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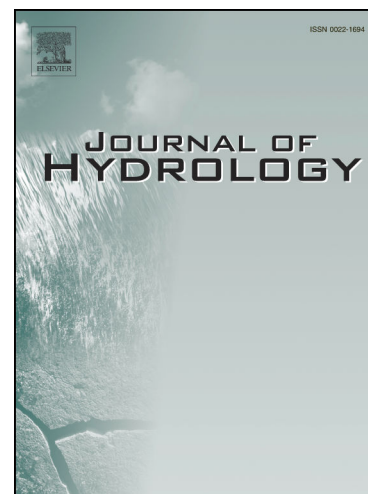
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2 **water isotopes**

3

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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}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}Rn
106 helps identify areas of high groundwater contribution because it degasses upon interaction with
107 the atmosphere. Thus, areas of high ^{222}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}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}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}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**

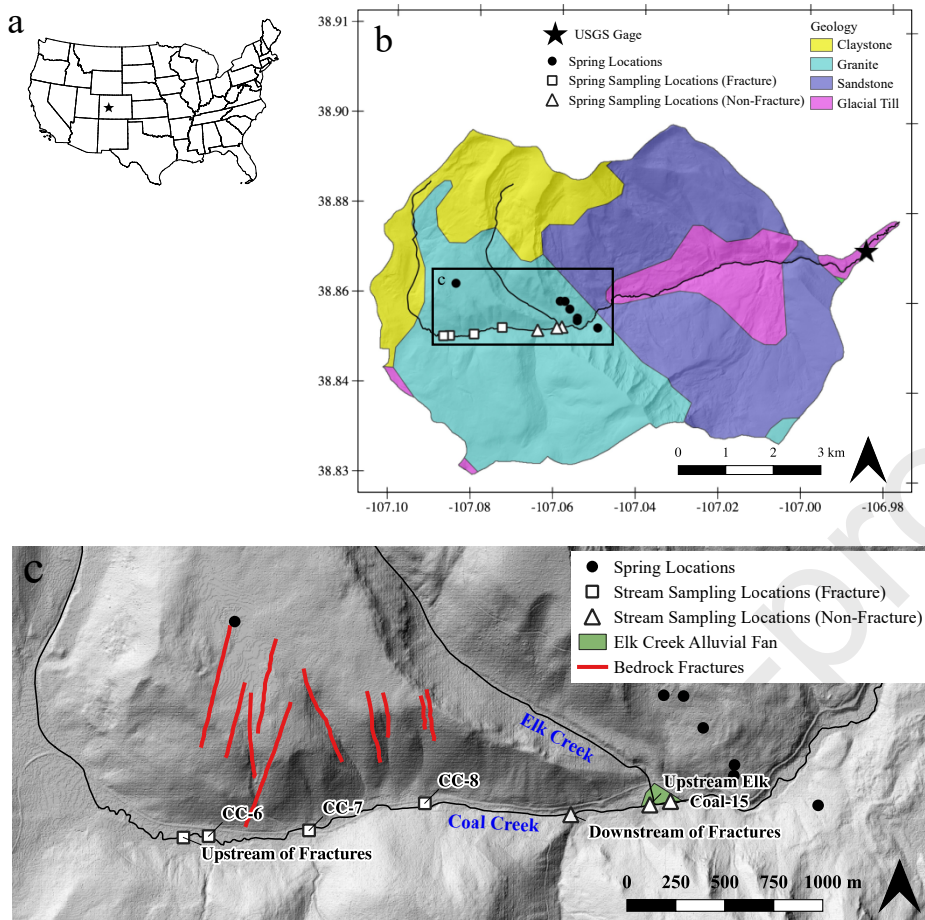
133 *2.1 Study Site*

134 Coal Creek is a small (53 km²), 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 km²), 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}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}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}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}Rn
202 and water isotopes.

203 2.2.1 Water Sampling

204 Locations in a stream with high ^{222}Rn concentrations indicate localized areas of
205 groundwater discharge. ^{222}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}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}Rn due to
211 the relatively low concentration of ^{222}Rn in stream water. Spring samples were collected in
212 smaller bottles given the high concentration of ^{222}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}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}Rn and the cap was sealed with
220 ParafilmTM. 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}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 3rd,
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 ^{222}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 ^{222}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 ^{222}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 ^{222}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 ^{222}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. ^{222}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 δ 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 δ_x is the $\delta^{18}\text{O}$ isotopic signature of stream water, and $\delta_{winterP}$, $\delta_{summerP}$, and δ_{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 (δ_{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}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}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 (m s^{-1}) is the
 294 precipitation rate, E (m s^{-1}) is the evaporation rate, Q_T ($\text{m}^3 \text{s}^{-1}$) is tributary discharge, q_{gi} (m s^{-1}) is
 295 the groundwater discharge gain flux, q_{go} (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}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 (mol m^{-3}) is the stream concentration, D ($\text{m}^2 \text{s}^{-1}$) is the longitudinal hydrodynamic
 301 dispersivity, A (m^2) is the stream cross-sectional area, C_{GW} (mol m^{-3}) is the local groundwater
 302 concentration, k (m s^{-1}) is the gas exchange velocity, C_{ATM} (mol m^{-3}) is the atmospheric
 303 equilibrium concentration of the tracer, λ (s^{-1}) is the decay coefficient, and C_T (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}Rn
 310 concentration along the stream reach. The groundwater concentration of ^{222}Rn , ^{222}Rn gas
 311 exchange velocity, and ^{222}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}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}Rn was set to zero. The ^{222}Rn
 327 decay coefficient was set to 3.82 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}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}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}Rn concentrations lead to underestimation of discharge
 338 and overestimation and ill-fitting of measured ^{222}Rn concentrations (Text S3; Figures S2 and S3),
 339 which is not surprising given that gas exchange velocity and groundwater ^{222}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}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 m m^{-1}), gas exchange velocities
 345 have been observed between 1 and 100 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 m d^{-1} (
 347 ≤ 10 times estimated gas exchange velocity using empirical equations (SI Text 2)) and
 348 groundwater ^{222}Rn concentrations between 100 and 600 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}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}Rn concentrations. To
 355 represent a range of conditions which may give optimal model performance, we evaluated
 356 groundwater ^{222}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}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}Rn concentration
 360 and minimum gas exchange velocity, and the maximum groundwater ^{222}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 (ms^{-1})	0	Field conditions
E	Evaporation (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 (m^2)	w*d	Stream discharge measurements
D	Dispersivity (m^2s^{-1}) ¹	0	Beisner et al. (2018)
k [†]	gas exchange velocity (ms^{-1})	Table 3	Estimated using MC simulation

Parameter	Definition	Value	Note
P	Precipitation (ms^{-1})	0	Field conditions
E	Evaporation (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 (m^2)	w*d	Stream discharge measurements
λ	Rn decay coefficient (s^{-1})	4.43×10^{-5}	Cook and Herczeg (2000)
C_{atm}	Atmospheric ^{222}Rn concentrations (pCi/L)	0	Field conditions
C_{gw}^{\dagger}	Groundwater ^{222}Rn concentrations	Table 3	Estimated using MC simulation
C_{tr}	^{222}Rn concentration in Elk Creek (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 3rd 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:

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

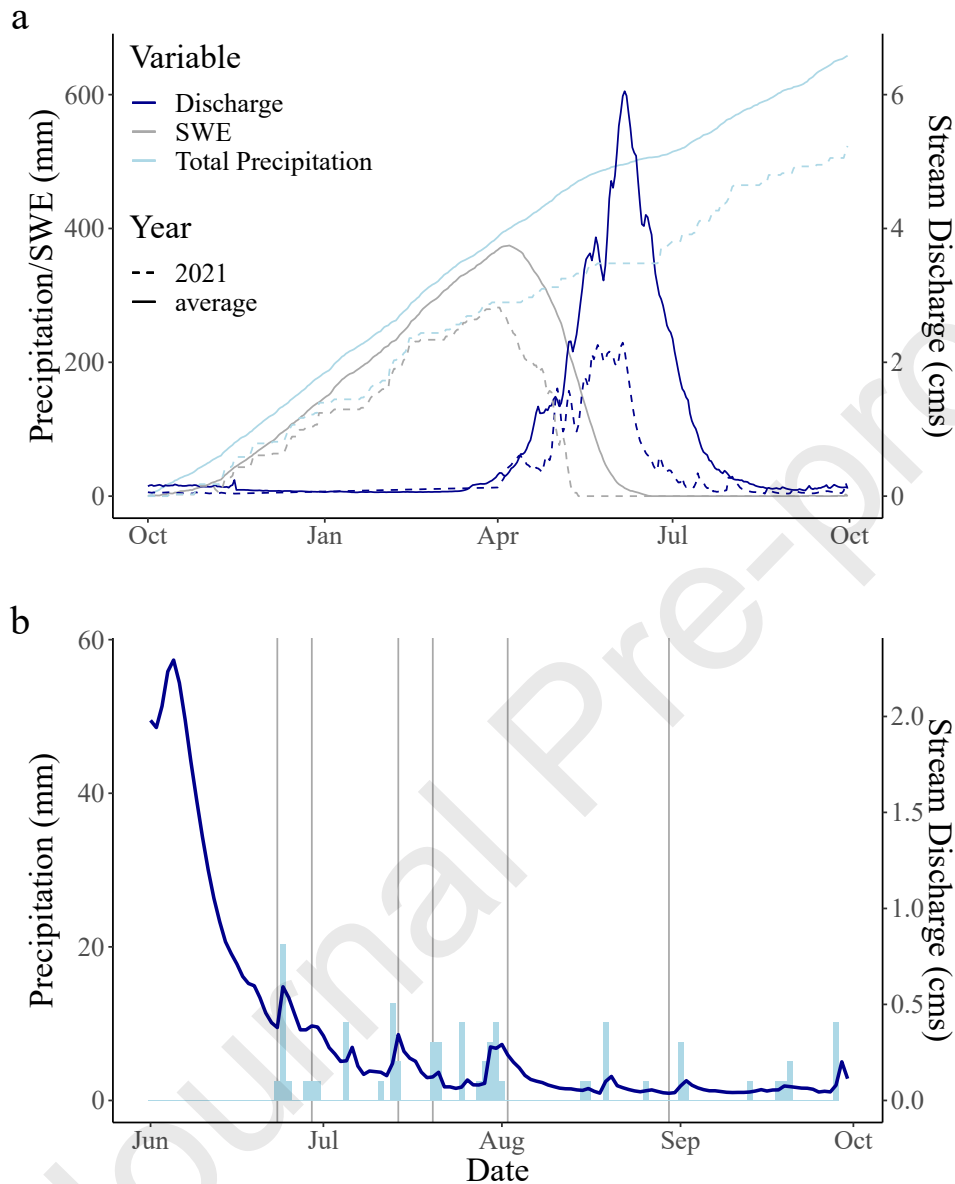
385 where t is time in days (in this study $t=1$ on June 1, 2021), P is precipitation (mm), Q is stream
 386 water discharge (mm), and ET is evapotranspiration (mm). Actual ET measurements are not
 387 available for Coal Creek; we use PET calculated from the Penman Monteith equation in our
 388 calculations 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 10th

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}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}Rn was measured at Upstream Elk and the
 420 lowest was measured at Downstream (Figure 3). ^{222}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).

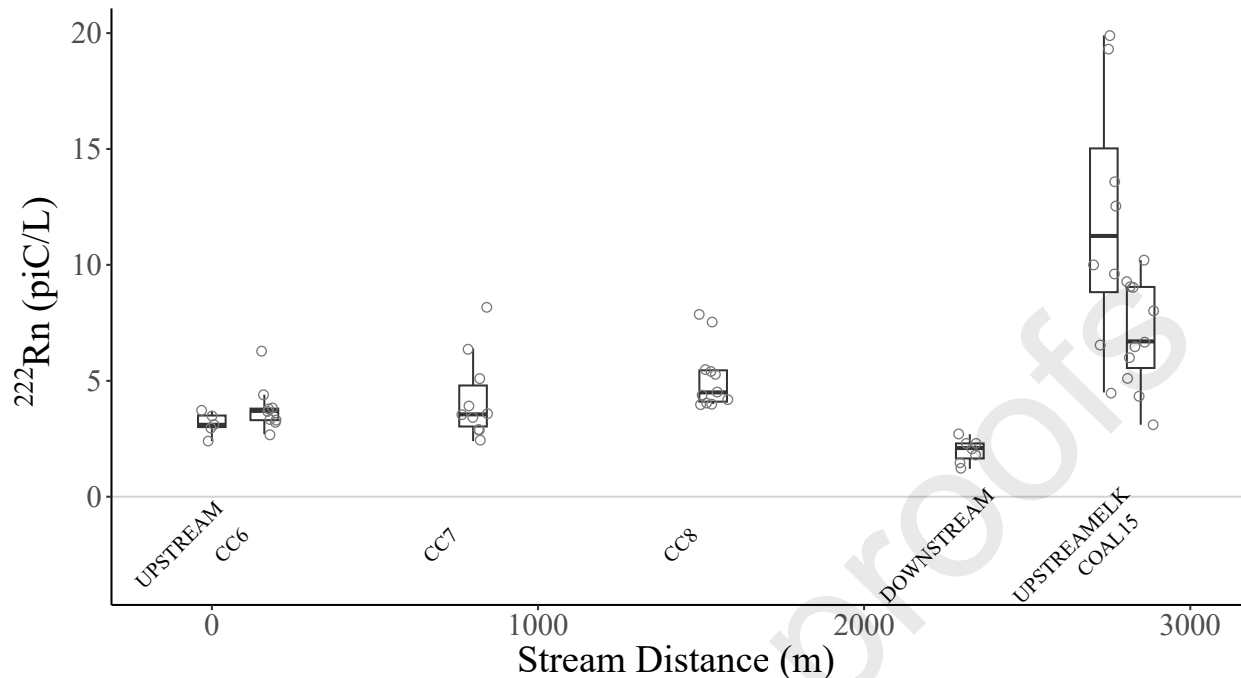
424 Table 2: Sites, times sampled, stream meter, and mean and deviation from mean (standard deviation/mean) of ^{222}Rn ,
 425 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ water isotope measurements.

Site	Class	Times Sampled	Stream Meter	^{222}Rn Mean (pCiL ⁻¹)	^{222}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 ⁺	11956	3	16	-16.1	1.86	-118.5	2.5
CC6	fracture	11 ⁺	11795	4	26	-15.8	5.70	-116.0	5.5
CC7	fracture	12 ⁺	11155	4	43	-15.6	4.49	-115.0	4.6
CC8	fracture	13 ⁺	10419	5	27	-15.6	4.49	-114.7	4.6
Downstream	fracture	9 ⁺	9632	2	25	-15.8	3.80	-116.4	3.4
Upstream Elk	non-fracture	9 ⁺	9221	12	46	-15.5	3.87	-114.2	4.0
Elk Creek	non-fracture	3 ⁺	9196	2	NA	-16.7	3.17	-122.3	3.82

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

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

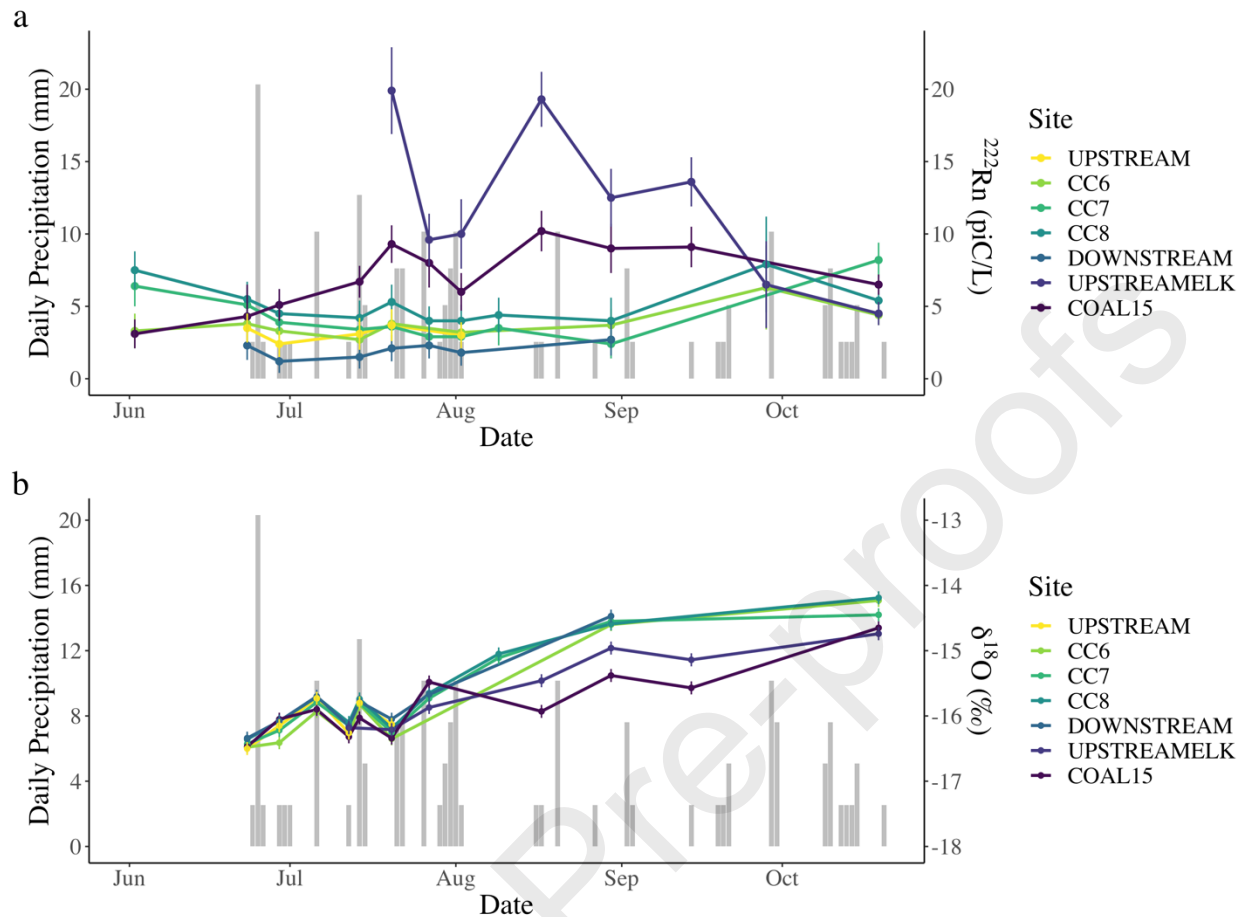
427 ‡ Indicates ²²²Rn and water isotope samples were collected on different days and that ²²²Rn concentrations were
428 collected in 250 mL glass vials. Unmarked spring samples were collected in 500 mL plastic bottles.



429

430 Figure 3. ^{222}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}Rn were not temporally consistent at all sites
 436 (Figure 4a). In general, fracture zone sites showed a decreasing trend in ^{222}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}Rn concentrations at Coal-15 were low in
 439 June and increased throughout the summer before decreasing again at the end of summer. ^{222}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}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}Rn concentrations coincided with periods of time with more precipitation.

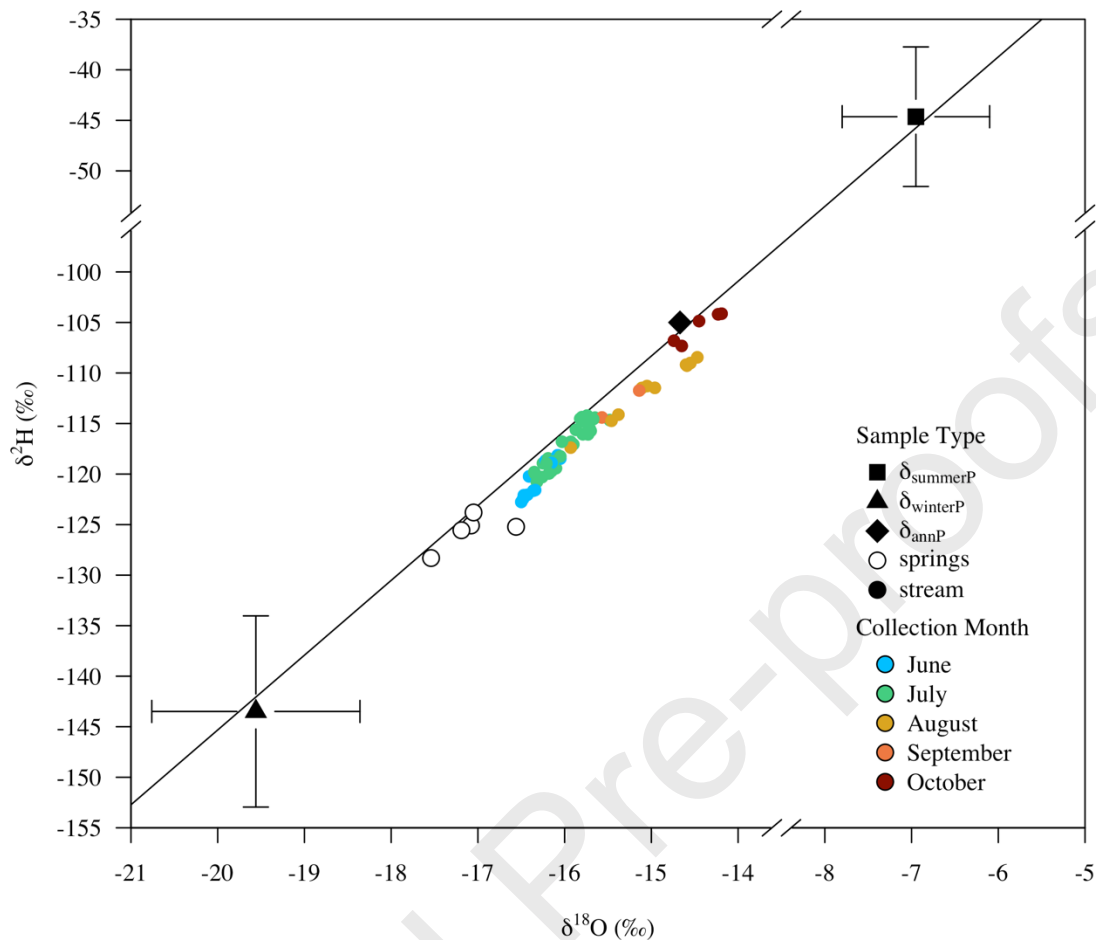


444

445 Figure 4. (a) ^{222}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}Rn concentrations, there was less distinct spatial variation in stream
 453 $\delta^{18}\text{O}$ values.

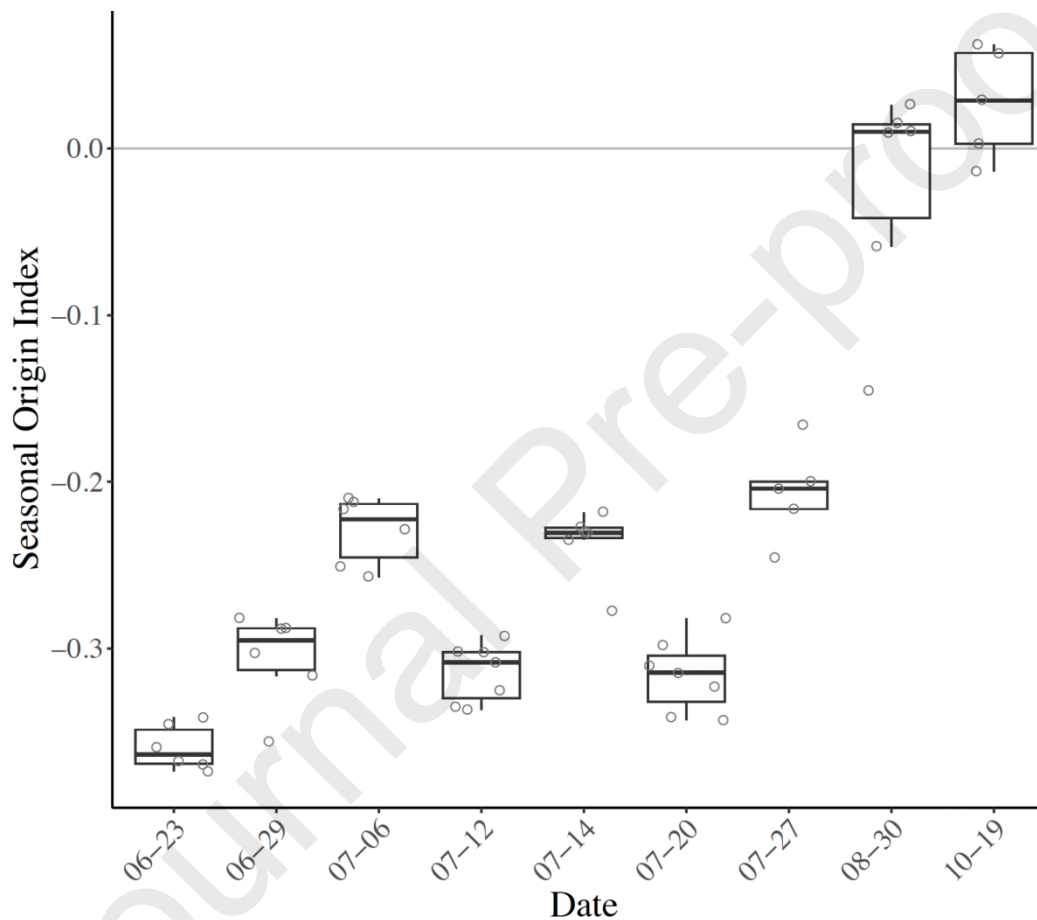


454

455 Figure 5: Dual isotope plots showing δ_{winterP} (weighted average snow, triangle), δ_{summerP} (weighted average
 456 rain, square), and δ_{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

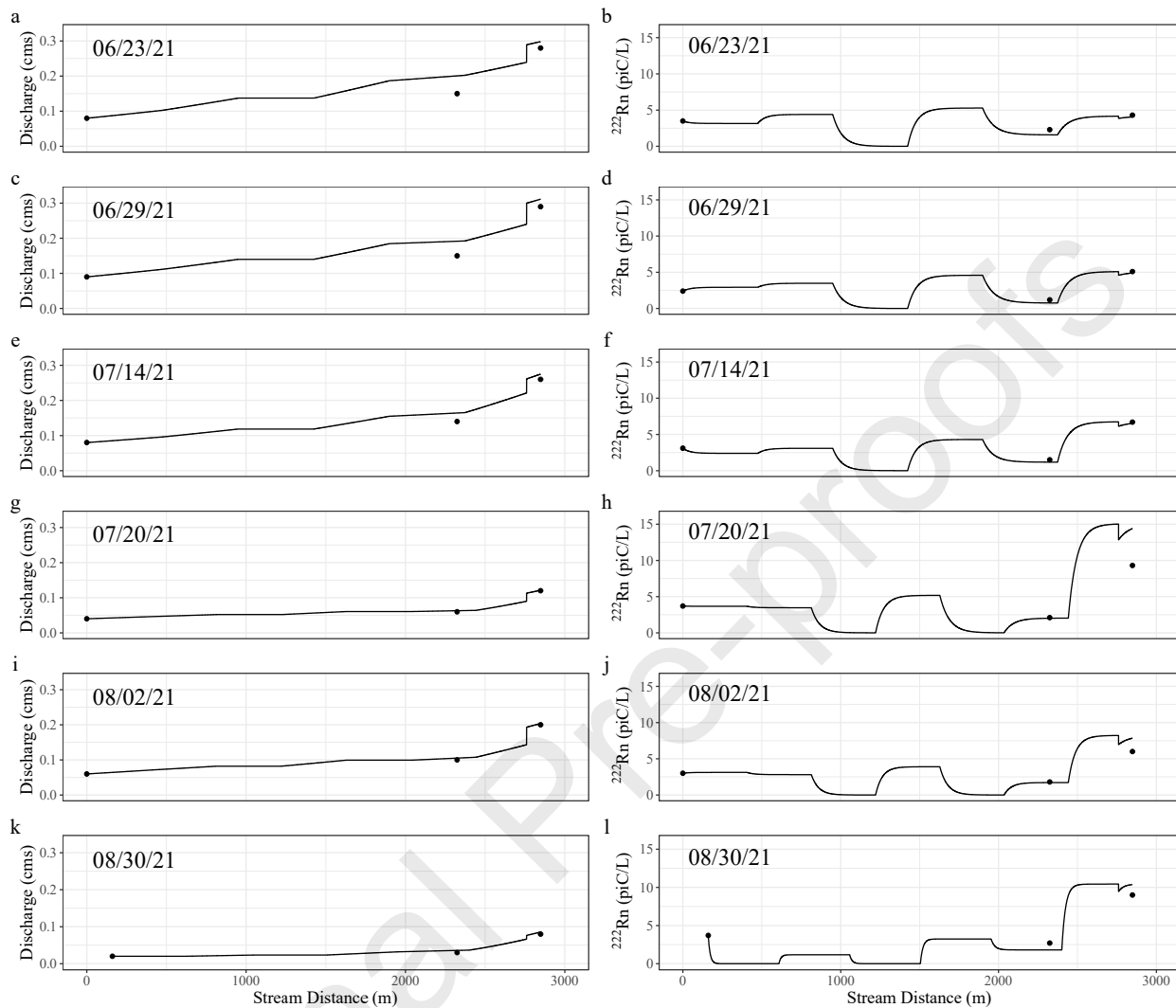
487 We used the StreamTran model to estimate groundwater flux into the stream between
 488 Upstream/CC6 and Coal-15 across six different dates throughout the summer. Monte Carlo
 489 simulations were used to estimate the gas exchange velocity and groundwater ^{222}Rn
 490 concentration for each synoptic 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 ²²²Rn
 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 ²²²Rn 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 ²²²Rn
 498 concentrations during 07/20 and 08/02.

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

Date	Median ²²² 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



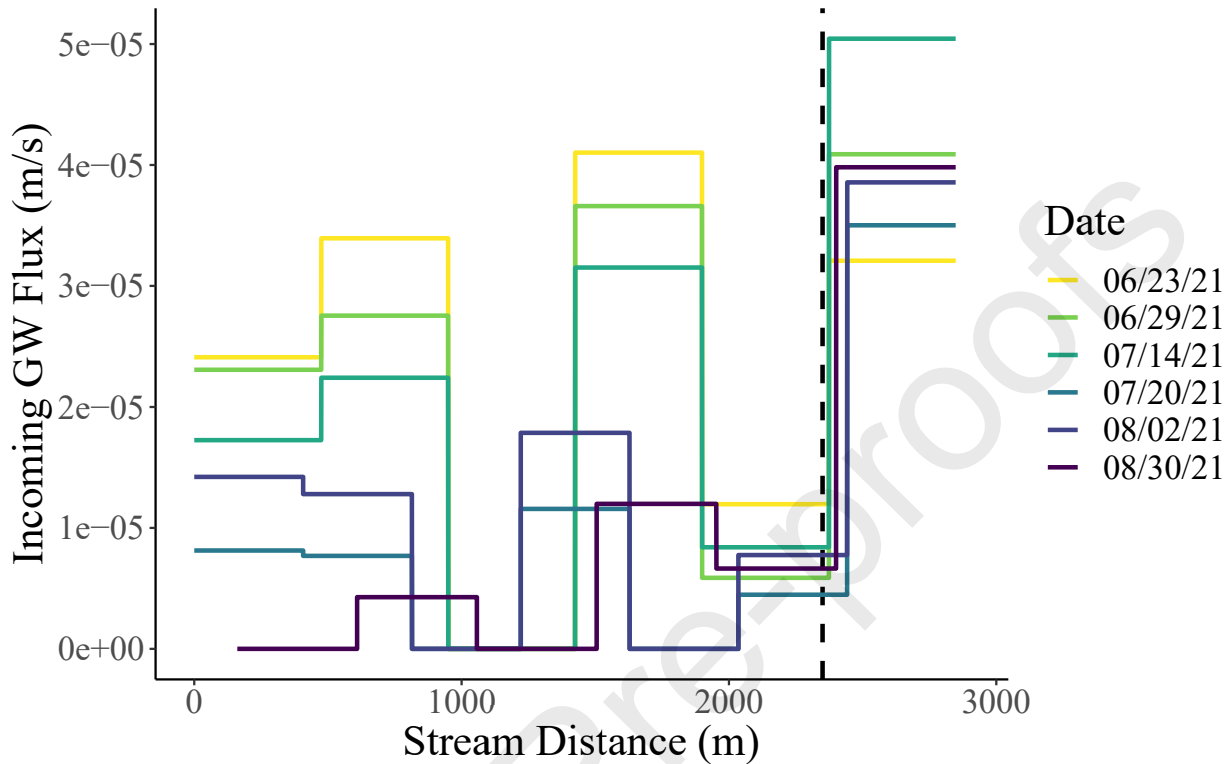
502

503 Figure 7: Stream discharge (a, c, e, g, i, k) and stream ^{222}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

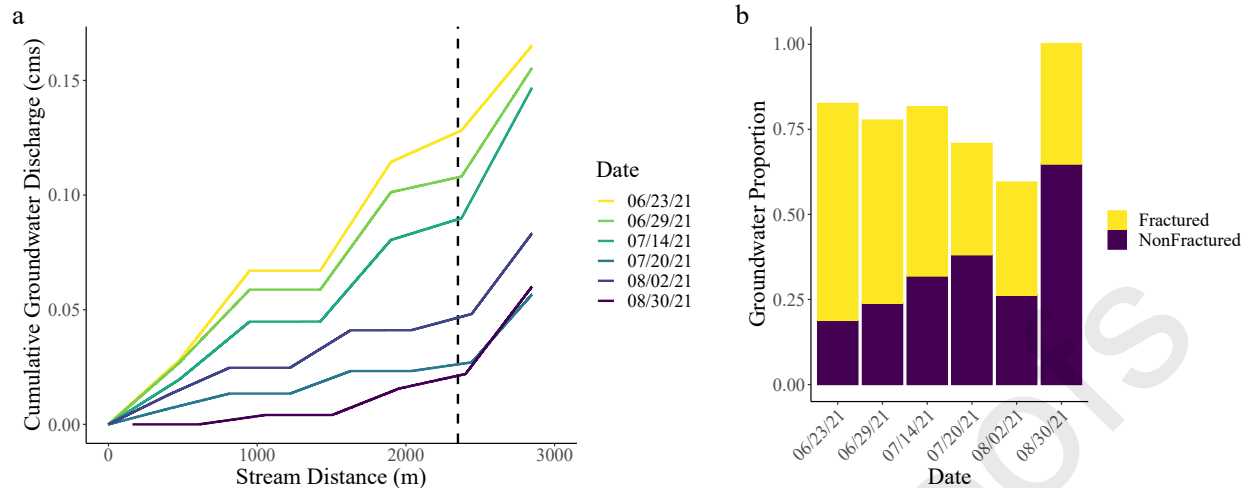
516 the non-fractured zone fan, and contribution from the fractured zone was more variable
 517 compared to the non-fractured zone contribution.



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.



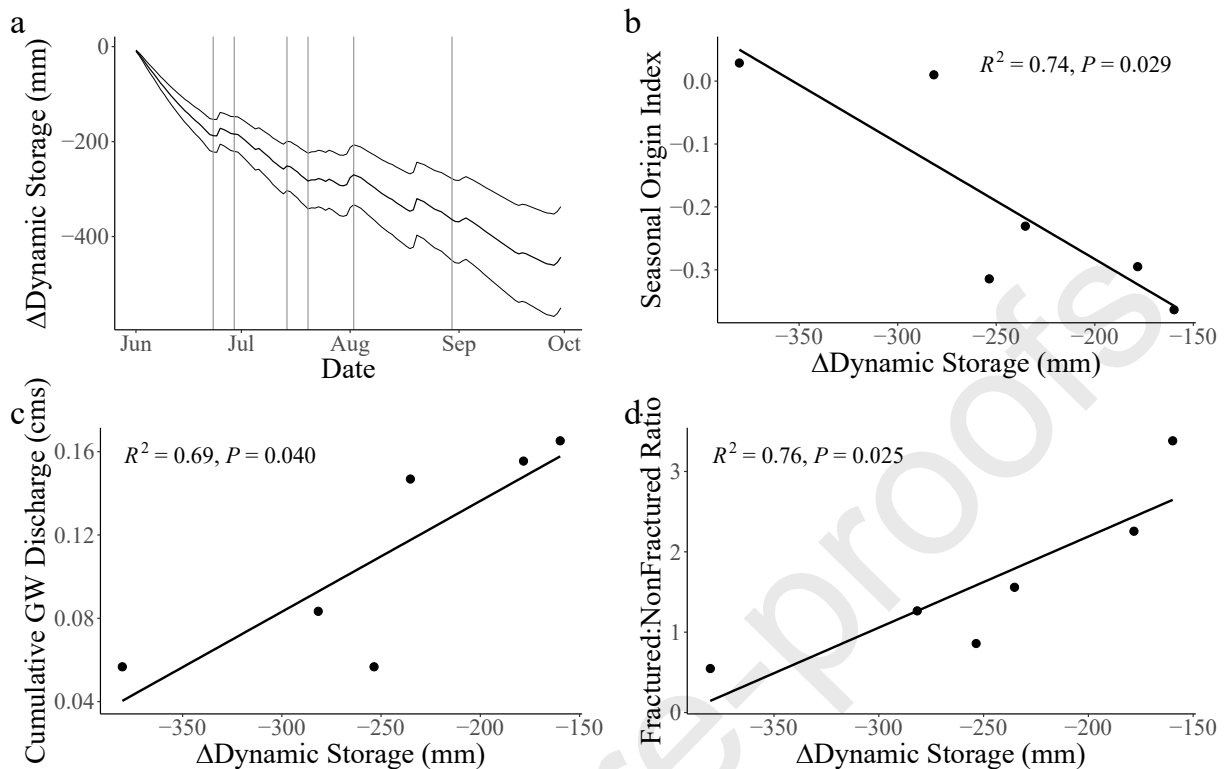
530

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}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 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

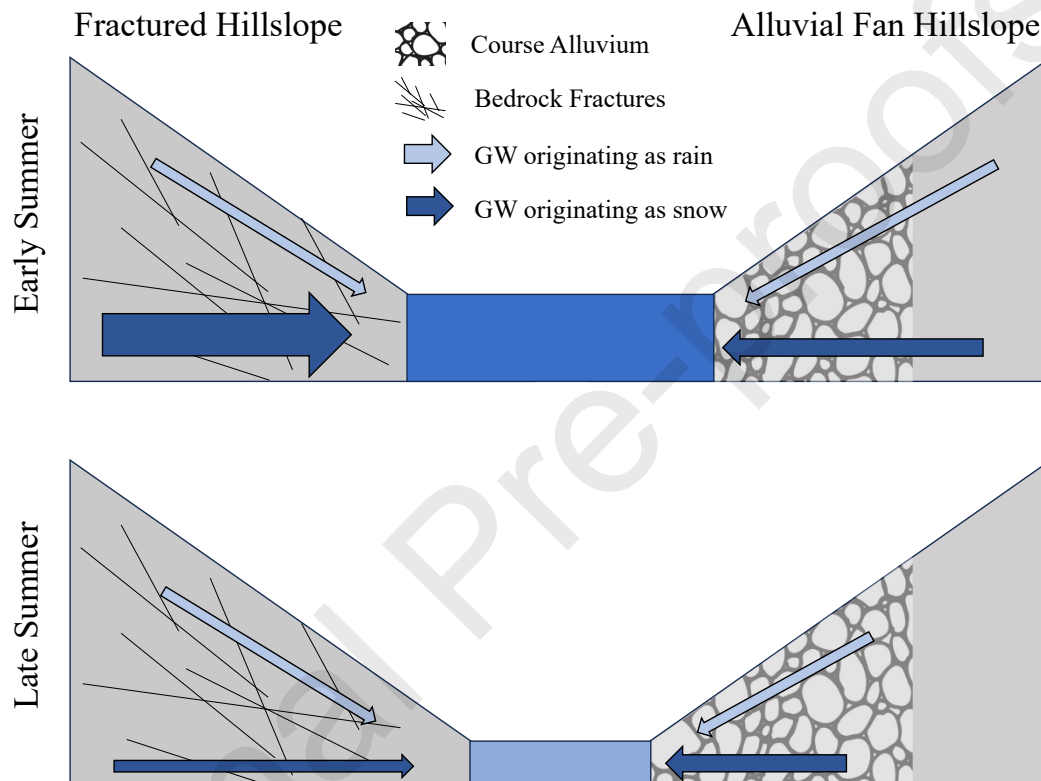
665 overlapped geology giving rise to permeable preferential flow paths (Gardner et al., 2011),
666 functioning similar to the fractures in Coal Creek.

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

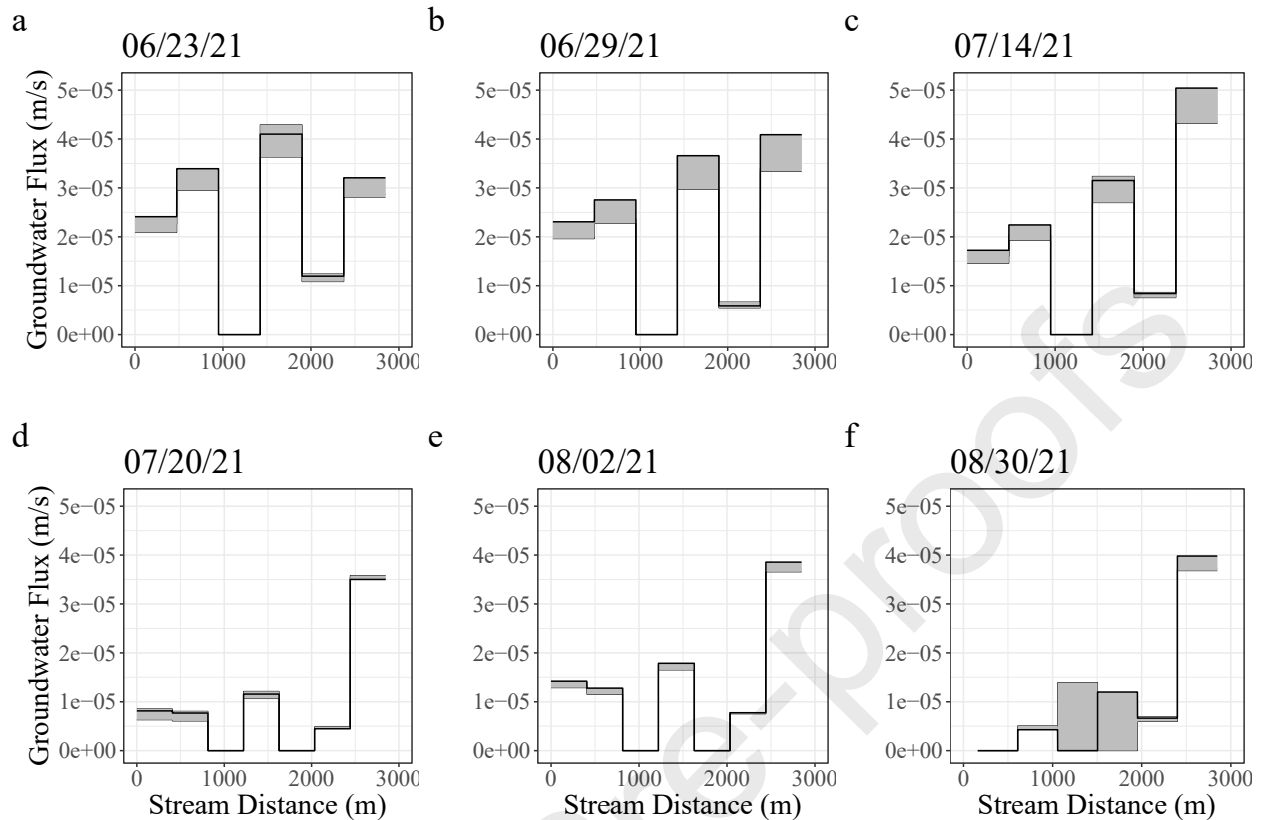
720 Figure 11: Conceptual diagram developed based on SOI that depicts groundwater originating from snow and rain
 721 recharging stream water under fractured and alluvial fan hillslopes during early and late summer. In early summer,
 722 groundwater that originated from snow (δ_{winterP}) dominated the 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 (δ_{winterP}) origin in early summer to greater rain origin (δ_{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}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}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}Rn concentration based on the
748 minimum and maximum ^{222}Rn concentration measured in springs in the watershed. From the MC
749 simulations, groundwater ^{222}Rn concentrations were generally estimated to be low relative to
750 measured ^{222}Rn concentrations, suggesting that groundwater contributing to Coal Creek was
751 relatively young (< 1 week).

752 Gas exchange velocity and groundwater ^{222}Rn concentration parameters exert opposite
753 effects on stream water concentrations: higher gas exchange velocities reduce instream ^{222}Rn
754 concentrations whereas higher groundwater ^{222}Rn concentrations increase instream ^{222}Rn
755 concentrations. We evaluated the relationship between estimated gas exchange velocities and
756 groundwater ^{222}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}Rn concentration values across the top 5% best model runs were
759 used to calibrate StreamTran. Pairings of the minimum groundwater ^{222}Rn concentration and
760 minimum gas exchange velocity, and the maximum groundwater ^{222}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}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}Rn and gas exchange velocity, and maximum paired groundwater ^{222}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}Rn concentrations are
 774 sensitive to the distance between sampling locations. Groundwater ^{222}Rn degasses upon contact
 775 with the atmosphere, and in small streams with high gas exchange velocity, changes in ^{222}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}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}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}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}Rn
804 concentration, and stream slope. It is well documented that groundwater ^{222}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}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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- 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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