figures S2 and S3),  
 339 which is not surprising given that gas exchange velocity and groundwater  $^{222}\text{Rn}$  concentrations  
 340 are highly variable (Ulseth et al., 2019; Mullinger et al., 2009). Therefore, we used Monte Carlo  
 341 simulations to estimate a range of gas exchange velocities and groundwater  $^{222}\text{Rn}$  concentrations.  
 342 Gas exchange velocity is highly dependent on-stream turbulence. For high-energy, montane  
 343 streams, the accuracy of empirical equations for estimating gas exchange velocity often  
 344 diminishes. For streams with slopes similar to Coal Creek ( $0.029 \text{ m m}^{-1}$ ), gas exchange velocities  
 345 have been observed between 1 and  $100 \text{ m d}^{-1}$  (Ulseth et al., 2019). Monte Carlo simulations were  
 346 run for each modeled sampling event using gas exchange velocities between 10 and  $105 \text{ m d}^{-1}$  (  
 347  $\leq 10$  times estimated gas exchange velocity using empirical equations (SI Text 2)) and  
 348 groundwater  $^{222}\text{Rn}$  concentrations between 100 and  $600 \text{ pCi L}^{-1}$  (approximate minimum and

349 maximum measured spring concentrations; Table 1). A total of 3,000 Monte Carlo simulations  
 350 per modeled synoptic event were run to estimate the gas exchange velocity and groundwater  
 351  $^{222}\text{Rn}$  concentration for each synoptic event. Model fit was evaluated using the Akaike  
 352 Information Criterion (AIC). AIC is an estimation of prediction error, generally used to compare  
 353 models and determine which is the best fit for the data (Bozdogan, 1987). Here, low AIC values  
 354 indicate better fit between measured and modeled discharge and  $^{222}\text{Rn}$  concentrations. To  
 355 represent a range of conditions which may give optimal model performance, we evaluated  
 356 groundwater  $^{222}\text{Rn}$  concentrations and gas exchange velocities from model runs within the top  
 357 5% of AIC values (150 runs for each synoptic event). The median values of groundwater  $^{222}\text{Rn}$   
 358 concentration and gas exchange velocity from the top 5% simulation runs were used to  
 359 parameterize the StreamTran model. Pairings of the minimum groundwater  $^{222}\text{Rn}$  concentration  
 360 and minimum gas exchange velocity, and the maximum groundwater  $^{222}\text{Rn}$  concentration and  
 361 maximum gas exchange velocity, from the top 5% best models were used to characterize  
 362 uncertainty around the MC estimated groundwater flux.

363 Table 1: Model input parameters.

| Parameter      | Definition  | Value    | Note                            |
|----------------|---|----------|---------------------------------|
| P              | Precipitation ( $\text{ms}^{-1}$ )                      | 0        | Field conditions                |
| E              | Evaporation ( $\text{ms}^{-1}$ )                        | Table S5 | Estimated using Penman-Monteith |
| w              | Width (m)   | Table S4 | Stream discharge measurements   |
| d              | Depth (m)   | Table S4 | Stream discharge measurements   |
| A              | Cross Sectional Area ( $\text{m}^2$ )                   | w*d      | Stream discharge measurements   |
| D              | Dispersivity ( $\text{m}^2\text{s}^{-1}$ ) <sup>1</sup> | 0        | Beisner et al. (2018)           |
| k <sup>†</sup> | gas exchange velocity ( $\text{ms}^{-1}$ )              | Table 3  | Estimated using MC simulation   |

| Parameter                 | Definition  | Value                 | Note  |
|---------------------------|---|-----------------------|---|
| P                         | Precipitation ( $\text{ms}^{-1}$ )                              | 0                     | Field conditions                            |
| E                         | Evaporation ( $\text{ms}^{-1}$ )                                | Table S5              | Estimated using Penman-Monteith             |
| w                         | Width (m)   | Table S4              | Stream discharge measurements               |
| d                         | Depth (m)   | Table S4              | Stream discharge measurements               |
| A                         | Cross Sectional Area ( $\text{m}^2$ )                           | w*d                   | Stream discharge measurements               |
| $\lambda$                 | Rn decay coefficient ( $\text{s}^{-1}$ )                        | $4.43 \times 10^{-5}$ | Cook and Herczeg (2000)                     |
| $C_{\text{atm}}$          | Atmospheric $^{222}\text{Rn}$ concentrations ( $\text{pCi/L}$ ) | 0                     | Field conditions                            |
| $C_{\text{gw}}^{\dagger}$ | Groundwater $^{222}\text{Rn}$ concentrations                    | Table 3               | Estimated using MC simulation               |
| $C_{\text{tr}}$           | $^{222}\text{Rn}$ concentration in Elk Creek ( $\text{pCi/L}$ ) | 2.1                   | Field conditions, measured on July 27, 2021 |

364 † indicates parameters that varied during optimization routine

#### 365 2.4.3.3 Discharge and stream geometry relationships

366 Discharge along the modeled stream reach is a required input for parameterization of  
 367 StreamTran. Discharge was measured five times throughout the summer at Upstream/CC6,



368 Downstream, and Coal-15. Upstream and CC6 are combined into one site because beginning  
 369 August 3<sup>rd</sup> measurements had to be moved downstream from Upstream to CC6 due to  
 370 construction of a new beaver dam. These two sites are 161 m apart. Since stream discharge is  
 371 responsive to monsoon rains, using measured discharge close to the sampling date is not  
 372 sufficient. Thus, linear regressions between each measured site and the USGS gage data were  
 373 performed to estimate discharge along the stream reach throughout the summer (Figure S1).

374 Width and depth were measured with discharge and are also required inputs along the  
 375 stream reach. However, these parameters are responsive to changes in discharge and thus to  
 376 precipitation inputs from monsoon rains. Width and depth were regressed against measured  
 377 discharge (Figure S1), and those relationships were used to estimate width and depth from  
 378 modeled discharge. Modeled discharge, width, and depth were used as inputs for each transect  
 379 run in StreamTran (Table S5).

#### 380 2.4.4 Estimation of dynamic storage

381 We estimated the change in dynamic storage of Coal Creek over the course of the  
 382 summer using a water balance analysis. The change in dynamic storage ( $dS$ ) was calculated as  
 383 follows:

$$384 \quad dS(t) = \sum_{t=1}^T (P(t) - Q(t) - ET(t)) \text{ (eq.4)}$$

385 where  $t$  is time in days (in this study  $t=1$  on June 1, 2021),  $P$  is precipitation (mm),  $Q$  is stream  
 386 water discharge (mm), and  $ET$  is evapotranspiration (mm). Actual  $ET$  measurements are not  
 387 available for Coal Creek; we use  $PET$  calculated from the Penman Monteith equation in our  
 388 calculations of  $dS$ . Coal Creek is a well-watered system and meets most of the assumptions  
 389 required for Penman Monteith. The  $dS$  was calculated at a daily time stamp between June 1 and  
 390 September 30. This water budget does not account for interbasin groundwater flow nor overland  
 391 flow out of the catchment that is not routed into the stream. Although this is a simplification of  
 392 the water budget, it represents the dominant processes that control water fluxes in montane  
 393 catchments (Ryken et al., 2021). Uncertainty around  $dS$  was estimated assuming a 10% error in  
 394 precipitation measurement (Larson, 1974; Ehsani and Behrangi, 2022), a 20% error in  $PET$   
 395 relative to  $AET$  (Hua et al., 2020; Westerhoff, 2015; Klingston et al., 2009), and a 13% error in  
 396 stream water discharge calculated as the average percent difference between measured and gage-  
 397 estimated discharge values for Coal Creek.

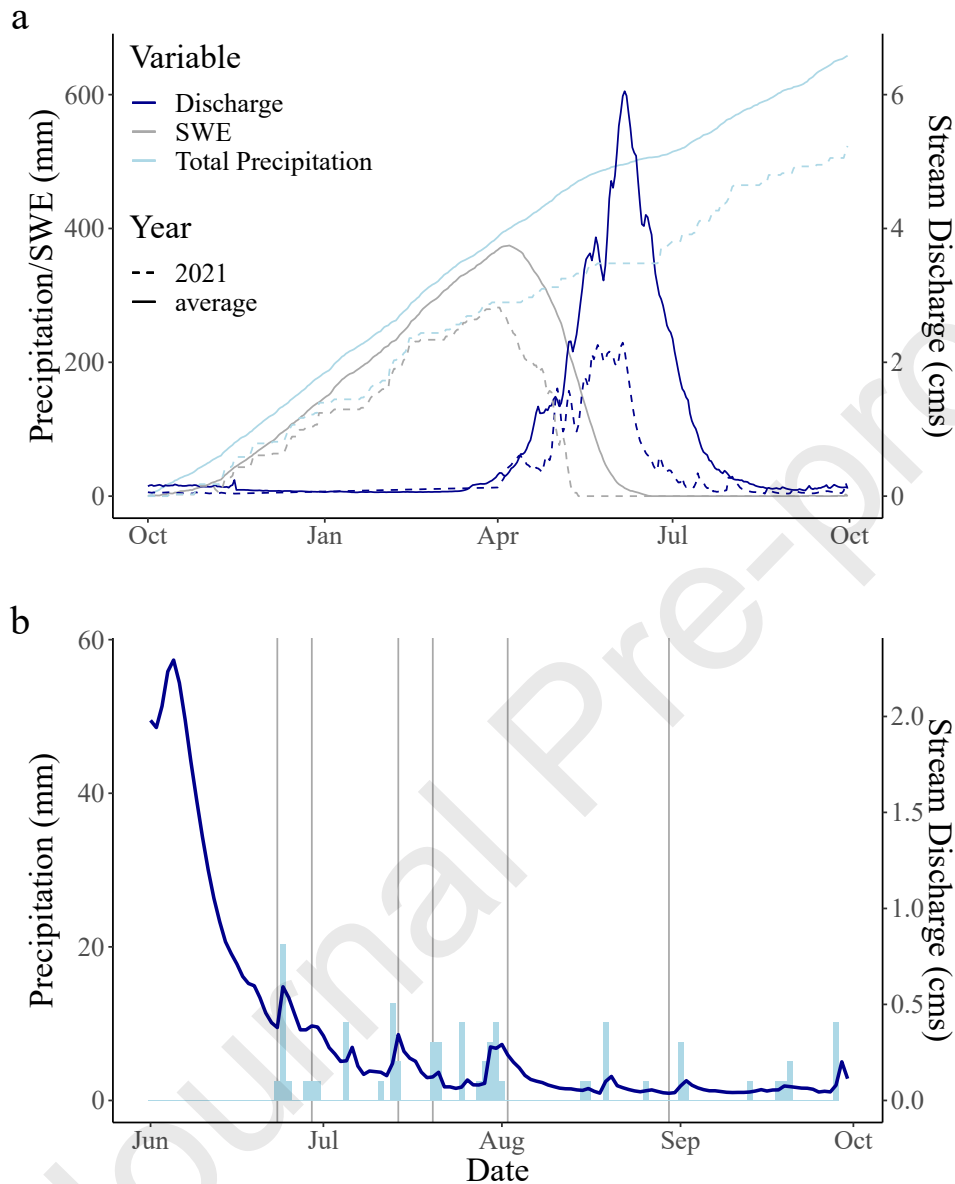
### 398 **3.0 Results**

#### 399 *3.1 Hydro-climatology of Coal Creek*

400 In Coal Creek, the 2021 water year was overall drier than average, receiving only 523  
 401 mm of precipitation, compared to the average 658 mm. However, the precipitation deficit was  
 402 confined predominantly to winter (October 1 – March 31) and spring (April 1-June 29), where  
 403 only 290 mm and 88 mm of precipitation fell, compared to the average 387 mm and 126 mm,  
 404 respectively. The total amount of rain during the summer (June 30-September 30) was equivalent  
 405 to the average (145 mm). The snow drought of 2021 led to 62% lower than average peak flows  
 406 ( $6.05 \text{ m}^3 \text{ s}^{-1}$ ) and 57% lower than average summer base flows ( $0.095 \text{ m}^3 \text{ s}^{-1}$ ; defined as the 10<sup>th</sup>



407 percentile flow between July 1 and September 30). Precipitation events during the summer of  
 408 2021 were generally concentrated between late June and July, with occasional precipitation  
 409 events occurring through the rest of the summer (Figure 2b).



410

411 Figure 2: (a) Average water year precipitation accumulation (left-hand axis), snow water equivalent (SWE, left-hand  
 412 axis), and stream discharge (right-hand axis) in Coal Creek. Dashed lines, but same color coding, show the  
 413 respective curves for the 2021 water year. (b) Precipitation events and stream discharge (same color scheme as  
 414 above) during summer sampling period (June 1 - September 30, 2021). Gray vertical lines indicate sampling dates  
 415 included in the model.

416 *3.2 Evaluating stream response to monsoon rains through synoptic stream chemistry sampling*

417 3.2.1 Radon Samples

418 Stream water  $^{222}\text{Rn}$  concentrations ranged from 2 to 20 pCi/L, while spring water samples  
 419 varied from 183 to 651 pCi/L. The highest stream  $^{222}\text{Rn}$  was measured at Upstream Elk and the  
 420 lowest was measured at Downstream (Figure 3).  $^{222}\text{Rn}$  was least variable at Upstream of  
 421 Fractures (deviation from mean (%Dev) < 20%), moderately variable at CC6, CC8, and  
 422 Downstream of Fractures (20% < %Dev < 30%), and highly variable at CC7, Upstream of Elk,  
 423 and Coal-15 (%Dev > 30%) (Table 1, Figure 3).

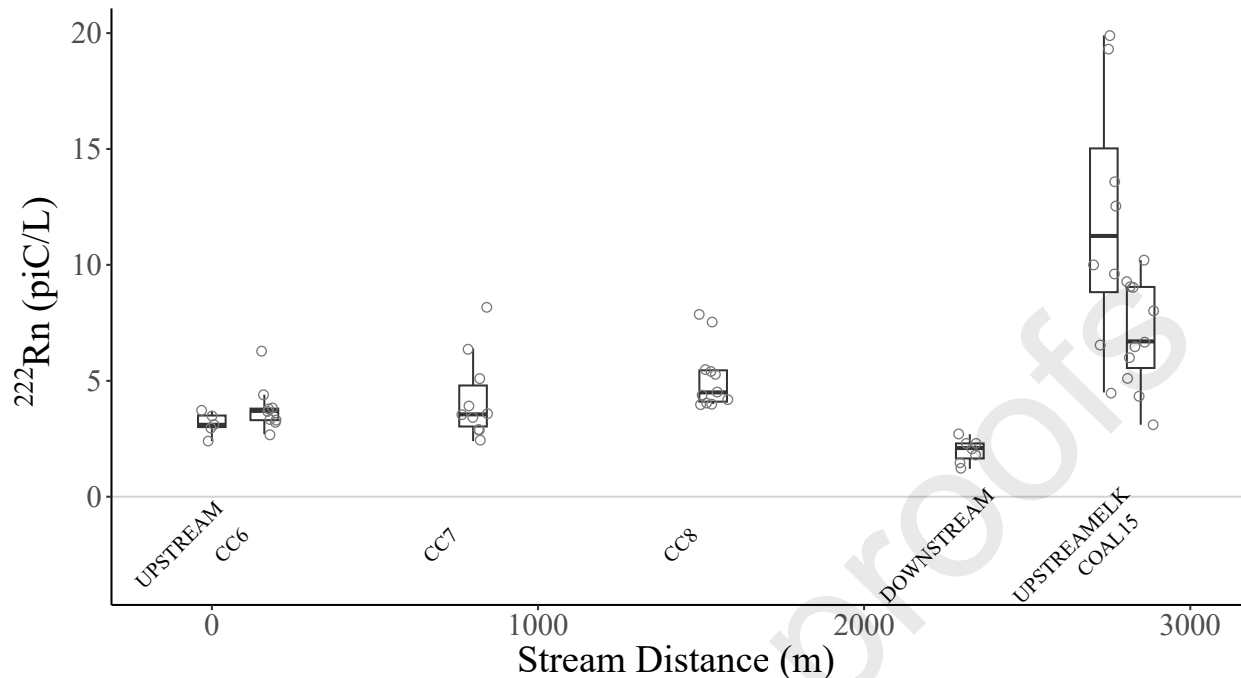
424 Table 2: Sites, times sampled, stream meter, and mean and deviation from mean (standard deviation/mean) of  $^{222}\text{Rn}$ ,  
 425  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  water isotope measurements.

| Site         | Class        | Times Sampled   | Stream Meter | $^{222}\text{Rn}$ Mean (pCiL <sup>-1</sup> ) | $^{222}\text{Rn}$ Dev. from Mean (%) | $\delta^{18}\text{O}$ Mean (‰) | $\delta^{18}\text{O}$ Dev from Mean (%) | $\delta^2\text{H}$ Mean (‰) | $\delta^2\text{H}$ Dev from Mean (%) |
|--------------|--------------|-----------------|--------------|--|--------------------------------------|--------------------------------|---|-----------------------------|--------------------------------------|
| Upstream     | fracture     | 7 <sup>+</sup>  | 11956        | 3  | 16                                   | -16.1                          | 1.86                                    | -118.5                      | 2.5                                  |
| CC6          | fracture     | 11 <sup>+</sup> | 11795        | 4  | 26                                   | -15.8                          | 5.70                                    | -116.0                      | 5.5                                  |
| CC7          | fracture     | 12 <sup>+</sup> | 11155        | 4  | 43                                   | -15.6                          | 4.49                                    | -115.0                      | 4.6                                  |
| CC8          | fracture     | 13 <sup>+</sup> | 10419        | 5  | 27                                   | -15.6                          | 4.49                                    | -114.7                      | 4.6                                  |
| Downstream   | fracture     | 9 <sup>+</sup>  | 9632         | 2  | 25                                   | -15.8                          | 3.80                                    | -116.4                      | 3.4                                  |
| Upstream Elk | non-fracture | 9 <sup>+</sup>  | 9221         | 12   | 46                                   | -15.5                          | 3.87                                    | -114.2                      | 4.0                                  |
| Elk Creek    | non-fracture | 3 <sup>+</sup>  | 9196         | 2  | NA                                   | -16.7                          | 3.17                                    | -122.3                      | 3.82                                 |

|                       |              |                 |      |     |    |       |      |            |     |
|-----------------------|--------------|-----------------|------|-----|----|-------|------|------------|-----|
| Coal15                | non-fracture | 13 <sup>†</sup> | 9108 | 7   | 33 | -15.6 | 3.21 | -<br>116.6 | 3.5 |
| Spring 1 <sup>‡</sup> | spring       | 1               | NA   | 208 | NA | NA    | NA   | NA         | NA  |
| Spring 2              | spring       | 1               | NA   | 619 | NA | -17.2 | NA   | -<br>125.6 | NA  |
| Spring 3 <sup>‡</sup> | spring       | 1               | NA   | 651 | NA | NA    | NA   | NA         | NA  |
| Spring 4              | spring       | 1               | NA   | NA  | NA | -17.1 | NA   | -<br>125.1 | NA  |
| Spring 5              | spring       | 1               | NA   | 608 | NA | -16.6 | NA   | -<br>125.2 | NA  |
| Spring 6 <sup>‡</sup> | spring       | 1               | NA   | 265 | NA | -17.5 | NA   | -<br>128.3 | NA  |
| Spring 7 <sup>‡</sup> | spring       | 1               | NA   | 183 | NA | -17.1 | NA   | -<br>123.8 | NA  |

426 † Number of samples analyzed for isotope data; <sup>222</sup>Rn analysis was conducted two fewer times than the listed value.

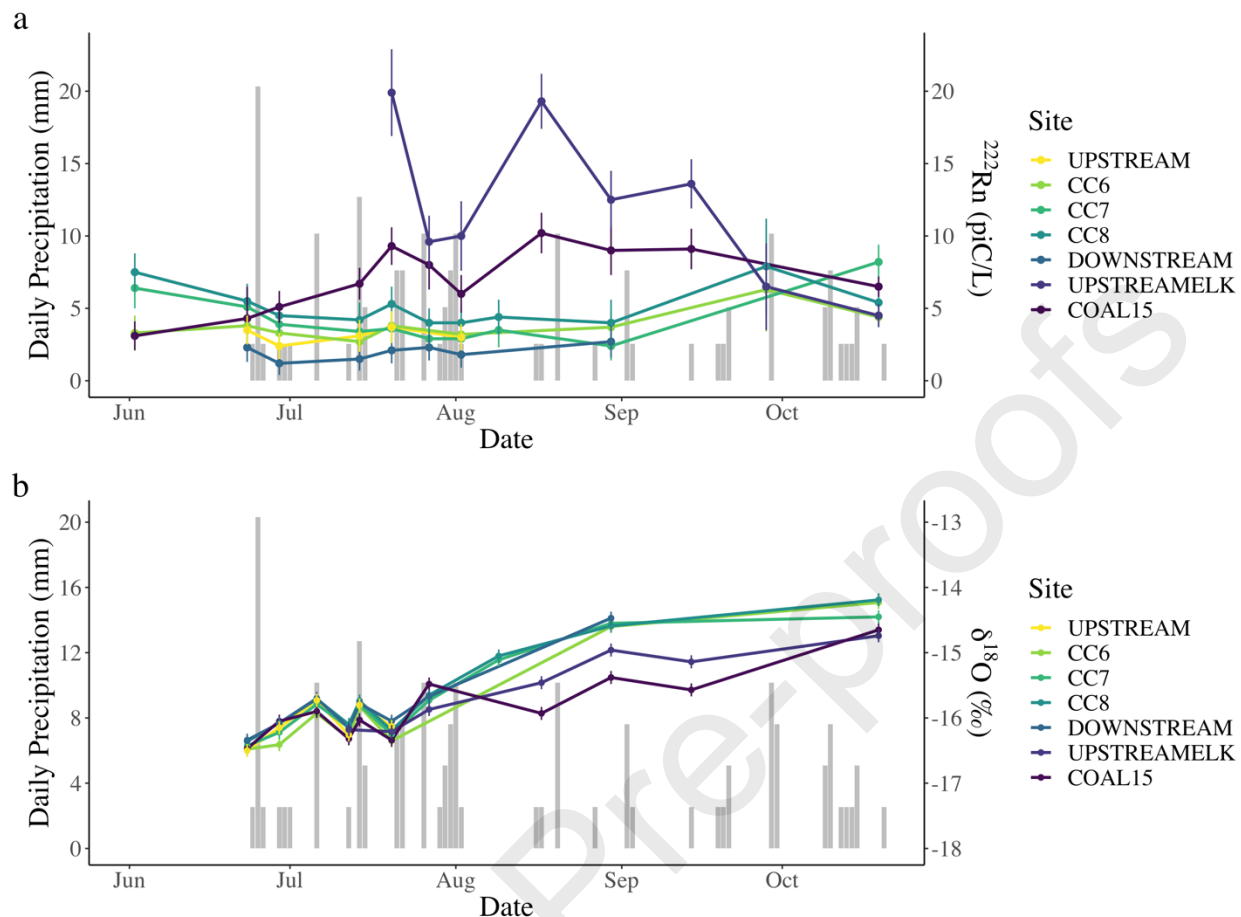
427 ‡ Indicates <sup>222</sup>Rn and water isotope samples were collected on different days and that <sup>222</sup>Rn concentrations were  
428 collected in 250 mL glass vials. Unmarked spring samples were collected in 500 mL plastic bottles.



429

430 Figure 3.  $^{222}\text{Rn}$  concentrations at surface water locations with distance downstream, not including Elk Creek.  
 431 Lower and upper lines of boxplot box are quartile 1 and 3, respectively. The middle line is the median. Vertical lines  
 432 indicate minimum and maximum, if less than  $\pm 1.5 \times \text{IQR}$ . Points outside  $\pm 1.5 \times \text{IQR}$  are  
 433 considered outliers and are plotted above/below vertical lines. Open points show all samples collected on a given  
 434 date.

435 Increasing or decreasing patterns of  $^{222}\text{Rn}$  were not temporally consistent at all sites  
 436 (Figure 4a). In general, fracture zone sites showed a decreasing trend in  $^{222}\text{Rn}$  concentration at  
 437 the beginning of the summer before flattening out in July, and then increased again in late  
 438 summer/early fall. Unlike the fracture zone sites,  $^{222}\text{Rn}$  concentrations at Coal-15 were low in  
 439 June and increased throughout the summer before decreasing again at the end of summer.  $^{222}\text{Rn}$   
 440 concentrations at Upstream Elk were also high during summer and declined at the end of the  
 441 summer. Across all sites, peaks in  $^{222}\text{Rn}$  were observed in mid-July, and non-fractured zone sites  
 442 there was an additional peak observed in mid-August peak. In general, peaks coincided with dry  
 443 periods while lower  $^{222}\text{Rn}$  concentrations coincided with periods of time with more precipitation.

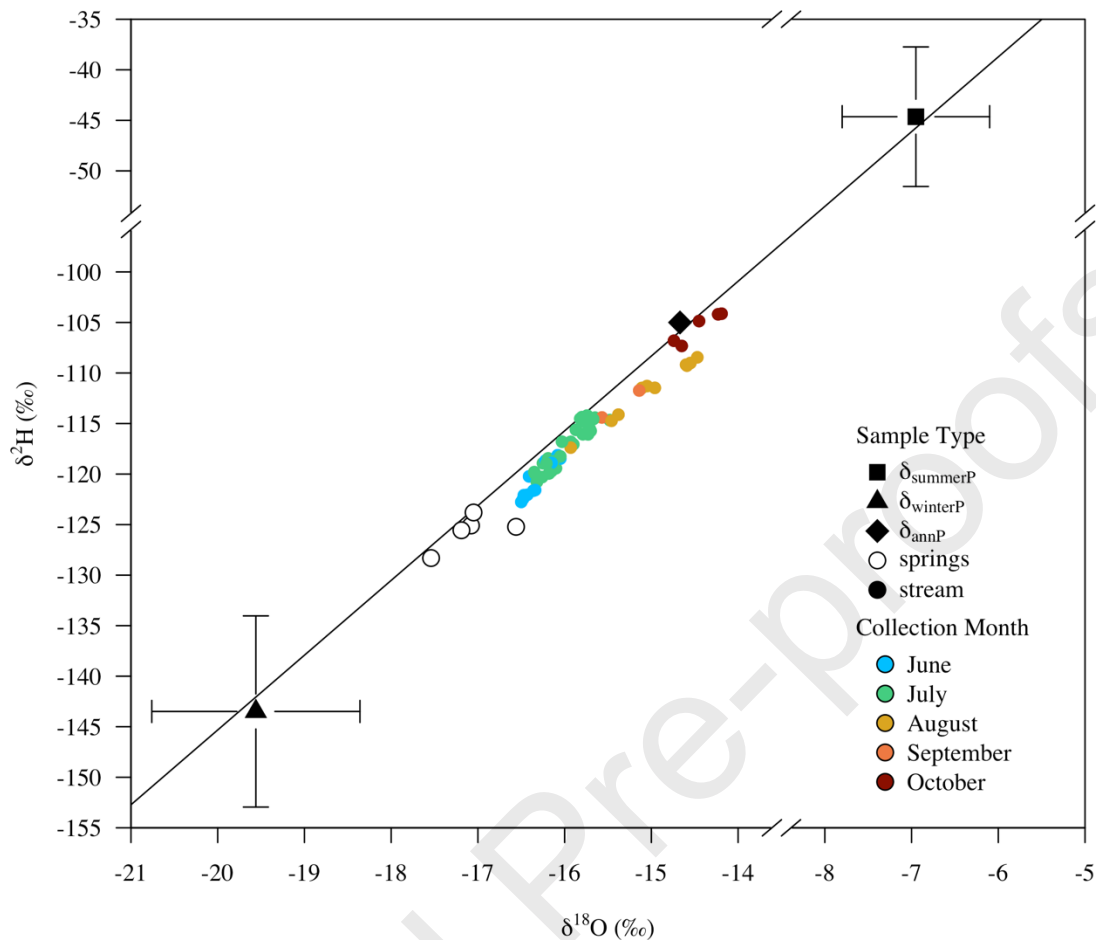


444

445 Figure 4. (a)  $^{222}\text{Rn}$  concentrations and (b)  $\delta^{18}\text{O}$  values and the analysis uncertainty (vertical lines) at sites (colored  
 446 lines) as compared to the daily precipitation at Coal Creek (gray bars).

### 447 3.2.2 Water Isotope Samples

448 Stream water  $\delta^{18}\text{O}$  values ranged from -16.5 to -14.2 ‰, while spring water samples were  
 449 consistently more depleted than stream water and varied from -17.54 to -16.56 ‰ (Figure 5).  
 450 Precipitation  $\delta^{18}\text{O}$  values ranged from -3.83 to -26.64 ‰ ( $\delta_{\text{annP}} = -14.67$  ‰); summer rain events  
 451 (2021  $\delta_{\text{summerP}} = -6.95$  ‰) were generally more enriched than winter snow events (2021  $\delta_{\text{winterP}} =$   
 452  $-19.56$  ‰). Compared to  $^{222}\text{Rn}$  concentrations, there was less distinct spatial variation in stream  
 453  $\delta^{18}\text{O}$  values.

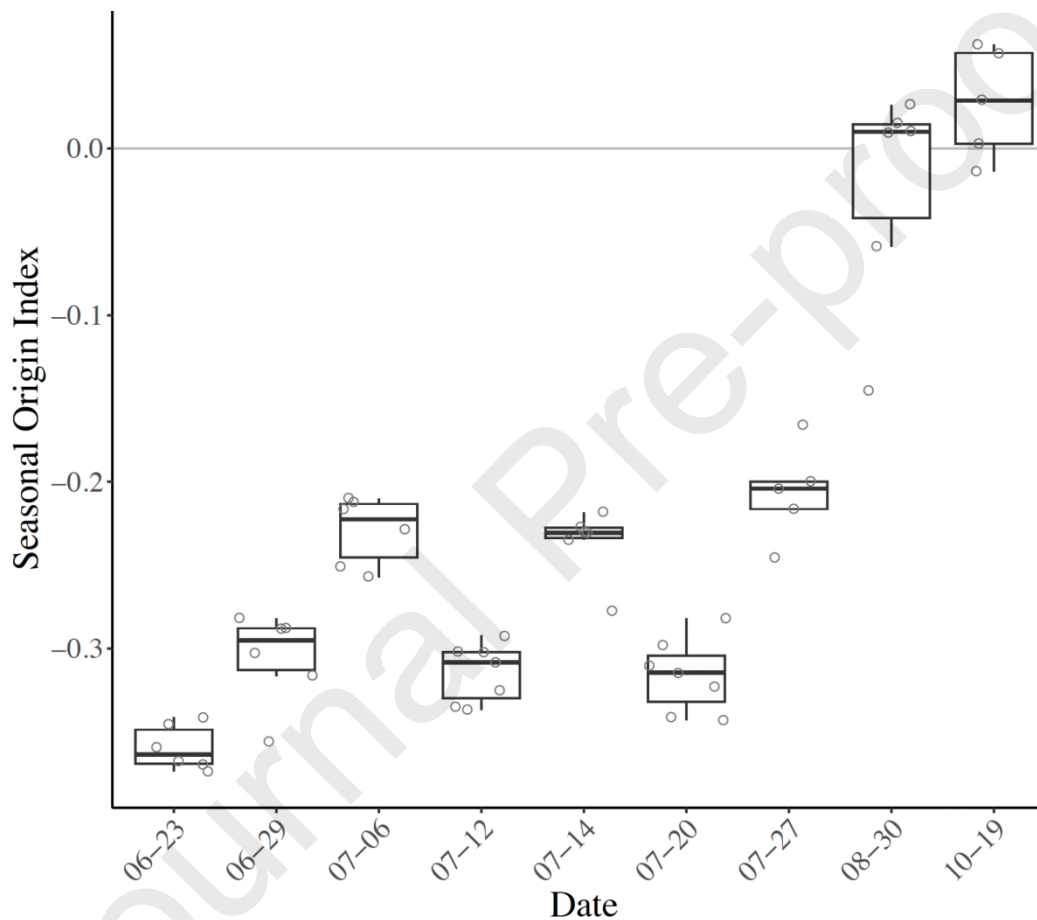


454

455 Figure 5: Dual isotope plots showing  $\delta_{\text{winterP}}$  (weighted average snow, triangle),  $\delta_{\text{summerP}}$  (weighted average  
 456 rain, square), and  $\delta_{\text{annP}}$  (weighted average annual precipitation, diamond), spring samples (open circles),  
 457 stream samples (colored circles), and the local meteoric water line (LMWL) (black line) (developed by  
 458 Carroll et al., 2018). Error bars around precipitation end members indicate weighted standard errors.  
 459 Colors indicate sample collection month.

460 There was a strong temporal variation in stream water isotope composition with more  
 461 depleted values measured at the beginning of summer and more enriched samples measured at  
 462 the end of summer (Figure 5). In general,  $\delta^{18}\text{O}$  enrichment was more pronounced in fracture zone  
 463 sites than the non-fractured zone sites, with fracture zone sites becoming more enriched later in  
 464 the summer in comparison to non-fractured zone sites. Across the entire stream transect in July,  
 465 variability in stream  $\delta^{18}\text{O}$  values were observed, where samples collected following precipitation  
 466 events (e.g., 07/06, 07/14, and 07/27) had more enriched isotopic compositions and samples  
 467 collected during drier periods (i.e., 07/12 and 07/20) had more depleted isotopic compositions  
 468 (Figure 4b). This suggests that during July, Coal Creek may be responding quickly to  
 469 precipitation events, but this stream response was not observed in sampling events outside of  
 470 July.

471 The patterns present in the temporal variation of  $\delta^{18}\text{O}$  (Figure 4b) are reflected in the  
 472 Seasonal Origin Index (SOI) (Figure 6). The SOI estimates the proportion of water in the stream  
 473 originating as winter (snow) vs summer (rain) precipitation (Figure 5). Within Coal Creek, the  
 474 SOI of most stream water samples were negative, with only late season mean SOI value falling  
 475 slightly above zero. SOI ranged from -0.37 to 0.06, with the most negative values observed  
 476 during the earliest sampling event and the positive values observed during the latest sampling  
 477 period. The variability in stream  $\delta^{18}\text{O}$  composition observed in Figure 4b is also present in  
 478 Figure 6 from dates 07/06 through 07/27. This is followed by an increase in SOI, indicating that  
 479 at the beginning of the summer, stream water origin is more snow-dominated and becomes less  
 480 snow-dominated throughout the summer.



481  
 482 Figure 6: Seasonal origin index (SOI) for stream samples at Coal Creek. Lower and upper lines of the boxplot box  
 483 are quartile 1 and 3, respectively. The middle line is the median. Vertical lines indicate minimum and maximum, if  
 484 less than  $\pm 1.5 \times \text{IQR}$ . Points outside  $\pm 1.5 \times \text{IQR}$  are considered outliers. Open points show all samples collected on  
 485 a given date. Horizontal gray line shows SOI of 0.

### 486 3.3 Model Parameterization and Performance

487 We used the StreamTran model to estimate groundwater flux into the stream between  
 488 Upstream/CC6 and Coal-15 across six different dates throughout the summer. Monte Carlo  
 489 simulations were used to estimate the gas exchange velocity and groundwater  $^{222}\text{Rn}$   
 490 concentration for each synoptic event. Values used to parameterize each synoptic event were the

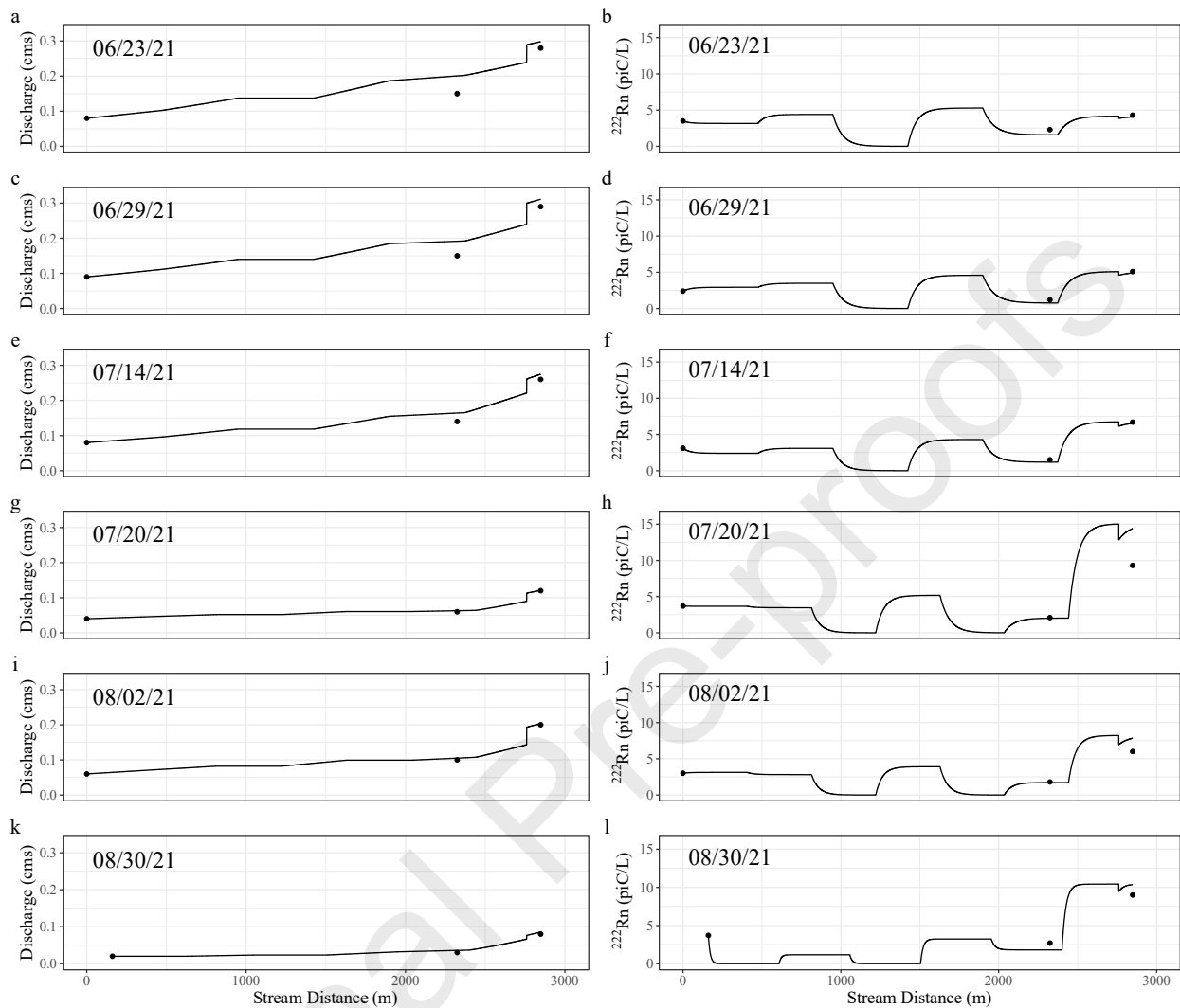


491 median of the top 5% best (lowest AIC) MC simulations (Table 3). Median groundwater <sup>222</sup>Rn  
 492 concentrations ranged from 130 to 256.5 and median gas exchange velocities ranged from 48.5  
 493 to 90. Model performance varied across modeled events, with the best performing model  
 494 representing stream conditions on 07/14 (AIC = 48.08) and the worst performing model  
 495 representing stream conditions on 07/20 (AIC = 73.14). Both modeled stream discharge and  
 496 stream <sup>222</sup>Rn concentrations generally agreed with measured values, with slight overprediction of  
 497 stream discharge during 06/23, 06/29, and 07/14, and slight overprediction of stream <sup>222</sup>Rn  
 498 concentrations during 07/20 and 08/02.

499 Table 3: Median output from top 5% Monte Carlo simulation runs for groundwater <sup>222</sup>Rn concentrations and gas  
 500 exchange velocity (GEV) for the six model dates. Final model AIC is shown as well.

| Date  | Median <sup>222</sup> Rn (pCi/L) | Median GEV (m/d) | Final Model AIC |
|-------|----------------------------------|------------------|-----------------|
| 06/23 | 139.5                            | 90.0             | 59.03           |
| 06/29 | 130.0                            | 86.5             | 54.98           |
| 07/14 | 137.0                            | 84.0             | 48.08           |
| 07/20 | 256.5                            | 48.5             | 73.14           |
| 08/02 | 188.5                            | 73.0             | 65.73           |
| 08/30 | 245.5                            | 77.5             | 60.08           |

501



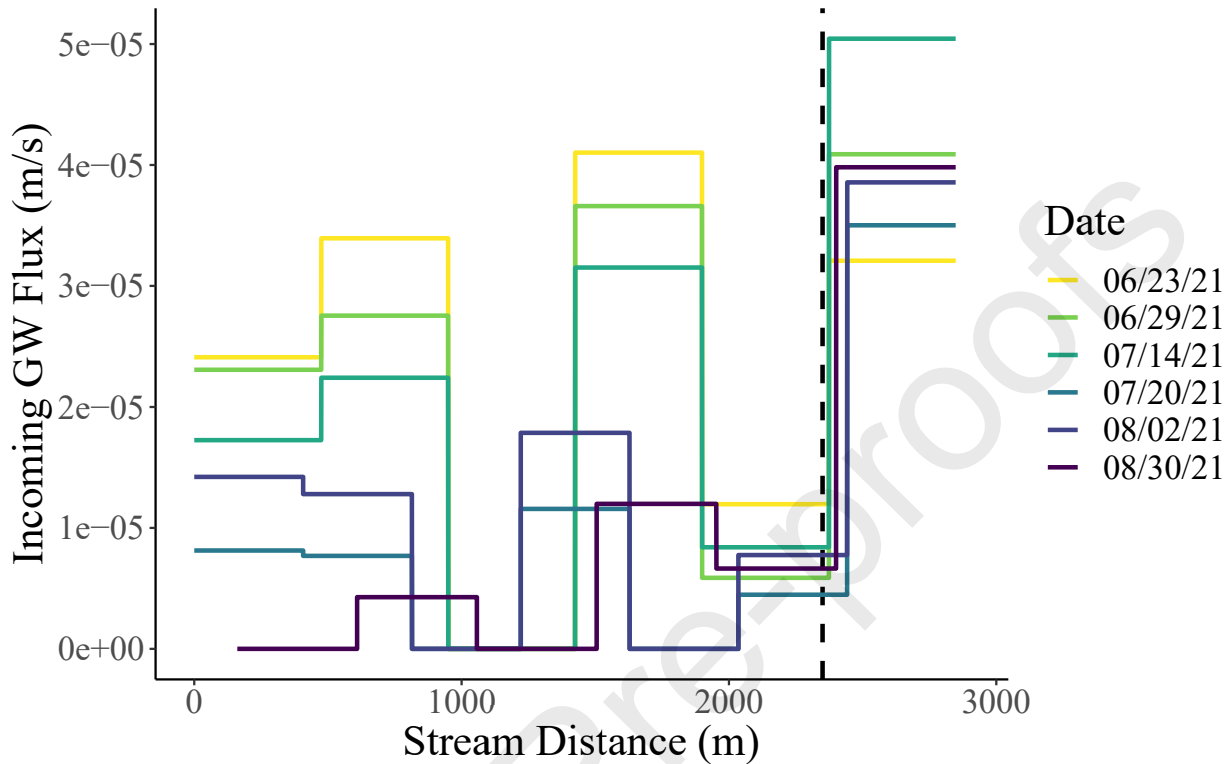
502

503 Figure 7: Stream discharge (a, c, e, g, i, k) and stream  $^{222}\text{Rn}$  concentration (b, d, f, h, j, l) measurements (points)  
 504 compared to StreamTran modeled values (line) along the stream reach.

### 505 3.4 Estimation of lateral groundwater flux through space and time

506 By evaluating the groundwater flux (Figure 8) we can quantitatively evaluate how  
 507 groundwater discharge varied in space and time. There were two distinct spikes in GW flux  
 508 along the fractured zone and consistently high GW flux in the non-fractured zone (Figure 8). We  
 509 categorized two different temporal behaviors: early summer (06/23-07/14) and late summer  
 510 (07/20-08/30). In general, during early summer, groundwater contributions between both the  
 511 fractured and non-fractured zones were similar. The highest flux from the fractures and lowest  
 512 flux from the non-fractured occurred on 06/23 and the lowest flux from the fractures and highest  
 513 flux from the non-fractured zone occurred on 07/14. There was similar spread between all three  
 514 early summer sampling dates across all three areas of groundwater contribution. In contrast,  
 515 during late summer, groundwater contribution from the fractured zone was lower than that from

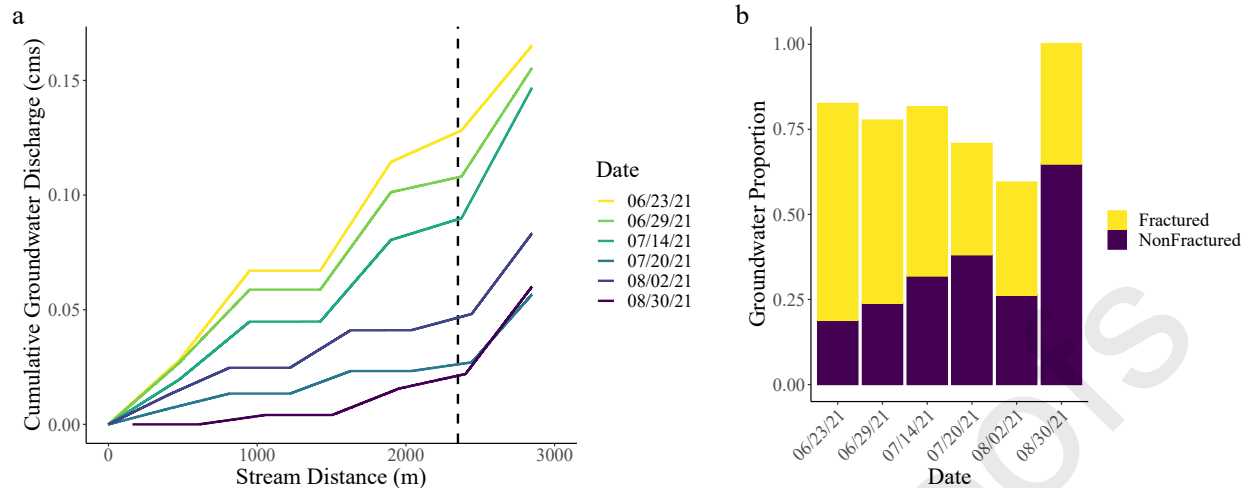
516 the non-fractured zone fan, and contribution from the fractured zone was more variable  
 517 compared to the non-fractured zone contribution.



518

519 Figure 8: Groundwater flux along stream reach for six different modeled dates (colored lines). Flux represents a  
 520 constant groundwater flow into the stream along each discretized section. Dashed line indicates the transition from  
 521 the fracture zone to non-fractured fan.

522 To convert to groundwater discharge, flux was multiplied by the average width of the  
 523 stream and 0.3 meters, which is the length of one discretized model unit. Cumulative  
 524 groundwater discharge shows a similar divide between early and late season sampling events  
 525 (Figure 9a). Early summer events show a larger absolute groundwater discharge and steeper and  
 526 steadier slope in groundwater discharge over the stream transect than late season events. Late  
 527 season events show a flatter slope in the upper portion of the stream transect, indicating less  
 528 groundwater discharge across the fracture zone, with a similar slope when compared to early  
 529 season sites along the non-fractured zone.



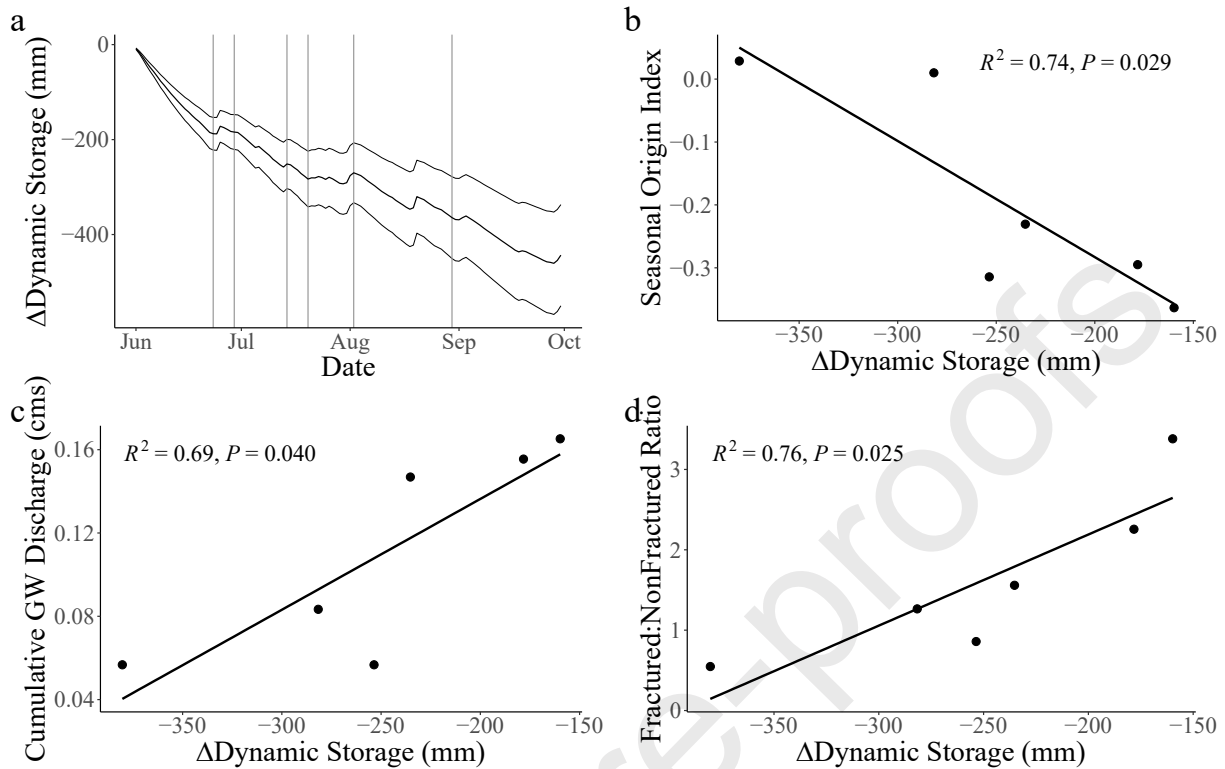
530

531 Figure 9: (a) Cumulative groundwater discharge ( $\text{m}^3 \text{s}^{-1}$ ) along the stream length of Coal Creek for six different  
 532 modeled dates (colored lines). This assumes that groundwater discharge above the most-upstream-sampled location  
 533 was zero. Dashed lines indicate transitions from fracture to non-fractured zone (2350 m). (b) The proportion of  
 534 increase in flow between Upstream/CC6 and Coal-15 attributed to groundwater for the six different modeled dates  
 535 colored according to the amount contributed from the fracture zone (< 2350 m, yellow) and the non-fractured zone  
 536 (> 2350 m, deep purple).

537 Across the six dates, the proportion of groundwater contribution to the modeled reach  
 538 ranged from 60% on August 2 to 95% on August 30 (Figure 9b). Water from the fracture zone  
 539 contributed between 35% and 77% of total groundwater with the highest proportional  
 540 contribution early in the summer. Water from the non-fractured zone contributed between 23%  
 541 and 65% of total groundwater with the highest proportional contribution later in the summer  
 542 (Figure 9b). Fracture zone contributions declined both volumetrically and proportionally  
 543 throughout the summer whereas non-fractured zone volumetric contributions stayed relatively  
 544 constant and increased their proportion.

### 545 3.5 Relating dynamic storage to SOI and groundwater discharge

546 We evaluated how catchment storage changed over the course of the summer using  
 547 changes in daily dynamic storage. Dynamic storage was highest during the beginning of the  
 548 summer and lowest at the end of the summer (Figure 10a). Over the course of the sampling  
 549 period used for modeling (6/23/21 to 8/30/21) dynamic storage declined by 176 mm, indicating  
 550 significant draining of the dynamic storage zone throughout the summer. We evaluated the  
 551 relationship between dynamic storage and SOI, cumulative groundwater discharge, and the ratio  
 552 of fractured zone to non-fractured zone groundwater discharge across the six modeled sampled  
 553 dates (Figure 10). We found significant relationships between dynamic storage and all three  
 554 parameters, indicating that periods of higher connectivity (i.e., higher dynamic storage) are  
 555 associated with more snow dominated streamflow and more groundwater discharge, specifically  
 556 originating from the fractured zone, into Coal Creek.



557

558 Figure 10: (a) Change in dynamic storage throughout the summer. Modeled sample dates are shown as vertical lines  
 559 and uncertainty around the calculated dynamic storage value is shaded grey. Panels b-d show the relationships  
 560 between change in dynamic storage and (b) seasonal origin index, (c) mean groundwater flux, and (d) the ratio of  
 561 fractured zone to non-fractured zone groundwater discharge.  $R^2$  and p-values for each relationship are shown in the  
 562 respective panel. All relationships are significant at the 0.05 level.

#### 563 4.0 Discussion

564 Changing subsurface connectivity due to variable moisture conditions is well documented  
 565 across diverse watersheds (Blume and van Meerveld, 2015; Covino, 2017). Hydrologic  
 566 connectivity describes how deep and shallow groundwater link to surface water, where in highly  
 567 connected watersheds streamflow is typically older and groundwater is typically more important  
 568 for streamflow generation (Kirchner, 2009; Ajami et al., 2011; Heidbüchel et al., 2013; McIntosh  
 569 et al., 2017). Thus, systems with lower connectivity typically rely on water in the shallow, or  
 570 dynamic, storage zone. Dynamic storage is part of overall catchment storage and defined as the  
 571 variation in storage between wet and dry periods (Spence, 2007; Kirchner, 2009; Sayama et al.,  
 572 2011; Dwivedi et al., 2018). Previous work at Coal Creek suggests that deep storage in the basin  
 573 is low, and the stream is supplied mostly from water originating in the dynamic storage zone  
 574 (Zhi et al., 2019; Johnson et al., 2023). During the summer of 2021, we sampled seven springs to  
 575 capture diverse groundwater chemistry across the catchment, yet median sampled spring  
 576 chemistry showed  $^{222}\text{Rn}$  concentrations three times higher than median modeled contributing  
 577 groundwater concentrations. This discrepancy in chemical signature between modeled  
 578 groundwater chemistry and spring samples indicate that deeper groundwater is not a major

579 contributor to the stream. Rather, streamflow generation at Coal Creek is dependent on shallow  
580 flow paths that propagate through the dynamic storage zone.

581 We used dynamic storage to understand subsurface connectivity, where periods of high  
582 dynamic storage are associated with high subsurface connectivity. Our results indicate that as the  
583 dynamic storage zone drains (i.e., high to low dynamic storage) throughout the summer, Coal  
584 Creek transitions from a high to low hydrologically connected system, relying more on shallow  
585 flow paths for streamflow (Figure 10a). This hypothesis is supported by water isotopic evidence  
586 that indicates a shift in the stream water source from snow dominance to a higher share of rain in  
587 Coal Creek throughout the summer (Figure 6), reductions in the responsiveness of groundwater  
588 discharge to the stream following precipitation events (Figure 4), and correlations between  
589 dynamic storage and SOI and GW discharge (Figure 10). Interestingly, despite the overall low  
590 storage and low connectivity of Coal Creek, groundwater inputs and isotopic responses along  
591 Coal Creek varied spatially and were related to changes in storage (Figure 8, Figure 10). These  
592 findings are discussed below in detail.

#### 593 *4.1 Stream water origin signals short residence time flow paths dominate in Coal Creek*

594 Coal Creek water origin shifts from more to less snow dominated throughout the summer,  
595 with values of SOI ranging from -0.37 to just above 0 (Figure 6). These values are similar to  
596 those observed in other monsoon-impacted and montane sites. For example, in the Xiangjiang  
597 River basin, China, SOI values ranged between -0.5 and 0 and progressively increased  
598 throughout the summer (Xiao et al., 2022). This suggests that summer precipitation in the  
599 Xiangjiang River basin is preferentially partitioned to ET, leaving predominantly winter  
600 precipitation to feed streamflow. However, SOI values have also been shown to exhibit more  
601 dramatic seasonal shifts, exemplified by Allen et al (2019a) across Swiss catchments. Here SOI  
602 values ranged from -1 to 1, indicating that more summer precipitation becomes streamflow in  
603 these catchments compared to Coal Creek.

604 At Coal Creek summer precipitation plays an increasingly important role in streamflow  
605 generation during dry periods and later in the summer (Figure 6). The increased reliance on  
606 summer precipitation for streamflow reflects a shift towards shallower flow paths driven by a  
607 decline in connectivity (Covino, 2017). We found a significant, negative relationship between  
608 SOI and dynamic storage, indicating that as dynamic storage drains (i.e., more negative dynamic  
609 storage values), SOI increases indicating a shift in stream water source towards a higher  
610 proportion of rain (Figure 10b). Shifting stream water source throughout the summer is well  
611 documented, with many catchments showing shifts towards deep groundwater (Rademacher et  
612 al., 2005; Zelazny et al., 2011), and some showing shifts towards shallower flow paths (Spencer  
613 et al., 2021; Bush et al., 2023). In catchments impacted by the North American monsoon,  
614 summer precipitation can be important for streamflow generation (Carroll et al., 2020). However,  
615 when ET demand is high, summer precipitation is often preferentially partitioned to plant uptake  
616 (Julander and Clayton, 2018), leading to winter precipitation dominating summer stream flows  
617 (Sprengrer et al, 2022; Xiao et al., 2022). For Coal Creek, increasing, but still negative, SOI  
618 values later in the summer indicate that although summer precipitation becomes more important  
619 throughout the summer, streamflow is still snow-dominated suggesting summer precipitation  
620 may be partitioned towards ET and away from stream flow generation.

621 Interestingly, we also observed stream responses to incoming precipitation during periods of  
 622 higher dynamic storage as well. In general, higher SOI values and more enriched  $\delta^{18}\text{O}$  values in  
 623 stream water followed precipitation events in early summer (Figure 4b, Figure 5). It is well  
 624 documented that precipitation can infiltrate quickly into the subsurface and, in highly permeable  
 625 areas, discharge into the stream (McDonnell et al., 1990, Wittenberg et al., 2019). We do not  
 626 observe this quick stream response to precipitation later in the summer, yet we observe an overall  
 627 enrichment of stream  $\delta^{18}\text{O}$  values and SOI. We hypothesize that this quick stream response to  
 628 precipitation is facilitated by rainfall moving through the bedrock fractures during periods of  
 629 high connectivity, which become disconnected from the stream during periods of low  
 630 connectivity and therefore no longer transport precipitation to Coal Creek. Later in the summer,  
 631 precipitation transport leading to enriched values of  $\delta^{18}\text{O}$ , and more positive SOI values, may  
 632 originate from shallow flow paths connected to the stream in high storage areas, such as the non-  
 633 fractured zone. Overall, our results suggest that the low-storage fractures respond quickly to  
 634 incoming precipitation during periods of high connectivity whereas high-storage areas of the  
 635 catchment may facilitate consistent transport of both summer precipitation through shallow flow  
 636 paths and snowmelt-recharged groundwater through deeper flow paths.

637 Climate predictions suggest that snowmelt will occur earlier (Clow, 2010; Kapnick and  
 638 Hall, 2012) and that the onset of monsoon rains will occur later (Cook and Seager, 2013) with  
 639 warming, leading to longer summer dry periods. At Coal Creek, where monsoon rains play an  
 640 important role in sustaining late summer flows, the shift in summer precipitation onset and  
 641 timing may lead to lower summer flows. In addition, increased ET (Mastrothodoros et al., 2020;  
 642 Milly and Dunne, 2020) may partition more precipitation away from streamflow generation  
 643 leading to further reductions in stream flow. With warming, groundwater is expected to become  
 644 more important for summer stream flows because of shifts in precipitation and melt timing  
 645 (Mayer and Naman, 2011; Ficklin et al., 2013; Segura et al., 2019), however in catchments like  
 646 Coal Creek lacking contributions from deep storage, localized groundwater inputs from high  
 647 storage features can provide significant amounts of flow to streams in the summer (Käser and  
 648 Hunkeler, 2014) and buffer declines in moisture throughout the summer (Herron and Wilson,  
 649 2001). Therefore, evaluating how local geology responds to changes in connectivity is critical for  
 650 understanding how Coal Creek streamflow may respond under warming conditions.

#### 651 *4.2 Groundwater contribution from fracture vs non-fracture zones show distinct temporal* 652 *variability*

653 We evaluated the spatial variability in connectivity along the Coal Creek transect through  
 654 both groundwater flux estimates and responsiveness to incoming precipitation. Groundwater flux  
 655 values ranged from 0 to  $5 \times 10^{-5} \text{ m s}^{-1}$ , and generally declined throughout the summer as dynamic  
 656 storage decreased (Figure 8, Figure 10c). Flux values ( $0$  to  $5 \times 10^{-5} \text{ m s}^{-1}$  or  $0$  to  $1.3 \text{ m}^3 \text{ m}^{-1} \text{ d}^{-1}$   
 657 (linear discharge at model unit width  $0.3 \text{ m}$ )) fall within the range of estimated groundwater  
 658 fluxes from other applications of this model. This paper is the first application of StreamTran in  
 659 a montane region, but linear discharge estimations from the Fitzroy River, Australia varied  
 660 between  $0$  and  $0.5 \text{ m}^3 \text{ m}^{-1} \text{ d}^{-1}$  (Gardner et al., 2011), and in the Daly River, Australia linear  
 661 discharge varied between  $0$  and nearly  $200 \text{ m}^3 \text{ m}^{-1} \text{ d}^{-1}$  (Smerdon et al., 2012). Higher groundwater  
 662 discharge has been observed along reaches near springs, where deeper, regional groundwater  
 663 discharges to streams (Smerdon et al., 2012; Beisner et al., 2018). In contrast, reaches with lower  
 664 discharge but more consistent groundwater contribution may reflect the presence of faults and



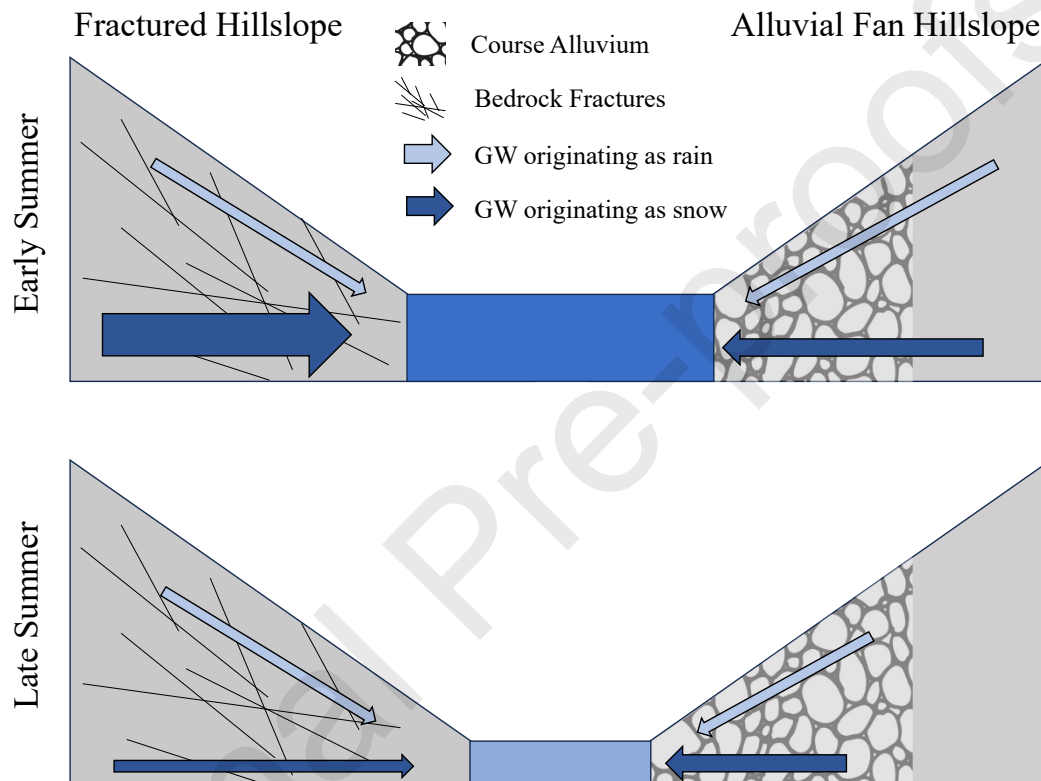
665 overlapped geology giving rise to permeable preferential flow paths (Gardner et al., 2011),  
666 functioning similar to the fractures in Coal Creek.

667 In Coal Creek, groundwater contributed between 60% and 93% of increased flow between  
668 the start and end of the modeled reach. The fracture zone contributed between 36% and 77% and  
669 the non-fractured zone contributed between 23% and 64% of groundwater influx (Figure 9).  
670 Groundwater flux through the fracture zone was highest during early summer when the  
671 subsurface is saturated from snowmelt and most hydrologically connected (Figure 8). As  
672 connectivity declined throughout the summer, groundwater fluxes through the fractures and the  
673 proportion of fracture zone contributions also declined. Studies that have evaluated how fracture  
674 flow changes with moisture conditions have found shallow fractured bedrock is highly sensitive  
675 to changes in seasonal moisture (Salve et al., 2012) and that fracture flow is significantly slower  
676 during periods of lower moisture (Flerchinger et al., 1993). In contrast, groundwater flux through  
677 the non-fractured zone is constant throughout the summer, regardless of subsurface connectivity.  
678 We used a ratio of fracture zone groundwater flux to non-fractured groundwater flux to evaluate  
679 how groundwater contribution from different features changed as connectivity declined and  
680 found a strong, significant, positive relationship between fracture: non-fractured groundwater  
681 flow and dynamic storage (Figure 10d). The fracture: non-fractured groundwater ratio ranged  
682 from  $> 3$  to  $< 1$  and declined as dynamic storage declined indicating that during periods of high  
683 connectivity the fracture zone was contributing over three times as much water as the non-  
684 fractured zone. In contrast during periods of low connectivity, the non-fractured zone contributed  
685 more than double what the fracture zone contributed indicating that this zone becomes a more  
686 important source of streamflow when dynamic storage is low. This indicates that groundwater in  
687 the non-fractured zone may be originating from an area with high subsurface storage that is  
688 hydraulically connected to the stream during periods of low connectivity (Figure 11).

689 Further evaluation of the local geology in the non-fractured zone revealed an alluvial fan at  
690 the base of Elk Creek, a perennial tributary to Coal Creek, which may facilitate the transport of  
691 water through the subsurface into the stream. Two known hydrologic factors could control  
692 subsurface flow through the alluvial fan: 1) water from Elk creek is recharging the alluvial fan  
693 and then discharges into this zone, and 2) the alluvial fan is storing and discharging water from a  
694 different source than Elk Creek. If water were directly being recharged from Elk Creek through  
695 subsurface flow paths, we would expect that the sampling sites in the non-fractured zone would  
696 have an isotopic signature that reflects mixing of upstream waters with Elk Creek over time,  
697 proportional to the contribution of water from the fractured vs non-fractured zone (Figure 9b).  
698 StreamTran model output indicates that groundwater contribution from the fan becomes  
699 increasingly important throughout the summer; if water from the fan was originating from Elk  
700 Creek, we would expect that the water at the Upstream Elk location would appear chemically  
701 similar to Elk Creek, especially later in the summer. Elk Creek remains depleted throughout the  
702 summer ( $\delta^{18}\text{O}$  mean = -16.7,  $\delta^{18}\text{O}$  SD = 0.5) whereas Upstream Elk becomes more enriched  
703 throughout the summer (Figure 4b). Additionally, Coal-15, the site downstream of Elk Creek, is  
704 consistently more depleted than the Upstream Elk site (Figure 4b), indicating that the water  
705 coming into Coal Creek from Elk Creek is more depleted than that of the water entering through  
706 the alluvial fan. We therefore conclude that the alluvial fan is storing water chemically different  
707 than Elk Creek.

708 Water flowing through the alluvial fan shows similar isotopic composition to fracture zone  
709 water during early summer (i.e., June and July) but begins to deviate starting in August, showing  
710 a more depleted signature than fracture zone samples. This suggests that alluvial fan groundwater

711 may be originating from deeper flow paths, transmitting isotopically depleted snowmelt into the  
 712 stream later in the summer due to high storage and hydrologic connectivity associated with the  
 713 fan (Figure 11). The high connectivity of the fan would allow for transport of groundwater into  
 714 the stream throughout the summer, consistent with the patterns observed in model output. This  
 715 behavior is also consistent with other studies quantifying the groundwater contribution of alluvial  
 716 fans to streams; fans have been shown to contribute significant amounts of water to streams (Liu  
 717 et al., 2004; Gordon et al., 2015), especially during low flow periods (Käser and Hunkeler,  
 718 2014).



719

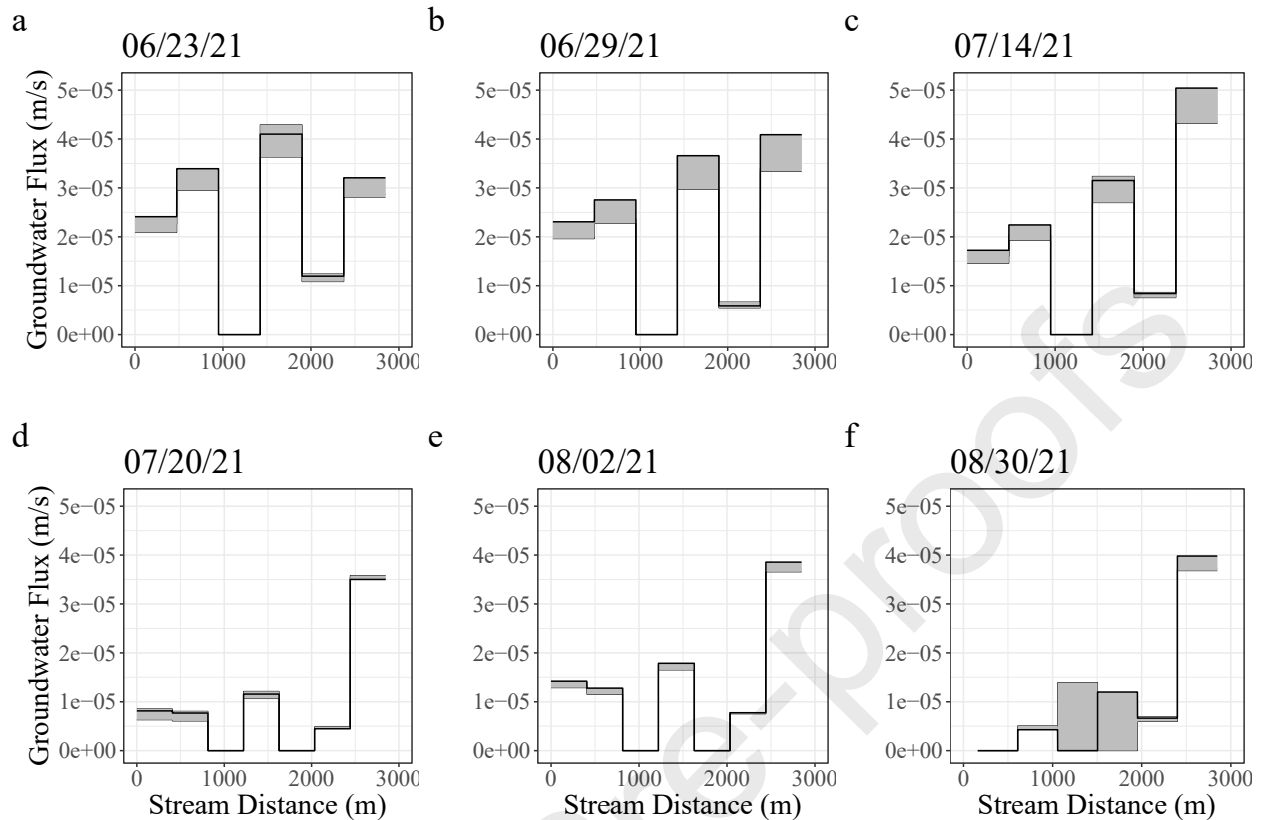
720 Figure 11: Conceptual diagram developed based on SOI that depicts groundwater originating from snow and rain  
 721 recharging stream water under fractured and alluvial fan hillslopes during early and late summer. In early summer,  
 722 groundwater that originated from snow ( $\delta_{\text{winterP}}$ ) dominated the fractured hillslope, while in late summer  
 723 groundwater flow declined and was equally composed of snow and rain. Unlike the fractured hillslope, groundwater  
 724 that originated from the alluvial fan was consistent in volume and its snow-dominated composition. Early in the  
 725 summer, the alluvial fan and area upslope of the fan contributed groundwater to the stream, while later in the  
 726 summer the upslope became disconnected and the alluvial fan was the dominant water source. Overall, stream water  
 727 composition moved from greater snow ( $\delta_{\text{winterP}}$ ) origin in early summer to greater rain origin ( $\delta_{\text{summerP}}$ ) in late  
 728 summer. Height of the arrows indicate the relative proportion of groundwater that originated from rain or snow to  
 729 the stream.

### 730 4.3 Modeling Limitations and Future Work

731 Our work points towards a need to understand localized groundwater contributions in  
 732 montane environments, especially those that rely on monsoonal precipitation for summer stream  
 733 flow generation. While the methods presented in this paper allow for both data driven and

734 modeling analysis of GW-SW interactions, there are several important limitations to consider.  
735 The largest sources of error in our model are groundwater  $^{222}\text{Rn}$  concentration and gas exchange  
736 velocity. Throughout the summer, we measured chemistry from seven springs to capture diverse  
737 groundwater behavior, yet when used in the model to predict stream flow and chemistry,  
738 modeled stream chemistry drastically diverged from measured stream chemistry. Thus, we  
739 concluded that groundwater feeding the springs was not the same groundwater directly  
740 contributing to Coal Creek. Gas exchange velocity can be measured using tracer injection tests  
741 (Wanninkhof et al., 1990; Maurice et al., 2017), however no tracer test was performed for this  
742 work. We used Monte Carlo (MC) simulations to estimate both the groundwater  $^{222}\text{Rn}$   
743 concentration and gas exchange velocity. MC bounds for gas exchange velocity were set based  
744 on gas exchange literature values for streams of similar size and slope as Coal Creek (Raymond  
745 et al., 2012; Ulseth et al., 2019). As expected, gas exchange values varied with discharge, with  
746 higher gas exchange values estimated during higher flow periods and lower gas exchange values  
747 measured during lower flow. Bounds were set for groundwater  $^{222}\text{Rn}$  concentration based on the  
748 minimum and maximum  $^{222}\text{Rn}$  concentration measured in springs in the watershed. From the MC  
749 simulations, groundwater  $^{222}\text{Rn}$  concentrations were generally estimated to be low relative to  
750 measured  $^{222}\text{Rn}$  concentrations, suggesting that groundwater contributing to Coal Creek was  
751 relatively young ( $< 1$  week).

752 Gas exchange velocity and groundwater  $^{222}\text{Rn}$  concentration parameters exert opposite  
753 effects on stream water concentrations: higher gas exchange velocities reduce instream  $^{222}\text{Rn}$   
754 concentrations whereas higher groundwater  $^{222}\text{Rn}$  concentrations increase instream  $^{222}\text{Rn}$   
755 concentrations. We evaluated the relationship between estimated gas exchange velocities and  
756 groundwater  $^{222}\text{Rn}$  concentrations and found they were negatively correlated and, as expected,  
757 gas exchange velocity was positively related to discharge (Figure S4). The median of gas  
758 exchange and groundwater  $^{222}\text{Rn}$  concentration values across the top 5% best model runs were  
759 used to calibrate StreamTran. Pairings of the minimum groundwater  $^{222}\text{Rn}$  concentration and  
760 minimum gas exchange velocity, and the maximum groundwater  $^{222}\text{Rn}$  concentration and  
761 maximum gas exchange velocity from the top 5% best models were used to characterize  
762 uncertainty around the MC estimated groundwater flux (Table S6). While there was variability in  
763 estimated GW flux across the range of values retained in the top 5% of AIC values (Figure 12),  
764 declining trends in groundwater flux throughout the summer and variability across the reach  
765 exceeded uncertainty. Visual inspection of model output using MC estimated values showed a  
766 good fit between measured and modeled stream discharge (Figure 7), however, near stream  
767 piezometers and tracer injection tests likely would have provided better constraints on values for  
768 groundwater  $^{222}\text{Rn}$  concentrations and gas exchange velocity.



769

770 Figure 12: Modeled groundwater fluxes (black line) and uncertainty (grey shading) estimated using the minimum  
 771 paired groundwater  $^{222}\text{Rn}$  and gas exchange velocity, and maximum paired groundwater  $^{222}\text{Rn}$  and gas exchange  
 772 velocity from the top 5% of AIC values from the Monte Carlo analysis for each modeled event.

773 In StreamTran, estimations of groundwater flux and stream water  $^{222}\text{Rn}$  concentrations are  
 774 sensitive to the distance between sampling locations. Groundwater  $^{222}\text{Rn}$  degasses upon contact  
 775 with the atmosphere, and in small streams with high gas exchange velocity, changes in  $^{222}\text{Rn}$  can  
 776 happen rapidly. The scale length describes how far apart samples should be taken given  
 777 discharge and stream geometry (Cook et al., 2006). Scale lengths in Coal Creek vary between 28  
 778 and 101 meters depending on stream reach location and discharge but are shorter than the  
 779 distances between samples we used (161 – 787 meters). We acknowledge that this sample design  
 780 may lead to an underestimation of groundwater inputs, especially in the portion of the reach  
 781 further upstream from sampling locations. However, the goal of using this model was to compare  
 782 how spatial groundwater discharge varied across time. While the reach length is longer than the  
 783 length scale, the sampling locations were held constant across the sampling events and therefore  
 784 we are still able to look at differences with time and interpret changes between events.

785 In addition to limitations imposed by data availability, StreamTran has several assumptions  
 786 that influence the predicted volume of groundwater discharge. StreamTran does not consider  
 787 hyporheic exchange, which can contribute substantial amounts of  $^{222}\text{Rn}$  to streams (Cook et al.,  
 788 2006; Bourke et al., 2014; Cartwright and Hoffman, 2016). Hyporheic exchange describes the  
 789 exchange of stream water through alluvial aquifers through flow paths that begin and end in the  
 790 stream channel (Gooseff, 2010). While we acknowledge that the omission of hyporheic exchange  
 791 in our model may lead to overestimations of groundwater flux, along reaches longer than

792 hyporheic flow paths (i.e., cm to tens of meters) (Boano et al., 2014), hyporheic exchange does  
793 not increase total stream flow. Along our modeled reach, streamflow increases substantially with  
794 limited input from tributaries, indicating groundwater contributions must be driving flow  
795 increases. StreamTran accounts for the gaining nature of the reach by fitting not only  $^{222}\text{Rn}$   
796 concentrations but also measured discharge. Therefore, the model fit is weighted toward  
797 groundwater discharge that increases stream flow, and we can be confident that increasing  
798 streamflow and peaks in  $^{222}\text{Rn}$  concentration indicate groundwater contribution and not Rn input  
799 from hyporheic exchange. Additionally, the groundwater fluxes estimated by the model are used  
800 for comparison over time; evaluating relative differences among synoptic events is valid even if  
801 estimations are high.

802 StreamTran assumes steady state conditions of spatially and temporally input parameters,  
803 including stream temperature, evaporation, gas exchange velocity, groundwater  $^{222}\text{Rn}$   
804 concentration, and stream slope. It is well documented that groundwater  $^{222}\text{Rn}$  concentration can  
805 be spatially variable at Coal Creek (Table 2) and in other streams (McClymont et al., 2012;  
806 Floriancic et al., 2018). Gas exchange velocity is influenced by factors such as turbulence, depth,  
807 slope, and stream temperature that vary across the modeled stream reach. Finally, StreamTran  
808 uses a linear interpolation of width, depth, and area and assumes a rectangular stream channel  
809 between measurement locations which erases much of the complex channel morphology present  
810 in small headwater streams (Schneider et al., 2015). When we included temporal variation of all  
811 input parameters between sampling dates using the Monte Carlo approach, we observed that  
812 patterns in modeled groundwater discharge in time and space outweigh the uncertainty  
813 introduced by steady state behavior (Figure 12). With similar datasets, this could be applied to  
814 other river systems (Beisner et al., 2018) to understand localized and regional groundwater  
815 contribution to streamflow.

816 Future work at Coal Creek could leverage this new model of groundwater flow to understand  
817 solute transport. The Coal Creek watershed, and many other watersheds in the Rocky Mountains,  
818 are heavily mined and mineralized leading to concerns about metal transport into streams. Coal  
819 Creek serves as the drinking water supply for the town of Crested Butte, and previous work has  
820 identified high concentrations of zinc, cadmium, and copper in stream water (Manning et al.,  
821 2007; Verplanck et al., 2009). A better understanding of fracture and alluvial fan groundwater  
822 contributions may help elucidate source and timing of metal fluxes into Coal Creek.

## 823 **5.0 Conclusion**

824 Understanding local controls on GW-SW interactions is critical as groundwater becomes  
825 more important for summer streamflow generation under warmer conditions. We used spatial  
826 and temporal  $^{222}\text{Rn}$  and water isotope sampling along a three km reach of a Colorado River  
827 headwater stream to assess how bedrock fractures control GW-SW interactions throughout the  
828 summer. The model application presented here is transferable to other stream reaches with  
829 similar geochemistry data to understand how streamflow generation processes shift through time  
830 and space. We characterized changes in subsurface hydrologic connectivity throughout the  
831 summer using dynamic storage, and found the catchment shifts from high to low hydrologic  
832 connectivity over the summer. We observed variable responses to declining connectivity  
833 between geologic features. During early summer, groundwater contributions through the fracture  
834 zone dominated groundwater flux along the reach but declined as summer progressed. In



835 contrast, groundwater contributions from the non-fractured zone were constant throughout the  
836 study and dominated in late summer when fracture contributions were low. We hypothesize that  
837 groundwater in the non-fractured zone is dominantly sourced from a high-storage alluvial fan at  
838 the base of Elk Creek that is connected to Coal Creek throughout the summer and provides  
839 consistent groundwater influx. Throughout the summer, streamflow origin shifted from more to  
840 less snow dominated reflecting the important role that monsoonal precipitation plays in  
841 streamflow generation during the late summer. At the catchment scale, we observed significant  
842 relationships between dynamic storage and water isotope values, groundwater discharge, and the  
843 ratio of fracture to non-fractured zone groundwater contribution indicating that periods of higher  
844 connectivity led to more snow dominated stream water, higher groundwater discharge, and a  
845 higher proportion of fracture zone groundwater in Coal Creek. Overall, we observed that at the  
846 catchment scale shallow flow paths became more important for streamflow generation during  
847 low hydrologic connectivity conditions, but local geologic features responded differently to  
848 changes in moisture based on their storage. Under warmer conditions, groundwater and monsoon  
849 rains may become more important for sustaining summer flows. Based on this work, we expect  
850 high storage features, such as alluvial fans, to become more important for sustaining streamflow  
851 under warming. Additionally, we expect a higher proportion of late season streamflow to  
852 originate from monsoon rains transported through shallow flow paths as deeper groundwater  
853 transported through low storage features may become disconnected from the stream earlier in the  
854 summer. To better understand streamflow generation processes in montane catchments,  
855 additional assessment of groundwater and stream response to warming and monsoon rain is  
856 critical.

#### 857 **Data Availability**

858 Data is available on ESS-DIVE: [doi:10.15485/2283437](https://doi.org/10.15485/2283437)

#### 859 **Code Availability**

860 Related code is available in Zenodo repository: <https://doi.org/10.5281/zenodo.10045527>

#### 861 **Competing Interests**

862 The contact author has declared that none of the authors has any competing interests.

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#### 869 **References**

870 Ajami, H., Troch, P. A., Maddock III, T., Meixner, T., & Eastoe, C. (2011). Quantifying  
871 mountain block recharge by means of catchment-scale storage-discharge relationships.  
872 *Water Resources Research*, 47(4). <https://doi.org/10.1029/2010WR009598>

- 873 Allen, S. T., Kirchner, J. W., Braun, S., Siegwolf, R. T. W., & Goldsmith, G. R. (2019). Seasonal  
874 origins of soil water used by trees. *Hydrology and Earth System Sciences*, 23(2), 1199–  
875 1210. <https://doi.org/10.5194/hess-23-1199-2019>
- 876 Allen, S. T., von Freyberg, J., Weiler, M., Goldsmith, G. R., & Kirchner, J. W. (2019). The  
877 Seasonal Origins of Streamwater in Switzerland. *Geophysical Research Letters*, 46(17–  
878 18), 10425–10434. <https://doi.org/10.1029/2019GL084552>
- 879 Andermann, C., Longuevergne, L., Bonnet, S., Crave, A., Davy, P., & Gloaguen, R. (2012).  
880 Impact of transient groundwater storage on the discharge of Himalayan rivers. *Nature*  
881 *Geoscience*, 5(2), 127–132. <https://doi.org/10.1038/ngeo1356>
- 882 Avery, E., Bibby, R., Visser, A., Esser, B., & Moran, J. (2018). Quantification of Groundwater  
883 Discharge in a Subalpine Stream Using Radon-222. *Water*, 10(2), Article 2.  
884 <https://doi.org/10.3390/w10020100>
- 885 Azmat, M., Liaqat, U. W., Qamar, M. U., & Awan, U. K. (2017). Impacts of changing climate  
886 and snow cover on the flow regime of Jhelum River, Western Himalayas. *Regional*  
887 *Environmental Change; Dordrecht*, 17(3), 813–825.  
888 <http://dx.doi.org.ezproxy.proxy.library.oregonstate.edu/10.1007/s10113-016-1072-6>
- 889 Banks, E. W., Simmons, C. T., Love, A. J., Cranswick, R., Werner, A. D., Bestland, E. A.,  
890 Wood, M., & Wilson, T. (2009). Fractured bedrock and saprolite hydrogeologic controls  
891 on groundwater/surface-water interaction: A conceptual model (Australia). *Hydrogeology*  
892 *Journal*, 17(8), 1969–1989. <https://doi.org/10.1007/s10040-009-0490-7>
- 893 Banks, E. W., Simmons, C. T., Love, A. J., & Shand, P. (2011). Assessing spatial and temporal  
894 connectivity between surface water and groundwater in a regional catchment: Implications  
895 for regional scale water quantity and quality. *Journal of Hydrology*, 404(1), 30–49.  
896 <https://doi.org/10.1016/j.jhydrol.2011.04.017>
- 897 Bavay, M., Lehning, M., Jonas, T., & Löwe, H. (2009). Simulations of future snow cover and  
898 discharge in Alpine headwater catchments. *Hydrological Processes*, 23(1), 95–108.  
899 <https://doi.org/10.1002/hyp.7195>
- 900 Beisner, K. R., Gardner, W. P., & Hunt, A. G. (2018). Geochemical characterization and  
901 modeling of regional groundwater contributing to the Verde River, Arizona between  
902 Mormon Pocket and the USGS Clarkdale gage. *Journal of Hydrology*, 564, 99–114.  
903 <https://doi.org/10.1016/j.jhydrol.2018.06.078>
- 904 Blume, T., & van Meerveld, H. J. (Ilja). (2015). From hillslope to stream: Methods to investigate  
905 subsurface connectivity. *WIREs Water*, 2(3), 177–198. <https://doi.org/10.1002/wat2.1071>
- 906 Boano, F., Harvey, J. W., Marion, A., Packman, A. I., Revelli, R., Ridolfi, L., & Wörman, A.  
907 (2014). Hyporheic flow and transport processes: Mechanisms, models, and biogeochemical  
908 implications. *Reviews of Geophysics*, 52(4), 603–679.  
909 <https://doi.org/10.1002/2012RG000417>



- 910 Bourke, S. A., Cook, P. G., Shanafield, M., Dogramaci, S., & Clark, J. F. (2014).  
911 Characterisation of hyporheic exchange in a losing stream using radon-222. *Journal of*  
912 *Hydrology*, 519, 94–105. <https://doi.org/10.1016/j.jhydrol.2014.06.057>
- 913 Bozdogan, H. (1987). Model selection and Akaike's Information Criterion (AIC): The general  
914 theory and its analytical extensions. *Psychometrika*, 52(3), 345–370.  
915 <https://doi.org/10.1007/BF02294361>
- 916 Brooks, P. D., Gelderloos, A., Wolf, M. A., Jamison, L. R., Strong, C., Solomon, D. K., Bowen,  
917 G. J., Burian, S., Tai, X., Arens, S., Briefer, L., Kirkham, T., & Stewart, J. (2021).  
918 Groundwater-Mediated Memory of Past Climate Controls Water Yield in Snowmelt-  
919 Dominated Catchments. *Water Resources Research*, 57(10), e2021WR030605.  
920 <https://doi.org/10.1029/2021WR030605>
- 921 Bush, S. A., Birch, A. L., Warix, S. R., Sullivan, P. L., Gooseff, M. N., McKnight, D. M., &  
922 Barnard, H. R. (2023). Dominant source areas shift seasonally from longitudinal to lateral  
923 contributions in a montane headwater stream. *Journal of Hydrology*, 617, 129134.  
924 <https://doi.org/10.1016/j.jhydrol.2023.129134>
- 925 Carroll, R. W. H., Bearup, L. A., Brown, W., Dong, W., Bill, M., & Williams, K. H. (2018).  
926 Factors controlling seasonal groundwater and solute flux from snow-dominated basins.  
927 *Hydrological Processes*, 32(14), 2187–2202. <https://doi.org/10.1002/hyp.13151>
- 928 Carroll, R. W. H., Gochis, D., & Williams, K. H. (2020). Efficiency of the Summer Monsoon in  
929 Generating Streamflow Within a Snow-Dominated Headwater Basin of the Colorado  
930 River. *Geophysical Research Letters*, 47(23), e2020GL090856.  
931 <https://doi.org/10.1029/2020GL090856>
- 932 Cartwright, I., & Hofmann, H. (2016). Using radon to understand parafluvial flows and the  
933 changing locations of groundwater inflows in the Avon River, southeast Australia.  
934 *Hydrology and Earth System Sciences*, 20(9), 3581–3600. [https://doi.org/10.5194/hess-20-](https://doi.org/10.5194/hess-20-3581-2016)  
935 [3581-2016](https://doi.org/10.5194/hess-20-3581-2016)
- 936 Cook, B. I., & Seager, R. (2013). The response of the North American Monsoon to increased  
937 greenhouse gas forcing. *Journal of Geophysical Research: Atmospheres*, 118(4), 1690–  
938 1699. <https://doi.org/10.1002/jgrd.50111>
- 939 Cook, P. G., & Herczeg, A. L. (2000). *Environmental tracers in subsurface hydrology*. Springer  
940 Science + Business Media, LLC.
- 941 Cook, P. G., Lamontagne, S., Berhane, D., & Clark, J. F. (2006). Quantifying groundwater  
942 discharge to Cockburn River, southeastern Australia, using dissolved gas tracers <sup>222</sup>Rn and  
943 SF<sub>6</sub>. *Water Resources Research*, 42(10). <https://doi.org/10.1029/2006WR004921>
- 944 Covino, T. (2017). Hydrologic connectivity as a framework for understanding biogeochemical  
945 flux through watersheds and along fluvial networks. *Geomorphology*, 277, 133–144.  
946 <https://doi.org/10.1016/j.geomorph.2016.09.030>

- 947 Cowie, R. M., Knowles, J. F., Dailey, K. R., Williams, M. W., Mills, T. J., & Molotch, N. P.  
 948 (2017). Sources of streamflow along a headwater catchment elevational gradient. *Journal*  
 949 *of Hydrology*, 549, 163–178. <https://doi.org/10.1016/j.jhydrol.2017.03.044>
- 950 Dwivedi, R., Meixner, T., McIntosh, J. C., Ferré, P. A. T., Eastoe, C. J., Niu, G.-Y., Minor, R.  
 951 L., Barron-Gafford, G. A., & Chorover, J. (2019). Hydrologic functioning of the deep  
 952 critical zone and contributions to streamflow in a high-elevation catchment: Testing of  
 953 multiple conceptual models. *Hydrological Processes*, 33(4), 476–494.  
 954 <https://doi.org/10.1002/hyp.13363>
- 955 Ehsani, M. R., & Behrangi, A. (2022). A comparison of correction factors for the systematic  
 956 gauge-measurement errors to improve the global land precipitation estimate. *Journal of*  
 957 *Hydrology*, 610, 127884. <https://doi.org/10.1016/j.jhydrol.2022.127884>
- 958 Ficklin, D. L., Stewart, I. T., & Maurer, E. P. (2013). Climate Change Impacts on Streamflow  
 959 and Subbasin-Scale Hydrology in the Upper Colorado River Basin. *PLOS ONE*, 8(8),  
 960 e71297. <https://doi.org/10.1371/journal.pone.0071297>
- 961 Fischer, B. M. C., Rinderer, M., Schneider, P., Ewen, T., & Seibert, J. (2015). Contributing  
 962 sources to baseflow in pre-alpine headwaters using spatial snapshot sampling.  
 963 *Hydrological Processes*, 29(26), 5321–5336. <https://doi.org/10.1002/hyp.10529>
- 964 Flerchinger, G., Deng, Y., & Cooley, K. (1993). *Groundwater response to snowmelt in a*  
 965 *mountainous watershed: Testing of a conceptual model*. [https://doi.org/10.1016/0022-](https://doi.org/10.1016/0022-1694(93)90146-Z)  
 966 [1694\(93\)90146-Z](https://doi.org/10.1016/0022-1694(93)90146-Z)
- 967 Floriancic, M. G., van Meerveld, I., Smoorenburg, M., Margreth, M., Naef, F., Kirchner, J. W.,  
 968 & Molnar, P. (2018). Spatio-temporal variability in contributions to low flows in the high  
 969 Alpine Poschiavino catchment. *Hydrological Processes*, 32(26), 3938–3953.  
 970 <https://doi.org/10.1002/hyp.13302>
- 971 Gardner, W. P., Harrington, G. A., Solomon, D. K., & Cook, P. G. (2011). Using terrigenic 4He  
 972 to identify and quantify regional groundwater discharge to streams. *Water Resources*  
 973 *Research*, 47(6). <https://doi.org/10.1029/2010WR010276>
- 974 Gaskill, D. L. (1991). *Geologic map of the Gothic Quadrangle, Gunnison County, Colorado*.
- 975 Genereux, D. P., Hemond, H. F., & Mulholland, P. J. (1993). Use of radon-222 and calcium as  
 976 tracers in a three-end-member mixing model for streamflow generation on the West Fork  
 977 of Walker Branch Watershed. *Journal of Hydrology*, 142(1), 167–211.  
 978 [https://doi.org/10.1016/0022-1694\(93\)90010-7](https://doi.org/10.1016/0022-1694(93)90010-7)
- 979 Gleeson, T., Manning, A. H., Popp, A., Zane, M., & Clark, J. F. (2018). The suitability of using  
 980 dissolved gases to determine groundwater discharge to high gradient streams. *Journal of*  
 981 *Hydrology*, 557, 561–572. <https://doi.org/10.1016/j.jhydrol.2017.12.022>

- 982 Gooseff, M. N. (2010). Defining Hyporheic Zones – Advancing Our Conceptual and Operational  
 983 Definitions of Where Stream Water and Groundwater Meet. *Geography Compass*, 4(8),  
 984 945–955. <https://doi.org/10.1111/j.1749-8198.2010.00364.x>
- 985 Gordon, R. P., Lautz, L. K., McKenzie, J. M., Mark, B. G., Chavez, D., & Baraer, M. (2015).  
 986 Sources and pathways of stream generation in tropical proglacial valleys of the Cordillera  
 987 Blanca, Peru. *Journal of Hydrology*, 522, 628–644.  
 988 <https://doi.org/10.1016/j.jhydrol.2015.01.013>
- 989 Guyer, J. E., Wheeler, D., & Warren, J. A. (2009). FiPy: Partial Differential Equations with  
 990 Python. *Computing in Science & Engineering*, 11(3), 6–15.  
 991 <https://doi.org/10.1109/MCSE.2009.52>
- 992 Heidbüchel, I., Troch, P. A., & Lyon, S. W. (2013). Separating physical and meteorological  
 993 controls of variable transit times in zero-order catchments. *Water Resources Research*,  
 994 49(11), 7644–7657. <https://doi.org/10.1002/2012WR013149>
- 995 Herron, N., & Wilson, C. (2001). A water balance approach to assessing the hydrologic buffering  
 996 potential of an alluvial fan. *Water Resources Research*, 37(2), 341–351.  
 997 <https://doi.org/10.1029/2000WR900253>
- 998 Hua, D., Hao, X., Zhang, Y., & Qin, J. (2020). Uncertainty assessment of potential  
 999 evapotranspiration in arid areas, as estimated by the Penman-Monteith method. *Journal of*  
 1000 *Arid Land*, 12(1), 166–180. <https://doi.org/10.1007/s40333-020-0093-7>
- 1001 Hubbard, S. S., Williams, K. H., Agarwal, D., Banfield, J., Beller, H., Bouskill, N., Brodie, E.,  
 1002 Carroll, R., Dafflon, B., Dwivedi, D., Falco, N., Faybishenko, B., Maxwell, R., Nico, P.,  
 1003 Steefel, C., Steltzer, H., Tokunaga, T., Tran, P. A., Wainwright, H., & Varadharajan, C.  
 1004 (2018). The East River, Colorado, Watershed: A Mountainous Community Testbed for  
 1005 Improving Predictive Understanding of Multiscale Hydrological–Biogeochemical  
 1006 Dynamics. *Vadose Zone Journal*, 17(1), 180061. <https://doi.org/10.2136/vzj2018.03.0061>
- 1007 Jencso, K. G., McGlynn, B. L., Gooseff, M. N., Bencala, K. E., & Wondzell, S. M. (2010).  
 1008 Hillslope hydrologic connectivity controls riparian groundwater turnover: Implications of  
 1009 catchment structure for riparian buffering and stream water sources. *Water Resources*  
 1010 *Research*, 46(10). <https://doi.org/10.1029/2009WR008818>
- 1011 Johnson, K. (2023). hydrokeira/CoalCreekGW\_JoH: Groundwater Flux Code: Coal Creek  
 1012 (v1.0.1). Zenodo. <https://doi.org/10.5281/zenodo.10045527>
- 1013 Johnson, K., Harpold, A., Carroll, R. W. H., Barnard, H., Raleigh, M. S., Segura, C., Li, L.,  
 1014 Williams, K. H., Dong, W., & Sullivan, P. L. (2023). Leveraging Groundwater Dynamics to  
 1015 Improve Predictions of Summer Low-Flow Discharges. *Water Resources Research*, 59(8),  
 1016 e2023WR035126. <https://doi.org/10.1029/2023WR035126>
- 1017 Julander, R. P., & Clayton, J. A. (2018). Determining the proportion of streamflow that is  
 1018 generated by cold season processes versus summer rainfall in Utah, USA. *Journal of*  
 1019 *Hydrology: Regional Studies*, 17, 36–46. <https://doi.org/10.1016/j.ejrh.2018.04.005>

- 1020 Kapnick, S., & Hall, A. (2012). Causes of recent changes in western North American snowpack.  
1021 *Climate Dynamics*, 38(9–10), 1885–1900. <https://doi.org/10.1007/s00382-011-1089-y>
- 1022 Käser, D., & Hunkeler, D. (2016). Contribution of alluvial groundwater to the outflow of  
1023 mountainous catchments. *Water Resources Research*, 52(2), 680–697.  
1024 <https://doi.org/10.1002/2014WR016730>
- 1025 Kingston, D. G., Todd, M. C., Taylor, R. G., Thompson, J. R., & Arnell, N. W. (2009).  
1026 Uncertainty in the estimation of potential evapotranspiration under climate change.  
1027 *Geophysical Research Letters*, 36(20). <https://doi.org/10.1029/2009GL040267>
- 1028 Kirchner, J. W. (2009). Catchments as simple dynamical systems: Catchment characterization,  
1029 rainfall-runoff modeling, and doing hydrology backward. *Water Resources Research*,  
1030 45(2). <https://doi.org/10.1029/2008WR006912>
- 1031 Larson, L. W., & Peck, E. L. (1974). Accuracy of precipitation measurements for hydrologic  
1032 modeling. *Water Resources Research*, 10(4), 857–863.  
1033 <https://doi.org/10.1029/WR010i004p00857>
- 1034 Liao, F., Cardenas, M. B., Ferencz, S. B., Chen, X., & Wang, G. (2021). Tracing Bank Storage  
1035 and Hyporheic Exchange Dynamics Using 222Rn: Virtual and Field Tests and Comparison  
1036 With Other Tracers. *Water Resources Research*, 57(5), e2020WR028960.  
1037 <https://doi.org/10.1029/2020WR028960>
- 1038 Liu, F., Williams, M. W., & Caine, N. (2004). Source waters and flow paths in an alpine  
1039 catchment, Colorado Front Range, United States. *Water Resources Research*, 40(9).  
1040 <https://doi.org/10.1029/2004WR003076>
- 1041 Ludwig, KR. User's manual for Isoplot version 3.75–4.15: A geochronological toolkit for  
1042 Microsoft Excel: Berkeley Geochronological Center Special Publication 5
- 1043 Manning, A.H., Verplanck, P.L., Mast, M.A., and Wanty, R.B., 2008, Hydrogeochemical  
1044 investigation of the Standard Mine vicinity, upper Elk Creek Basin, Colorado: U.S.  
1045 Geological Survey Scientific Investigations Report 2007–5265, 131 p.
- 1046 Mastrotheodoros, T., Pappas, C., Molnar, P., Burlando, P., Manoli, G., Parajka, J., Rigon, R.,  
1047 Szeles, B., Bottazzi, M., Hadjidoukas, P., & Fatichi, S. (2020). More green and less blue  
1048 water in the Alps during warmer summers. *Nature Climate Change*, 10(2), Article 2.  
1049 <https://doi.org/10.1038/s41558-019-0676-5>
- 1050 Maurice, L., Rawlins, B. G., Farr, G., Bell, R., & Goody, D. C. (2017). The Influence of Flow  
1051 and Bed Slope on Gas Transfer in Steep Streams and Their Implications for Evasion of  
1052 CO<sub>2</sub>. *Journal of Geophysical Research: Biogeosciences*, 122(11), 2862–2875.  
1053 <https://doi.org/10.1002/2017JG004045>
- 1054 Mayer, T. D., & Naman, S. W. (2011). Streamflow Response to Climate as Influenced by  
1055 Geology and Elevation1. *JAWRA Journal of the American Water Resources Association*,  
1056 47(4), 724–738. <https://doi.org/10.1111/j.1752-1688.2011.00537.x>

- 1057 McClymont, A. F., Hayashi, M., Bentley, L. R., & Liard, J. (2012). Locating and characterising  
1058 groundwater storage areas within an alpine watershed using time-lapse gravity, GPR and  
1059 seismic refraction methods. *Hydrological Processes*, 26(12), 1792–1804.  
1060 <https://doi.org/10.1002/hyp.9316>
- 1061 McDonnell, J. J. (1990). A Rationale for Old Water Discharge Through Macropores in a Steep,  
1062 Humid Catchment. *Water Resources Research*, 26(11), 2821–2832.  
1063 <https://doi.org/10.1029/WR026i011p02821>
- 1064 McIntosh, J. C., Schaumberg, C., Perdrial, J., Harpold, A., Vázquez-Ortega, A., Rasmussen, C.,  
1065 Vinson, D., Zapata-Rios, X., Brooks, P. D., Meixner, T., Pelletier, J., Derry, L., &  
1066 Chorover, J. (2017). Geochemical evolution of the Critical Zone across variable time  
1067 scales informs concentration-discharge relationships: Jemez River Basin Critical Zone  
1068 Observatory. *Water Resources Research*, 53(5), 4169–4196.  
1069 <https://doi.org/10.1002/2016WR019712>
- 1070 Milly, P. C. D., & Dunne, K. A. (2020). Colorado River flow dwindles as warming-driven loss  
1071 of reflective snow energizes evaporation. *Science (New York, N.Y.)*, 367(6483), 1252–  
1072 1255. <https://doi.org/10.1126/science.aay9187>
- 1073 Mote, P. W., Li, S., Lettenmaier, D. P., Xiao, M., & Engel, R. (2018). Dramatic declines in  
1074 snowpack in the western US. *Npj Climate and Atmospheric Science*, 1(1), 2.  
1075 <https://doi.org/10.1038/s41612-018-0012-1>
- 1076 Mullinger, N. J., Pates, J. M., Binley, A. M., & Crook, N. P. (2009). Controls on the spatial and  
1077 temporal variability of 222Rn in riparian groundwater in a lowland Chalk catchment.  
1078 *Journal of Hydrology*, 376(1), 58–69. <https://doi.org/10.1016/j.jhydrol.2009.07.015>
- 1079 Oxtobee, J. P. A., & Novakowski, K. S. (2003). Ground Water/Surface Water Interaction in a  
1080 Fractured Rock Aquifer. *Groundwater*, 41(5), 667–681. <https://doi.org/10.1111/j.1745-6584.2003.tb02405.x>
- 1082 Peterson, R. N., Santos, I. R., & Burnett, W. C. (2010). Evaluating groundwater discharge to  
1083 tidal rivers based on a Rn-222 time-series approach. *Estuarine, Coastal and Shelf  
1084 Science*, 86(2), 165–178. <https://doi.org/10.1016/j.ecss.2009.10.022>
- 1085 Rademacher, L. K., Clark, J. F., Clow, D. W., & Hudson, G. B. (2005). Old groundwater  
1086 influence on stream hydrochemistry and catchment response times in a small Sierra  
1087 Nevada catchment: Sagehen Creek, California. *Water Resources Research*, 41(2).  
1088 <https://doi.org/10.1029/2003WR002805>
- 1089 Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P., Laursen, A. E.,  
1090 McDowell, W. H., & Newbold, D. (2012). Scaling the gas transfer velocity and hydraulic  
1091 geometry in streams and small rivers. *Limnology and Oceanography: Fluids and  
1092 Environments*, 2(1), 41–53. <https://doi.org/10.1215/21573689-1597669>



- 1093 Ryken, A. C., Gochis, D., & Maxwell, R. M. (2022). Unravelling groundwater contributions to  
1094 evapotranspiration and constraining water fluxes in a high-elevation catchment.  
1095 *Hydrological Processes*, 36(1), e14449. <https://doi.org/10.1002/hyp.14449>
- 1096 Safeeq, M., Grant, G. E., Lewis, S. L., & Tague, Christina. L. (2013). Coupling snowpack and  
1097 groundwater dynamics to interpret historical streamflow trends in the western United States:  
1098 COUPLING SNOWPACK AND GROUNDWATER DYNAMICS TO INTERPRET  
1099 STREAMFLOW. *Hydrological Processes*, 27(5), 655–668.  
1100 <https://doi.org/10.1002/hyp.9628>
- 1101 Salve, R., Rempe, D. M., & Dietrich, W. E. (2012). Rain, rock moisture dynamics, and the rapid  
1102 response of perched groundwater in weathered, fractured argillite underlying a steep  
1103 hillslope. *Water Resources Research*, 48(11). <https://doi.org/10.1029/2012WR012583>
- 1104 Sayama, T., McDonnell, J. J., Dhakal, A., & Sullivan, K. (2011). How much water can a  
1105 watershed store? *Hydrological Processes*, 25(25), 3899–3908.  
1106 <https://doi.org/10.1002/hyp.8288>
- 1107 Schmidt, A., Gibson, J. J., Santos, I. R., Schubert, M., Tattier, K., & Weiss, H. (2010). The  
1108 contribution of groundwater discharge to the overall water budget of two typical Boreal  
1109 lakes in Alberta/Canada estimated from a radon mass balance. *Hydrology and Earth  
1110 System Sciences*, 14(1), 79–89. <https://doi.org/10.5194/hess-14-79-2010>
- 1111 Schneider, J. M., Rickenmann, D., Turowski, J. M., & Kirchner, J. W. (2015). Self-adjustment of  
1112 stream bed roughness and flow velocity in a steep mountain channel. *Water Resources  
1113 Research*, 51(10), 7838–7859. <https://doi.org/10.1002/2015WR016934>
- 1114 Schubert, M., Siebert, C., Knoeller, K., Roediger, T., Schmidt, A., & Gilfedder, B. (2020).  
1115 Investigating Groundwater Discharge into a Major River under Low Flow Conditions  
1116 Based on a Radon Mass Balance Supported by Tritium Data. *Water*, 12(10), 2838.  
1117 <https://doi.org/10.3390/w12102838>
- 1118 Segura, C., Noone, D., Warren, D., Jones, J. A., Tenny, J., & Ganio, L. M. (2019). Climate,  
1119 Landforms, and Geology Affect Baseflow Sources in a Mountain Catchment. *Water  
1120 Resources Research*, 55(7), 5238–5254. <https://doi.org/10.1029/2018WR023551>
- 1121 Singh, N. K., Emanuel, R. E., & McGlynn, B. L. (2016). Variability in isotopic composition of  
1122 base flow in two headwater streams of the southern Appalachians. *Water Resources  
1123 Research*, 52(6), 4264–4279. <https://doi.org/10.1002/2015WR018463>
- 1124 Smerdon, B. D., & Gardner, W. P. (2022). Characterizing groundwater flow paths in an  
1125 undeveloped region through synoptic river sampling for environmental tracers.  
1126 *Hydrological Processes*, 36(1), e14464. <https://doi.org/10.1002/hyp.14464>
- 1127 Smerdon, B. D., Payton Gardner, W., Harrington, G. A., & Tickell, S. J. (2012). Identifying the  
1128 contribution of regional groundwater to the baseflow of a tropical river (Daly River,  
1129 Australia). *Journal of Hydrology*, 464–465, 107–115.  
1130 <https://doi.org/10.1016/j.jhydrol.2012.06.058>

- 1131 Somers, L. D., & McKenzie, J. M. (2020a). A review of groundwater in high mountain  
1132 environments. *WIREs Water*, 7(6), e1475. <https://doi.org/10.1002/wat2.1475>
- 1133 Somers, L. D., & McKenzie, J. M. (2020b). A review of groundwater in high mountain  
1134 environments. *WIREs Water*, 7(6), e1475. <https://doi.org/10.1002/wat2.1475>
- 1135 Somers, L. D., McKenzie, J. M., Mark, B. G., Lagos, P., Ng, G.-H. C., Wickert, A. D., Yarleque,  
1136 C., Baraër, M., & Silva, Y. (2019). Groundwater Buffers Decreasing Glacier Melt in an  
1137 Andean Watershed—But Not Forever. *Geophysical Research Letters*, 46(22), 13016–  
1138 13026. <https://doi.org/10.1029/2019GL084730>
- 1139 Spence, C. (2007). On the relation between dynamic storage and runoff: A discussion on  
1140 thresholds, efficiency, and function. *Water Resources Research*, 43(12).  
1141 <https://doi.org/10.1029/2006WR005645>
- 1142 Spencer, S. A., Anderson, A. E., Silins, U., & Collins, A. L. (2021). Hillslope and groundwater  
1143 contributions to streamflow in a Rocky Mountain watershed underlain by glacial till and  
1144 fractured sedimentary bedrock. *Hydrology and Earth System Sciences*, 25(1), 237–255.  
1145 <https://doi.org/10.5194/hess-25-237-2021>
- 1146 Sprenger, M., Carroll, R. W. H., Denedy-Frank, J., Siirila-Woodburn, E. R., Newcomer, M. E.,  
1147 Brown, W., Newman, A., Beutler, C., Bill, M., Hubbard, S. S., & Williams, K. H. (2022).  
1148 Variability of Snow and Rainfall Partitioning Into Evapotranspiration and Summer  
1149 Runoff Across Nine Mountainous Catchments. *Geophysical Research Letters*, 49(13),  
1150 e2022GL099324. <https://doi.org/10.1029/2022GL099324>
- 1151 Stewart, I. T., Cayan, D. R., & Dettinger, M. D. (2005). Changes toward Earlier Streamflow  
1152 Timing across Western North America. *Journal of Climate*, 18(8), 1136–1155.  
1153 <https://doi.org/10.1175/JCLI3321.1>
- 1154 Ulseth, A. J., Hall, R. O., Boix Canadell, M., Madinger, H. L., Niayifar, A., & Battin, T. J.  
1155 (2019). Distinct air–water gas exchange regimes in low- and high-energy streams. *Nature*  
1156 *Geoscience*, 12(4), Article 4. <https://doi.org/10.1038/s41561-019-0324-8>
- 1157 Verplanck, P.L., Manning, A.H., Graves, J.T., McCleskey, R.B., Todorov, Todor, and Lamothe,  
1158 P.J., 2010, Geochemistry of Standard Mine waters, Gunnison County, Colorado, July  
1159 2009: U.S. Geological Survey Open-File Report 2009–1292, 21 p.
- 1160 Viviroli, D., Dürr, H. H., Messerli, B., Meybeck, M., & Weingartner, R. (2007). Mountains of  
1161 the world, water towers for humanity: Typology, mapping, and global significance.  
1162 *Water Resources Research*, 43(7). <https://doi.org/10.1029/2006WR005653>
- 1163 Viviroli, D., Kummu, M., Meybeck, M., Kallio, M., & Wada, Y. (2020). Increasing dependence  
1164 of lowland populations on mountain water resources. *Nature Sustainability*, 3(11), Article  
1165 11. <https://doi.org/10.1038/s41893-020-0559-9>



- 1166 Wanninkhof, R., Mulholland, P. J., & Elwood, J. W. (1990). Gas exchange rates for a first-order  
 1167 stream determined with deliberate and natural tracers. *Water Resources Research*, 26(7),  
 1168 1621–1630. <https://doi.org/10.1029/WR026i007p01621>
- 1169 Webb, J. R., Santos, I. R., Robson, B., Macdonald, B., Jeffrey, L., & Maher, D. T. (2017).  
 1170 Constraining the annual groundwater contribution to the water balance of an agricultural  
 1171 floodplain using radon: The importance of floods. *Water Resources Research*, 53(1),  
 1172 544–562. <https://doi.org/10.1002/2016WR019735>
- 1173 Westerhoff, R. S. (2015). Using uncertainty of Penman and Penman–Monteith methods in  
 1174 combined satellite and ground-based evapotranspiration estimates. *Remote Sensing of*  
 1175 *Environment*, 169, 102–112. <https://doi.org/10.1016/j.rse.2015.07.021>
- 1176 Wittenberg, H., Aksoy, H., & Miegel, K. (2019). Fast response of groundwater to heavy rainfall.  
 1177 *Journal of Hydrology*, 571, 837–842. <https://doi.org/10.1016/j.jhydrol.2019.02.037>
- 1178 Xiao, X., Zhang, X., Wu, H., Zhang, C., & Han, L. (2022). Stable isotopes of surface water and  
 1179 groundwater in a typical subtropical basin in south-central China: Insights into the young  
 1180 water fraction and its seasonal origin. *Hydrological Processes*, 36(4), e14574.  
 1181 <https://doi.org/10.1002/hyp.14574>
- 1182 Żelazny, M., Astel, A., Wolanin, A., & Małek, S. (2011a). Spatiotemporal dynamics of spring  
 1183 and stream water chemistry in a high-mountain area. *Environmental Pollution*, 159(5),  
 1184 1048–1057. <https://doi.org/10.1016/j.envpol.2010.11.021>
- 1185 Żelazny, M., Astel, A., Wolanin, A., & Małek, S. (2011b). Spatiotemporal dynamics of spring  
 1186 and stream water chemistry in a high-mountain area. *Environmental Pollution*, 159(5),  
 1187 1048–1057. <https://doi.org/10.1016/j.envpol.2010.11.021>
- 1188 Zhi, W., Li, L., Dong, W., Brown, W., Kaye, J., Steefel, C., & Williams, K. H. (2019). Distinct  
 1189 Source Water Chemistry Shapes Contrasting Concentration-Discharge Patterns. *Water*  
 1190 *Resources Research*, 55(5), 4233–4251. <https://doi.org/10.1029/2018WR024257>
- 1191 Zuecco, G., Penna, D., & Borga, M. (2018). Runoff generation in mountain catchments: Long-  
 1192 term hydrological monitoring in the Rio Vauz Catchment, Italy. *Cuadernos de*  
 1193 *Investigación Geográfica*, 44(2), Article 2. <https://doi.org/10.18172/cig.3327>
- 1194 Geologic features (e.g., fractures and alluvial fans) can play an important role in the locations  
 1195 and volumes of groundwater discharge and degree of groundwater-surface water (GW-SW)  
 1196 interactions. However, the role of these features in controlling GW-SW dynamics and  
 1197 streamflow generation processes are not well constrained. GW-SW interactions and streamflow  
 1198 generation processes are further complicated by variability in precipitation inputs from summer  
 1199 and fall monsoon rains, as well as declines in snowpack and changing melt dynamics driven by  
 1200 warming temperatures. Using high spatial and temporal resolution radon and water stable isotope  
 1201 sampling and a 1D groundwater flux model, we evaluated how groundwater contributions and  
 1202 GW-SW interactions varied along a stream reach impacted by fractures (fractured-zone) and  
 1203 below the fractured hillslope (non-fractured zone) in Coal Creek, a Colorado River headwater  
 1204 stream affected by summer monsoons. During early summer, groundwater contributions from the

1205 fractured zone dominated, but declined throughout the summer. Groundwater contributions from  
1206 the non-fractured zone were constant throughout the summer and became proportionally more  
1207 important later in the summer. We hypothesize that groundwater in the non-fractured zone is  
1208 dominantly sourced from a high-storage alluvial fan at the base of a tributary that is connected to  
1209 Coal Creek throughout the summer and provides consistent groundwater influx. Water isotope  
1210 data revealed that Coal Creek responds quickly to incoming precipitation early in the summer,  
1211 and summer precipitation becomes more important for streamflow generation later in the  
1212 summer. We quantified the change in catchment dynamic storage and found it negatively related  
1213 to stream water isotope values, and positively related to modeled groundwater discharge and the  
1214 ratio of fractured zone to non-fractured zone groundwater. We interpret these relationships as  
1215 declining hydrologic connectivity throughout the summer leading to late summer streamflow  
1216 supported predominantly by shallow flow paths, with variable response to drying from geologic  
1217 features based on their storage. As groundwater becomes more important for sustaining summer  
1218 flows, quantifying local geologic controls on groundwater inputs and their response to variable  
1219 moisture conditions may become critical for accurate predictions of streamflow.

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- 1222 **1.** Hydrologic connectivity shifts from high to low throughout the summer.  
1223 **2.** Shallow flow paths are important for late summer streamflow generation.  
1224 **3.** Spatial origin of groundwater discharge varies with hydrologic connectivity.  
1225 **4.** Dynamic storage explains variability in groundwater flux and stream water origin.

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