

AN ABSTRACT OF THE THESIS OF

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presented on January 30, 2024

Title: Drivers of Relative Streamflow Contribution in Mountainous Headwater Streams

Abstract approved:

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Characterizations of the spatial and temporal variability of runoff generation processes in headwater systems contribute to understanding of how physiography and meteorological factors affect flow paths and streamflow contributions to downstream systems. Water stable isotope ratios were used to evaluate runoff generation processes across headwater streams draining contrasting terrain in a forested headwater system in the H.J. Andrews Experimental Forest, OR. Eight years (2015–2023) of weekly precipitation and one year of stream grab samples at 10 catchments (0.7–62.4 km²) were used in this investigation. Results indicated a strong climate control in the annual variability of average precipitation isotopic signatures. As such, precipitation was the most depleted in 2017, a cold year with high precipitation (2598 mm) and snow water equivalent (SWE) above the long-term median. Conversely, 2020 a warm year with low precipitation (1721 mm) and SWE below the long-term median, exhibited the highest enrichment in a water year. Precipitation inputs were consistently more depleted in late fall, winter, and early spring and consistently, more enriched in late spring, summer, and early fall. Stream and precipitation d-excess signatures were similar in fall and winter and different for spring and summer, indicating that precipitation inputs on fall and winter contributed the most to streamflow. While for a given stream, the temporal variability in stream isotopic signatures was low, the spatial variability in stream isotopic signatures was high across

catchments and driven in part by elevation. The stream with the most depleted isotopic signature was Cold Creek, a high elevation spring-fed stream in the snow zone and the stream with the most enriched isotopic signature was Nostoc Creek, located at lower elevation in the transient snow zone. End-member mixing analysis indicated that Cold Creek contributed between 7 and 90% of the Lookout Creek flow. In contrast, Nostoc and Longer Creeks were found to contribute less than 43% to the Lookout Creek streamflow at their confluences to the main stem. Overall, water contributions to the Lookout Creek at the gauging station (62.4 km²) were high for Cold, Longer, and Mack Creeks during low flows conditions ranging and from 31% to 63%. Considering drainage area, Cold and Longer Creeks supplied more water per unit area than the other tributary. Collectively, our findings demonstrated strong variability across headwater with significant implication for understanding how meteorological and physiographic features impact downstream streamflow contributions. This underscores the complexity of environmental systems and highlights the need for integrated hydrological and chemical approaches to effectively manage and protect headwater streams in the face of ongoing environmental challenges.

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Drivers of Relative Streamflow Contribution in Mountainous Headwater Streams

by
Jaime Ortega

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented January 30, 2024
Commencement June 2024

Master of Science thesis of Jaime Ortega presented on January 30, 2024

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Jaime Ortega, Author

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor Dr. Catalina Segura, for guiding me through this exciting research experience. I would also like to thank my committee members: Dr. Pamela Sullivan, Dr. Renee Brooks, and Dr. Molly Kile for your expertise and feedback.

Thank you to the Panamanian government (SENACYT) for funding my master's studies and to the National Science foundation for financially support my field work and lab analysis. Thank you to the LTER community of the HJ Andrews Experimental Forest, specifically Mark Schulze for logistical support and site access. Thank you to the Keck Lab, particularly Chris J. Russo and Jesse Muratli, for helping me in the analysis of cation samples. Thank you to Jessica Specht (member of the Sullivan Lab) for her assistance in the analysis of the anion samples. Thank you to the Sullivan Lab, specifically Sidney Bush and Keira Johnson, for her assistance in the stream chemistry analysis.

I would like to thank Catchment Processes Laboratory for all the assistance with lab and field work, and research discussion. Thank you to the Water Resources graduate cohort and Peavy 380 office mates for making my graduate school experience joyful, and for all the academic and moral support in this last three years.

An immense thank you to my family back in Panama for keeping motivated during difficult moments and for their unconditional love. A special thank you to my cousin Gloribel Cespedes for her guidance during the scholarship application process and for selling me the idea to study abroad.

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1. Introduction

The headwaters of mountainous river systems include numerous streams that play an important role in nutrient cycling, stream water quality (Alexander et al., 2007; Isokangas et al., 2019), aquatic biodiversity (Freeman et al., 2007; Meyer et al., 2007), and the streamflow availability to downstream reaches (Segura et al., 2019). Given the climatic and physiographic complexity of these systems, we need to better understand what factors control local water flow paths dynamics, streamflow generation, and headwater streamflow and solutes contributions to higher order streams. For example, interannual precipitation variability can result in changes in water transit time (Segura, 2021). Likewise, variability in physiography (geology, geomorphology, and topography) can drive contrasting groundwater discharge (Winter, 2007) and water flow paths (McGuire et al., 2005; Segura et al., 2019).

Streams in the Pacific Northwest (PNW) of the United States are influenced by two hydrological regimes: rain-dominated and snow-dominated regimes (Moore & Wondzell, 2005). Each regime exhibits distinctive seasonal streamflow distributions. Rain-dominated catchments located at intermediate elevations are characterized by high flows in the winter and in the late spring/early summer following precipitation events. Snow-dominated catchments at high elevations exhibit low flow periods in the winter season as snow accumulates, and large peak flow in spring/early summer season with snowmelt (Hamlet, 2001). With climate change predictions for low to no snow futures (Siirila-Woodburn et al., 2021), headwater streams whose low flow conditions are currently dependent on snowfall (Dierauer et al., 2018; Johnson, Harpold, et al., 2023) might experience a change in their streamflow distribution; specifically, streamflow dynamics may more closely mirror a rain and rain-on snow dominated systems due to a decrease in the proportion of snowfall to rainfall and earlier snowmelt onset during the spring season in response to warming temperatures (Barnhart et al., 2020; Knowles et al., 2006).

In addition to the form of precipitation (rain vs snow), seasonal streamflow is strongly influenced by the underlying geology. Headwater streams often have complex subsurface structure coupled with well-defined stream channels (Benito, 2013) that result in significant differences in seasonal discharge (Leuthold et al., 2021). As such, hydrologic response (runoff generation and water storage) is strongly influenced by the geologic setting and geomorphic processes (Litwin et al., 2022). For instance, subsurface features such as fractures (Fan et al., 2007; Johnson et al., in review), lithology (Nickolas et al., 2017), and mass movement processes (Brideau & Roberts,

2015) can impact water movement from hillslopes to a catchment scale; influencing water transit (McGuire et al., 2005), stream network development (Moore & Wondzell, 2005), summer baseflow (Segura et al., 2019), and aquifer recharge (Grant, 1997). Despite our current understanding of the relevance of the subsurface architecture on runoff generation process, our ability to predict water flow paths in headwater streams is still limited.

Conservative tracers such as water stable isotope ratios ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) have been widely used to infer hydrological processes influenced by surface/subsurface features in the landscape and meteorological conditions. Recent work has demonstrated that the surface water isotopic signature is remarkably conditioned by the changes in elevation (McGill et al., 2020), and local conditions at the sampling site (Bowen & Good, 2015). Regarding elevation, the rainout effect indicates a progressive isotopic depletion of the heavy isotopes in the cloud vapor as it travels inland or along a mountain range (Clark & Fritz, 1997; Dansgaard, 1964). As such concentration of the heavy isotopes often decreases with elevation and isotopic lapse rates with negative slopes, are used to describe the variation in the precipitation isotopic ratios with elevation (Poage and Chamberlain, 2001). Lapse rates have been estimated based on isotope ratios in precipitation and surface water (e.g., streams) for many regions such as the Andean Plateau (Bershaw et al., 2016), the Himalayas (Biggs et al., 2015), Central Asia (Fan et al., 2015; Wu et al., 2019), the upper Colorado River-USA (Sprenger et al., 2023), Italy (Vespasiano et al., 2015) British Columbia-Canada (Wassenaar et al., 2011), and the Willamette Valley-USA (Brooks et al., 2012). Observation of precipitation and stream isotope ratios have also been used to estimate transit times and water contributions from two different sources in time (hydrograph separation) or from two different sources in space using end-member mixing models.

End-member mixing analysis (EMMA) using water stable isotopes has been pivotal in hydrological research. This approach has allowed defining details in the runoff generation process such as the contributions of “old” or “new” water or water transit times (e.g., McGuire & McDonnell, 2006) that are not evident from the hydrometric record alone (Beven & Binley, 1992; Dunn, Bacon, et al., 2008; Fenicia et al., 2008; Seibert & McDonnell, 2002). Two component hydrograph separation is a mass balance approach that has been used for over 50 years (Pinder & Jones, 1969; Sklash & Farvolden, 1979) in investigations worldwide (Birkel & Soulsby, 2015; Sklash & Farvolden, 1979). Another application of these models is to investigate the variability in spatial water contributions, such as the relative contribution of tributaries to a mainstream

(Nickolas et al., 2017; Segura et al., 2019). In such cases, tributaries to a stream represent different end-members to the mainstream (mixture) of a catchment. These investigations can provide quantitative information about seasonal and spatial variation in runoff generation processes which is relevant to variations in mainstream water sources and to downstream water availability. This information is critical for headwater streams in which runoff processes can widely vary, given that both physiography and meteorological conditions can change over very short distances.

Using hydrometric observations and hydrological tracers, the goal of this study was to characterize the relative streamflow contribution of three tributaries to a main channel in a mountain stream system. To assess the influence of water inputs, we evaluated the precipitation isotopic values between 2015 and 2023 in terms of seasonal and annual variability. Subsequently, the spatiotemporal variability was analyzed in terms of different surface/subsurface flowpaths and runoff generation mechanisms through the lenses of known differences in geology, geomorphology, and seasonal precipitation variability. In this study we address the following questions:

1. How does the streamflow contribution oscillate seasonally from headwater streams to downstream reaches, draining catchments with distinctive terrain features?
2. How does precipitation isotopic signature vary on seasonal and annual basis between 2015 and 2023?
3. How do the isotopic signatures of each study catchment change spatially and temporally based on potential water sources and landscape characteristics?

We expect that the stream water isotopic signature and discharge by catchment will be influenced by i) seasonal precipitation, and elevation gradient (rainout effect) and ii) hydrologic connectivity (water linkage regions through subsurface water flow), and water transit time that arise from the variability in geologic and geomorphic setting.

2. Materials and Methods

2.1 Study Area

The study was conducted at the H.J. Andrews Experimental Forest (hereafter Lookout Creek), a Long-Term Ecological Research (LTER) program site sponsored by the National Science Foundation. Lookout Creek catchment (Figure 1) is a fifth-order stream that drains 64 km² located in the Western Cascades of Oregon (44°12' N, 122°7' W). The Lookout Creek catchment is divided into three principal catchments McRae, Upper Lookout, and Lower Lookout Creek. Upper Lookout has four major tributaries that contribute to streamflow generation, from west to east: Nostoc, Mack, Longer, and Cold Creeks (see black outline Figure 1). The drainage pattern is dendritic, with high elevations dominated by first and second order streams that represent a significant portion of the drainage network length. The elevation gradient in Lookout Creek varies between 411 to 1632 m with a mean slope of 24° (44.5%), and a mean elevation of 972 m.

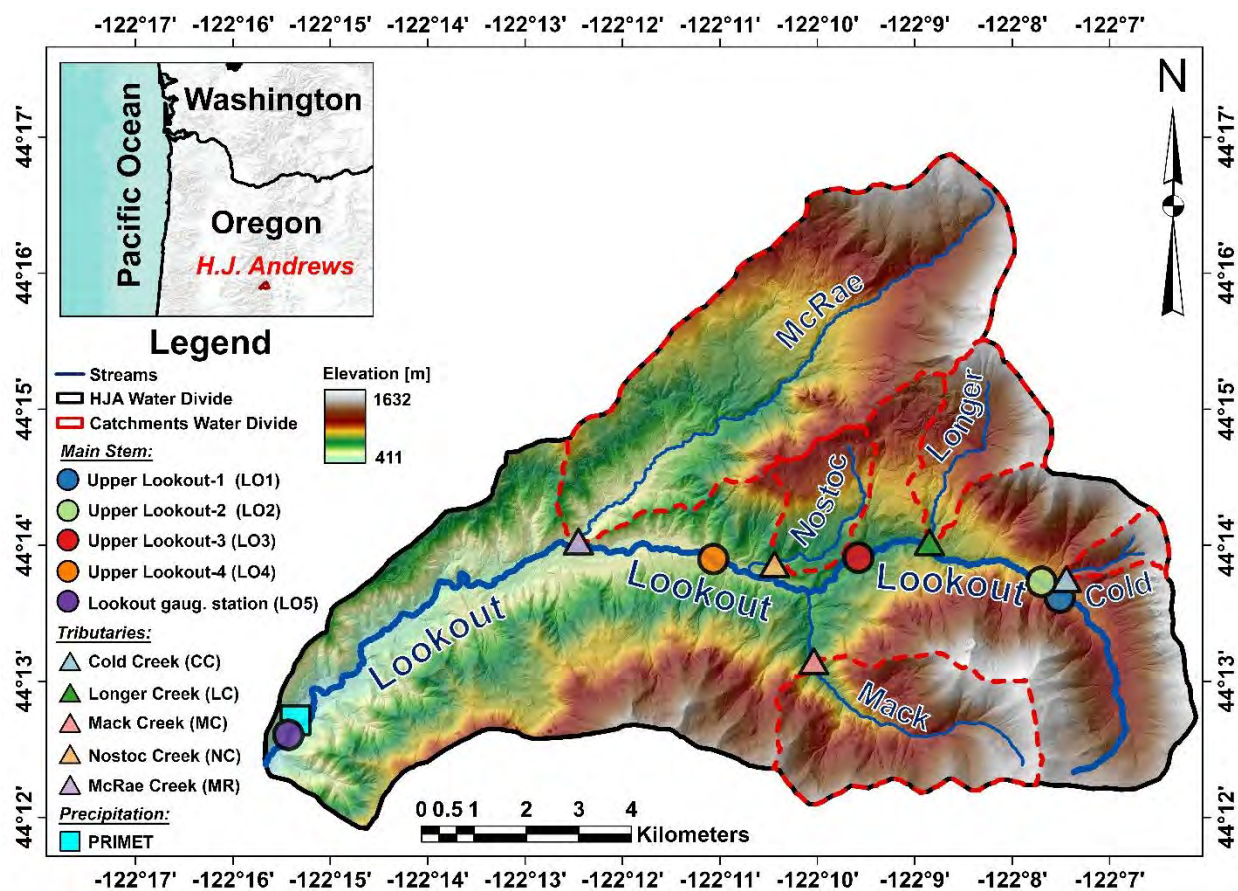


Figure 1. Location of Lookout Creek catchment in Oregon, indicating sample collection sites across the different tributaries and main stems catchments in the Lookout Creek catchment.

2.1.1 Climatology

The climate is Mediterranean with wet winters and dry summers, and it is subjected to maritime influence, affected mainly by subtropical, Pacific, and Gulf of Alaska air masses depending upon the season (Greenland, 1993; J. W. Smith, 2017). Meteorological data in Lookout Creek can be constrained by a series of stations at different elevations, PRIMET at 430 m, H15MET at 909 m, and UPLMET 1295 m. Precipitation increases with elevation as does the proportion of snowfall (McKee & Bierlmaier, 1987). The temperature is affected by elevation, aspect, and topography across Lookout, with the average annual air temperature (water year: 1998-2022) is 8.8 °C, oscillating from 5.9 °C at 1295 m elevation to greater than 9.0 °C at 430 m elevation. Furthermore, daily maximum and minimum temperatures range from 40 °C in July to -20 °C in December. The mean annual precipitation for Lookout Creek (water year: 1996–2022) is 2300 mm, varying from 2194 mm at lower elevations to over 2697 mm at higher elevations (1295 m). Most precipitation is received in winter (December, January, February) with 42% (969 mm) followed by spring (March, April, May) with 26% (603 mm) of the total annual precipitation. The snowpack depth varies depending on the meteorological conditions. For elevations between 400–800 m (transient snow zone), the snowpack (shallow deep) persists no more than 1–2 weeks. Above 800 m (seasonal snow zone), the snowpack (up to 3 m deep) could last up to 6 months (from November to April or June) (Bierlmaier & McKee, 1989; Jones & Perkins, 2010). Snow water equivalent (water year: 2003–2020) ranges from less than 20 mm (PRIMET) to more than 800 mm (UPLMET), with annual median SWE peaks between 105 to 993 mm.

2.1.2 Geology and Geomorphology

The Lookout Creek catchment (Figures 2 and 3) is underlain by rocks of volcanic origin (extrusive and intrusive), which erupted in the late Oligocene to early Miocene period, and it is divided in three formations Pliocascade volcanics (Lava-1), Sardine (Lava-2 and Ash), and Little Butte (Pyro). These types of rocks include lava flows, ash flows, air falls tufts, cinder beds, and water-worked tuffaceous sediments. In general, Lookout Creek has been subjected to different phases of volcanism intermingled with periods dominated by weathering, erosion, and the reworking of volcanic material (Swanson & James, 1975).

At high elevation (> 900 m), the most dominant rock types are andesitic and basaltic lava flows, subaqueous lava flows, and fluvial and lacustrine silt, sand, and gravel. This fringe zone coincides with the headwater area of upper McRae, and Upper Lookout Creek (Cold, Longer, and Mack Creek). At mid-elevations (600 to 900 m), exposures of andesitic and basaltic lava flows, ash flow tuffs, and flow rock capped stuff are found within McRae and Upper Lookout Creek (Longer and Nostoc Creek). At lower elevations (< 600 m), tuffaceous silt and sand lacustrine sediments, basaltic flows, and pyroclastic flow are found from the confluence of between McRae and Upper Lookout Creek to the outlet of the Lookout Creek catchment (Table 1).

In general terms, the Lookout Creek catchment is composed of moderate ($15\text{--}30^\circ$) slopes with a catchment orientation from southeast to southwest (main channel path). Some of the tributary catchments such as Cold, Longer, Mack, and Nostoc Creeks, located in the Upper Lookout Creek, exhibited average slopes that oscillates from 26 to 19% with different catchment orientations. The occurrence of deep-seated and massive earth movement (rotation slumps, earthflows, and others) in the Lookout Creek catchment has generated anomalous drainage patterns, poorly drainage depressions, vegetation disturbed by ground movement, temporal blockage, or diversion of the main channel. Likewise, shallow soil mass movement have taken place, specifically in soils derived from basaltic rock through the occurrence of debris slides, avalanches, torrents, and small earthflows. These earth mass movements have a notorious presence in the main channel and adjacent areas of it. Longer Creek is the catchment with more exposure of these mass earth movements, specifically earthflow, followed by Nostoc and McRae Creeks. Furthermore, the main channel of the Lookout Creek is affected by these geomorphic processes, starting from the farthest point upstream at 885 m to lowest point downstream at 489 m where the susceptibility to debris flow increases (Johnson, Harpold, et al., 2023). Glacial erosion has taken place in the Lookout Creek catchment, creating U-shape valleys, in the Upper Lookout (above 700 m) subbasin, pointing out north and northeast-facing ridges (Swanson & James, 1975). This landscape feature is present at Cold and Longer Creeks, where headwaters begin their path downstream, conditioned by these ridge orientations.

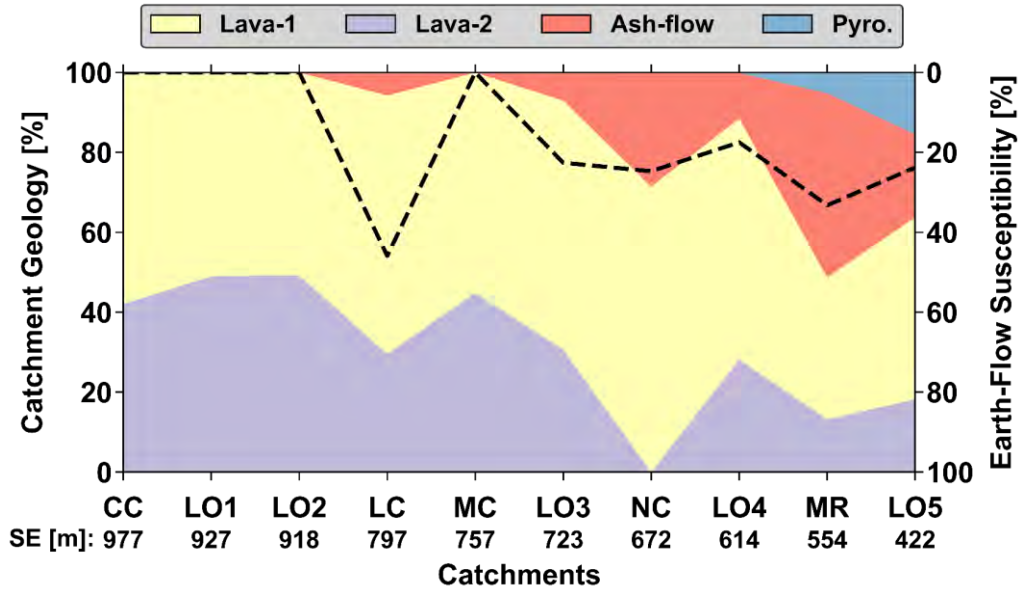


Figure 2. Percent of catchments areas with earth-flow susceptibility (dashed black line) and areas composed of different geologic units. Tributaries include Cold (CC), Longer (LC), Mack (MC), Nostoc (NC), and McRae (MR), while sites along Lookout Creek (LO) ranges from upstream (1) to downstream (5). SE represents site elevation where samples were collected.

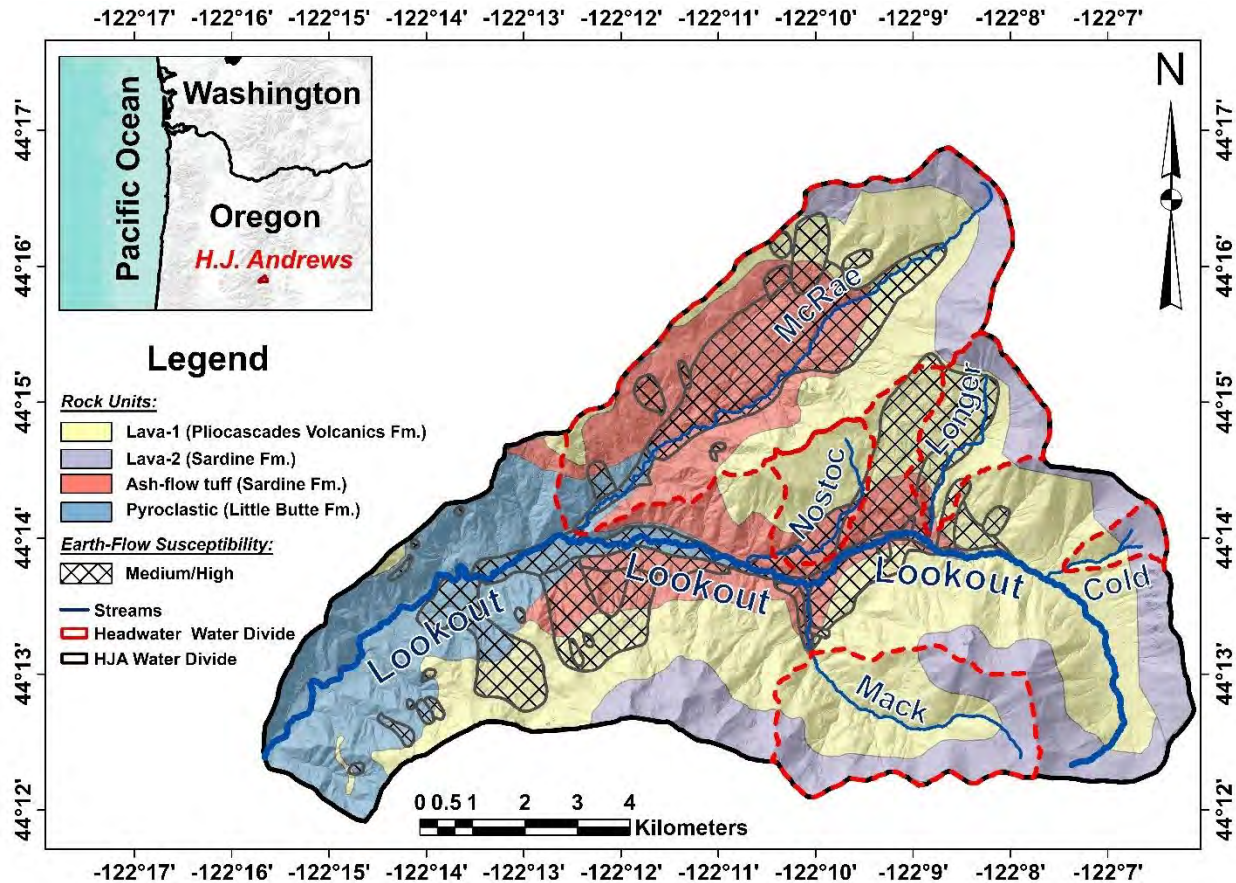


Figure 3. Geology (lithology) and earth-flow susceptibility areas in the Lookout Creek catchment.

2.1.3 Vegetation

The vegetation of the Lookout Creek was mainly old-growth coniferous with a 400–500 year-old stand dominated by species such as Douglas-fir (*Pseudotsuga menziesii*), Western hemlock (*Tsuga heterophylla*), and Noble fir (*Abies procera*). Multiple disturbances have played a role in altering the landscape including: 1) logging operations between 1950 and 1995 that resulted in 25% clearcut of the Lookout Creek catchment (~16 km²), with an associated 136 km of forest roads constructed (Goodman et al., 2023). 2) flooding in 1964–65 and 1996 in concert with forestry activities resulted in significant mass wasting (Goodman et al., 2023). 3) wildfires have also impacted the catchment (Tepley et al., 2014). The most significant fires occurred around 1840's and 1900's, more recently the 2020 Holiday Farm Fire, and the 2023 Lookout Fire affected large areas of the catchment.

2.1.4 Hydrography

The seasonal streamflow distribution of Lookout Creek was typical of a transient snow (mixed rain-snow) dominated system with high flows in both winter and late spring. The annual median streamflow (water year: 1950–2022) at the Lookout Creek USGS gauging station (No. 14161500) was 3.36 m³/s with an average annual runoff of 1728 mm. Monthly average streamflow ranged from 0.40 m³/s to 6.50 m³/s. Discharge was highest in winter (mean= 5.96 m³/s) and lowest in summer (mean=0.59 m³/s). Winter flows coincided with the maximum precipitation events (November–January), and late spring/early summer flows were related to snowpack melting.

2.2 Fields Methods

We established 10 sampling sites (Table 1, Figure 1) to characterize the spatiotemporal stream isotopic signature of tributaries to Lookout Creek and to estimate their relative streamflow contribution. The sites were chosen to represent variable drainage area, precipitation regime, and streamflow contribution (Figure 1). Five sites were located in tributaries: Cold (CC), Longer (LC), Mack (MC), Nostoc (NC), and McRae (MR) Creeks with drainage areas between 0.7 and 15.6 km² and with catchment mean elevation between 913 and 1297 m (Table 1). Five additional sampling sites were established along the main stem of the Lookout Creek (LO1–LO5) with drainage areas between 5.5 and 62.4 km². The aim of this design was to evaluate the streamflow

contribution from the defined headwater streams to downstream in the main channel. The precipitation isotopic ratios were analyzed from the meteorological station PRIMET (430 m).

Surface water grab samples at 10 locations were collected weekly between May 2022 and May 2023, while composite precipitation samples were collected weekly at PRIMET between November 2014 and May 2023. Precipitation samples were collected in a Palmex Rain Sampler (Rain Sampler Palmex Ltd., Croatia) equipped to avoid evaporation (Gröning et al., 2012). Each week, accumulated precipitation volume was measured, and a subsample collected for isotopic analysis. This resulted in 317 composite precipitation samples and 278 grab stream samples. Water samples were collected in 20 ml borosilicate glass vials with conical inserts and capped without headspace, storing them in non-sunlight and cool conditions ($<15^{\circ}\text{C}$) to prevent isotopic fractionation (evaporation).

2.3 Statistical Methods

We were interested in the arithmetic and volume-weighted average, standard deviation, standard error from the isotopic composition of the grab (stream) and precipitation samples in the study period. All statistical analyses were done in Python version 3.9.12, using NumPy and pandas packages (Harris et al., 2020; The pandas development team, 2023).

We fit a simple linear regression model to estimate the isotopic lapse rate (slope) between stream average isotopic signature (response variable) and catchment mean elevation for each study sampling site, using NumPy package (Harris et al., 2020). We conducted a weighted linear regression analysis to estimate regression coefficients (slope and intercept) between the precipitation isotopic signature of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ to estimate the general (2015–2023) Local Meteoric Water Line (LMWL) and the LMWL by season (spring, summer, fall, and winter). We assigned weights based on the precipitation volume measured as described above, using Statsmodels package (Seabold & Perktold, 2010). We applied an ANCOVA analysis to evaluate if the general and seasonal LMWLs were statistically different from the Global Meteoric Water Line (GMWL) through the regression coefficients, specifically slopes (Statsmodels package, Seabold & Perktold, 2010).

Table 1. LiDAR derived topographic characteristics, lithology, and available streamflow record of the study catchments.

Catchment	Da	Max. Elev.	Min. Elev.	WME	Mean Slope	Dominant Lithology*			Mass Movement Presence**	Available Streamflow Record	
	km²	m	m	m	° [%]	% of occupied area			Type	Water years	
Tributaries	CC	0.69	1570	977	1297	27 [51]	Lava-1 [42%]	[58%], Lava-2	-	2 [2021–2023]	
	LC	2.74	1601	797	1178	23 [42]	Lava-1 [30%]	[62%], Lava-2	Earthflow [46%]	1 [2022–2023]	
	MC	5.75	1619	757	1197	28 [53]	Lava-1 [45%]	[55%], Lava-2	Shallow soil, headwall scarp	28 [1996–2023]	
	NC	1.96	1153	672	913	19 [34]	Lava-1 [71%], Ash [29%]			Earthflow [25%], shallow soil, headwall scarp	-
	MR	15.58	1632	554	984	22 [40]	Ash [46%], Lava-1 [36]			Earthflow [33%], shallow soil	-
Main Stem	LO1	5.53	1620	927	1257	24 [44]	Lava-1 [49%]	[51%], Lava-2	-	-	
	LO2	6.32	1620	918	1258	25 [46]	Lava-1 [49%]	[51%], Lava-2	-	-	
	LO3	15.63	1620	723	1170	24 [44]	Lava-1 [62%], Ash [31%]			Earthflow [23%], shallow soil	-
	LO4	30.67	1620	614	1106	25 [46]	Lava-1 [28%]	[60%], Lava-2	Earthflow [17%], shallow soil	-	
	LO5	62.42	1632	422	979	25 [46]	Lava-1 [18%]	[46%], Lava-2	Earthflow [24%], shallow soil	74 [1950–2023]	

Da: drainage area; Max Elev: maximum elevation; Min Elev: minimum elevation; WME: catchment mean elevation.

LiDAR information obtained from a raster file created by HJ Andrews Elevation Surfaces (2023).

* Dominant lithology information obtained from a vector file created by Swanson (2005).

** Mass movement presences obtained from Andrews Forest LTER Site & Swanson, (2013).

2.4 Isotopic Analysis

Water stable isotope ratios were used as tracers to understand water sources and to quantify tributary contributions to the main stem of the Lookout Creek. As such, grab and precipitation samples were analyzed for stable isotope ratios ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) using a Picarro L2130-I cavity ring down spectroscopy liquid and vapor isotopic analyzer (Picarro Inc, CA). Samples were run under the high precision mode, with six injections per sample. The initial three injections were discarded to account for any memory effects. For calibration purposes we used two internal standards with $\delta^{18}\text{O}$ between -14.6 and -7.7‰ and $\delta^2\text{H}$ between -105.6 and -50.7‰. Additionally, a third internal standard was employed to estimate the accuracy of the analysis ($\delta^{18}\text{O}$: -11.1 and $\delta^2\text{H}$: -80.1). The calibration of all internal standards was performed against the International Atomic Energy Agency's (IAEA) primary standards, specifically the Vienna Standard Mean Ocean Water (VSMOW2, with $\delta^{18}\text{O}$ = 0.0‰ and $\delta^2\text{H}$ = 0.0‰), Greenland Ice Sheet Precipitation (GISP, with $\delta^{18}\text{O}$ = -24.8‰ and $\delta^2\text{H}$ = -189.5‰), and Standard Light Antarctic Precipitation (SLAP2, with $\delta^{18}\text{O}$ = -55.5‰ and $\delta^2\text{H}$ = -427.5‰). Following the methodology suggested by Brooks et al. (2022), the precision (one standard deviation based on 102 duplicated samples) was 0.02‰ for $\delta^{18}\text{O}$, 0.09‰ for $\delta^2\text{H}$, and 0.15‰ for deuterium excess. The accuracy of the analyses was assessed by comparing 33 estimated values to a known internal standard, resulting in an accuracy of 0.01 ± 0.04 ‰ for $\delta^{18}\text{O}$ and 0.08 ± 0.25 ‰ for $\delta^2\text{H}$.

Isotope ratios ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were reported in parts per thousand (‰) deviation relative to VSMOW2.

$$\delta(\text{‰}) = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} - 1 \right) * 1000 \quad (1)$$

where R_{sample} and R_{standard} are the isotope ratio ($^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$) of the sample and standard (VSMOW2). Volume-weighted averages (precipitation) are indicated with a doubled overbar ($\overline{\overline{\delta^{18}\text{O}}}$ and $\overline{\overline{\delta^2\text{H}}}$) and the arithmetic average isotopic composition (streams) were presented with an overbar ($\overline{\delta^{18}\text{O}}$ and $\overline{\delta^2\text{H}}$), distinguishing from individual isotopic samples ($\delta^{18}\text{O}$ and $\delta^2\text{H}$).

2.4.1 Precipitation Isotopic Analysis

To understand how meteorological processes (precipitation form and seasonality) affect the precipitation isotopic composition, weekly precipitation samples have been collected at PRIMET since water year 2015. This period included a wide range of meteorological conditions. The annual volume-weighted precipitation isotopic signature was computed, considering the (1) amount of precipitation accumulated in the rain gage between the last and current sample (Ppt_i), (2) isotopic signature of the current sample (δ_i), and (3) total annual precipitation ($\sum_{i=1}^n Ppt_i$):

$$\overline{\delta(^{18}\text{O}/^2\text{H})} = \frac{\sum_{i=1}^n \delta_i * Ppt_i}{\sum_{i=1}^n Ppt_i} \quad (2)$$

To represent the long-term relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ at PRIMET, the LMWL was defined based on a weighted least squares regression (WLSR) (Hughes & Crawford, 2012) where weights were based on recorded precipitation volumes for each sample period. The GMWL was considered for comparative purposes (Craig, 1961). The equations are represented as following:

$$\delta^2\text{H} [\text{LMWL}] = (a * \delta^{18}\text{O}) + b \quad (3)$$

$$a = \frac{\sum_{i=1}^n Ppt_i y_i x_i - \frac{\sum_{i=1}^n Ppt_i x_i \sum_{i=1}^n Ppt_i y_i}{\sum Ppt_i}}{\sum_{i=1}^n Ppt_i x_i^2 - \frac{(\sum_{i=1}^n Ppt_i x_i)^2}{\sum Ppt_i}} \quad (4)$$

$$b = \frac{\sum_{i=1}^n Ppt_i y_i - a \sum_{i=1}^n Ppt_i x_i}{\sum Ppt_i} \quad (5)$$

$$\delta^2\text{H} [\text{GMWL}] = (8 * \delta^{18}\text{O}) + 10 \quad (6)$$

where a and b are the model parameters (slope and intercept). y_i and x_i are the isotopic signature (‰, $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively) of the i^{th} sample from the n samples collected in that water year. Ppt_i is the total amount of precipitation (mm) to the i^{th} sample from the n samples collected in that water year.

2.4.2 Stream Isotopic Analysis

We evaluated the spatial and temporal variation in stream isotope ratios ($\delta^{18}\text{O}$, $\delta^2\text{H}$) and d-excess ($d = \delta^2\text{H} - 8 * \delta^{18}\text{O}$). We also calculated the isotopic lapse rate–linear relation between

mean catchments elevation and average isotopic composition (Beria et al., 2018; Brooks et al., 2012)–for all the investigated catchments to assess how the isotopic values gradually varied with elevation. Moreover, we estimated the relative streamflow contribution of the different tributaries in the Lookout Creek catchment based on a two-end member mixing model on each tracer ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) (Nickolas et al., 2017; Segura et al., 2019):

$$Q_t C_t = Q_1 C_1 + Q_2 C_2 \quad (7)$$

$$F_1 = \frac{C_t - C_2}{C_1 - C_2} = \frac{Q_1}{Q_t} \quad (8)$$

$$F_2 = \frac{C_t - C_1}{C_2 - C_1} = \frac{Q_2}{Q_t} \quad (9)$$

$$F_1 + F_2 = 1 \quad (10)$$

where Q_t is the discharge downstream of the two tributaries, Q_1 , and Q_2 , are the discharge of end-members 1 and 2, C_t is the tracer concentration for the sample downstream of end-members 1 and 2, and C_1 and C_2 are the tracer concentration of end-members 1 and 2. F_1 and F_2 represent the fractions of the total flow downstream of end-member 1 and 2.

2.4.3 Water Age Computations

To have a roughly approximation of the hydrologic connectivity, water contribution, and relative age differences among the study catchments; we computed the damping ratio (DR) as a proxy for transit time for all investigated catchments:

$$\text{DR} = \frac{\text{SD}_{\text{Stream}} (\delta^{18}\text{O} \text{ or } \delta^2\text{H})}{\text{SD}_{\text{Ppt}} (\delta^{18}\text{O} \text{ or } \delta^2\text{H})} \quad (11)$$

where $\text{SD}_{\text{stream}}$ is the standard deviation of the stream isotopic signature. SD_{ppt} is the standard deviation of the precipitation isotopic signature (Bansah & Ali, 2019; Sanchez-Murillo et al., 2015; Soulsby et al., 2015).

2.5 Streamflow and Unit Discharge Analysis

For our purposes, streamflow records were obtained and calculated from a timeframe that spanned from May 2022 to May 2023. Two of the sampling locations have long-term streamflow

data: LO5 (USGS No. 14161500) and MC (Mack Creek: long-term site of the HJ Andrews Forest gage) (Table 1). Two of the investigated tributaries (Cold and Longer Creeks), were instrumented with pressure transducers (Solinst Canada Ltd.) installed in uniform cross-sections. Stage heights at 15 minutes resolution were obtained after barometric compensation. To estimate discharge, rating curves were developed based on pair measurement of stage and discharge. Discharge was calculated applying the velocity-area method (Dingman, 2015) using either a FlowTracker (SonTek, Xylem Inc.) or a pigmy meter (Performance Results Plus, Inc.) to measure velocity. Stage height–discharge rating curves were developed based on nine discharge measurements in Cold Creek and five discharge measurements at Longer Creek, covering a wide range in discharge levels (Appendix C). In both cases the rating curve was a power-law relation (Herschy, 2009):

$$Q = a (H - H_o)^b \quad (12)$$

where Q is the discharge, m^3/s , a, b are coefficients, H is the stage height, and H_o is the reference stage height (i.e., it is the stage at zero flow-datum correction).

To extrapolate the rating curve for high flows where no streamflow measurements were performed, we used the stage velocity-stage area method. Discharge was estimated as the product of cross-sectional area (A) and velocity (V_m). Both A and V_m are estimated as a function of stage height (H) (González, 2010). In the case of Cold Creek, the extrapolation was performed for a stage height above 0.15 m ($0.11 m^3/s$) and for Longer Creek the extrapolation was carried out for a stage height above 0.22 m ($0.40 m^3/s$). Streamflow contributions from the upstream gauged tributaries to the Lookout Creek at the gauging station were calculated based on the relative monthly average discharge from each tributary divided by the total discharge recorded at gauging station, expressed as following:

$$Q_{\text{Partial}} = \left(\frac{\sum_{i=1}^n Q_{\text{Tributary } i} + Q_{\text{Tributary } i+n}}{Q_{\text{Main stem}}} \right) * 100 \quad (13)$$

3. Results

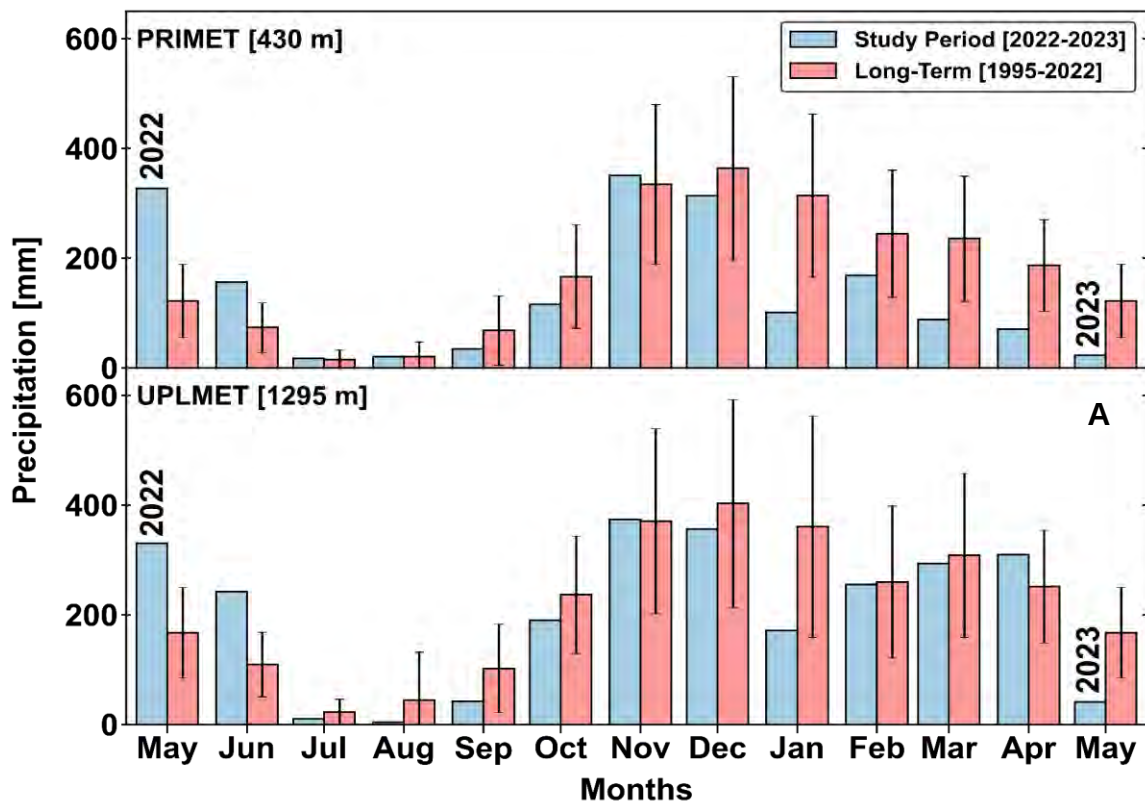
3.1 Precipitation-Streamflow Description

Between May 2022 and May 2023, the total annual precipitation at PRIMET (isotopic rain sampler) was lower than the long-term average data, receiving 1785 mm, compared to the average 2265 mm (1995–2022). Similarly, precipitation at UPLMET (highest elevation station) was slightly lower than the long-term average data, receiving 2619 mm, compared to the average 2802 mm (1995–2022). At the monthly basis, May and November 2022 had the highest monthly precipitations; conversely, May 2023 had 87% less precipitation compared to precipitation in May 2022 (Figure 4A). Annual streamflow in Lookout Creek between May 2022 and May 2023 was 3.12 m³/s and below the long-term (1950–2022) annual average (3.43 m³/s). May, June, July, August, and April were the months with a monthly average discharge above the long-term record (Figure 4B). Seasonally, spring (March-May) had over 25% more streamflow than long term values while winter (December-February) had 47% lower streamflow compared to the seasonal long-term average. Snowmelt processes occurring in high elevations during late spring triggered high flows in May and June. On the other hand, winter flow (Nov–Feb) was lower than the long-term averages. Snowpack (UPLMET) varied greatly in the last years (water year: 1996–2023) with SWE peaks that ranging from 240 mm (2005) to 1570 (2023) mm across a water years. In 2015, the HJ Andrews (No SWE recorded in the Met station, mechanical issues) and surrounding area experienced a severe snow drought (Segura et al., 2019), while in 2017 (1270 mm) and 2023 (1570) were above the median peak SWE (920 mm).

The average streamflow (Figure 5A) for the gauged catchments (CC, LC, MC, and LO5) varied between 0.08 and 3.18 m³/s with distinct monthly streamflow distribution. Cold Creek showed the highest discharge in May 2022 (0.18 m³/s) and the lowest in February 2023 (0.05 m³/s). In Longer Creek monthly streamflow was highest in May 2023 (0.23 m³/s) and lowest in October 2023 (0.09 m³/s); however, this stream was only monitored between October 2022 and May 2023. Mack Creek (MC) and Lookout Creek (LO5) displayed similar patterns with maximum monthly streamflow in May 2022 (0.96 m³/s in MC and 8.20 m³/s in LO5) and minimum streamflow in September 2022 (0.03 m³/s in MC and 0.32 m³/s in LO5).

Specific discharge (Figure 6A) was highest in Cold Creek with an annual mean specific discharge of 122 l/s/km². Mack, Longer, and Lookout at the gauging station had an annual mean

specific discharge between 50.59 and of 60.13 l/s/km². Cold Creek had the maximum total annual runoff of 4197 mm, most of it in May 2022 (680 mm). The total runoff was 2062 mm in Mack Creek, 1870 mm Longer Creek, and 1735 mm in Lookout at the gauging station. Furthermore, flow duration curves showed (Figure 5B) discharges at high extremes (equaled or exceeded for 1% of the time) ranged from 237 l/s (CC) to 18,077 l/s(LO5) and discharge under low flow conditions (equaled or exceeded for 99% of the time) ranged from 22 l/s (MC) to 269 l/s (LO5). Streamflow contribution from these tributaries (CC, MC, LC) to Lookout Creek at gauging station (LO5, Figure 1) ranged from 31% to 63% during periods of low flow (July-October) (Figure 6B). In contrast, throughout the remaining months (November-June), the proportional contribution dropped considerably, with the relative contribution not exceeding 22%, as observed in May 2023.



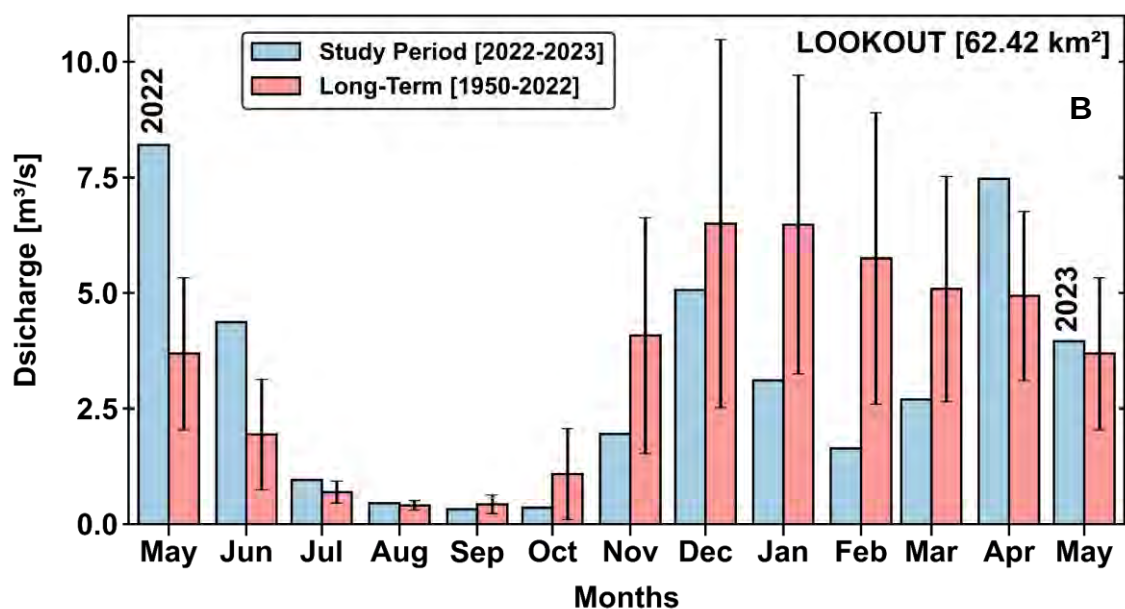
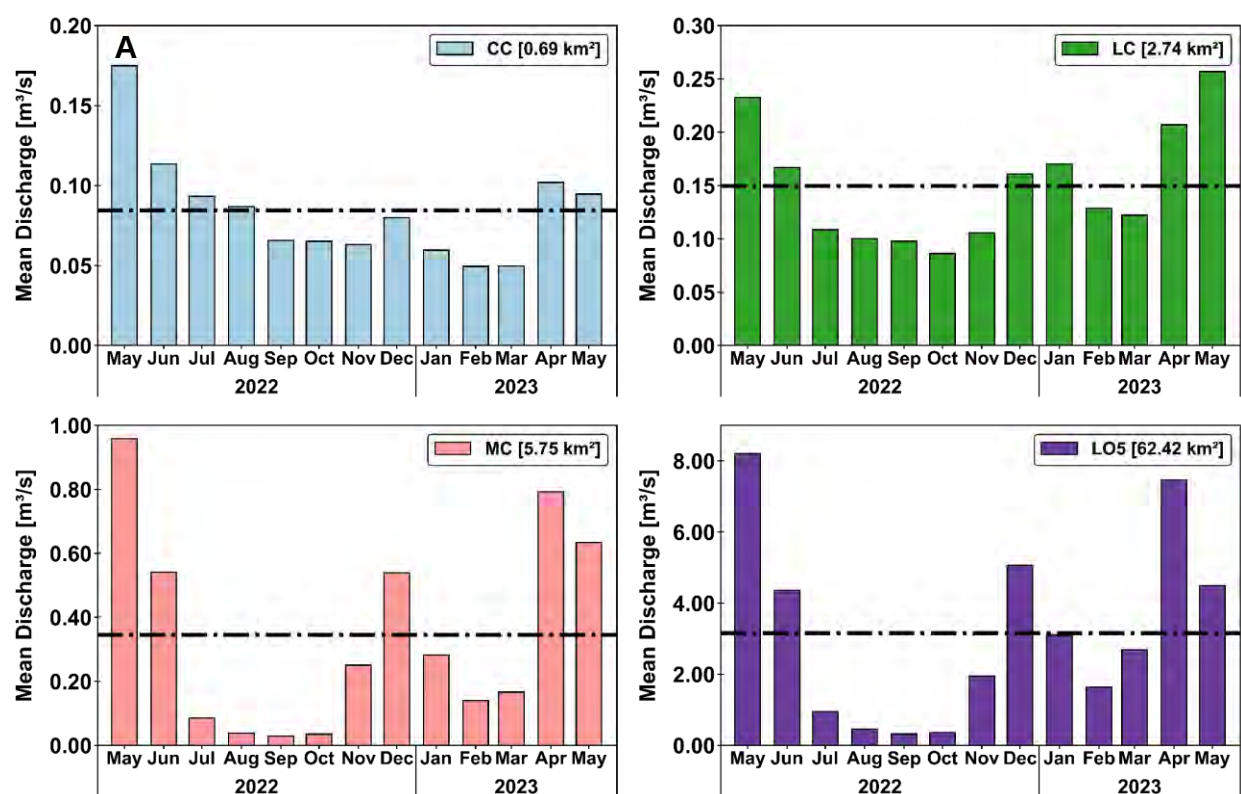


Figure 4. Monthly precipitation (A: PRIMET and UPLMET) and discharge (B: Lookout at the gauging station No. 14161500) distribution from the long-term data and study period. The error bars indicate the monthly standard deviation.



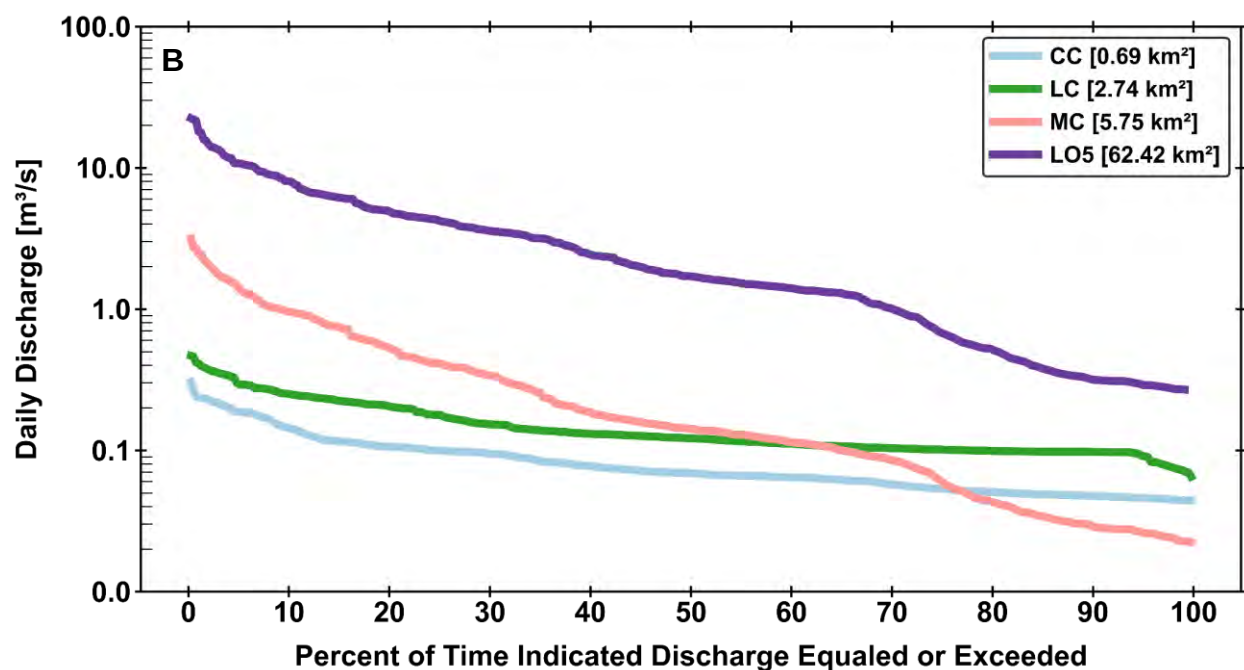
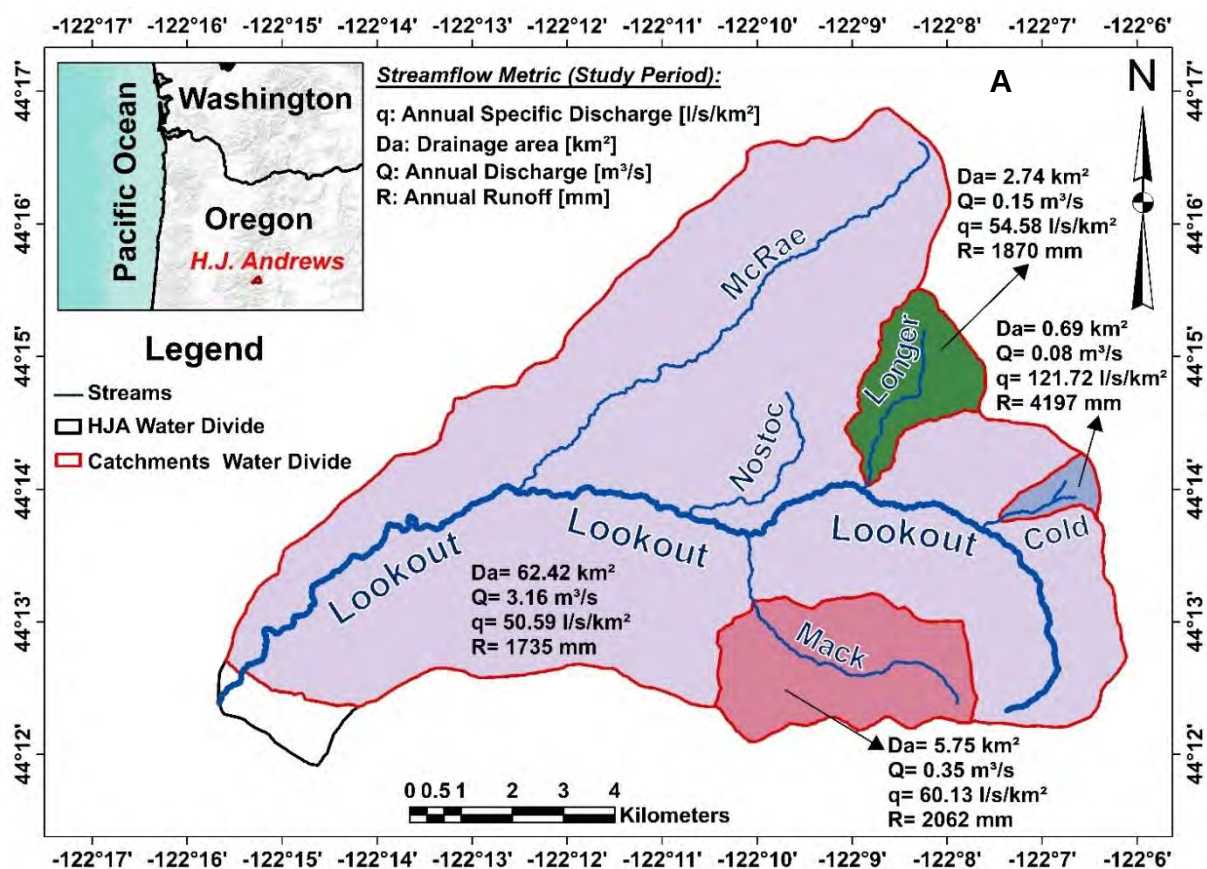


Figure 5. Streamflow distribution (A) and flow duration curve (B) by gauged catchment (Cold, Longer, Mack Creeks, and Lookout Creek at gauging station) during the study period (May 2022- May 2023).



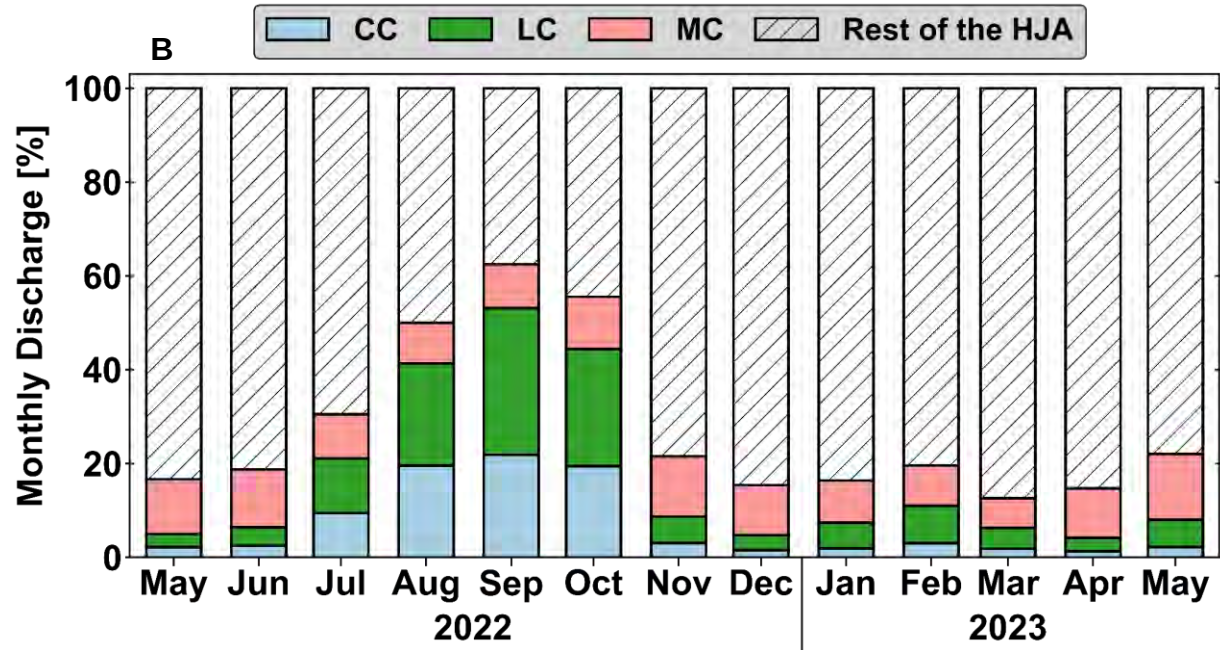


Figure 6. (A) Summary of streamflow metrics (annual discharge, specific discharge, and runoff) by catchments based on the study period. (B) Relative monthly streamflow contribution (%) from Cold (CC), Longer (LC), and Mack (MC) Creeks to the Lookout Creek at the gauging station (LO5).

3.2 Precipitation Isotopic Analysis

Precipitation water isotope ratios sampled weekly between 2015 and 2023 varied between -145.3 and -1.9‰ for $\delta^2\text{H}$, -19.3 and 3.7‰ for $\delta^{18}\text{O}$, and -31.4 and 20.8‰ for $d - \text{excess}$. The volume weighted average precipitation isotopic ratios (2015–2023) were $-71.8 \pm 20.5\text{‰}$ for $\overline{\delta^2\text{H}}$, $10.3 \pm 2.6\text{‰}$ for $\overline{\delta^{18}\text{O}}$, and $10.8 \pm 4.5\text{‰}$ for $\overline{d - \text{excess}}$ (Table 2). In 2017, the weighted average precipitation isotopic composition was the most depleted, while 2020 exhibited the highest enrichment across water years (Figure 7). The $d - \text{excess}$ values for each individual sample illustrated that 51% (161) of the total precipitation isotopic samples (317) were below 10‰ (Dansgaard, 1964), indicating evaporative influence during the precipitation process and different moisture sources. The 2015–2023 LMWL (Figure 8) had a similar slope ($7.8 \pm 0.1\text{‰}$) and intercept ($9.2 \pm 1.0\text{‰}$) to the GMWL ($\delta^2\text{H} = 8 * \delta^{18}\text{O} + 10$). The analysis of covariance (ANCOVA) revealed that the differences in slopes between the LMWL and GMWL exhibited no statistically significant differences ($p\text{-value} = 0.051$), indicating that the meteoric water lines can be considered parallel to each other.

This isotopic variability between depleted and enriched years was influenced by the seasonal snowfall, specifically a year characterized by significant amounts and prolonged seasonal snowfall results in a depleted precipitation isotopic composition. The 2023 water year, during which we collected the stream grab samples had a snow water equivalent above the median that resulted in a depleted isotopic signature compared to most years since 2015 (Table 2). Indeed, precipitation in 2023 was the second most depleted year in record (Figure 9A and 9B); however, the 2023 values are based on only a partial year, missing summer values which tend to be enriched relative to other seasons.

Seasonally, precipitation isotopic signature portrayed a typical change based on the local meteorological conditions and moisture (Figure 9C). Spring and winter precipitation isotopic values (green and blue dots) are the most depleted and given that many corresponded to high precipitation volumes (size of the marker), they strongly influenced the moving weighted average (black line). In contrast, fall and summer isotope values (brown and yellow dots) were the most enriched; however, many of these samples were low in volume (size of the marker), exerting relatively lower influence in the moving average compared to the winter samples. The seasonal LMWL regression coefficients varied (Table 3) from the general LMWL and GMWL, oscillating from $7.2 \pm 0.6\text{‰}$ (summer) to $8.0 \pm 0.1\text{‰}$ (winter) for slope and from $1.3 \pm 1.9\text{‰}$ to $12.3 \pm 1.4\text{‰}$ for intercept. Moreover, the variations in slopes observed among each seasonal LMWL and the GMWL showed no statistically significant differences ($p\text{-value} > 0.05$), as confirmed by an ANCOVA analysis (Table 3).

Certain precipitation events during spring and summer had low d-excess falling well below the LMWL, indicating evaporative enrichment of the precipitation (Figure 8). In winter and fall season, precipitation events had a higher d-excess values than the ones exhibited in spring and summer seasons. Additionally, the isotopic signature difference between winter and summer season of was $+3\text{‰}$ for $\overline{\delta^{18}\text{O}}$ and $+21\text{‰}$ for $\overline{\delta^2\text{H}}$. Seasonal d-excess samples revealed that spring ($n=75$) and summer ($n=25$) experienced the highest proportion of samples with d-excess $< 10\text{‰}$, reaching 83% and 79%, respectively. In contrast, fall ($n=24$) and winter ($n=37$) exhibited the lowest percentages, with 27% and 36% of total samples showing d-excess $< 10\text{‰}$.

These data collectively indicated that the precipitation isotopic signature is significantly conditioned by seasonality, highlighting the (1) strong influence of winter and fall season storm

events associated with depletion signatures, and (2) low d-excess precipitation events during spring and summer season related to enrichment signatures. Likewise, a typical water year dominated by rainfall or snowfall would consequently impact the resulting isotopic signature characterized by enrichment or depletion.

Table 2. Volume weighted average and standard deviation precipitation isotopic signature by water year.

Water Year	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	$\bar{d} \pm \sigma$	Min ($\delta^{18}\text{O}, \delta^2\text{H}, d$)	Max ($\delta^{18}\text{O}, \delta^2\text{H}, d$)	n
	‰	‰	‰	‰	‰	
2015	-9.5 ± 1.7	-66.7 ± 14.2	9.0 ± 3.7	-13.1, -98.9, -12.9	-2.8, -34.9, 5.8	32 (1)*
2016	-10.3 ± 2.8	-71.6 ± 22.9	10.7 ± 4.3	-19.3, -145.3, -16.7	-0.7, -22.3, 9.4	40
2017	-11.5 ± 2.6	-80.4 ± 22.3	11.2 ± 3.8	-17.0, -123.6, 0.2,	-2.5, -19.6, 12.8	38 (3)*
2018	-10.5 ± 2.4	-71.8 ± 19.5	11.9 ± 3.8	-16.8, -124.1, -31.4	3.7, -1.9, 10.2	39
2019	-10.6 ± 2.7	-74.6 ± 22.4	10.1 ± 5.7	-18.4, -137.9, -4.3	-3.2, -30.0, 9.2	33 (15)*
2020	-9.2 ± 2.8	-63.0 ± 20.3	10.3 ± 5.4	-15.2, -108.4, -25.0	-0.4, -27.8, 12.8	38 (1)*
2021	-10.0 ± 2.4	-69.0 ± 20.1	11.1 ± 3.9	-15.2, -111.6, 5.6	-3.5, -22.3, 10.2	36
2022	-10.4 ± 2.2	-71.9 ± 16.3	11.2 ± 4.8	-13.8, -98.3, -8.7	-2.6, -29.5, 12.1	39
2023	-10.7 ± 2.2	-74.0 ± 16.4	11.8 ± 3.8	-14.2, -102.8, -3.9	-5.5, -47.7, 11.0	22**
2015-2023	-10.3 ± 2.6	-71.8 ± 20.5	10.8 ± 4.5	-19.3, -145.3, -31.4	3.7, -1.9, 12.8	317

$\bar{d}$ is the d-excess weighted average; n is total number of samples.

* number in parenthesis is the number of samples estimated using isotopes values from a rain sampler located in Corvallis, OR, administered by the EPA.

** No completed water year (10/01/2022 – 05/23/2023).

Table 3. Summary of regression coefficients and p-values of the statistical comparison (ANCOVA) between the GMWL and seasonal Local Meteoric Water Line (LMWL).

Season*	$a \pm \sigma$	$b \pm \sigma$	R^2	p-value ($\delta^{18}\text{O}-\delta^2\text{H}$)	p-value (LMWL-GMWL)*
Fall	7.9 ± 0.1	12.3 ± 1.4	0.97	<0.001	0.174
Winter	8.0 ± 0.1	11.6 ± 1.7	0.97	<0.001	0.191
Spring	7.4 ± 0.2	1.3 ± 1.9	0.95	<0.001	0.168
Summer	7.2 ± 0.6	2.1 ± 5.0	0.85	<0.001	0.162
2015-2023	7.8 ± 0.1	9.2 ± 1.0	0.95	<0.001	0.051

Seasons were defined: spring (03/20-06/20), summer (06/21-09/22), fall (09/23-12/20), and winter (12/21-03/19). a is the slope, b is the intercept, and σ is the standard deviation.

* p-values obtained from ANCOVA analysis between the dependent variable ($\delta^{18}\text{O}$) and covariates ($\delta^2\text{H}$: fitted values of LMWL and GMWL).

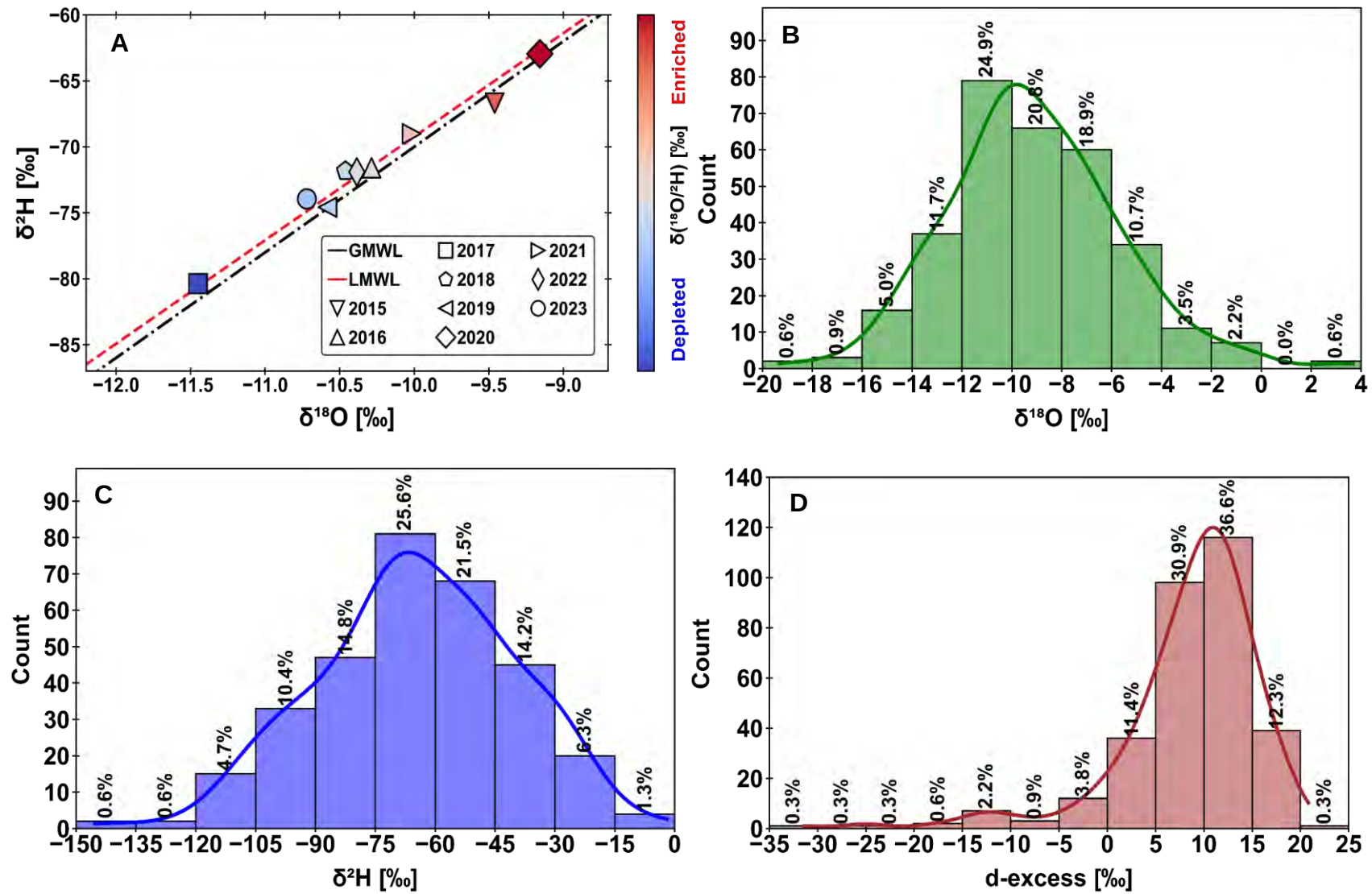


Figure 7. Dual annual volume weighted average precipitation isotopic signature (A), and frequency distribution histogram of $\delta^{18}\text{O}$ (B), $\delta^2\text{H}$ (C), and $d\text{-excess}$ (D).

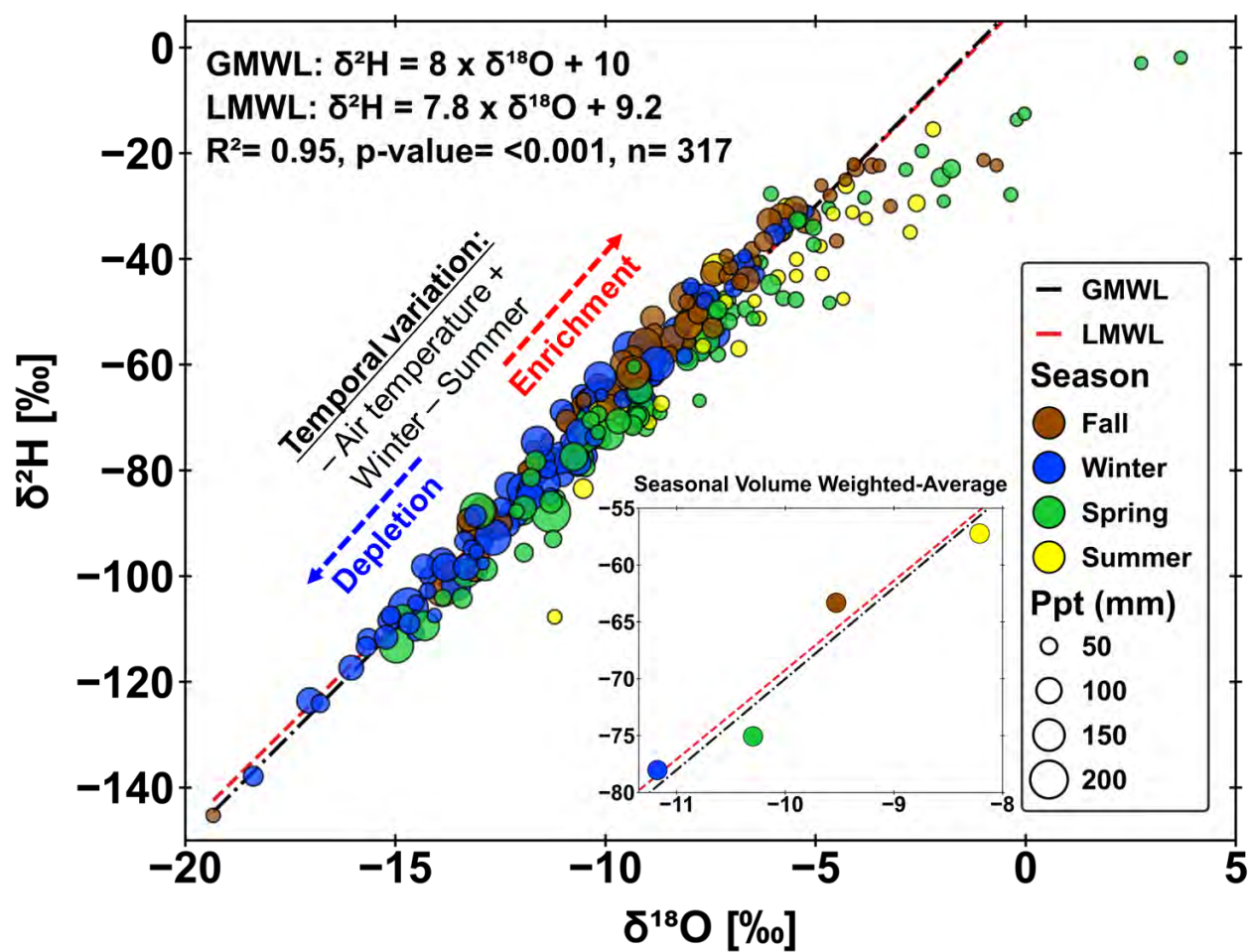


Figure 8. Relationship between the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the 317 weekly precipitation samples. All samples were included in the analysis. Red and black represent the Local Meteoric and Global Water Meteoric Water Line, respectively.

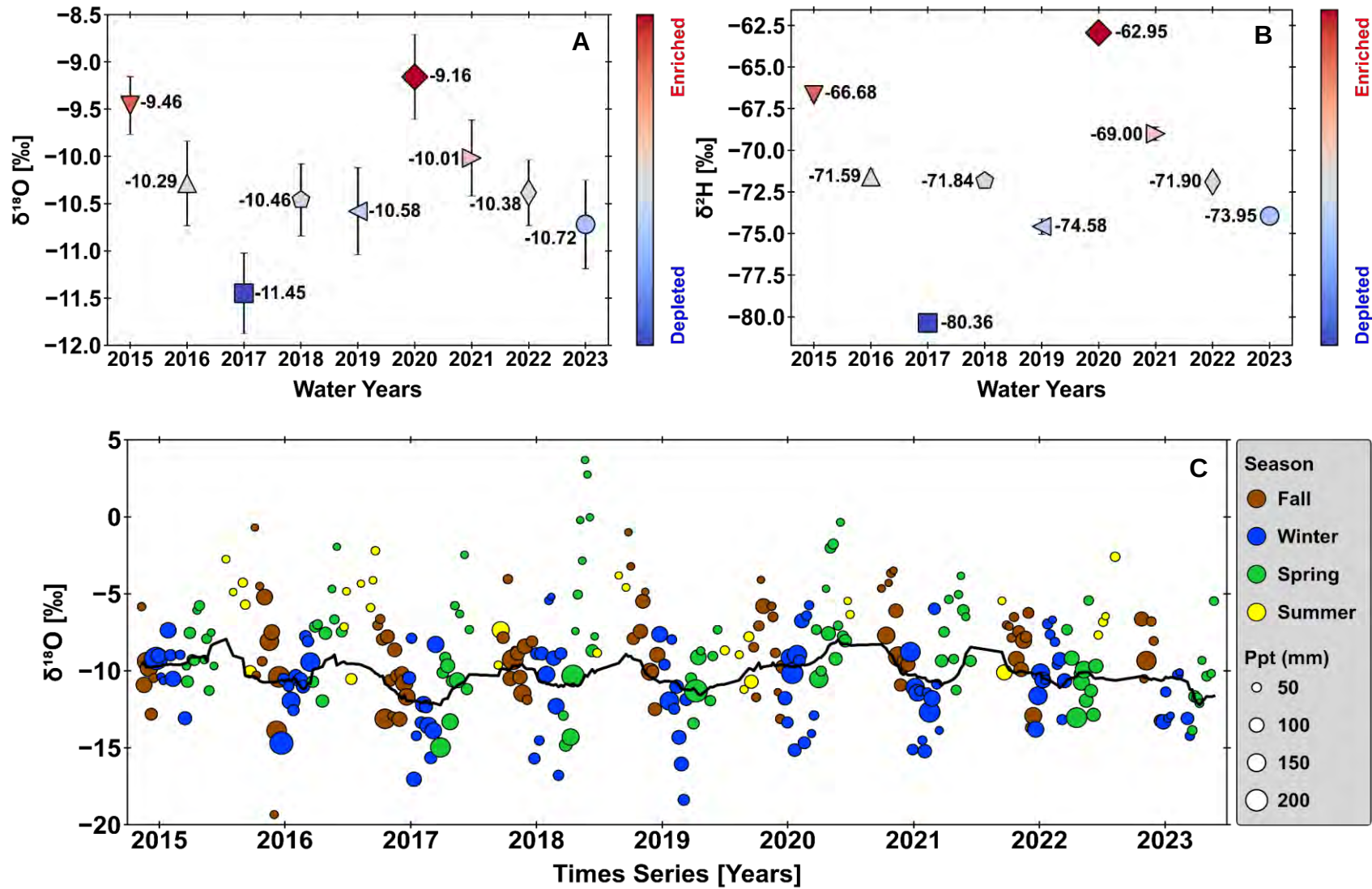


Figure 9. Annual volume weighted average precipitation isotopic composition by isotope (A: $\overline{\delta^{18}\text{O}}$ and B: $\overline{\delta^2\text{H}}$) with the standard error represented by errors bars. Precipitation isotopic signature (C: $\delta^{18}\text{O}$) throughout time (water years: 2015–2023). Black line is the volume weighted moving average with a window of 25 values.

3.3 Streamflow Isotopic Analysis

3.3.1 Temporal Analysis

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the grab tributary stream samples (CC, LC, MC, NC, and MR) varied from -80.7 to -67.3‰ for $\delta^2\text{H}$, from -11.8 to -10.0‰ for $\delta^{18}\text{O}$, and from 10.2 to 14.6‰ for d-excess. The mean values were $\overline{\delta^2\text{H}} = -74.2 \pm 2.3\text{‰}$, $\overline{\delta^{18}\text{O}} = -10.9 \pm 0.4\text{‰}$, and $\overline{d} = 13.0 \pm 0.6\text{‰}$. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the main Lookout stream (LO1–LO5), were in general more enriched than in the tributaries. $\delta^2\text{H}$ varied from -79.7 to -67.3‰, $\delta^{18}\text{O}$ varied from -11.7 to -10.0‰, and d-excess varied from 10.2 to 14.6‰. The mean values were $\overline{\delta^2\text{H}} = -74.5 \pm 2.4\text{‰}$, $\overline{\delta^{18}\text{O}} = -10.9 \pm 0.3\text{‰}$, and $\overline{d} = -13.1 \pm 0.6\text{‰}$ (Table 4). Cold Creek (CC), the most upstream catchment, had the most depleted isotopic values throughout the study period. Conversely, Longer (LC) and Nostoc (NC) Creeks, had more enriched isotopic values than Cold Creek. Stream grab samples in the main stem sampling sites showed that the second most upstream catchment, Upper Lookout Creek-2 (LO2), had the most depleted isotopic signature across time, specifically during July–October. The most downstream catchment, Lookout Creek at the gauging station (LO5), showed similar depletion trends during July–October, probably conditioned from the mixing or streamflow contributions coming from the headwaters (Figure 10B).

3.3.1 Spatial Analysis

Stream isotopic values considerable varied indicating heterogeneity across catchments (Figure 11A and 11B). Cold Creek had the most depleted average isotopic signature ($\overline{\delta^{18}\text{O}} = -11.4\text{‰}$; $\overline{\delta^2\text{H}} = -78.2\text{‰}$). In contrast, Nostoc Creek had the most enriched average isotopic signature ($\overline{\delta^{18}\text{O}} = -10.6\text{‰}$; $\overline{\delta^2\text{H}} = -72.6\text{‰}$). In the main stem, Upper Lookout-2 (LO2) had the most depleted average isotopic signature ($\overline{\delta^{18}\text{O}} = -11.2\text{‰}$; $\overline{\delta^2\text{H}} = -76.3\text{‰}$) and Lookout Creek at the gauging station (LO5) had the most enriched average signature ($\overline{\delta^{18}\text{O}} = -10.8\text{‰}$; $\overline{\delta^2\text{H}} = -73.3\text{‰}$) (Table 4). Not surprisingly elevation is inversely related to mean isotope ratios. The catchment with the lowest mean elevation (NC) had on average more enriched isotope values and the highest elevation catchment (CC). Despite this general trend some sites displayed different median isotope values than those expected solely based on elevation. For example, even though the mean catchment elevations of LO1 and LO2 is very similar, the mean isotope values in LO1 are markedly more enriched than the mean isotope values in LO2 (Figure 12).

The relationships between mean catchment elevation and stream isotope ratios ($\delta^2\text{H}$, $\delta^{18}\text{O}$, and d-excess) were moderate strong. R-squared (R^2) varied between 0.59 and 0.68 (p-values 0.003–0.010). Seasonally, these relationships were also strong (Table 7). The isotopic lapse rates for the study period isotopic were $-0.16\text{‰}/100\text{ m}$ for $\delta^{18}\text{O}$, $-1.08\text{‰}/100\text{ m}$ for $\delta^2\text{H}$, and $0.18\text{‰}/100\text{ m}$ for d – excess. Seasonal isotopic lapse rates had similar pattern as those including the complete study period (Table 7).

3.3.2 Water Stable Isotope Relationship (Dual isotopes)

All stream average isotopic signatures plotted to the left (above) of the GMWL and LMWL (PRIMET), indicating no evaporative influence (d-excess $>10\text{‰}$) (Figure 11A). This is also reflected in the high stream average d-excess values across all catchments (d-excess $>12\text{‰}$), which is higher than the weighted-average precipitation (2015–2023) d-excess ($10.8 \pm 4.5\text{‰}$); however, we found seasonal differences. Stream ($12.1\text{--}13.8\text{‰}$) and precipitation d-excess signatures were similar for fall ($11.4 \pm 3.5\text{‰}$, p-value= 0.05) and winter ($12.9 \pm 3.0\text{‰}$, p-value= <0.01). Conversely, precipitation d-excess values for spring ($7.3 \pm 4.7\text{‰}$, p-value= <0.01) and summer ($8.5 \pm 7.6\text{‰}$, p-value= <0.01) differed from the corresponding stream values ($12.0\text{--}13.7\text{‰}$) (Figure 10A).

The average isotopic signature of each catchment varied seasonally (Figure 13). Tributaries catchments had a more stable isotopic signature over time. Cold Creek (CC) was the catchment with the most depleted isotopic values throughout the study period. Mack (MC), Nostoc (NC) and McRae (MR) Creeks were the most enriched catchments in the four seasons with most of their isotopic values oriented towards enrichment. Furthermore, Longer Creek (LC) was the catchment with less isotopic variability from the all-sampling catchments over time. The main Lookout stem catchments exhibited a higher isotopic variation than the tributary catchments over time. As such, Upper Lookout-2 Creek (LO2) had the most depleted isotopic signature in this group, pointing out the summer and early fall season, as representative of this pattern. The remaining main stem catchments (LO1, LO3, LO4, and LO5) displayed isotopic values that ranged from depletion to enrichment (Figure 14).

3.3.3 End-Member Mixing Analysis (Isotopic Hydrograph Separation)

End-member mixing analysis based on $\overline{\delta^{18}\text{O}}$ and $\overline{\delta^2\text{H}}$, was used to estimate the streamflow contribution of Cold (CC, 0.69 km^2), Longer (LC, 2.74 km^2), and Nostoc (NC, 1.96 km^2) Creeks

to Lookout Creek. For Cold Creek, we considered Upper Lookout-1 (LO1, 5.53 km²) and CC as the two end-members, and Upper Lookout-2 (LO2, 6.32 km²) as the outlet (mixture of LO1 and CC). The relative streamflow contribution of Cold Creek to LO2 during baseflow conditions (June–September) ranged from 70 to 90% with a monthly isotopic signature of LO2 (mixing model) oriented towards CC, indicating those contributions (Figure 15A). In contrast, the streamflow contribution from LO1 to LO2 in May, June, January, and February varied from 65 to 100% (Figure 15A). For Longer Creek, we considered LO2 as an end-member with LC, and Upper Lookout-3 Creek (LO3, 15.63 km²) as the outlet. The only month that Longer Creek contributed more than LO2 was October with 84% as illustrated by an isotopic signature at the outlet (LO3) aligned in direction of LC. In November, January, and February, LO2 was responsible for contributing over 70% of the water downstream the main stem (LO3, Figure 15B). Lastly, for Nostoc Creek, we used LO3 as an end-member with NC, and Upper Lookout-4 Creek (LO4, 30.67 km²) as the outlet. Nostoc Creek never contributed more than LO3 with an average contribution of 32%. On the other hand, the streamflow contribution of LO3 was above 62% in those months and the average monthly isotopic signature of the outlet (LO4) was conditioned by the coming isotopic signature of LO3 in the four months of analysis (Figure 15C). However, in the groups of Longer and Nostoc Creeks, samples were only collected between October 2022 and February 2023—no samples collected in spring or summer.

Considering drainage area, Cold (CC, 0.69 km²) and Longer (LC, 2.74 km²) Creeks supplied more water per unit area than the other end-members (Upper Lookout Creeks, 5.53 and 6.32 km²) during low flow conditions. In August and September, Cold Creek (CC) delivered 37 and 70 times more water than LO1 per unit area. On the other hand, Longer Creek (LC) supplied 12 times more water than LO2 in October (LO2 is an end-member for Longer Creek).

Monthly discharge was estimated based on the streamflow contribution, partitioning between end-members and outlet, specifically for the first group. During low flow conditions, Cold Creek contributed from 65.6 to 93.6 l/s to LO2. In contrast, LO1 supplied 14.16 to 40.33 l/s to LO2. However, LO1 contributed more than 6000 l/s during January, while CC only contributed less than 10 l/s. Discharge was not estimated for Longer and Nostoc Creeks because the sampled sites above and below the confluence with the Upper Lookout Creeks (LO2, LO3, LO4) were far (up-downstream distance) to capture the isotopic composting coming from these two tributaries.

The collected time series of water isotopes allowed to estimate the relative contribution of event and pre-event water for a storm in November 2022, which was the first large precipitation event after the long dry summer. The event occurred between 01-Nov-2022 and 06-Nov-2022 and recorded a rainfall of 170 mm in PRIMET. The time series indicated that for most catchments the stream isotopic values became more enriched (closer in magnitude to the incoming precipitation) during the mentioned storm (Figure 16A). The volume weighted incoming precipitation-event water was $\overline{\delta^{18}\text{O}} = -9.4\text{‰}$ and $\overline{\delta^2\text{H}} = -61.8\text{‰}$. End-member mixing analysis indicated that the event water contribution was between 44–52% for Cold, Mack, and Nostoc Creeks, and 35–45% for all Lookout Creek sites (LO1–LO5). In contrast, the event water contribution was only 17% for Longer Creek (i.e., 83% of the water corresponded to pre-event water) (Table 5). Hydrograph storm across the four gauged catchments (CC, LC, MC, and LO5) indicated that peak streamflow occurred on 11/04 (CC and LC) and 11/05 (MC and LO5). Maximum discharges were recorded at 0.49 m³/s (CC), 0.20 m³/s (LC), 6.28 m³/s (MC), and 30.58 m³/s (LO5). Notably, the catchment experiencing the highest increase in streamflow proportion between the peak rainfall and discharge was MC (136), followed by LO5 (58), CC (7), and the lowest proportion observed in LC (3).

3.3.4 Water Age Computations

The damping ratios for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were strongly correlated (Figure 16B). In terms of $\delta^{18}\text{O}$, damping ratios varied between 0.03 (LC) and 0.10 (LO1), where lower values indicate more damping of isotope values for the stream relative to the precipitation input. Across tributaries, the average damping ratio was 0.05 (MC and MR had the highest with 0.07 and LC had the lowest with 0.03). Across the main stem catchments, the average damping ratio was higher (0.09) than at the tributaries (LO1 had the highest with 0.10 and LO5 had the lowest with 0.07). These results implied that the water flowing in the main stem are more temporally variable than the water draining out of the tributary catchments (Table 6), which traditionally would be interpreted as younger water, but as illustrated with the end-member mixing is largely the result of increased isotopic variance due to changing tributary contributions. Moreover, the average isotopic values in certain catchments (CC, LC, and LO1–LO4) were more depleted than the isotopic values of the annual weighted-average precipitation for the water year 2023. On the contrary, catchments like

MC, NC, MR, and LO5 exhibited average stream isotope values that were either lower or comparable to the annual weighted precipitation.

These data and metrics together illustrated spatial and temporal variations in the stream isotopic signatures across all catchments. Cold Creek (CC), a spring-fed stream, showed the most depleted isotopic signature among all catchments throughout the study period. In contrast, Nostoc Creek (NC), situated at a lower elevation than Cold Creek, exhibited the most enriched isotopic signature over both space and time. Longitudinally, from headwaters to the outlet, most of the main stem catchments (LO1–LO5) displayed a depletion-enrichment isotopic pattern. Additionally, average stream isotopic signatures ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were inversely related to mean catchment elevation. Based on a dual isotopic plot and seasonal LMWL, the stream isotopic signature was mainly influenced by fall and winter seasonal storm events, coinciding with the highest weighted-average precipitation d-excess associated to these seasons. Based on an isotopic hydrograph separation (IHS), Cold and Longer Creeks supplied more water per unit area than other end-members, particularly in during low flow conditions.

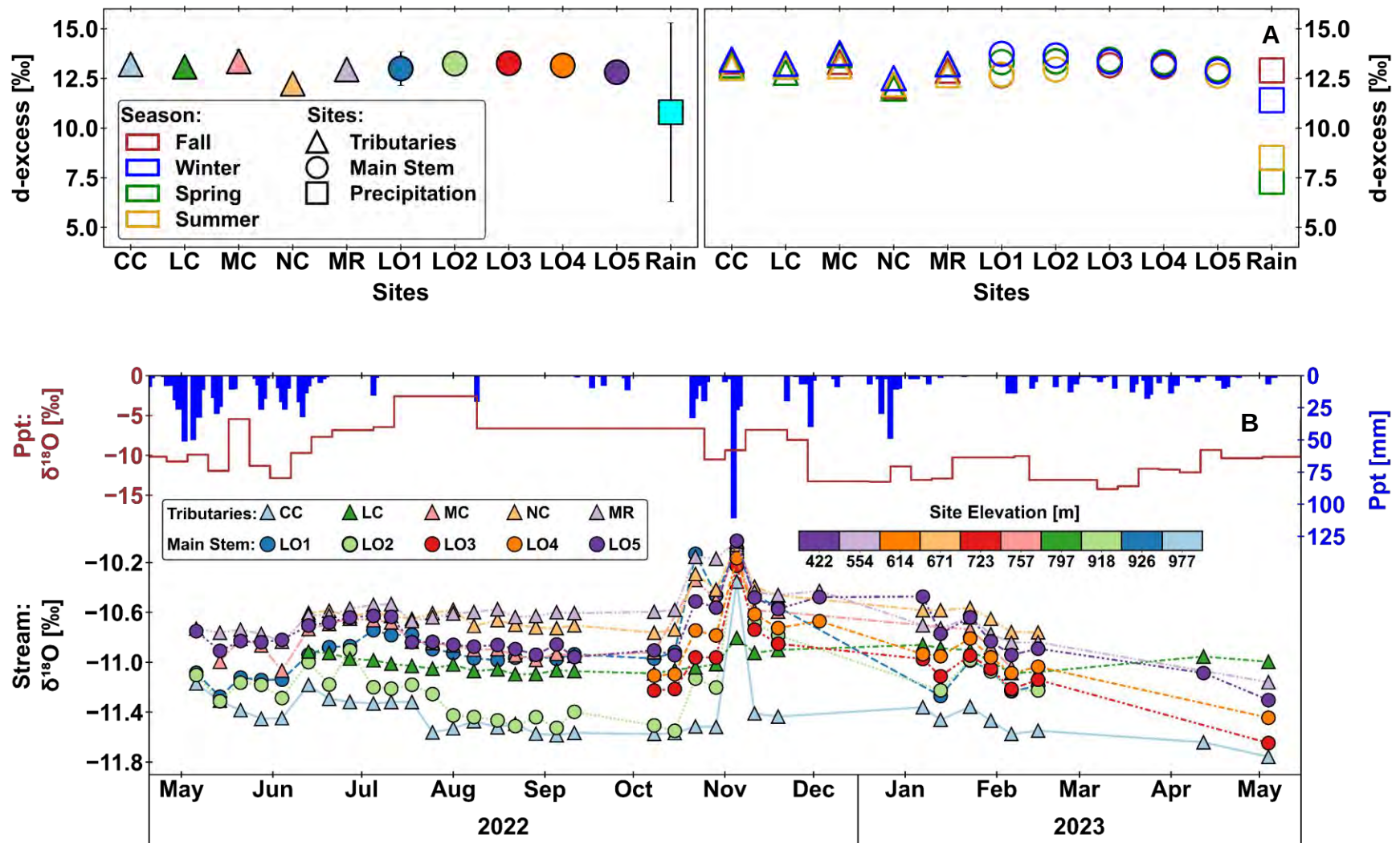


Figure 10. Average and weighted-average d-excess across all catchments and PRIMET (Rain, A); filled and unfilled dots represent study period average and seasonal averages, and error bars mean standard deviation. Stream isotopic signature (B) throughout time (May 2022 – May 2023). Precipitation isotopic signature (brown line) and daily precipitation (blue bars) corresponds to PRIMET.

Table 4. Summary of arithmetic mean isotope ratios ($\overline{\delta^{18}\text{O}}$, $\overline{\delta^2\text{H}}$), deuterium excess ($\bar{d}$), and standard deviation (σ) from grab stream samples collected between May 2022 and May 2023.

	Site	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	$\bar{d} \pm \sigma$	Min ($\delta^{18}\text{O}$, $\delta^2\text{H}$, d)	Max ($\delta^{18}\text{O}$, $\delta^2\text{H}$, d)	n*
		‰	‰	‰	‰	‰	
Tributaries	CC	-11.4 ± 0.2	-78.2 ± 1.7	13.2 ± 0.5	-11.8, -80.7, 12	-10.4, -69.6, 13.9	34
	LC	-11.0 ± 0.1	-74.9 ± 0.6	13.1 ± 0.2	-11.1, -75.4, 12.6	-10.8, -73.2, 13.4	29
	MC	-10.7 ± 0.2	-72.9 ± 1.6	13.4 ± 0.6	-11.1, -74.2, 12.2	-10.1, -67.5, 14.5	27
	NC	-10.6 ± 0.2	-72.6 ± 1.2	12.2 ± 0.3	-10.8, -73.8, 11.4	-10.1, -68.2, 12.7	27
	MR	-10.6 ± 0.2	-72.0 ± 1.5	13.0 ± 0.5	-11.2, -75.9, 12.0	-10.0, -67.3, 14.2	34
	Average [Max, Min]	-10.9 ± 0.4	-74.2 ± 2.3	13.0 ± 0.6	[-11.8, -80.7, 11.4]	[-10.0, -67.3, 14.5]	151
Main Stem	LO1	-10.9 ± 0.3	-74.2 ± 2.0	13.0 ± 0.9	-11.3, -77.2, 10.2	-10.1, -67.5, 14.3	31
	LO2	-11.2 ± 0.3	-76.3 ± 2.4	13.2 ± 0.6	-11.6, -79.0, 11.9	-10.1, -67.7, 14.6	31
	LO3	-11.0 ± 0.3	-74.9 ± 2.5	13.3 ± 0.10	-11.7, -79.7, 12.7	-10.2, -68.3, 13.5	14
	LO4	-10.9 ± 0.3	-73.9 ± 2.3	13.2 ± 0.2	-11.4, -78.2, 12.6	-10.2, -68.1, 13.4	15
	LO5	-10.8 ± 0.2	-73.3 ± 1.7	12.8 ± 0.5	-11.3, -77.0, 11.6	-10.0, -67.3, 14.0	35
	Average [Max, Min]	-11.0 ± 0.3	-74.5 ± 2.4	13.1 ± 0.6	[-11.7, -79.7, 10.2]	[-10.0, -67.3, 14.6]	126

$\bar{d}$ is the d-excess average.

* They represent the total number of samples.

Table 5. Hydrograph separation in the event and pre-event water for a fall storm event between 11/01/2023 and 11/06/2023.

	Site	Stream: $\delta^{18}\text{O}_{\text{pe}}$ *	Stream: $\delta^{18}\text{O}_{\text{e}}$ **	Ppt: $\delta^{18}\text{O}_{\text{pe}}$ ***	Q_{pe}	Q_{e}
		‰	‰	‰	%	%
Tributaries	CC	-11.6	-10.4	-9.4	44	56
	LC	-11.1	-10.8	-9.4	83	17
	MC	-10.9	-10.1	-9.4	47	53
	NC	-10.8	-10.1	-9.4	48	52
	MR	-10.6	-10.0	-9.4	52	48
Main Stem	LO1	-11.0	-10.1	-9.4	43	57
	LO2	-11.5	-10.1	-9.4	35	65
	LO3	-11.2	-10.2	-9.4	45	55
	LO4	-11.1	-10.2	-9.4	44	56
	LO5	-10.9	-10.0	-9.4	41	59

Event water isotopic signature was assumed as precipitation at PRIMET.

Q_{pe} is the streamflow contribution by baseflow and Q_{e} is the streamflow contribution by storm event.

* Stream isotopic composition of the pre-event ($\delta^{18}\text{O}_{\text{pe}}$) corresponds to 10/08/2022.

** Stream isotopic composition of the storm event ($\delta^{18}\text{O}_{\text{e}}$) corresponds to 11/05/2022.

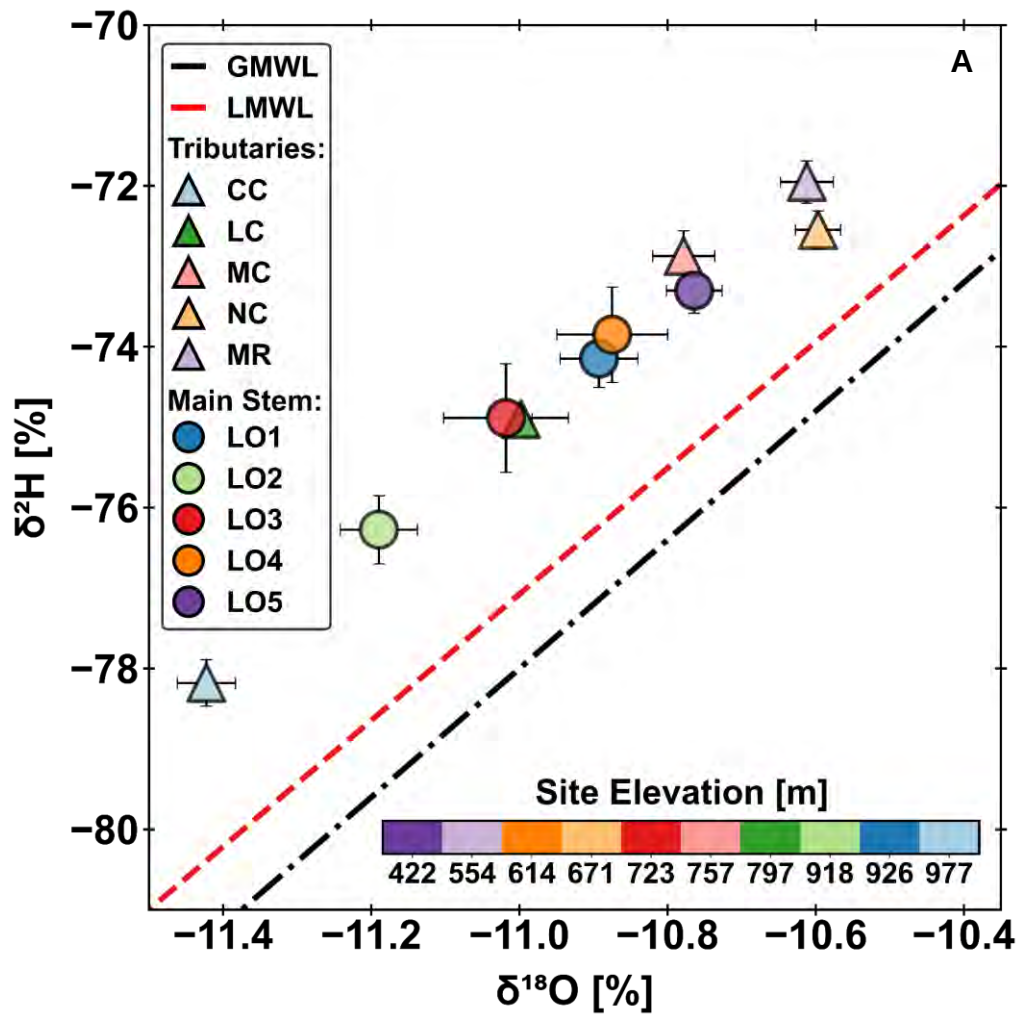
*** Weighted precipitation isotopic composition refers to isotopic samples between 10/26/2022 and 11/02/2022.

Table 6. Damping ratio values based on the study period for the 10 analyzed catchments.

	Site*	SD_δ ¹⁸ O	SD_δ ² H	DR_δ ¹⁸ O	DR_δ ² H
		‰	‰	-	-
Tributaries	CC	0.13	0.76	0.05	0.04
	LC	0.07	0.51	0.03	0.03
	MC	0.18	1.25	0.07	0.07
	NC	0.12	0.89	0.05	0.05
	MR	0.18	1.30	0.07	0.07
Main Stem	LO1	0.25	1.57	0.10	0.08
	LO2	0.22	1.77	0.09	0.09
	LO3	0.23	1.73	0.09	0.09
	LO4	0.22	1.70	0.09	0.09
	LO5	0.18	1.31	0.07	0.07

Precipitation weighted standard deviation was δ¹⁸O: 2.48‰ and δ²H: 18.65‰

* Stream isotopic signature of 11/05/2022 was not included in the calculation due to a storm event occurred in the previous days at the collection date.



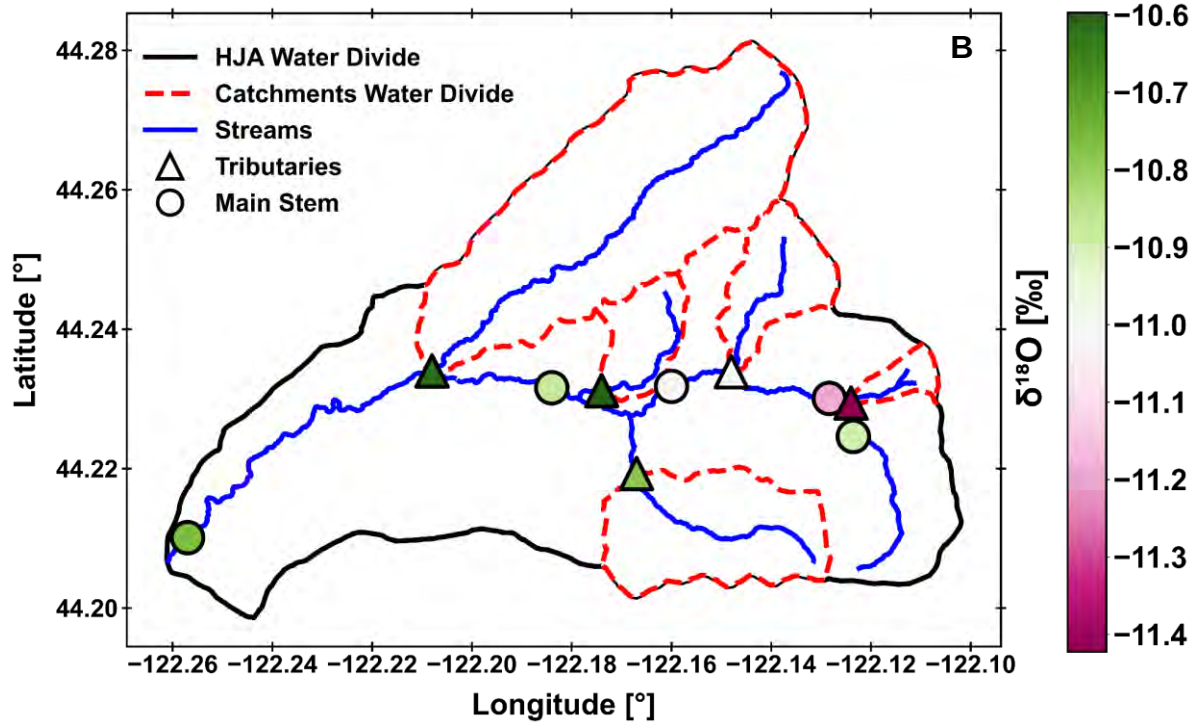


Figure 11. (A) Dual stream average isotopic signature ($\overline{\delta^{18}\text{O}}$ and $\overline{\delta^2\text{H}}$) relationship across all study catchments. Black and red line represents GMWL and LMWL. Error bars are the standard error. (B) Spatial distribution of the average stream isotopic signature ($\overline{\delta^{18}\text{O}}$) over the study period. Red and black water divide represent headwater streams and HJ Andrews Forest Boundary.

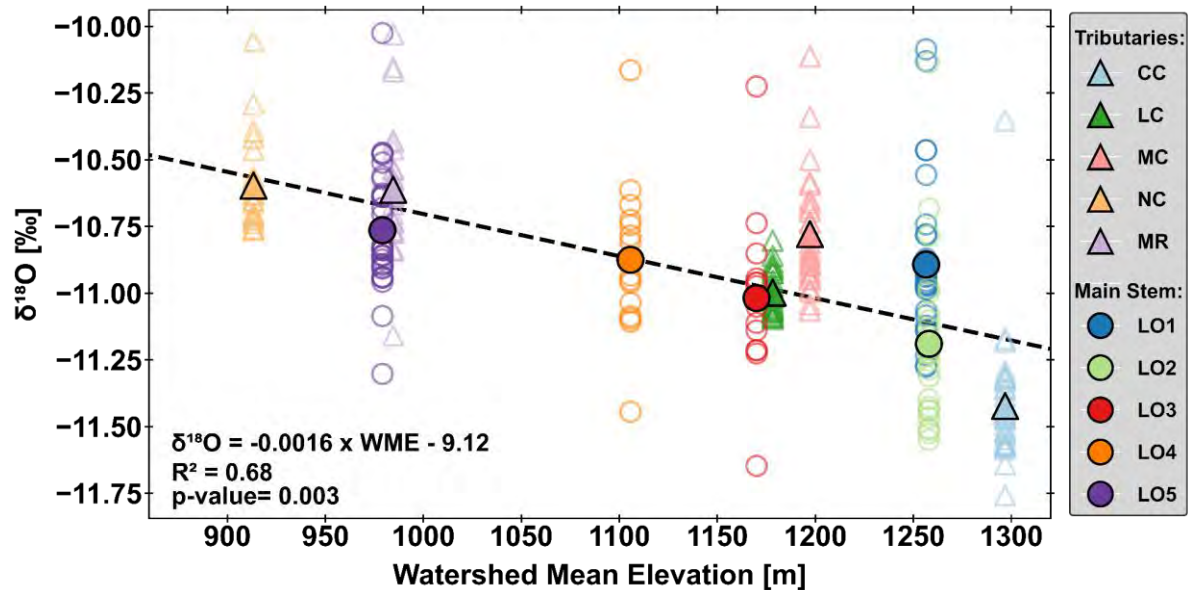


Figure 12. Relationship between mean catchment elevation and stream average isotopic signature ($\delta^{18}\text{O}$) by study catchment. Filled and unfilled markers represent the average and individual sample values. Linear regression line (dashed black line) was estimated using the average isotopic signature of each sampled site.

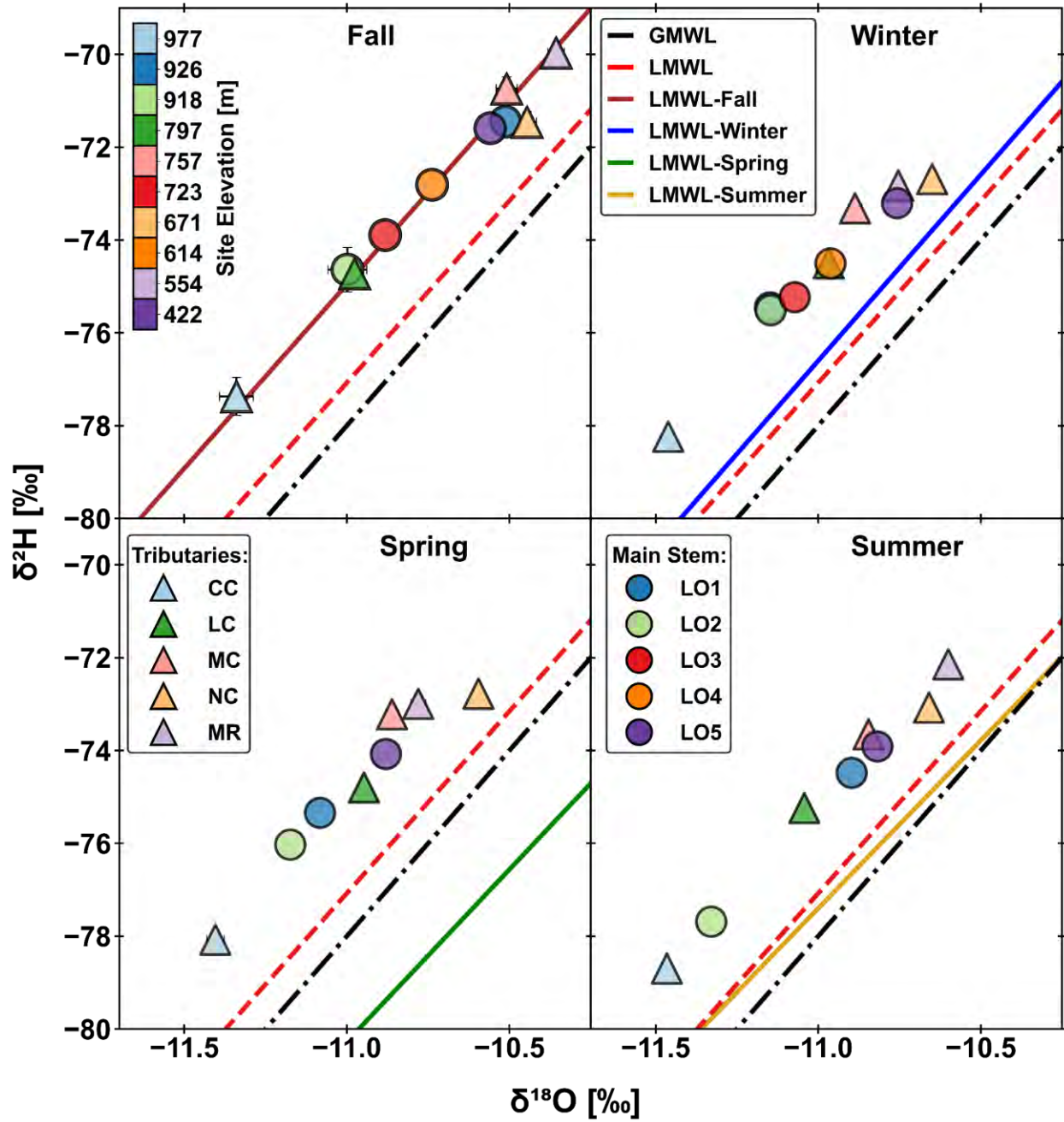


Figure 13. Dual seasonal average stream isotopic signature ($\overline{\delta^{18}O}$ and $\overline{\delta^2H}$) relationship across all study catchments. Black and red line represents GMWL and LMWL. Error bars portrayed standard error.

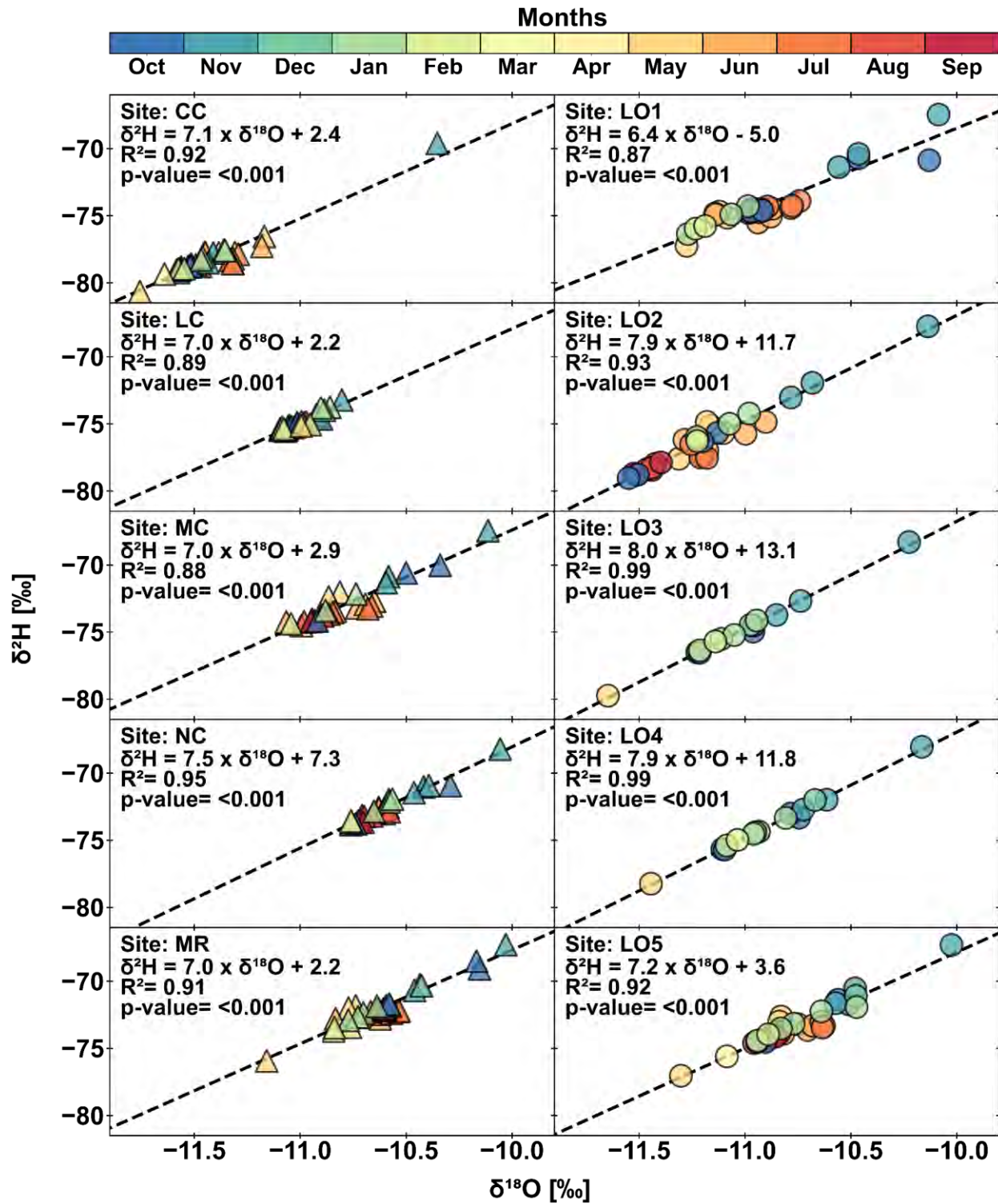


Figure 14. Dual individual stream isotopic signature ($\delta^{18}O$ and δ^2H) relationship by study catchments. Linear regression line (dashed black line) was estimated using the isotopic signature of each sampled site. Left and right column represent tributaries and main stem catchment, respectively.

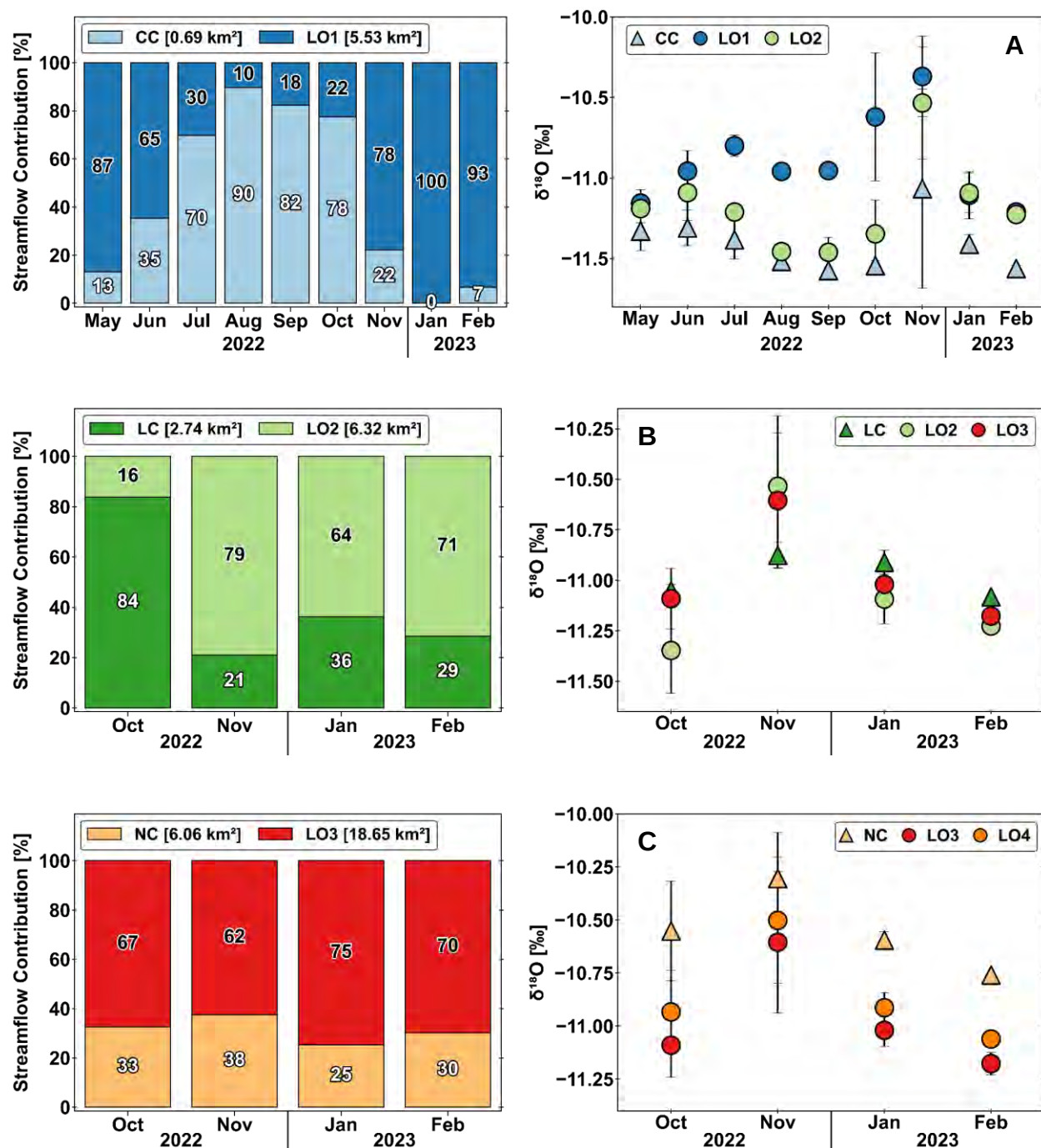


Figure 15. Streamflow contribution to Lookout Creek from A: Cold Creek (CC) considering LO1 and LO2; B: Long Creek (LC) considering LO2, LO3, and C: Nostoc Creek (NC) considering LO3, LO4. Bar plots represent the monthly streamflow contribution (%) and scatter plots represent stream average isotopic signature (‰) with error bars representing standard deviation.

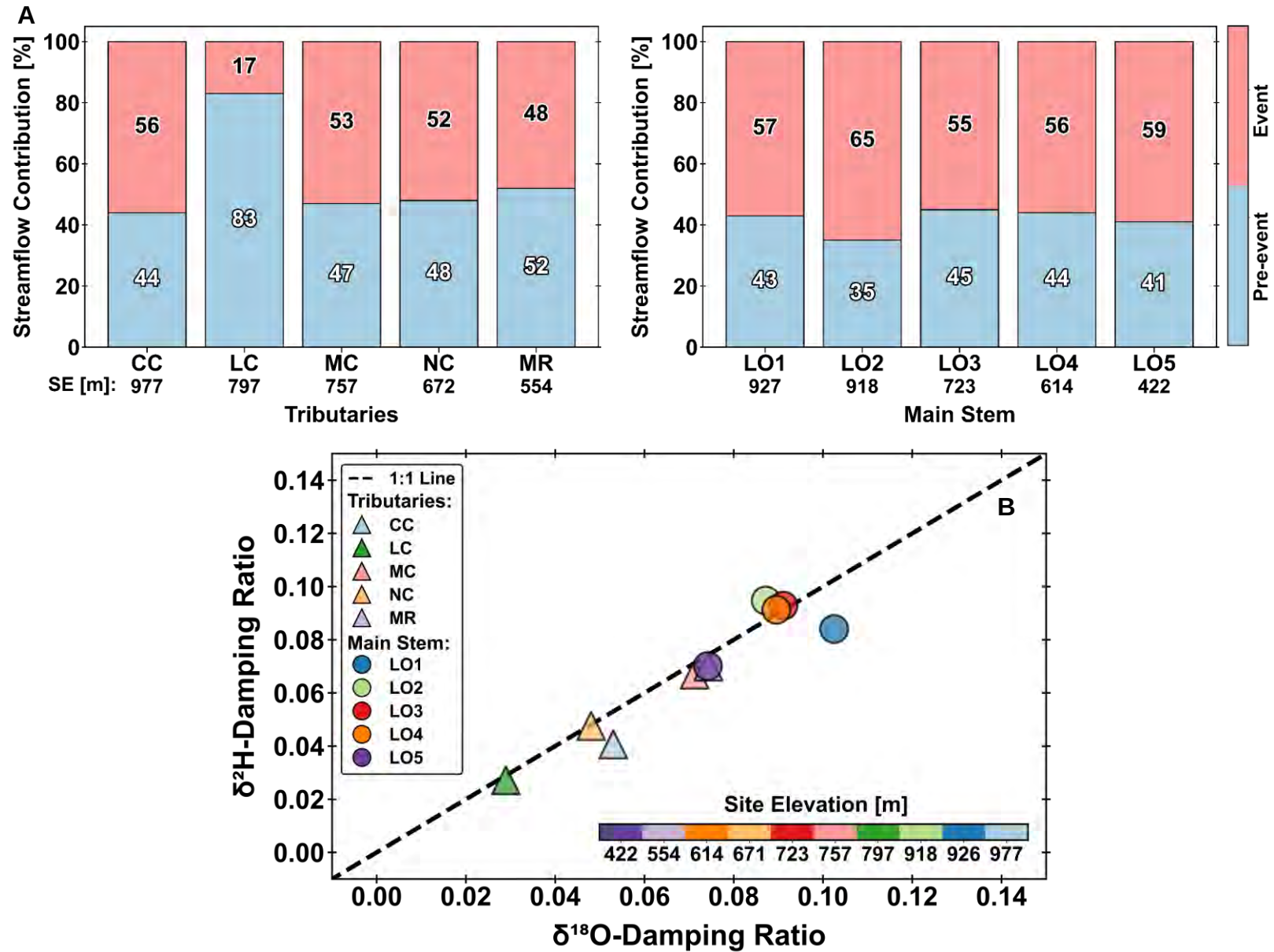


Figure 16. Hydrograph separation from the storm event in November 2023 (A) and damping ratio by analyzed catchment for the study period (B). Ratios were compared relative to the 1:1 line (solid black diagonal line).

Table 7. Seasonal isotopic lapse rate by isotopic signature.

Isotope	Reg. Coeff.	Study Period	Fall	Winter	Spring	Summer
$\delta^{18}\text{O}$	$a \pm \sigma$	-0.0016 ± 0.0012	-0.0016 ± 0.0019	-0.0016 ± 0.0009	-0.0014 ± 0.0010	-0.0016 ± 0.0014
	$b \pm \sigma$	-9.12 ± 1.38	-8.94 ± 2.19	-9.15 ± 10.00	-9.34 ± 1.12	-9.10 ± 1.60
	R^2	0.68	0.46	0.81	0.74	0.65
	p-value	0.003	0.032	0.000	0.006	0.016
$\delta^2\text{H}$	$a \pm \sigma$	-0.0108 ± 0.0101	-0.0107 ± 0.0149	-0.0103 ± 0.0081	-0.0094 ± 0.0087	-0.0115 ± 0.0113
	$b \pm \sigma$	-62.10 ± 11.50	-60.76 ± 16.95	-62.83 ± 9.30	-64.05 ± 9.90	-61.83 ± 12.87
	R^2	0.59	0.39	0.67	0.61	0.58
	p-value	0.010	0.053	0.004	0.022	0.028
d – excess	$a \pm \sigma$	0.0018 ± 0.0017	0.002 ± 0.0024	0.0026 ± 0.0017	0.0021 ± 0.0031	0.0016 ± 0.0015
	$b \pm \sigma$	10.89 ± 1.97	10.47 ± 2.68	10.37 ± 1.90	10.65 ± 3.49	10.96 ± 1.71
	R^2	0.60	0.47	0.75	0.39	0.61
	p-value	0.009	0.028	0.001	0.096	0.023

Seasons were defined: spring (03/20-06/20), summer (06/21-09/22), Fall (09/23-12/20), and winter (12/21-03/19).

a is the slope, b is the intercept, and σ is the standard deviation.

4. Discussion

4.1 Inter-Annual and Seasonal Variations in the Precipitation Isotopic Signature

Precipitation isotopic signatures at PRIMET (430 m) between 2015 and 2023 were influenced by seasonal snowfall, and spring and summer storm events (Figure 9C). Year-to-year analyses (Figure 8A) highlighted that the isotopic composition can be used as a proxy to preliminarily identify a drought (enriched) from a wet (depleted) water year, considering a water year with a snow water equivalent above the long-term median. A water year such as 2017 (wet-cold), and 2015 or 2020 (dry-hot) were clear examples of this precipitation isotopic tendency, pointing out the highest inter-annual isotopic difference of 2.3‰ for $\delta^{18}\text{O}$ and 17.4‰ for $\delta^2\text{H}$ between 2017 and 2020.

Individual precipitation isotopic samples along the general Local Meteoric Water Line (LMWL) illustrated the effects of seasonal precipitation and air temperature (Rozanski et al., 1993; D. F. Smith et al., 2021). Depleted signatures were associated with colder air temperatures typical of late fall, winter, and early spring season. In contrast, warmer temperatures were related with enriched precipitation events characteristic of late spring, summer, and early fall season (Figure 7). A considerable number of spring and summer precipitation events deviated from the general LMWL and GMWL, indicating the influence of nonequilibrium processes such as evaporation (d-excess <10‰) (Dansgaard, 1964), during their travel time from the cloud to the ground. Conversely, most of the fall and winter precipitation samples were distributed along the LMWL and GMWL revealing equilibrium process and lower air temperature when air masses condense (Beria et al., 2018).

4.2 Meteorological and Landscape Factors Influencing the Spatial-Temporal Stream Isotopic Signature

Stream isotopic signatures displayed significant variation (Figure 11) among catchments, underscoring the influence elevation (orographic uplifting) and physiographic (geology and geomorphology) as controls of subsurface storage. Average stream isotopic values for some catchments (CC, LC, and LO1–LO4) were more depleted than the annual weighted-average precipitation isotopic of the water year 2023 (SWE slightly above the long-term median). This suggests that the water flowing in the sampled sites likely comprises a mixture of current precipitation and older inputs stored in the subsurface. In contrast, the average stream isotope

values for catchments such as MC, NC, MR, and LO5 was lower or similar to the annual weighted precipitation, indicating that the predominant source of water draining in these catchments was recent precipitation.

Previous work by Brooks et al. (2012) reported that the stream isotopic signature in the Willamette Basin was significantly explained by spatial variation (catchment mean elevation) with a minimal seasonal variation due to the lack of systematic seasonal change in the precipitation isotopic signature and a residence time that remove temporal variation. In our analysis we found that the stream isotopic signature had a minimal temporal variation, indicating a consistent water source in each study catchment, homogenous mixing throughout the subsurface after precipitation infiltrates the soil, and limited influence of variance in precipitation isotopic signature into the streams. However, seasonal precipitation d-excess, particularly during fall and winter, unveiled the significant influence exerted by large storm events (rainfall or snowfall) with high d-excess values on the stream isotopic signatures. In other words, these large storm events had a higher contribution to the streamflow compared to occasional smaller precipitation events during late spring and summer. These large storm events with high d-excess values and lower isotopic ratios are characterized by low air temperature, cloud condensation temperature, mixing of different air masses from colder regions, and higher vertical vapor transport (Araguás-Araguás et al., 2000; Beria et al., 2018).

The average isotopic signature among streams was more variable than temporal variance within a stream. This isotopic variation was driven by the catchment mean elevation (WME) characterized by lower isotopic signatures with higher WME. The isotopic-elevation pattern, commonly identified as the rainout effect (Clark & Fritz, 1997; Dansgaard, 1964), was represented by the study period and seasonal stream isotopic lapse rates. This behavior showed an inverse relationship between catchment mean elevation and isotopic signature for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, excluding d-excess which showed a positive relationship as catchment mean elevation increased due to subcloud evaporation (Bershaw et al., 2016).

Damping ratios—a proxy of transit time—were systematically lower for the analyzed tributaries than for the main stem indicating longer flow paths and higher subsurface storage in these systems (McGuire et al., 2005; Segura, 2021). The fact that the damping ratio increased downstream was a result of spatial mixing of tributaries and not from a decrease in transit time

(see section 4.4), suggesting that care must be taken when interpreting damping ratios for transit time alone. The transit time interpretation is most appropriate in first order streams, and in smaller catchments. Our results aligned with the damping ratios found by (Sanchez-Murillo et al., 2015) of 0.05 in a pristine forested catchment in Idaho.

4.3 The Role of Groundwater in the Runoff Generation in Headwater Streams

Some studies have emphasized the significant role that groundwater flux have in headwater systems defining the point of origin in the stream (Winter, 2007), connecting an confined (perched) aquifer to the stream through flowpaths (Maltby & Barker, 2009), and maintaining a steady flow during low flows conditions (Fetter & Kremer, 2022). Based on the degree of flatness (slope) of the flow duration curve (Figure 5B), Cold and Longer Creeks (spring-fed streams) appear to receive greater contributions of groundwater, maintaining flows constant throughout time, not subjected to annual fluctuations, and indicating heterogeneous permeability in the subsurface (Bryan, 1919; Manga, 2001). In contrast, Mack Creek and Lookout Creek at the gauging station had steeper flow duration curves, likely associated to lower contribution of groundwater in their average discharges and greater dependence in precipitation storm events (Winter, 2007). We speculated that Longer Creek's groundwater contribution comes from the consolidated material zone (Lava-2, higher elevation), being slowly and constantly released, as a result of the higher water storage capacity. Conversely, runoff-fed stream such as Mack and Lookout Creek at the gauging station, appear to be more dependent on rainfall inputs due to a greater difference between high and low flows. Although Nostoc and McRae Creeks were not gauged, their similar isotopic variability to Mack and Lookout Creeks, implies similar hydrology character.

4.4 Influences of Headwater Streams in the Streamflow Contribution to Downstream Reaches

End-member mixing analysis through an isotopic hydrograph separation (IHS), elucidated the significant streamflow contribution of headwater streams, such as Cold and Longer Creeks (spring-fed streams), during low flow conditions (July–October), representing a substantial contribution ranging from 21 to 53% of the overall discharge flowing through the Lookout Creek at the gauging station (LO5). In contrast, during high flows conditions (November, January, February, May, and June), streamflow contributions from Cold and Longer Creeks were not higher than 11% at LO5, suggesting that most of the flow in the Lookout Creek catchment was carried

by water coming from the upstream main stem catchments (LO1 and LO2), diminishing the discharge contribution from the headwater streams (CC and LC).

Cold (CC, 0.69 km²) and Longer (LC, 2.74 km²) Creeks had the largest discharge per unit area compared to Mack Creek (MC, 5.75 km²) and Lookout Creek at the gauging station (LO5, 62.42 km²). On a monthly basis, the specific discharge in the gauged catchments exhibits a relatively consistent pattern, with Cold and Longer Creeks showing a lower variability compared to other catchments. Conversely, MC and LO5 displayed a greater fluctuation in the streamflow distribution over time, especially in the transitions between high and low flow periods. The observed streamflow contributions and specific discharges demonstrated that hydrogeological catchments (subsurface water divide) are larger than the hydrological catchment (surface water divide). In other words, surface drainage area is not a metric to define the streamflow contribution of a stream (Nickolas et al., 2017). Cold Creek is a clear example of this discrepancy between water divides suggesting that the underlying geology (variable permeability) plays an important role in the movement of water in the subsurface.

5. Conclusions

A comprehensive analysis of the inter-annual and seasonal variability in precipitation and stream isotopic signatures provided insights into the hydrological dynamics of headwater stream systems and unveiled the significant role of small tributaries in maintaining flow in the Lookout Creek catchment, specifically during low flow conditions.

The results underscore the significance of the precipitation isotopic composition as a proxy for identifying drought and wet water years, revealing distinctive patterns associated with seasonal variations and local meteorological conditions. Likewise, a typical water year dominated by rainfall or snowfall also impacts the resulting isotopic signature, characterized by either enrichment or depletion.

Stream isotopic signatures across catchments showed potential hydrological mechanisms governing runoff generation processes, influenced mainly by elevation (rainout effect), seasonal precipitation (fall and winter storm events), and geology (lithology; variable permeability) and geomorphic features (deep-seated mass movement) that control subsurface storage. Spatial heterogeneity was evident in the diverse isotopic signatures observed across catchments.

The role of groundwater in headwater streams was relevant in terms of discharge contributions, maintaining steady flows throughout time and reducing streamflow interannual variation. Spring-fed streams (Cold and Longer Creeks) were characterized by water moving in the subsurface coming from the consolidated material zone (lava flows; variable permeable material), while other streams exhibited a higher dependence on precipitation events. Furthermore, these findings collectively suggested that subsurface water divide did not coincide with the surface water divide throughout time.

6. References

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7. Appendix

Appendix A: Precipitation Isotopic Signature at PRIMET

Appendix A. 1: Local Meteoric Water Line (LMWL) parameters for each water year.

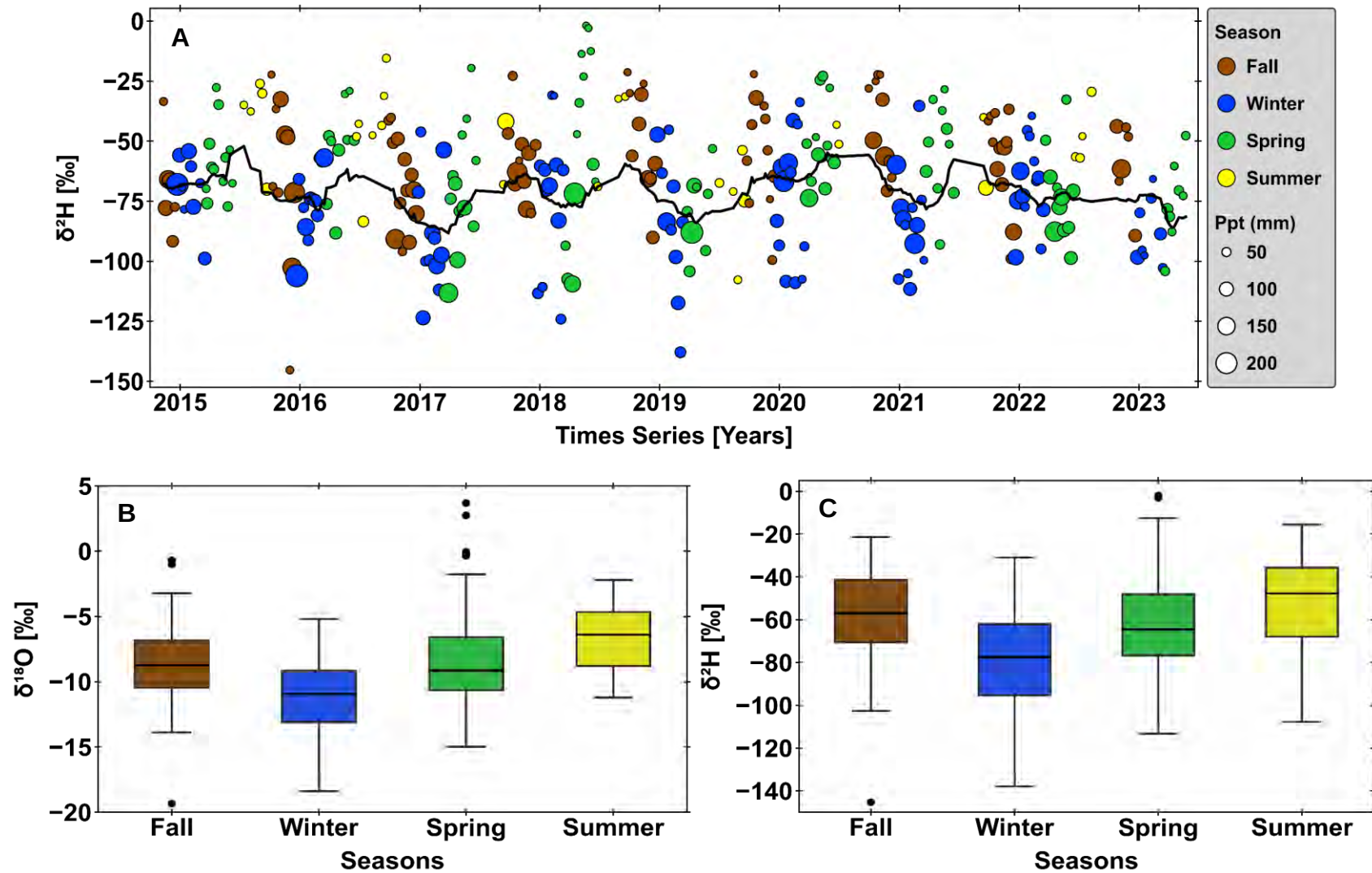
Water Year	$a \pm \sigma$	$b \pm \sigma$	R^2	p-value
2015	7.9 ± 0.4	8.1 ± 3.8	0.93	<0.001
2016	7.9 ± 0.2	10.1 ± 2.6	0.97	<0.001
2017	8.4 ± 0.2	15.4 ± 2.7	0.97	<0.001
2018	8.0 ± 0.2	12.0 ± 2.8	0.96	<0.001
2019	8.2 ± 0.4	12.2 ± 4.2	0.94	<0.001
2020	7.1 ± 0.3	2.1 ± 2.8	0.94	<0.001
2021	8.2 ± 0.3	13.1 ± 2.8	0.96	<0.001
2022	7.2 ± 0.3	2.9 ± 3.6	0.92	<0.001
2023	7.6 ± 0.3	7.2 ± 3.7	0.96	<0.001
2015-2023	7.8 ± 0.1	9.2 ± 1.0	0.95	<0.01

Appendix A.2: Volume weighted average and standard deviation precipitation isotopic signature by season.

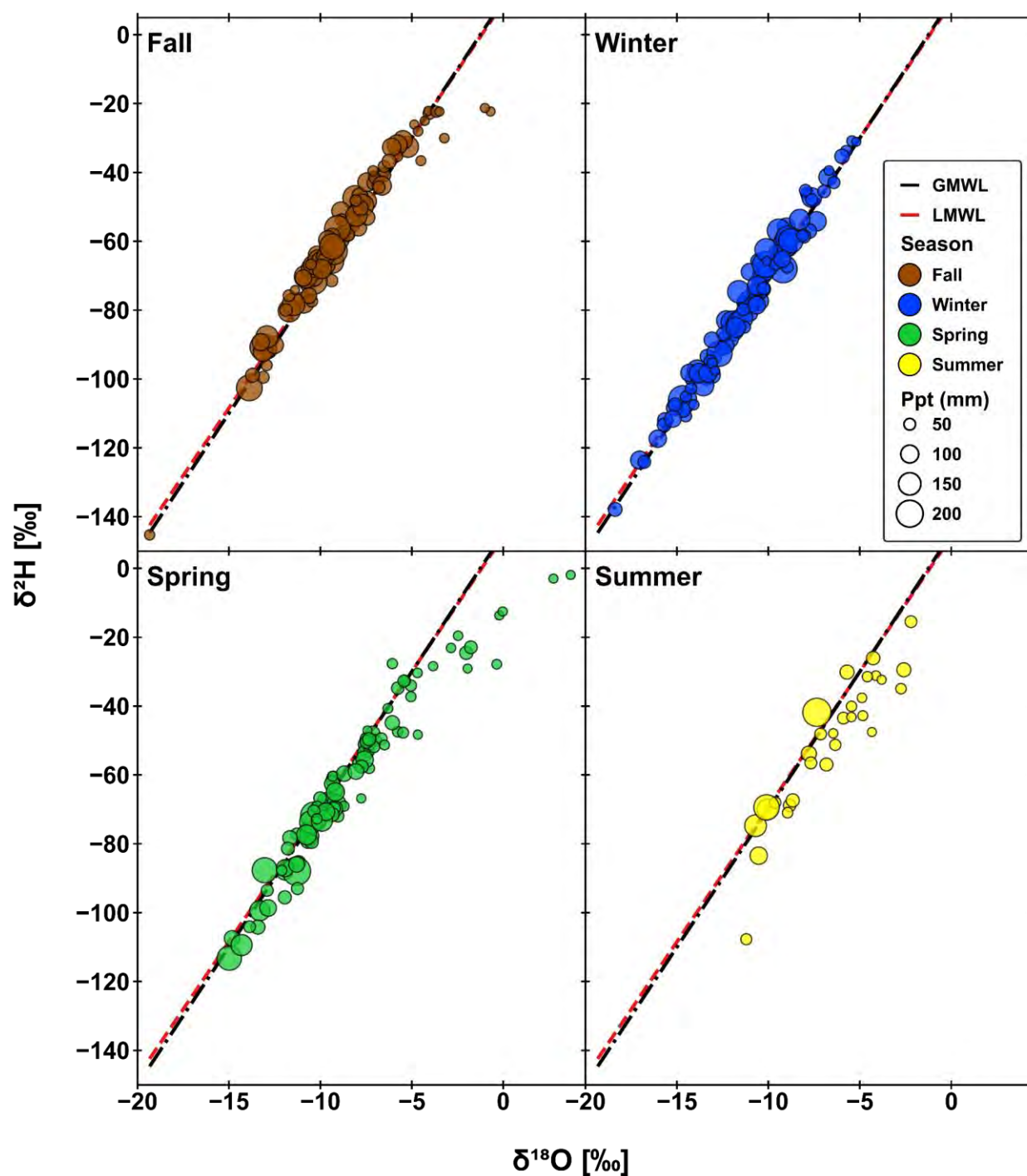
Season	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^{2}\text{H}} \pm \sigma$	$\overline{d} \pm \sigma$	Min ($\delta^{18}\text{O}, \delta^{2}\text{H}, \overline{d}$)	Max ($\delta^{18}\text{O}, \delta^{2}\text{H}, \overline{d}$)
	‰	‰	‰	‰	‰
Spring	-10.3 ± 2.6	-75.1 ± 19.8	7.3 ± 4.7	-15.0, -113.2, -31.4	3.7, -1.90, 6.6
Summer	-8.2 ± 2.4	-57.2 ± 18.7	8.5 ± 7.6	-11.2, -107.7, -18.1	-2.2, -15.5, 2.2
Fall	-9.5 ± 2.3	-63.3 ± 18.1	12.9 ± 3.0	-19.3, -145.3, -16.7	-0.7, -22.3, 9.4
Winter	-11.2 ± 2.5	-78.0 ± 19.9	11.4 ± 3.5	-18.4, -137.9, 9.2	-5.2, -31.1, 10.5

$\overline{d}$ is the d-excess weighted average.

Seasons were defined: spring (03/20-06/20), summer (06/21-09/22), fall (09/23-12/20), and winter (12/21-03/19).



Appendix A.3: Precipitation isotopic signature (A: $\delta^2\text{H}$) throughout time (water years: 2015 – 2023). Black line is the volume weighted moving average with a window of 25 values. Box plot distribution of the precipitation stable isotopes (B: $\delta^{18}\text{O}$ and C: $\delta^2\text{H}$) by season.



Appendix A.4: Precipitation isotopic signature grouped by precipitation magnitude and seasons (water year: 2015 – 2023). Red line is the Local Meteoric Water Line (LMWL), and black line is the Global meteoric Water Line (GMWL).

Appendix B: Stream Isotopic Signature by Catchment.

Appendix B. 1: Summary of arithmetic mean ($\overline{\delta^{18}\text{O}}$, $\overline{\delta^2\text{H}}$) and standard deviation of (σ) by catchment and season (fall and winter) between May 2022 and May 2023.

Fall*					Winter*				
	Site	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	$\bar{d} \pm \sigma$	Site	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	$\bar{d} \pm \sigma$	
		‰	‰	‰		‰	‰	‰	
Tributaries	CC	-11.3 ± 0.4	-77.4 ± 3.5	13.3 ± 0.2	CC	-11.5 ± 0.1	-78.2 ± 0.6	13.5 ± 0.1	
	LC	-11.0 ± 0.1	-74.7 ± 0.8	13.1 ± 0.2	LC	-11.0 ± 0.1	-74.5 ± 0.7	13.2 ± 0.2	
	MC	-10.5 ± 0.3	-70.7 ± 2.2	13.3 ± 0.4	MC	-10.9 ± 0.2	-73.3 ± 1.1	13.8 ± 0.2	
	NC	-10.5 ± 0.3	-71.5 ± 1.9	12.1 ± 0.3	NC	-10.7 ± 0.1	-72.7 ± 0.8	12.5 ± 0.1	
	MR	-10.4 ± 0.2	-70.0 ± 1.6	12.9 ± 0.3	MR	-10.8 ± 0.1	-72.8 ± 0.7	13.2 ± 0.1	
Main Stem	LO1	-10.5 ± 0.3	-71.5 ± 2.5	12.7 ± 1.1	LO1	-11.2 ± 0.1	-75.5 ± 0.8	13.7 ± 0.1	
	LO2	-11.0 ± 0.5	-74.6 ± 4.0	13.3 ± 0.1	LO2	-11.2 ± 0.1	-75.5 ± 0.9	13.7 ± 0.1	
	LO3	-10.9 ± 0.3	-73.9 ± 2.8	13.2 ± 0.2	LO3	-11.1 ± 0.1	-75.2 ± 0.8	13.3 ± 0.1	
	LO4	-10.7 ± 0.3	-72.8 ± 2.4	13.1 ± 0.2	LO4	-11.0 ± 0.1	-74.5 ± 0.7	13.2 ± 0.1	
	LO5	-10.6 ± 0.3	-71.6 ± 2.3	12.9 ± 0.3	LO5	-10.8 ± 0.2	-73.2 ± 1.0	12.9 ± 0.5	
Average		-10.7	-72.9	13.0	Average		-11.0	-74.6	13.3
Max		-10.4	-70.0	13.3	Max		-10.7	-72.7	13.8
Min		-11.3	-77.4	12.1	Min		-11.5	-78.2	12.5

* Fall: 09/23-12/20, and winter: 12/21-03/19.

Appendix B. 2: Summary of arithmetic mean ($\overline{\delta^{18}\text{O}}$, $\overline{\delta^2\text{H}}$) and standard deviation of (σ) by catchment and season (spring and summer) between May 2022 and May 2023.

Spring*					Summer*				
	Site	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	$\bar{d} \pm \sigma$	Site	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	$\bar{d} \pm \sigma$	
		‰	‰	‰		‰	‰	‰	
Tributaries	CC	-11.4 ± 0.2	-78.1 ± 1.2	13.2 ± 0.6	CC	-11.5 ± 0.1	-78.7 ± 0.3	13.0 ± 0.7	
	LC	-11.0 ± 0.0	-74.8 ± 0.4	12.8 ± 0.1	LC	-11.0 ± 0.0	-75.2 ± 0.2	13.1 ± 0.2	
	MC	-10.9 ± 0.2	-73.2 ± 1.0	13.7 ± 0.9	MC	-10.9 ± 0.1	-73.7 ± 0.5	13.1 ± 0.5	
	NC	-10.6 ± 0.0	-72.8 ± 0.4	12.0 ± 0.2	NC	-10.7 ± 0.1	-73.1 ± 0.4	12.2 ± 0.2	
	MR	-10.8 ± 0.2	-73.0 ± 1.3	13.2 ± 0.7	MR	-10.6 ± 0.0	-72.1 ± 0.1	12.7 ± 0.4	
Main Stem	LO1	-11.1 ± 0.1	-75.3 ± 0.9	13.3 ± 1	LO1	-10.9 ± 0.1	-74.5 ± 0.3	12.7 ± 0.5	
	LO2	-11.2 ± 0.1	-76.0 ± 1.0	13.4 ± 0.9	LO2	-11.3 ± 0.2	-77.7 ± 1.1	12.9 ± 0.6	
	LO3**	-11.6	-79.7	13.4	LO3	-	-	-	
	LO4**	-11.4	-78.2	13.3	LO4	-	-	-	
	LO5	-10.9 ± 0.2	-74.1 ± 1.4	13.0 ± 0.7	LO5	-10.8 ± 0.1	-74.0 ± 0.5	12.6 ± 0.5	
Average		-11.0	-74.7	13.1	Average		-11.0	-74.9	12.8
Max		-10.6	-72.8	13.7	Max		-10.6	-72.1	13.1
Min		-11.4	-78.1	12.0	Min		-11.5	-78.7	12.2

* Spring: 03/20-06/20), summer: 06/21-09/22.

** Sites without standard deviations were based on a single measurement.

Appendix B. 3: Partitioning of LO2 into streamflow contributions from CC and LO1 using $\overline{\delta^{18}\text{O}}$ and $\overline{\delta^2\text{H}}$.

Month	CC	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	Q_{CC}	LO1	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	Q_{LO1}
	%	‰	‰	l/s	%	‰	‰	l/s
May	13	-11.3 ± 0.1	-77.5 ± 0.6	174.2	87	-11.2 ± 0.1	-75.5 ± 1.2	1168.1
Jun	35	-11.3 ± 0.1	-77.8 ± 0.4	113.5	65	-11.0 ± 0.1	-75.0 ± 0.4	207.7
Jul	70	-11.4 ± 0.1	-78.6 ± 0.2	93.6	30	-10.8 ± 0.1	-74.2 ± 0.2	40.3
Aug	90	-11.5 ± 0.0	-78.8 ± 0.1	87.1	10	-11.0 ± 0.0	-74.6 ± 0.1	10.0
Sep	82	-11.6 ± 0.0	-79.0 ± 0.1	66.1	18	-11.0 ± 0.0	-74.7 ± 0.0	14.2
Oct	78	-11.5 ± 0.0	-78.9 ± 0.3	65.6	22	-10.6 ± 0.4	-72.7 ± 2.2	19.0
Nov	22	-11.1 ± 0.6	-75.3 ± 4.9	63.6	78	-10.4 ± 0.3	-69.8 ± 2.0	222.4
Jan	0	-11.4 ± 0.0	-77.9 ± 0.4	0.0	100	-11.1 ± 0.2	-75.2 ± 1.1	6013.2
Feb	7	-11.6 ± 0.0	-79.0 ± 0.0	50.0	93	-11.2 ± 0.0	-75.9 ± 0.1	697.3

Appendix B. 4: Partitioning of LO3 into streamflow contributions from NC and LO2 using $\overline{\delta^{18}\text{O}}$ and $\overline{\delta^2\text{H}}$.

Month	LC	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	LO2	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$
	%	‰	‰	%	‰	‰
Oct	84	-11.1 ± 0.0	-75.2 ± 0.2	16	-11.4 ± 0.2	-77.4 ± 0.2
Nov	21	-10.9 ± 0.1	-74.1 ± 0.7	79	-10.5 ± 0.4	-70.9 ± 0.7
Jan	36	-10.9 ± 0.1	-74.1 ± 0.5	64	-11.1 ± 0.1	-75.1 ± 0.5
Feb	29	-11.1 ± 0.0	-75.3 ± 0.1	71	-11.2 ± 0.00	-76.1 ± 0.1

Appendix B. 5: Partitioning of LO4 into streamflow contributions from NC and LO3 using $\overline{\delta^{18}\text{O}}$ and $\overline{\delta^2\text{H}}$.

Month	NC	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$	LO3	$\overline{\delta^{18}\text{O}} \pm \sigma$	$\overline{\delta^2\text{H}} \pm \sigma$
	%	‰	‰	%	‰	‰
Oct	33	-10.6 ± 0.2	-72.40 ± 1.6	67	-11.1 ± 0.2	-75.6 ± 1.0
Nov	38	-10.3 ± 0.2	-70.20 ± 1.7	62	-10.6 ± 0.3	-71.6 ± 2.9
Jan	25	-10.6 ± 0.0	-72.23 ± 0.4	75	-11.0 ± 0.1	-74.8 ± 0.6
Feb	30	-10.8 ± 0.0	-73.61 ± 0.1	70	-11.2 ± 0.1	-76.0 ± 0.5

Appendix B. 6: Monthly stream isotopic signature ($\overline{\delta^{18}O}$) by study catchment.

Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
CC	-11.4	-11.6	-	-	-11.4	-11.3	-11.4	-11.5	-11.6	-11.5	-11.1	-
LC	-10.9	-11.1	-	-	-	-10.9	-11.0	-11.1	-11.1	-11.0	-10.9	-
MC	-10.8	-11.0*	-	-	-10.9	-10.8	-10.8	-10.9	-10.9	-10.6	-10.4	-
NC	-10.6	-10.8	-	-	-	-10.6	-10.6	-10.7	-10.7	-10.6	-10.3	-
MR	-10.7	-10.8	-	-	-10.8	-10.7	-10.6	-10.6	-10.6	-10.4	-10.3	-
LO1	-11.1	-11.2	-	-	-11.2	-11.0	-10.8	-11.0	-11.0	-10.6	-10.4	-
LO2	-11.1	-11.2	-	-	-11.2	-11.1	-11.2	-11.5	-11.5	-11.4	-10.5	-
LO3	-11.0	-11.2	-	-	-11.6*	-	-	-	-	-11.1	-10.6	-
LO4	-10.9	-11.1	-	-	-11.4*	-	-	-	-	-10.9	-10.5	-
LO5	-10.7	-10.9	-	-	-10.93	-10.7	-10.7	-10.9	-10.9	-10.7	-10.4	-
Max	-10.6	-10.8	-	-	-10.8	-10.6	-10.6	-10.6	-10.6	-10.4	-10.3	-
Min	-11.4	-11.6	-	-	-11.7	-11.3	-11.4	-11.5	-11.6	-11.5	-11.0	-

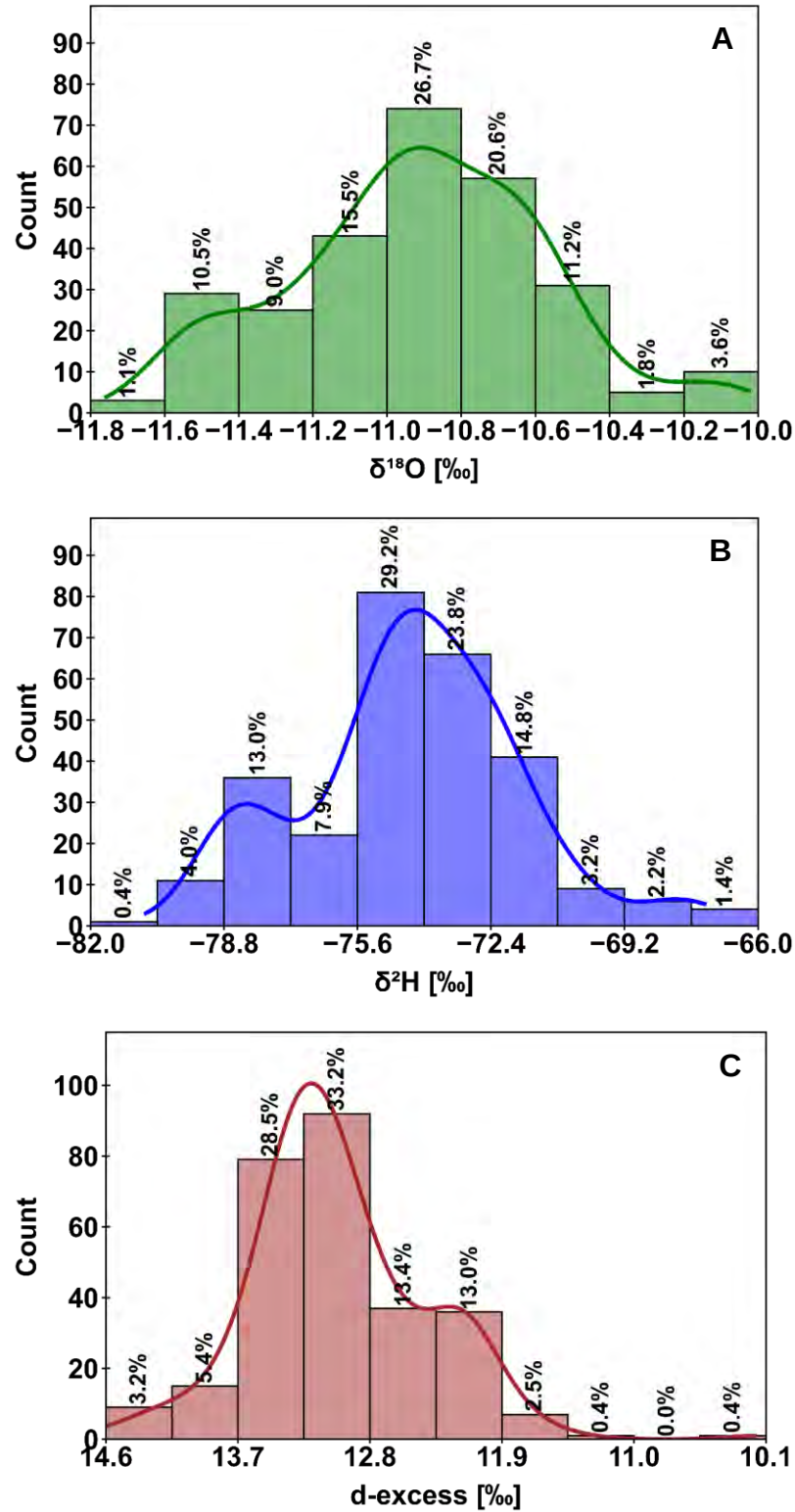
Appendix B. 7: Monthly stream isotopic signature ($\overline{\delta^2H}$) by study catchment.

Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
CC	-77.9	-79.0	-	-	-78.1	77.8	-78.6	-78.8	-79.0	-78.9	-75.3	-
LC	-74.1	-75.3	-	-	-	74.6	-75.1	-75.3	-75.5	-75.2	-74.1	-
MC	-72.8	-74.4*	-	-	-73.0	73.3	-73.3	-73.9	-74.2	-71.6	-69.9	-
NC	-72.2	-73.6	-	-	-	72.7	-72.7	-73.2	-73.6	-72.4	-70.2	-
MR	-72.5	-73.6	-	-	-73.2	72.6	-72.2	-72.1	-72.1	-70.3	-69.4	-
LO1	-75.2	-75.9	-	-	-75.5	75.0	-74.2	-74.6	-74.7	-72.7	-69.8	-
LO2	-75.1	-76.1	-	-	-75.8	76.0	-77.2	-78.4	-78.3	-77.4	-70.9	-
LO3	-74.8	-76.0	-	-	-79.7*	-	-	-	-	-75.6	-71.6	-
LO4	-74.2	-75.2	-	-	-78.2*	-	-	-	-	-74.4	-70.9	-
LO5	-72.7	-74.2	-	-	-74.0	73.5	-73.6	-74.2	-74.4	-73.0	-69.8	-
Max	-72.2	-73.6	-	-	-73.0	77.8	-72.2	-72.1	-72.1	-70.3	-69.4	-
Min	-77.9	-79.0	-	-	-78.1	72.6	-78.6	-78.8	-79.0	-78.9	-75.3	-

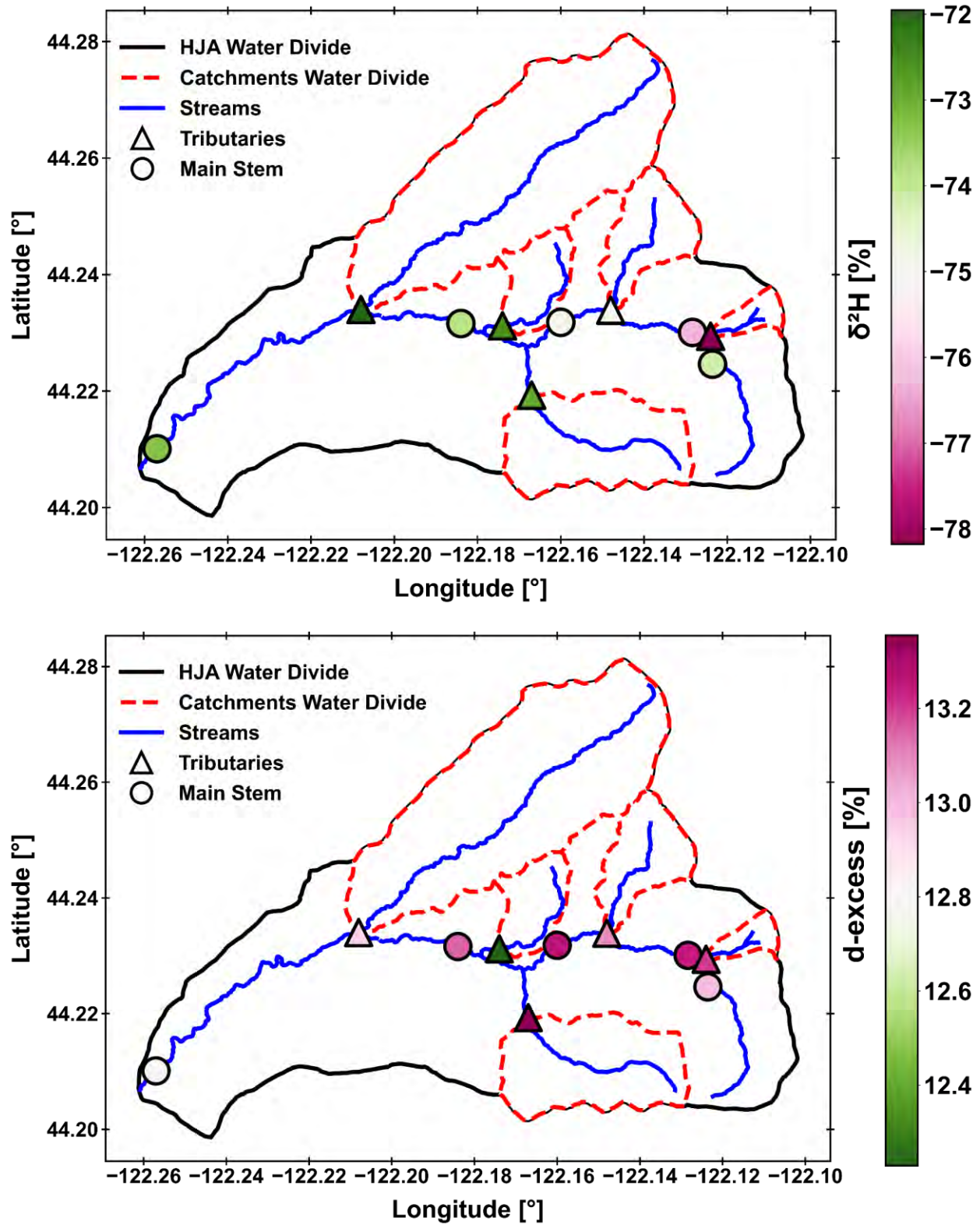
Appendix B. 8: Monthly stream isotopic signature ($\overline{d} - excess$) by study catchment.

Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
CC	13.4	13.5	-	-	13.2	12.7	12.5	13.4	13.6	13.4	13.2	-
LC	13.2	13.3	-	-	-	12.9	13.1	13.2	13.1	13.2	13.0	-
MC	13.7	14.0*	-	-	14.2	13.0	12.7	13.5	13.3	13.1	13.6	-
NC	12.5	12.5	-	-	-	12.1	12.2	12.2	12.1	12.0	12.2	-
MR	13.2	13.2	-	-	13.5	12.7	12.5	12.8	12.7	12.7	13.1	-
LO1	13.7	13.8	-	-	13.8	12.7	12.2	13.1	12.9	12.2	13.2	-
LO2	13.6	13.7	-	-	13.7	12.8	12.5	13.3	13.4	13.3	13.4	-
LO3	13.3	13.4	-	-	13.4*	-	-	-	-	13.1	13.3	-
LO4	13.1	13.3	-	-	13.3*	-	-	-	-	13.0	13.1	-
LO5	12.7	13.1	-	-	13.4	12.2	12.3	12.9	12.9	12.8	13.1	-
Max	13.7	13.8	-	-	14.2	13.0	13.1	13.5	13.6	13.4	13.6	-
Min	12.5	12.5	-	-	13.2	12.1	12.2	12.2	12.1	12.0	12.2	-

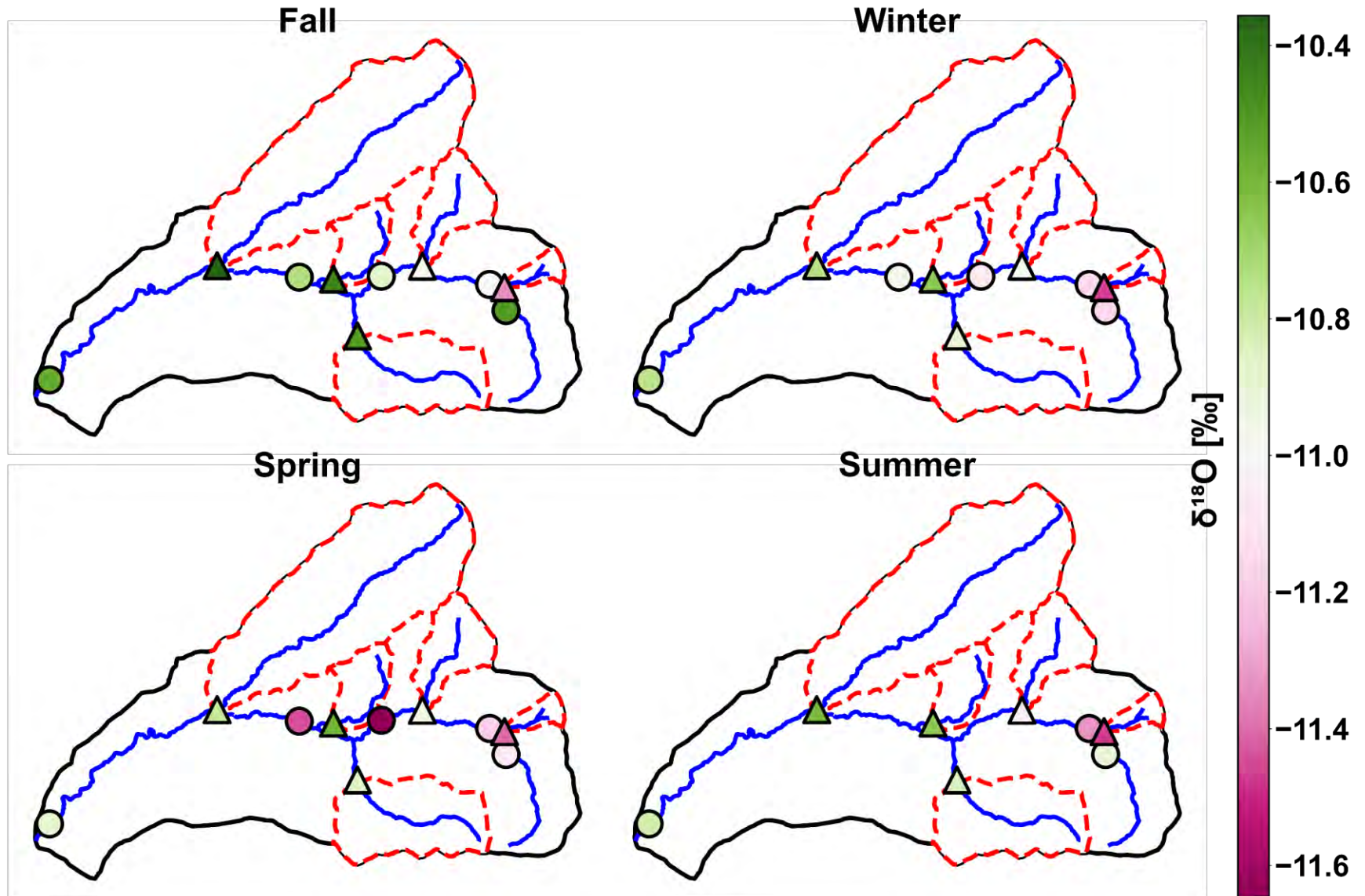
* Values were based on a single measurement.

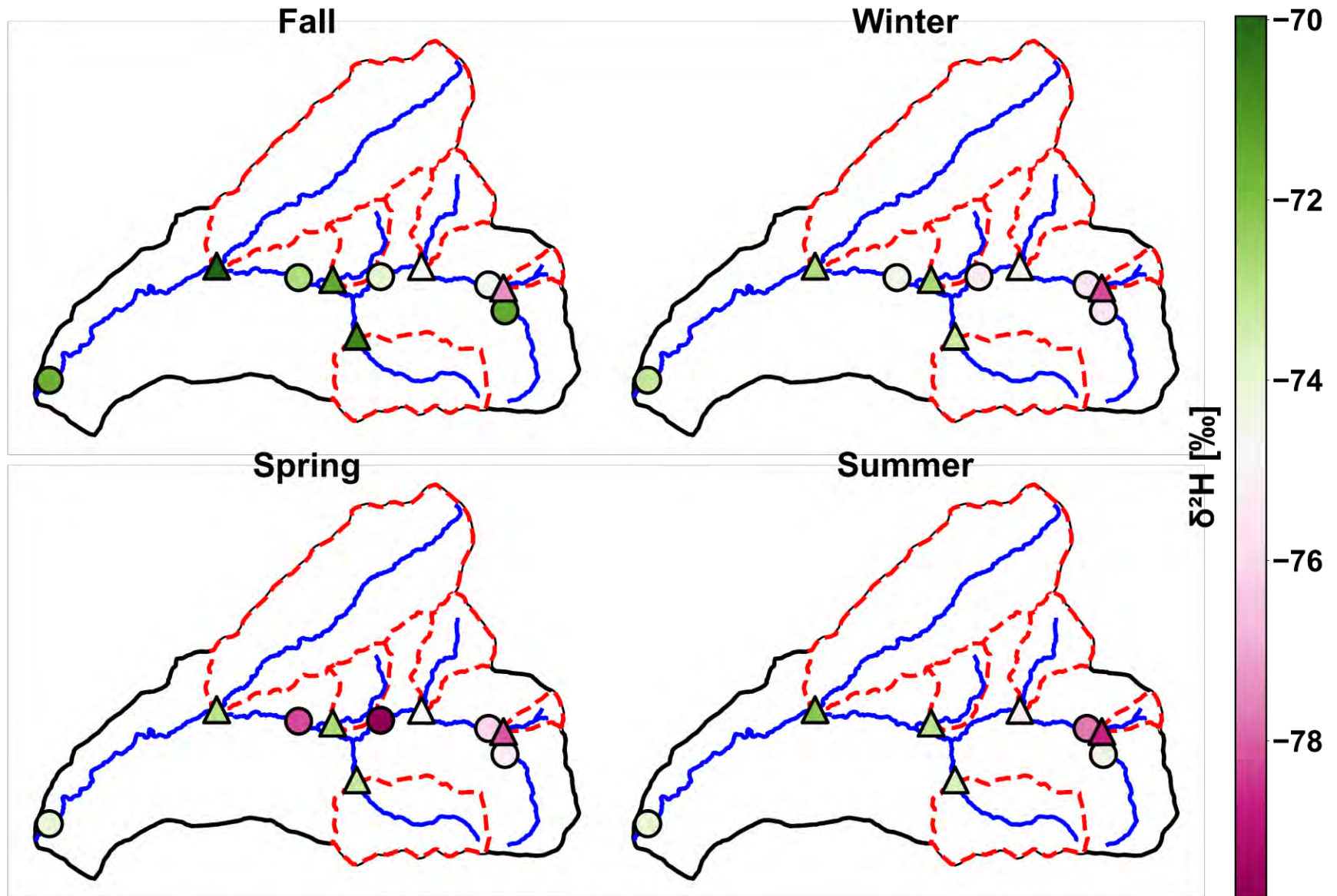


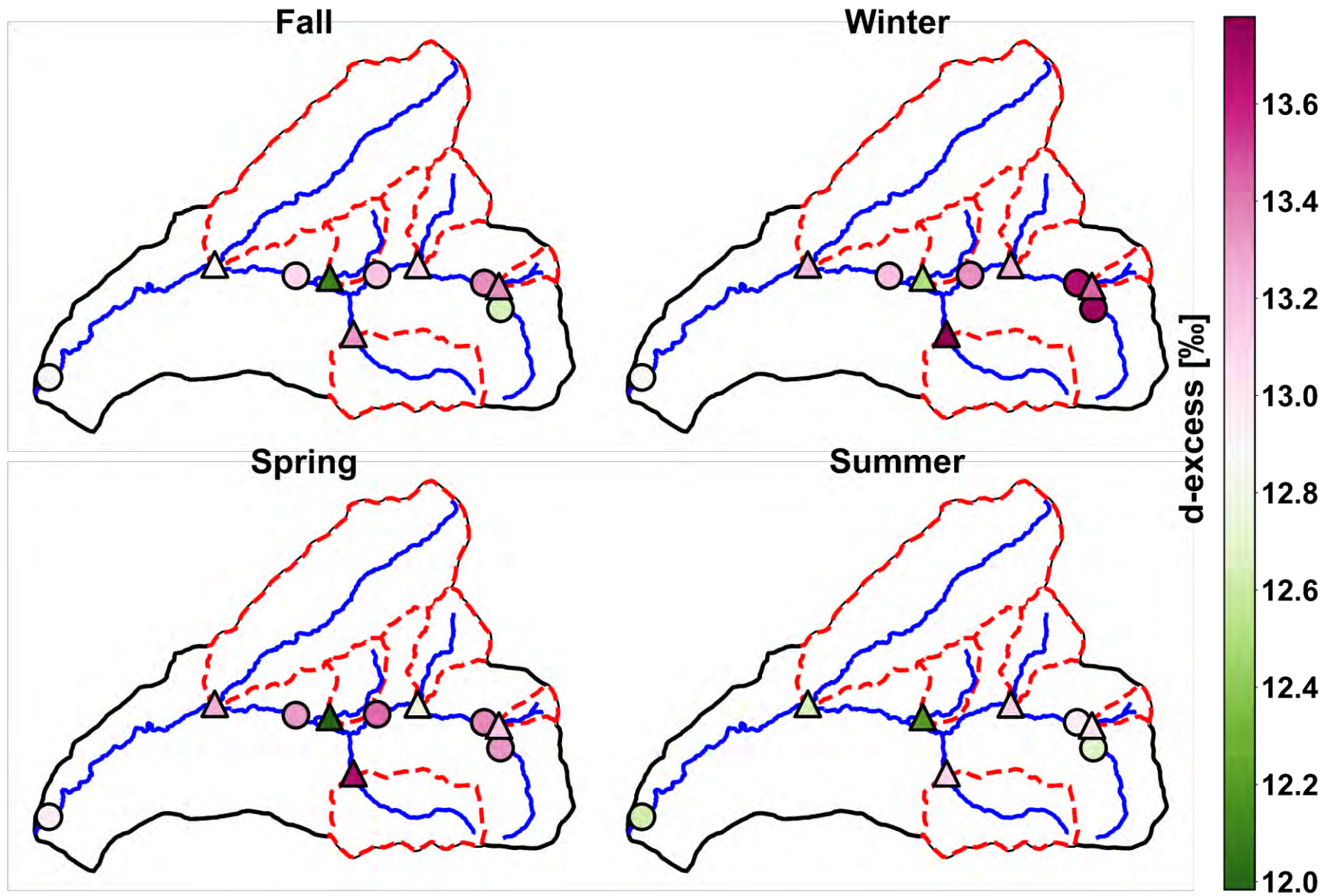
Appendix B. 9: Frequency distribution histogram of the stream isotopic signature for $\delta^{18}\text{O}$ (A), $\delta^2\text{H}$ (B) $d - excess$ (C), considering all catchments.



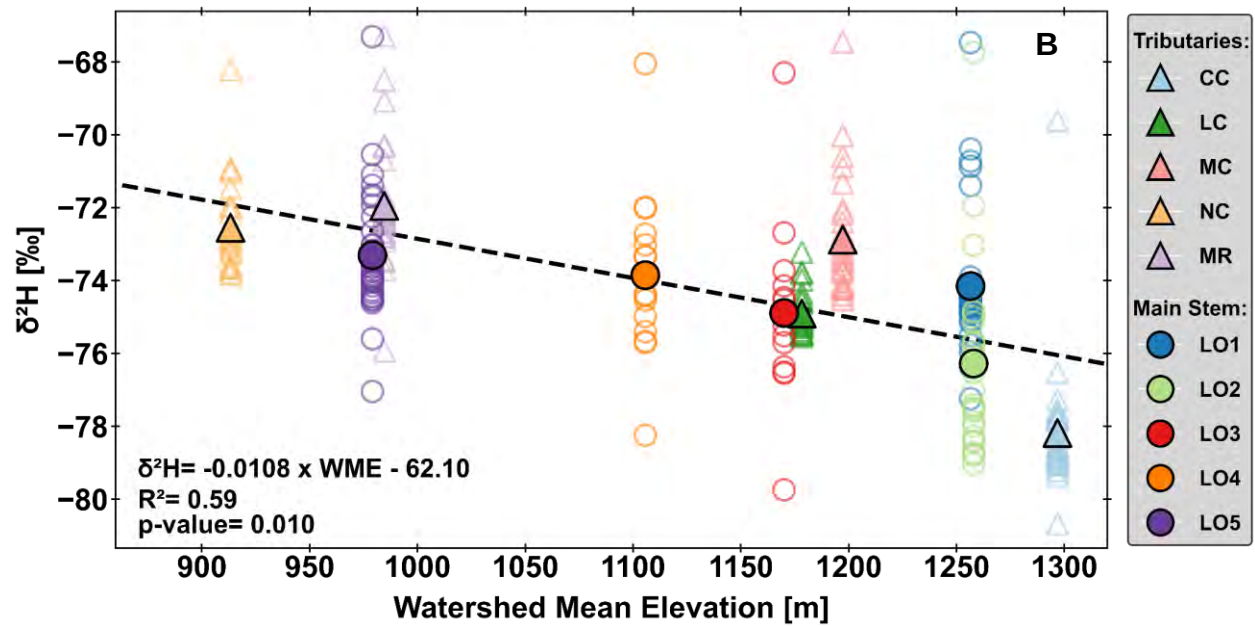
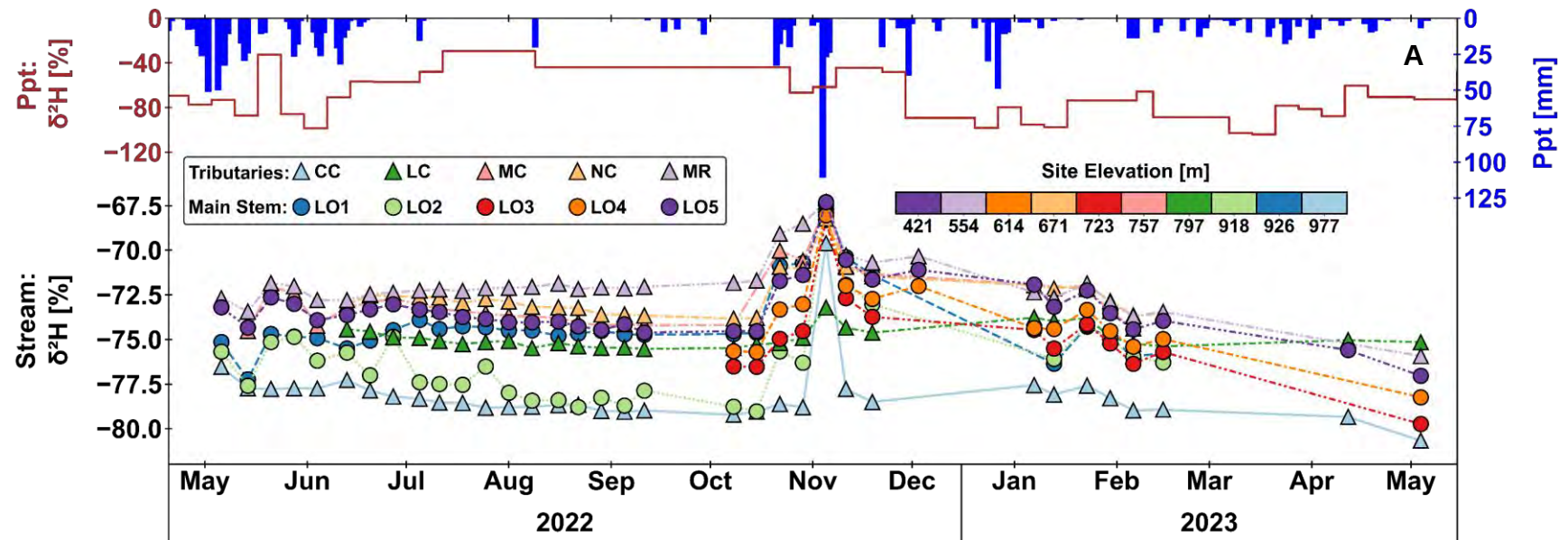
Appendix B. 10: Spatial distribution of the average stream isotopic signature ($\overline{\delta^2H}$ and $\overline{d-excess}$) over the study period. Red and black water divide (lines) represent headwater streams and HJ Andrews.

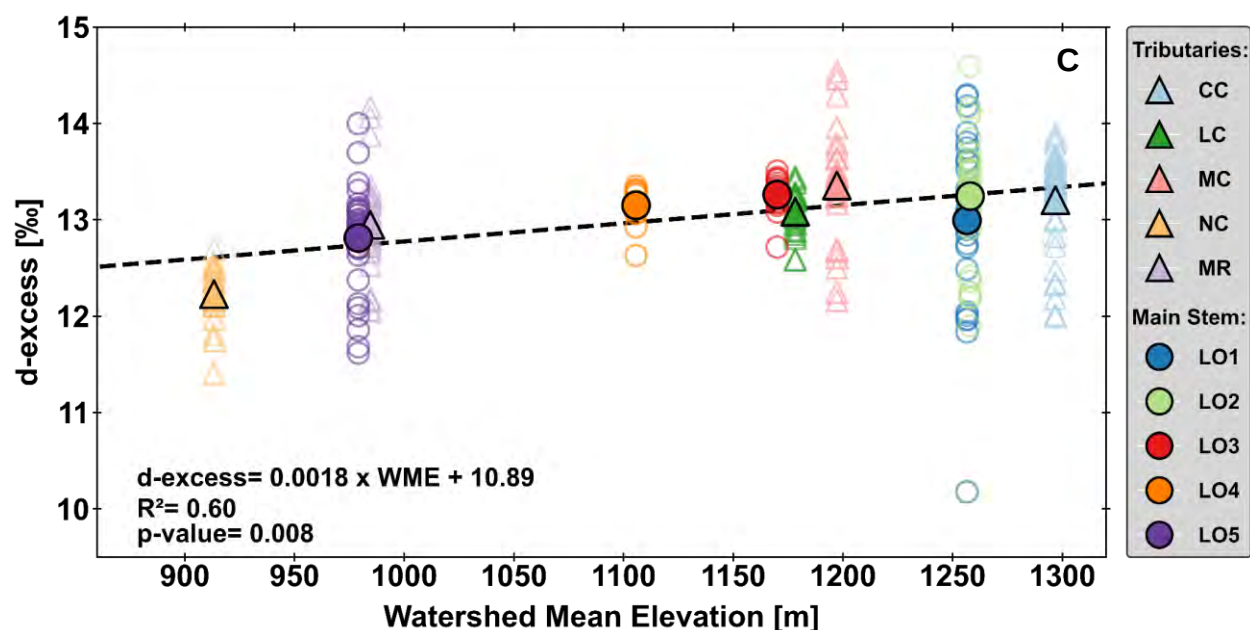




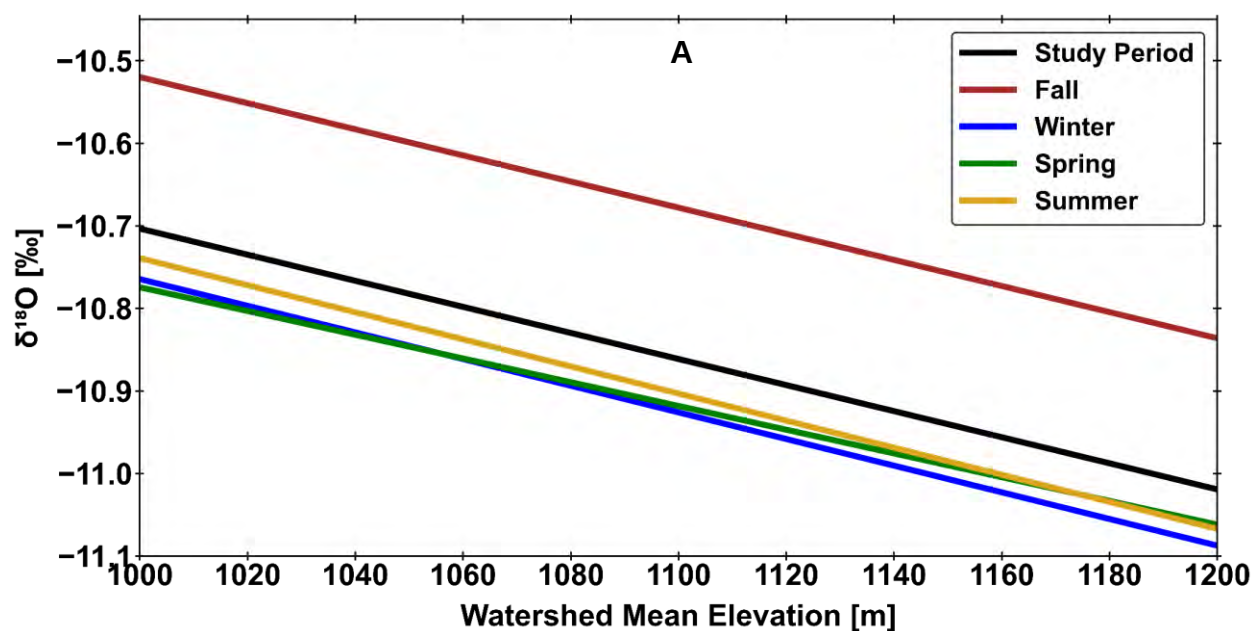


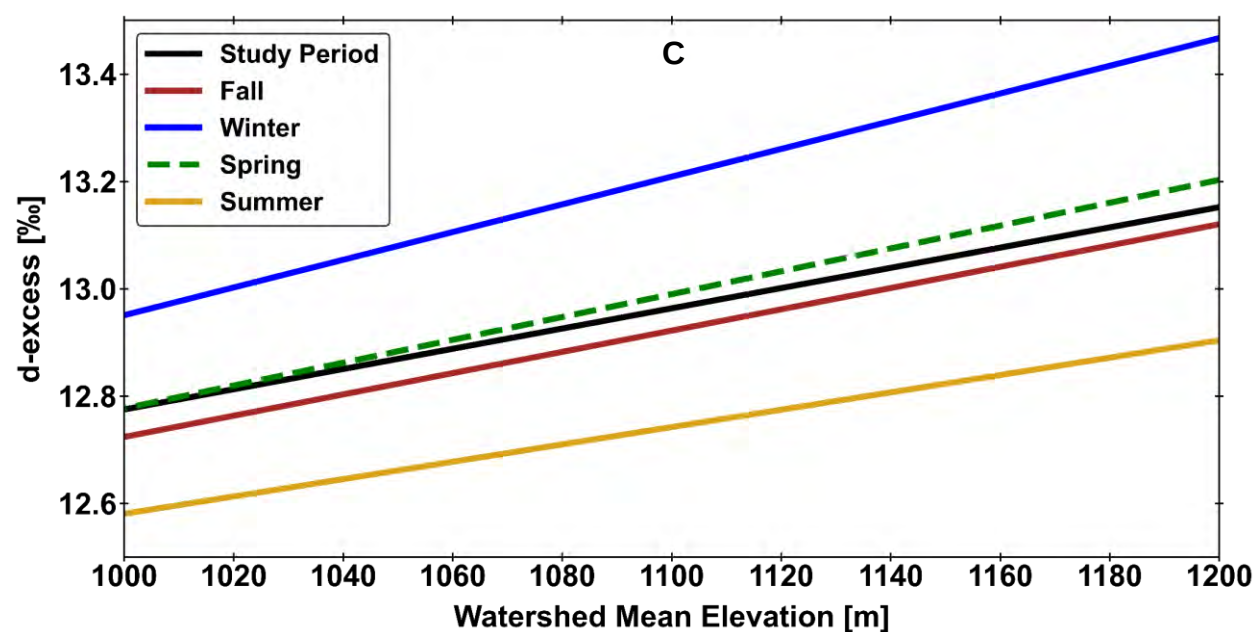
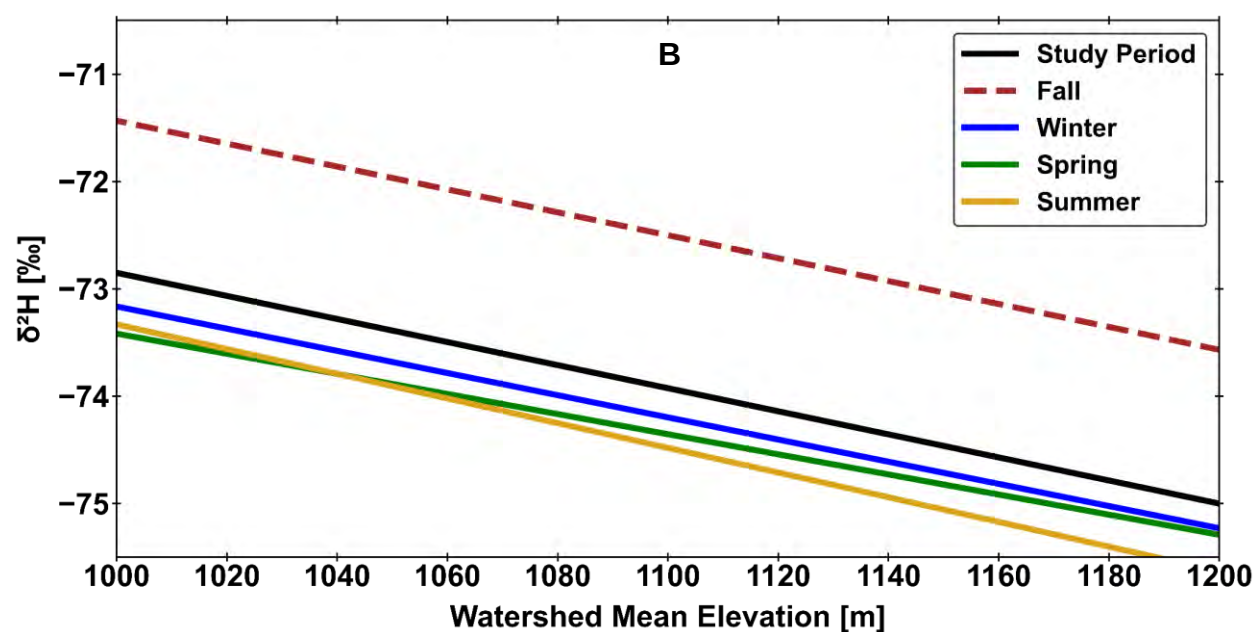
Appendix B. 11: Spatial-temporal distribution of the seasonal average stream isotopic signature ($\overline{\delta^{18}O}$, $\overline{\delta^{2}H}$, $\overline{d-excess}$) over the study period. Red dashed and black water divide (lines) represent headwater streams and HJ Andrews.





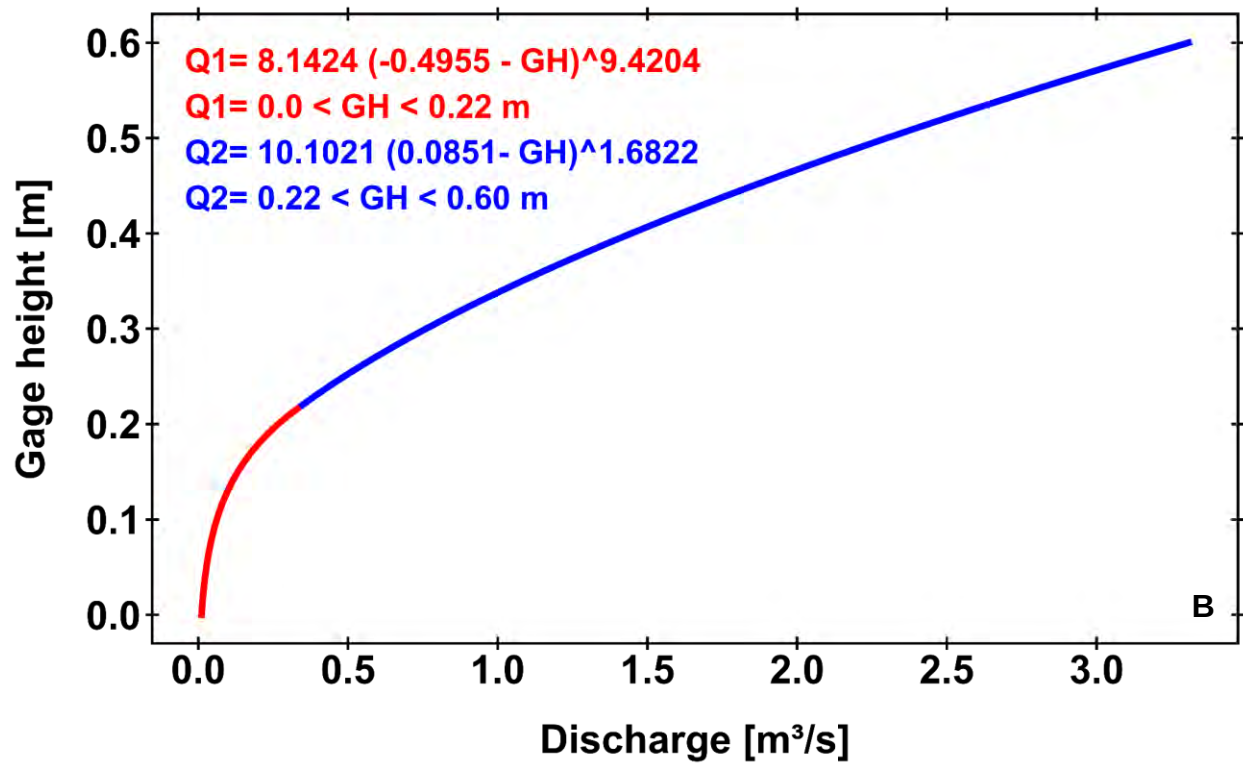
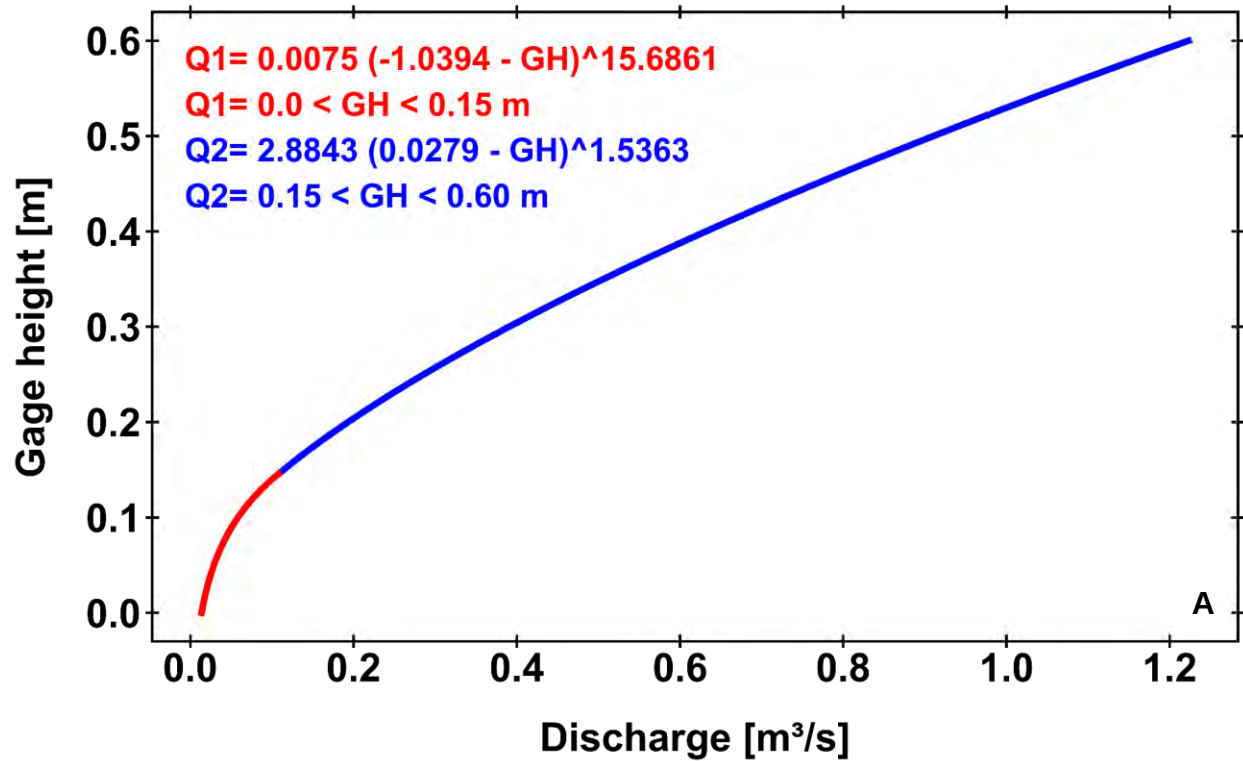
Appendix B. 12: Stream isotopic signature (A) throughout time (May 2022 – May 2023) for each catchment. Relationship between catchment mean elevation and water stable isotopes ($\delta^2\text{H}$, and $d\text{-excess}$) by catchment (B). Filled and unfilled markers represent the average and individual sample values. Linear regression line (dashed black line) was estimated using the average isotopic signature of each sampled site.





Appendix B. 13: Isotopic lapse rates by season and stable isotope. Dashed lines indicate p-value greater than 0.05 (no statistical significance) and straight lines represents p-value less than 0.05 (statistical significance).

Appendix C: Streamflow Analysis



Appendix C. 1: Rating curves of Cold (A) and Longer (B) Creeks.

Appendix C. 2: General hydrologic information by catchment (Cold and Longer Creek).

Month	Cold Creek (CC, 0.69 km²)					Month	Longer Creek (LC, 2.74 km²)*				
	Q	q	Runoff				Q	q	Runoff		
	m³/s	l/s/km²	mm	%	MCM		m³/s	l/s/km²	m³/s	%	MCM
May-22	0.18	252.22	678.77	16.17	0.47	May-22	0.23	84.86	227.30	12.16	0.62
Jun-22	0.11	163.55	425.94	10.15	0.29	Jun-22	0.17	60.92	157.91	8.44	0.43
Jul-22	0.09	134.48	361.90	8.62	0.25	Jul-22	0.11	39.65	106.19	5.68	0.29
Aug-22	0.09	125.15	336.79	8.02	0.23	Aug-22	0.10	36.55	97.89	5.24	0.27
Sep-22	0.07	94.60	246.36	5.87	0.17	Sep-22	0.10	35.69	92.51	4.95	0.25
Oct-22	0.07	93.87	252.61	6.02	0.17	Oct-22	0.09	31.47	84.29	4.51	0.23
Nov-22	0.06	91.03	237.07	5.65	0.16	Nov-22	0.11	38.54	99.89	5.34	0.27
Dec-22	0.08	115.16	309.93	7.38	0.21	Dec-22	0.16	58.73	157.30	8.41	0.43
Jan-23	0.06	85.95	231.32	5.51	0.16	Jan-23	0.17	62.19	166.56	8.91	0.46
Feb-23	0.05	71.25	173.18	4.13	0.12	Feb-23	0.13	46.90	113.46	6.07	0.31
Mar-23	0.05	71.62	192.75	4.59	0.13	Mar-23	0.12	44.63	119.54	6.39	0.33
Apr-23	0.10	147.06	382.99	9.13	0.26	Apr-23	0.21	75.58	195.90	10.48	0.54
May-23	0.10	136.50	367.35	8.75	0.25	May-23	0.26	93.80	251.23	13.44	0.69
Average	0.08	121.72	322.84	7.69	0.22	Average	0.15	54.58	143.84	7.69	0.39
Total	-	-	4196.97	100.00	2.90	Total	-	-	1869.97	100.00	5.12

Q is discharge, q is specific discharge, MCM is millions of cubic meters.

* Streamflow between May 2022 to September 2022 in Longer Creek (LC) was estimated using daily flows from the Lookout Creek at Gauging station (LO5):

$$Q_{LC} = (0.01707 * Q_{LO5}) + 0.0923, R^2 = 0.65, p - \text{value} = < 0.01.$$

Appendix C. 3: General hydrologic information by catchment (Mack Creek and Lookout Creek at gauging station).

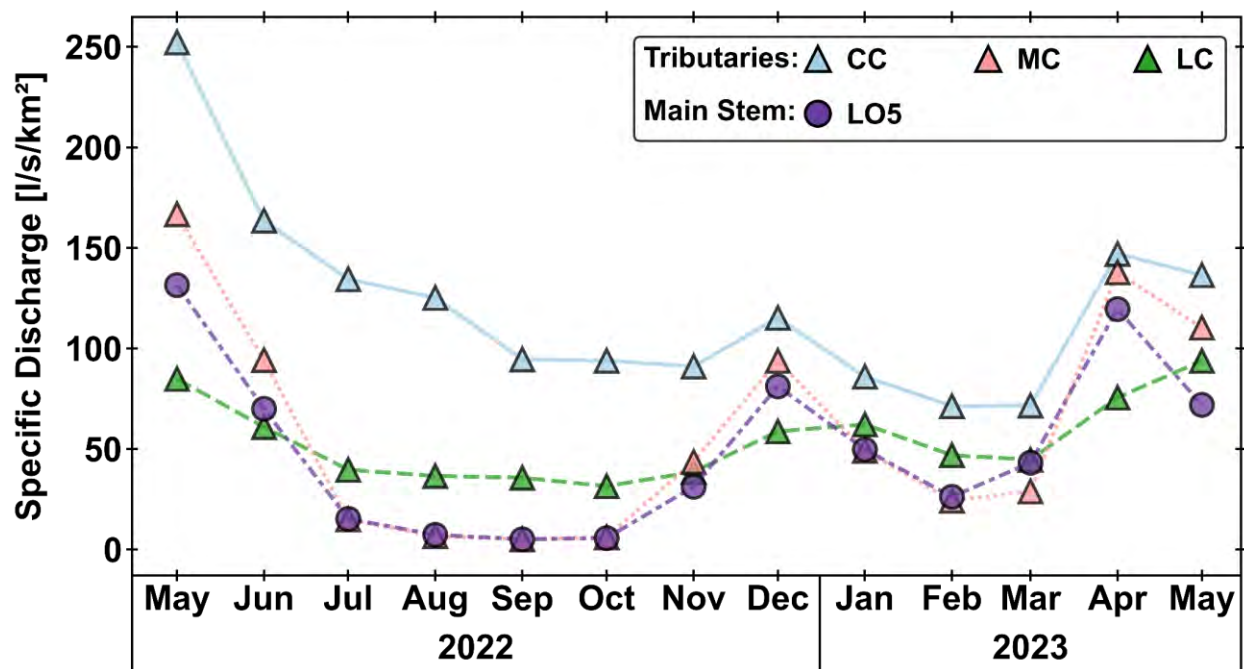
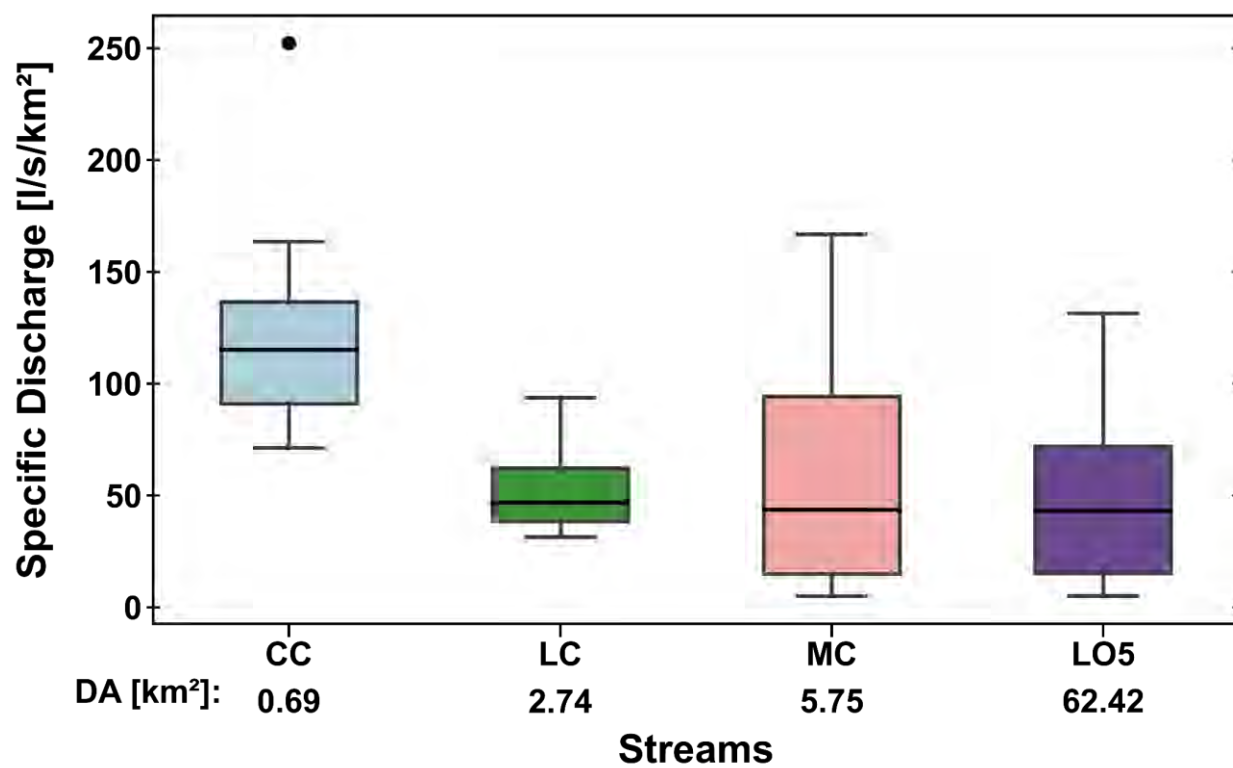
Month	Mack Creek (MC, 5.75 km ²)					Month	Lookout Creek at Gauging station (LO5, 62.42 km ²)				
	Q	q	Runoff				Q	q	Runoff		
	m ³ /s	l/s/km ²	mm	%	MCM		m ³ /s	l/s/km ²	mm	%	MCM
May-22	0.96	166.80	446.55	21.66	2.57	May-22	8.21	131.49	352.18	20.30	21.98
Jun-22	0.54	94.19	244.03	11.83	1.40	Jun-22	4.37	69.94	181.29	10.45	11.31
Jul-22	0.09	14.91	39.91	1.94	0.23	Jul-22	0.95	15.25	40.85	2.35	2.55
Aug-22	0.04	6.68	17.88	0.87	0.10	Aug-22	0.46	7.29	19.53	1.13	1.22
Sep-22	0.03	5.03	13.03	0.63	0.07	Sep-22	0.32	5.08	13.17	0.76	0.82
Oct-22	0.04	6.09	16.30	0.79	0.09	Oct-22	0.36	5.69	15.23	0.88	0.95
Nov-22	0.25	43.61	112.98	5.48	0.65	Nov-22	1.95	31.20	80.88	4.66	5.05
Dec-22	0.54	93.81	251.13	12.18	1.44	Dec-22	5.06	81.15	217.37	12.53	13.56
Jan-23	0.28	49.12	131.49	6.38	0.76	Jan-23	3.11	49.77	133.32	7.68	8.32
Feb-23	0.14	24.33	58.82	2.85	0.34	Feb-23	1.63	26.19	63.35	3.65	3.95
Mar-23	0.17	28.95	77.49	3.76	0.45	Mar-23	2.69	43.14	115.55	6.66	7.21
Apr-23	0.79	137.84	357.11	17.32	2.05	Apr-23	7.46	119.54	309.86	17.86	19.34
May-23	0.63	110.31	295.32	14.32	1.70	May-23	4.49	71.95	192.70	11.10	12.03
Average	0.35	60.13	158.62	7.69	0.91	Average	3.16	50.59	133.48	7.69	8.33
Total	-	-	2062.04	100.00	11.86	Total	-	-	1735.27	100.00	108.29

Q is discharge, q is specific discharge, MCM is millions of cubic meters.

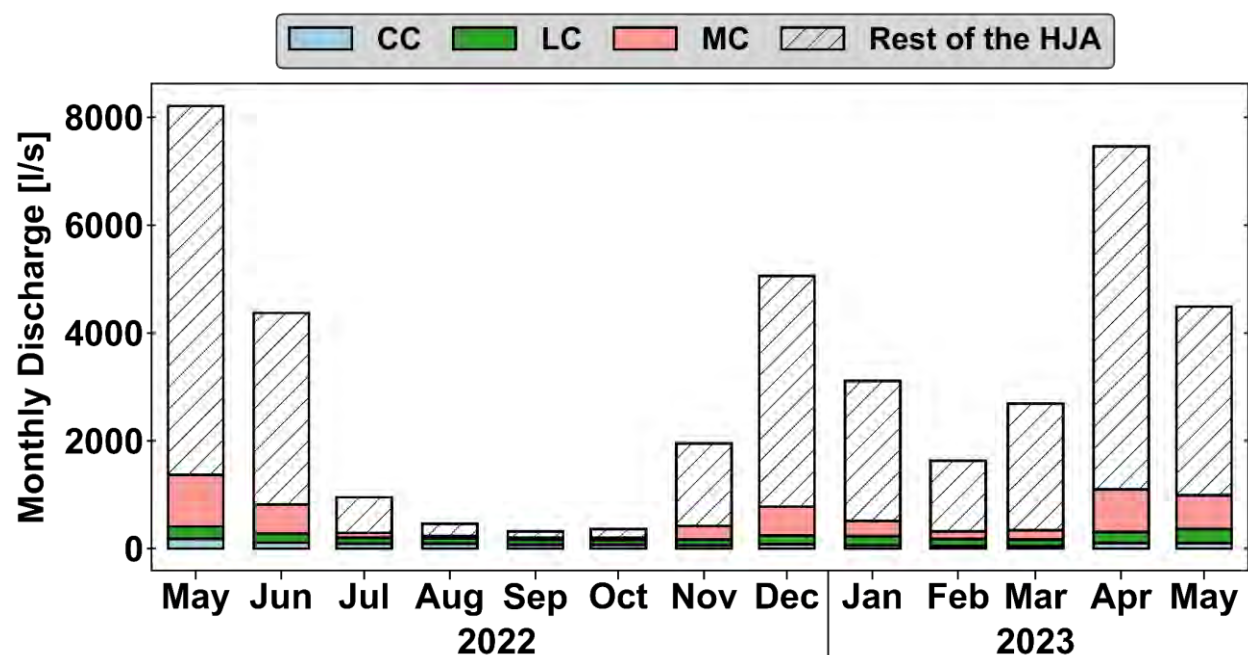
Appendix C. 4: Daily streamflow characteristics by gauging catchments derived from the flow duration curve analysis.

% Flow*	Cold Creek (0.69 km ²)		Longer Creek (2.74 km ²)		Mack Creek (5.75 km ²)		Lookout Creek at Gauging station (62.42 km ²)	
	Q	q	Q	q	Q	q	Q	q
	m ³ /s	l/s/km ²	m ³ /s	l/s/km ²	m ³ /s	l/s/km ²	m ³ /s	l/s/km ²
5	0.19	271.61	0.29	107.36	1.41	246.00	10.73	171.88
10	0.14	208.16	0.25	91.72	0.96	166.21	8.04	128.75
15	0.12	167.45	0.22	81.64	0.74	129.15	6.15	98.54
20	0.11	153.34	0.21	74.77	0.53	92.16	4.91	78.70
25	0.10	143.81	0.18	64.83	0.41	71.72	4.20	67.27
30	0.09	136.85	0.15	55.63	0.34	58.82	3.58	57.29
35	0.08	121.51	0.14	50.52	0.26	44.62	3.17	50.71
40	0.08	111.60	0.13	47.69	0.19	32.51	2.44	39.05
45	0.07	103.89	0.13	46.18	0.16	27.51	1.99	31.84
50	0.07	100.02	0.12	44.30	0.14	24.68	1.70	27.27
55	0.07	95.84	0.12	42.17	0.13	22.39	1.52	24.40
60	0.06	93.07	0.11	40.57	0.11	19.88	1.40	22.45
65	0.06	89.50	0.11	39.02	0.10	17.41	1.30	20.76
70	0.06	83.15	0.10	37.76	0.09	14.75	1.01	16.15
75	0.05	77.39	0.10	36.91	0.06	10.43	0.68	10.81
80	0.05	73.40	0.10	36.14	0.04	7.46	0.52	8.24
85	0.05	70.60	0.10	35.72	0.03	5.91	0.38	6.06
90	0.05	68.88	0.10	35.54	0.03	4.99	0.32	5.06

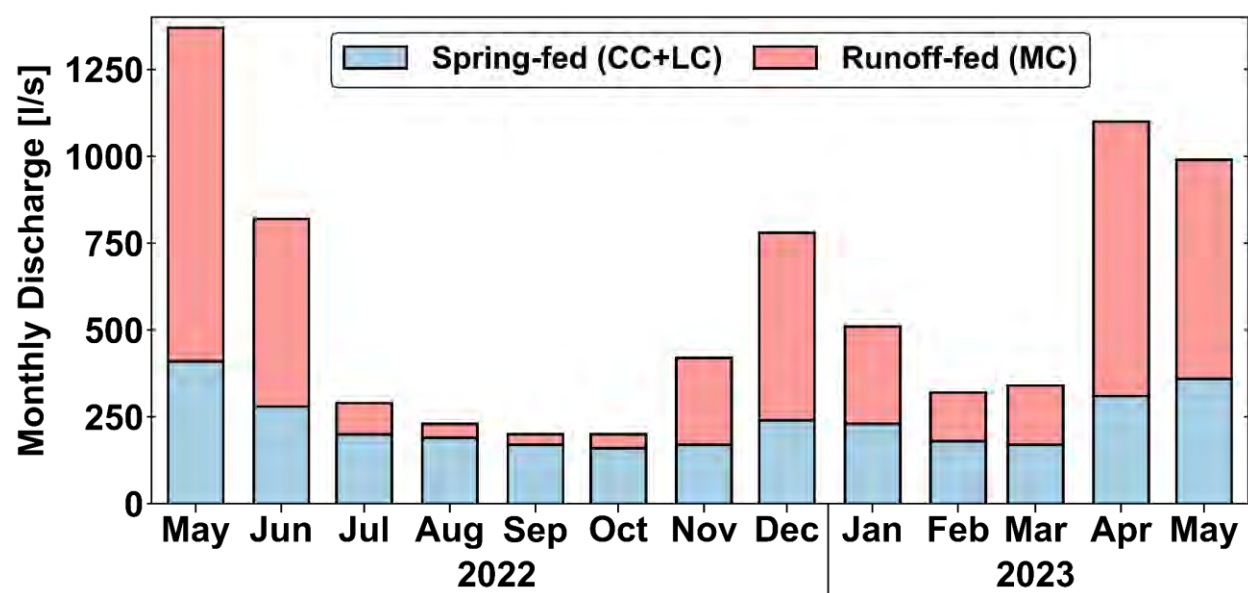
* % time flow equaled or exceeded ($X \geq Q$)



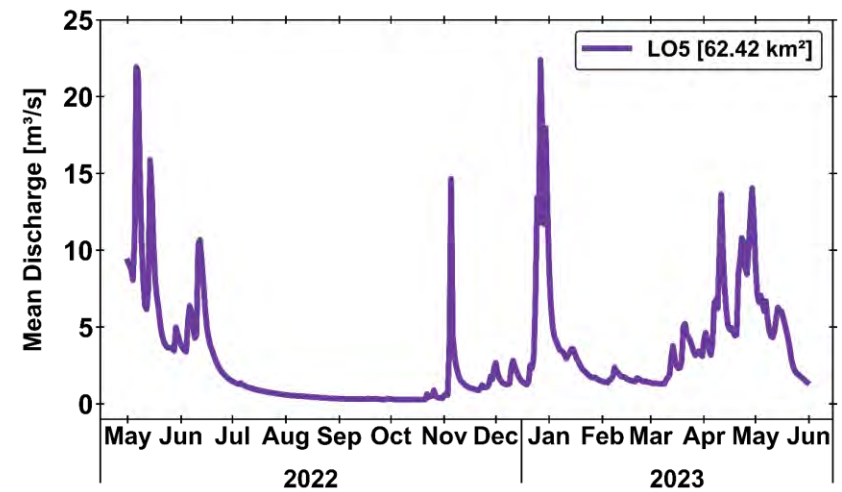
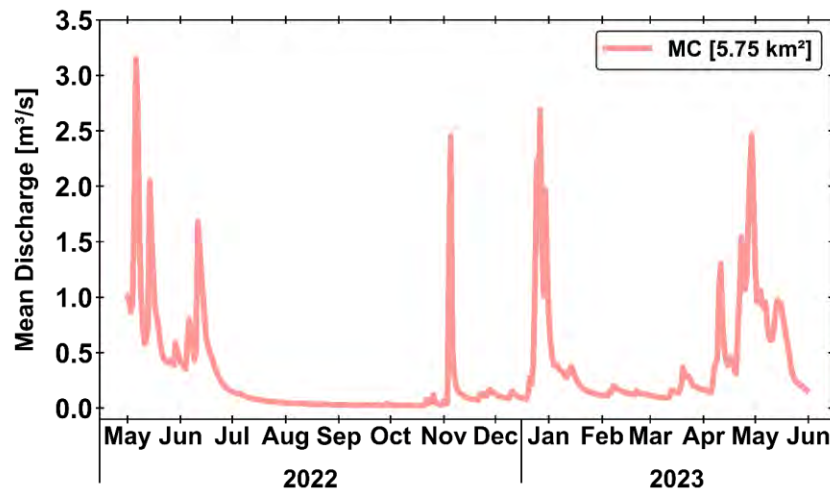
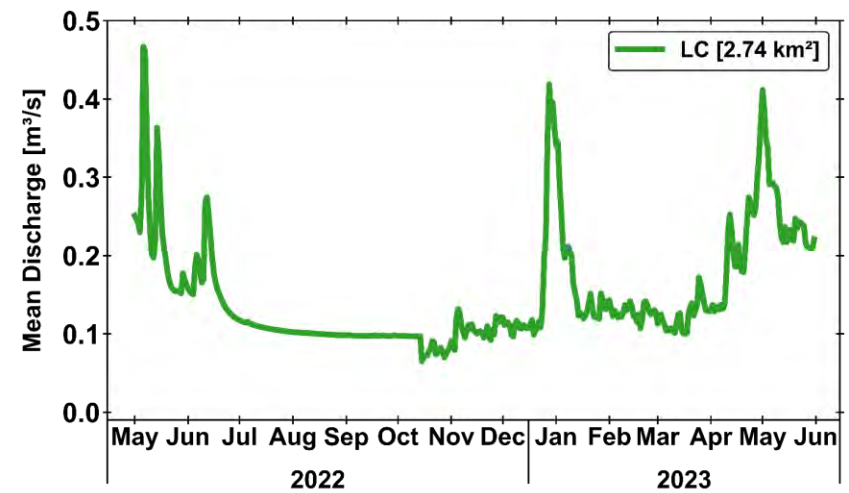
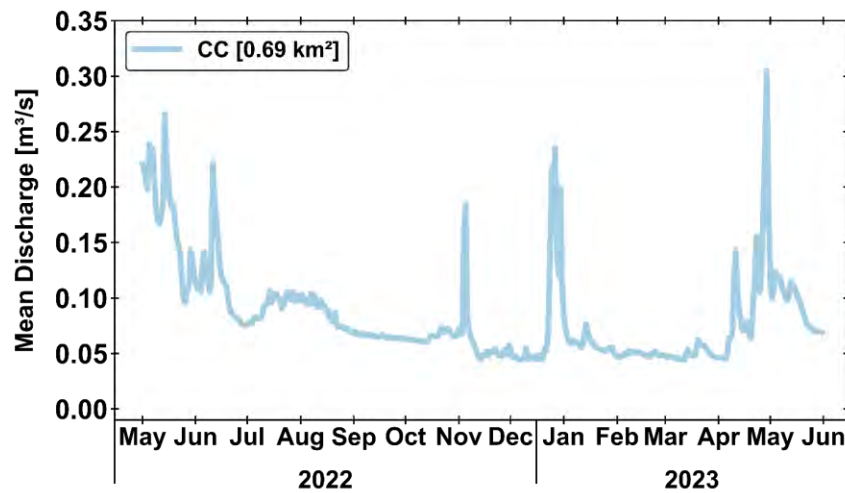
Appendix C. 5: Box plot (A) and monthly specific discharge distribution by study catchment (B).



Appendix C. 6: Relative monthly streamflow contribution (l/s) from Cold (CC), Longer (LC), and Mack (MC) Creeks to the Lookout Creek at the gauging station (LO5).



Appendix C. 7: Relative monthly streamflow (l/s) contribution from spring-fed (Cold and Longer Creeks, CC-LC) and runoff-fed streams (Mack Creek, MC) to the Lookout Creek at the gauging station (LO5).



Appendix C. 8: Daily streamflows distribution by gauging catchments for the study period.

Appendix D: Precipitation–Stream Chemistry Analysis

1.0 Materials and Methods

1.1 Study Area

The study was conducted at the H.J. Andrews Experimental Forest (hereafter Lookout Creek), a Long-Term Ecological Research (LTER) program site supported sponsored by the National Science Foundation. Lookout Creek catchment (Figure 1) is a fifth-order stream that drains 64 km² located in the Western Cascades of Oregon (44°12' N, 122°7' W). The Lookout Creek catchment is divided into three principal catchments McRae, Upper Lookout, and Lower Lookout Creek. Upper Lookout has four major tributaries that contribute to stream flow generation, from west to east: Nostoc, Mack, Longer, and Cold Creeks (see red outline Figure 1). The drainage pattern is dendritic, with high elevations dominated by first and second order streams that represent a significant portion of the drainage network length. The elevation gradient in Lookout Creek varies between 411 to 1,612 m with a mean slope of 24° (44.5%), and a mean elevation of 972 m.

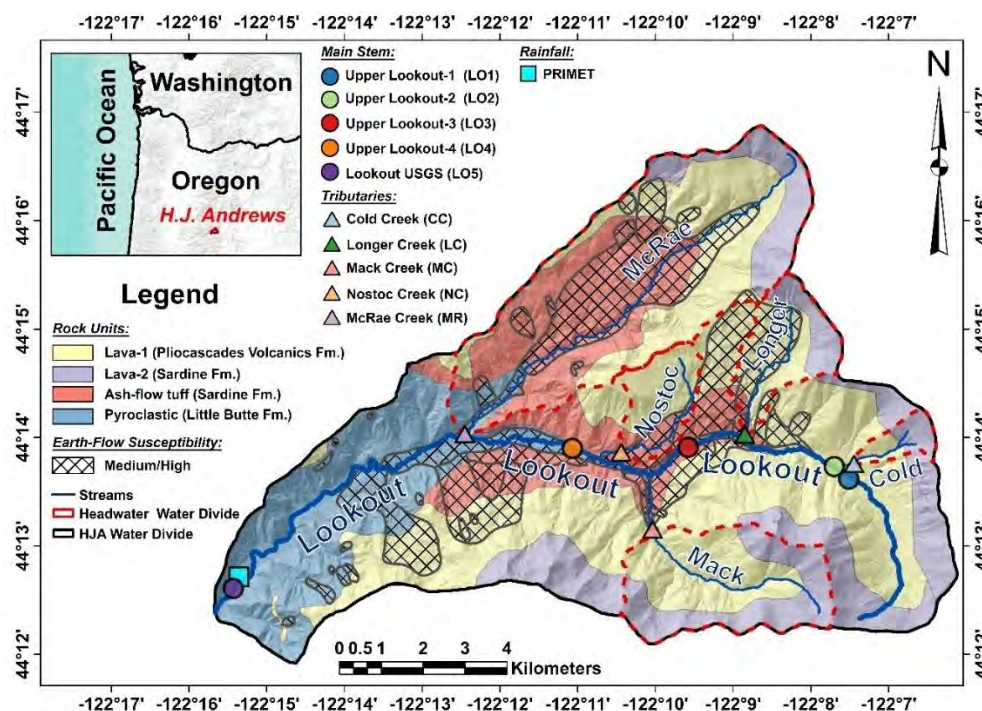


Figure 1. Location of Lookout Creek catchment in Oregon, indicating geology (lithology) and sample collection sites across the study catchments in the Lookout Creek.

1.1.1 Climatology

The climate is Mediterranean with wet winters and dry summers, and it is subjected to maritime influence, affected mainly by subtropical, Pacific, and Gulf of Alaska air masses depending upon the season (Greenland, 1993; Smith, 2017). Meteorological data in Lookout Creek can be constrained by a series of stations at different elevations, PRIMET at 430 m, H15MET at 909 m, and UPLMET 1295 m. Precipitation increases with elevation as does the proportion of snowfall (McKee & Bierlmaier, 1987). The temperature is affected by elevation, aspect, and topography across Lookout, with the average annual air temperature (water year: 1998-2022) is 8.8 °C, oscillating from 5.9 °C at 1295 m elevation to greater than 9.0 °C at 430 m elevation. Furthermore, daily maximum and minimum temperatures range from 40 °C in July to -20 °C in December. The mean annual precipitation for Lookout Creek (water year: 1996-2022) is 2300 mm, varying from 2194 mm at lower elevations to over 2697 mm at higher elevations (1295 m). Most precipitation is received in winter (December, January, February) with 42 % (969 mm) followed by spring (March, April, May) with 26% (603 mm) of the total annual precipitation. The snowpack depth varies depending on the meteorological conditions. For elevations between 400 – 800 m (transient snow zone), the snowpack (shallow deep) persists no more than 1–2 weeks. Above 800 m (seasonal snow zone), the snowpack (up to 3 m deep) could last up to 6 months (from November to April or June) (Bierlmaier & McKee, 1989; Jones & Perkins, 2010). Snow water equivalent (water year: 2003-2020) ranges from less than 20 mm (PRIMET) to more than 800 mm (UPLMET), with maximum median SWE peaks between 105 to 993 mm.

1.1.2 Geology and Geomorphology

The Lookout Creek catchment (Figure 1 and 2) is underlain by rocks of volcanic origin (extrusive and intrusive), which erupted in the late Oligocene to early Miocene period, and it is divided in three formations Pliocascade volcanics (Lava-1), Sardine (Lava-2 and Ash), and Little Butte (Pyro). These types of rocks include lava flows, ash flows, air falls tufts, cinder beds, and water-worked tuffaceous sediments. In general, Lookout Creek basin has been subjected to different phases of volcanism intermingled with periods dominated by weathering, erosion, and the reworking of volcanic material (Swanson & James, 1975).

At high elevation (> 900 m), the most dominant rock types are andesitic and basaltic lava flows, subaqueous lava flows, and fluvial and lacustrine silt, sand, and gravel. This fringe zone coincides

with the headwater area of upper McRae, and Upper Lookout Creek (Cold, Longer, and Mack Creek). At mid-elevations (600 to 900 m), there are exposure of andesitic and basaltic lava flows, ash flow tuffs, and flow rock capped stuff, which underlain in McRae and Upper Lookout Creek (Longer and Nostoc Creek). At lower elevations (< 600 m), tuffaceous silt and sand lacustrine sediments, basaltic flows, and pyroclastic flow is found from the confluence of between McRae and Upper Lookout Creek to the outlet of the Lookout Creek Catchment (Table 1). The chemical composition of basaltic and andesitic lava flow is mainly dominated by a significant percentage presence of the elements such as Fe, Mg, and Ca, and low presence of K and Na with low silica content (Nelson, 2017). Furthermore, it has zones of variable permeability, specifically at the top and bottom with vesicular and broken zones, and low permeability in mid-zones, considering a vertical profile with a defined thickness (Miller, 1999; Nelson, 2017).

In general terms, the Lookout Creek catchment is composed of moderately ($15\text{-}30^\circ$) slopes with a catchment orientation from southeast to southwest (main channel path). Some of the tributary catchments such as Cold, Longer, Mack, and Nostoc Creeks, located in the Upper Lookout Creek, exhibited average slopes that oscillate from 26 to 19% with different catchment orientations. The occurrence of deep-seated and massive earth movement (rotation slumps, earthflows, and others) in the Lookout Creek basin has generated anomalous drainage patterns, poorly drainage depressions, vegetations disturbed by ground movement, temporal blockage, or diversion of the main channel. These earth mass movements have a notorious presence in the main channel and adjacent areas of it. Longer Creek is the catchment with more exposure of these mass earth movements, specifically earthflow, followed by Nostoc and McRae Creeks. Furthermore, the main channel of the Lookout Creek is affected by these geomorphic processes, starting from the farthest point upstream at 885 m to lowest point downstream at 489 m where the susceptibility to debris flow increases (K. Johnson et al., 2023). Glacial erosion has taken place in the Lookout Creek catchment, creating U-shape valleys, exactly in the Upper Lookout (above 700 m) subbasin, pointing out north and northeast-facing ridges (Swanson & James, 1975). This landscape feature is present Cold and Longer Creek where headwater begins their path downstream, conditioned by these ridge orientations.

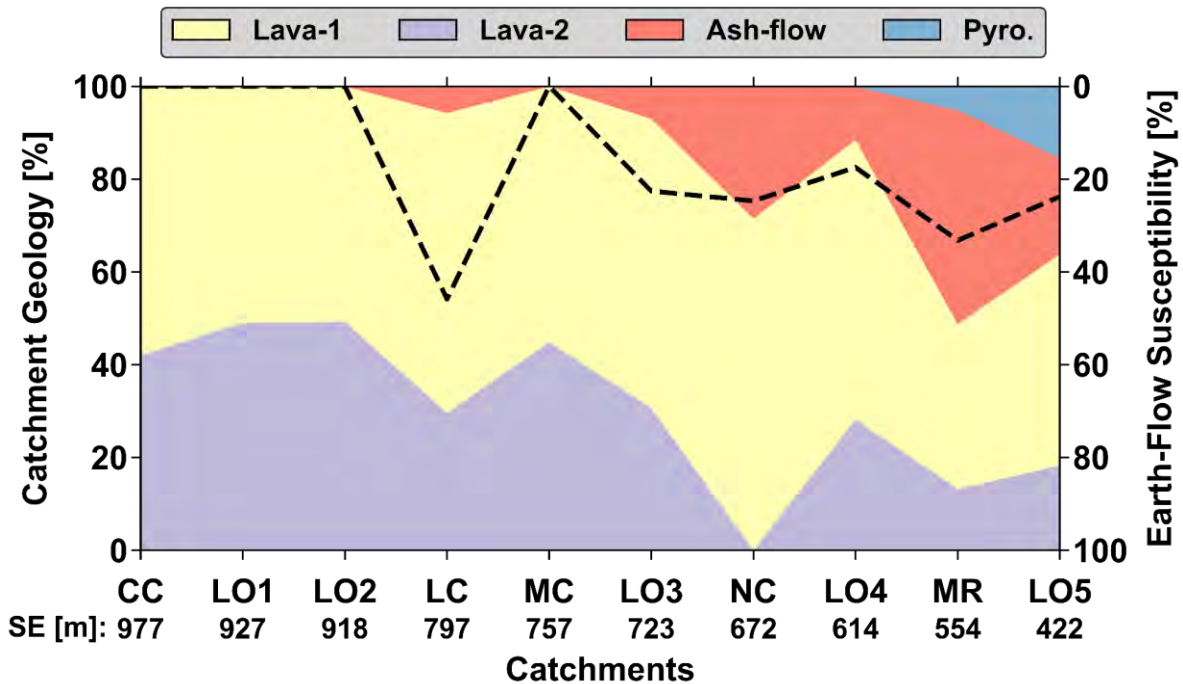


Figure 2. Percent of catchments areas with earth-flow susceptibility and areas composed of different geologic units. Tributaries include Cold (CC), Longer (LC), Mack (MC), Nostoc (NC), and McRae (MR), while sites along Lookout Creek (LO) range from upstream (1) to downstream (5). SE represents site elevation where samples were collected.

1.1.3 Vegetation

The vegetation of the Lookout Creek is mainly old-growth coniferous with a 400 – 500 year-old stand dominated by species such as Douglas-fir (*Pseudotsuga menziesii*), Western hemlock (*Tsuga heterophylla*), and Noble fir (*Abies procera*). Multiple disturbances have played a role in altering the landscape including: 1) logging operations between 1950 and 1995 incorporating a 25% clearcutting of the Lookout catchment (~16 km²), with an associated 136 km of forest roads constructed (Swanson et al., 1980). (2) flooding in 1964-65 and 1996 in concert with forestry activities resulted in significant mass wasting (Goodman et al., 2023). 3) wildfires have also impacted the catchment (Tepley et al., 2014). The most significant fires occurred around 1840's and 1900's, more recently the 2020 Holiday Farm Fire and the 2023 Lookout Fire affected large areas of the basin.

1.1.4 Hydrography

The seasonal streamflow distribution of Lookout Creek is typical of a transient snow (mixed rain-snow) dominated system with high flows in both winter and late spring. The annual median streamflow (water year: 1950-2022) at the Lookout Creek at the Gauging station (No.

14161500) is 3.36 m³/s with an average annual runoff of 1728 mm. Monthly average streamflow ranges from 0.40 m³/s to 6.50 m³/s. Discharge is highest in winter (mean= 5.96 m³/s) and lowest in summer (mean=0.59 m³/s). Winter flows coincide with the maximum precipitation events (November – January), and late spring/early summer flows are related to snowpack melting as air temperatures increase as the season progresses.

1.2 Fields Methods

To evaluate the hydrochemical interactions and estimate the relative streamflow contribution of the study catchments, we established 10 sampling sites (Table 1) in the Lookout Creek stream network based on its drainage area, precipitation regime, and streamflow contribution (Figure 1). Five sites were assigned to tributaries located in the Upper Lookout and McRae Creek. These tributaries were Cold (CC), Longer (LC), Mack (MC), Nostoc (NC), and McRae (MR) Creek. The drainage areas of these catchments vary from 0.69 to 15.6 km² with a catchment mean elevation between 913 and 1297 m. Five additional sampling sites were established in the main stem of the Lookout Creek (LO1, LO2, LO3, LO4, LO5). The aim of this design is to evaluate the streamflow contribution from the defined headwater streams, downstream in the main channel. Likewise, the precipitation isotopic signature was analyzed from the meteorological station PRIMET (430 m).

Grab (10) and precipitation (1) samples were weekly collected in a timeframe of 12 months (May 2022-May 2023). The collection sample campaign resulted in 21 composite precipitation samples and 277 grab stream samples. Two stream water samples were collected and filtered (0.45 µm nylon filter) into a 60 ml Nalgene screw top bottle by site. One sample was acidified with nitric acid for cation preservation and the other one remained non acidified for anion analysis. Stream samples were collected at the middle of the stream during low flow conditions and within a wading distance from banks during high flow conditions. On the other hand, precipitation samples were collected in a Stratus Precision Rain Gauge (Stratus, US) installed at PRIMET.

1.3 Statistical Methods

We were interested in the arithmetic and volume weighted-average, standard deviation, standard error, and coefficient of variation from the solute concentrations (cations and anions) of the grab (stream) and precipitation samples in the study period. All statistical analyses were done

in Python version 3.9.12, using NumPy and pandas packages (Harris et al., 2020; The pandas development team, 2023).

We fit a power-law relationship to evaluate chemostatic and chemodynamic behavior through the slope of this function between the interest solute concentrations and daily discharge, using NumPy package (Harris et al., 2020). We applied an PCA (Principal Component Analysis, multivariate dimensionality technique) to identify and quantify which water sources or catchments (end-members) contributed most to the variability in the data set, using `sklearn.decomposition.PCA` package (Pedregosa et al., 2012).

Table 1. LiDAR derived topographic characteristics, lithology, and available streamflow record of the study catchments.

Catchment	Da	Max. Elev.	Min. Elev.	WME	Mean Slope	Dominant Lithology*			Mass Movement Presence	Available Streamflow Record	
	km²	m	m	m	° [%]	% of occupied area			Type	Water years	
Tributaries	CC	0.69	1570	977	1297	27 [51]	Lava-1 [42%]	[58%], Lava-2	-	2 [2021-2023]	
	LC	2.74	1601	797	1178	23 [42]	Lava-1 [30%]	[62%], Lava-2	Earthflow [46%]	1 [2022-2023]	
	MC	5.75	1619	757	1197	28 [53]	Lava-1 [45%]	[55%], Lava-2	Earthflow, shallow soil, headwall scarp	28 [1996-2023]	
	NC	1.96	1153	672	913	19 [34]	Lava-1 [71%], Ash [29%]			Earthflow [25%], shallow soil, headwall scarp	-
	MR	15.58	1632	554	984	22 [40]	Ash [46%], Lava-1 [36%]			Earthflow [33%], shallow soil	-
Main Stem	LO1	5.53	1620	927	1257	24 [44]	Lava-1 [49%]	[51%], Lava-2	-	-	
	LO2	6.32	1620	918	1258	25 [46]	Lava-1 [49%]	[51%], Lava-2	-	-	
	LO3	15.63	1620	723	1170	24 [44]	Lava-1 [62%], Ash [31%]			Earthflow [23%], shallow soil	-
	LO4	30.67	1620	614	1106	25 [46]	Lava-1 [28%]	[60%], Lava-2	Earthflow [17%], shallow soil	-	
	LO5	62.42	1632	422	979	25 [46]	Lava-1 [18%]	[46%], Lava-2	Earthflow [24%], shallow soil	74 [1950-2023]	

Da: drainage area; Max Elev: maximum elevation; Min Elev: minimum elevation; WME: catchment mean elevation.

LiDAR information obtained from a raster file created by *HJ Andrews Elevation Surfaces* (2023)

* Dominant lithology information obtained from a vector file created by Swanson (2005).

1.4 Precipitation-Streamflow Description

To assess the degree of similarity or deviation (whether above or below the average) of precipitation, snow water equivalent, and discharge (Andrews Forest LTER Site et al., 2019; S. L. Johnson et al., 2020) between the study period (May 2022-2023) and long-term record of the HJ Andrews; monthly and annual precipitation (1995-2022) data was calculated from the meteorological stations PRIMET (430 m) and UPLMET (1295 m). Likewise, the median peak of the snow water equivalent (SWE) across water years (1996-2023) from the meteorological station UPLMET (1295 m) was defined to compare the maximum daily SWE recorded during the study period indicating how much snow was received during that specific timeframe. Annual and monthly streamflow distributions were calculated from the long-term (1950–2022) record of the USGS Gauging station at Lookout Creek (No. 14161500, 62.42 Km²).

1.5 Precipitation-Stream Water Chemical Analysis

Grab and precipitation samples were analyzed for cations (Si^{4+} , Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+}) and anions (Cl^{-} and SO_4^{2-}) analytes using a Spectro ARCOS MultiView (AMETEK, Czech Republic) equipped with an optical emission spectrometer with true radial or axial observation of inductively coupled plasma (ICP-OES) and a Dionne Aquion Ion Chromatography (IC) System (ThermoFisher Scientific, US). Matrix-matched standards were used to generate linear calibration relationship and an external certified standard was used to assess accuracy in each run, giving results of $\pm 5\%$. Solutes were reported in mg/l (ppm) with weighted average (precipitation) and arithmetic average concentration (streams) presented with an overbar (e.g., $\overline{\text{Ca}^{2+}}$), distinguishing from individual solutes samples. In total 276 grab stream, 20 precipitation, and 10 duplicates samples were collected during the sampling campaign.

To evaluate which solute showed the maximum and minimum concentration during the study period and how it seasonally varied, the annual and seasonal weighted-average precipitation chemical signature was calculated. With reference to the stream chemistry, we evaluated the spatiotemporal chemical behavior, relative streamflow contribution, and individual concentrations for each study catchment, coupling with precipitation and soil water chemistry (i.e., WS 10 data exclusively used in the PCA analysis, from 9/16/2022 to 11/26/2022). The annual and seasonal weighted-average precipitation ($\overline{\text{Solute}}$) was calculated considering the (1) amount of precipitation

recorded in the rain gage between the last and current sample (Ppt_i), (2) chemical concentration of the analyzed solute ($Solute_i$), and (3) total precipitation ($\sum_{i=1}^n Ppt_i$):

$$\overline{Solute} = \frac{\sum_{i=1}^n Solute_i * Ppt_i}{\sum_{i=1}^n Ppt_i} \quad (14)$$

1.5.1 Concentration-Discharge Analysis

To evaluate flushing and dilution trends through chemostatic or chemodynamic behaviors, considering solute concentrations and discharge, we applied two statistical approaches in the gauged catchments. The first method assessed the susceptibility of solute concentration to changes in the discharge distribution (export pattern) based on the slope of a power-law relationship between the solute concentration (C) and discharge (Q) ($C = aQ^b$, where a and b are constants) (Godsey et al., 2009). A slope approaching zero (i.e., $b \sim 0$) is interpreted as a chemostatic behavior, implying that the catchment exhibits less solutes concentration variability (constant) as streamflow varies throughout time (high and low flows). On the contrary, when a slope is not equal to zero (i.e., $b \neq 0$), is defined as a chemodynamic behavior (flushing or dilution) of the system, suggesting that solute concentration is sensitive to changes in discharge. The second approach considers the ratio between the solute concentration (Cv_c) and discharge (Cv_Q) coefficient of variation (regime), where chemostatic behavior was related with a $Cv_c/Cv_Q < 0.5$ and chemodynamic behavior was associated with a $Cv_c/Cv_Q \geq 0.5$ (Cartwright, 2020; Musolff et al., 2015; Sullivan et al., 2019; Thompson et al., 2011).

We assessed the total dissolved load and yield for each analyzed solute across the gauged catchments following the methodology described by Biedenharn et al. (2000) and Nash (1994), highlighting which solute had the most significant loading during the analyzed study period. A solute rating curve ($Q_s = aQ^b$, where a and b are constants; Q_s and Q are solute load [ton/days] and discharge [m^3/s]) was generated between discharge and solute concentration to obtain solute loads associated with each individual daily flows. Consequently, a magnitude-frequency analysis was performed to illustrate the relative amounts of transported load by various range of flows.

1.5.2 End-Member Mixing Analysis (Hydrograph Separation based on PCA)

To reveal the dominant underlying geology in each study catchment and evaluate the relative streamflow contribution of upstream tributaries and water sources, we used two

approaches. The first method, molar ratios, were used to investigate clustering behavior between catchments to identify potential water sources, and to understand how solute concentration ratios were conditioned by the underlying geology features in each system (Stewart et al., 2022). To fulfill this goal, we applied an Na-normalized elemental molar ratios (Ca/Na, Mg/Na, K/Na, Cl/Na, SO₄/Na) to remove the changes in absolute concentration due to dilution and evaporation process, correcting molar ratios by their respective charges, following the methodology stated by Gaillardet et al. (1999) and Sun et al. (2014).

We also used multivariate analysis, specifically Principal Component Analysis (PCA), following the procedures described by Christophersen and Hooper (1992). This approach enables to project the stream water observations in an orthogonal space (mixing space) identifying unknown potential end-members, circumscribing the data. Six solutes (Si⁴⁺, Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻, and SO₄²⁻) were included in the analysis due to their detectable levels and assuming they were conservatively mixed. All stream water chemistry samples were subjected to an outlier removal (compromised samples due to field collection or laboratory procedures), considering a ± 2.0 standard deviation units (Bush et al., 2023), to avoid discrepancy in the results. We eliminated 14% (38) of samples of the total dataset (276). Consequently, cleaned data was scaled to a standard score (mean= 0 and STD= 1) to reduce the weight effect between high and low sample concentrations. Finally, the PCA was performed, generating the resulting eigenvectors and eigenvalues (loading scores) in each defined cluster. The numbers of PCs retained in each cluster, was examined by the eigenvectors displayed in a scree plot (PCs above the elbow) as described by Bush et al. (2023) and Johnson et al. (2023). In total, 4 clusters were established to assess the streamflow contribution of tributaries (CC, LC, NC, and MR) over the main stem catchments, considering the closet upstream and downstream sites in the main stem of the Lookout Creek (LO1–LO4), precipitation inputs (PRIMET), and soil water chemistry (WS10). Precipitation chemistry samples were seasonally weighted from a total of 21 samples (no outlier removal was applied) collected throughout the study period, introducing four groups of solute concentrations in the PCA. We also included soil water chemistry data (17 samples after outlier removal) collected between 10/3/2002 and 11/26/2002 from WS 10 (McGuire, 2020). This addition was motivated by the absence of recent water chemistry information from this end-member and the enhanced ability to constrain the stream chemistry samples within the mixing spaces.

End-members criteria selection in each defined mixing space, was established considering their capacity to explain the mixture of the stream water samples, enclosing stream water observations in a line (two end-members) or in a triangle (three end-members) represented in an orthogonal plane. Finally, to determine the relative streamflow contribution using the defined end-members and catchment of interest (target values) in each mixing space, hydrograph separation based on the principal components one (PC1) and two (PC2) as tracers (eigenvalues), was performed applying the following equation, considering two and three end-members: +

$$f_1 = \frac{PC_{stream}^1 - PC_2^1}{PC_1^1 - PC_2^1} \quad (15)$$

$$f_2 = 1 - f_1 \quad (16)$$

$$f_1 = \frac{[(PC_{stream}^1 - PC_3^1)(PC_2^2 - PC_3^2)] - [(PC_2^1 - PC_3^1)(PC_{stream}^2 - PC_3^2)]}{[(PC_1^1 - PC_3^1)(PC_2^2 - PC_3^2)] - [(PC_2^1 - PC_3^1)(PC_1^2 - PC_3^2)]} \quad (17)$$

$$f_2 = \left[\left(\frac{PC_{stream}^1 - PC_3^1}{PC_2^1 - PC_3^1} \right) - \left(\frac{PC_1^1 - PC_3^1}{PC_2^1 - PC_3^1} \right) \right] * f_1 \quad (18)$$

$$f_3 = 1 - f_1 - f_2 \quad (19)$$

where f_x is the streamflow flow proportion of the end-member x to target component. PC_x^i is the eigenvalue (loading score) of the principal component i of end member x .

There were some instances in which the target component lied outside of the mixing domain defined by the end-members, resulting in a negative fraction of the streamflow contribution. In this case, the negative fraction was adjusted slightly positive greater than zero, implying that the contribution was completely dominated by a single end-member.

Tracer selections were considered based on: (1) the solutes with higher loading score resulting from the percent of explained variance of the first and second principal components (PCs, $+>>0$ or $-<<0$), and (2) consistency with conservative mixing hypothesis (collinearity behavior, non-uptake, or release in the system) between solutes was analyzed through bivariate scatter plot, considering a $R^2 > 0.5$ with p-values < 0.01 .

2. Results

2.1 Precipitation-Streamflow Description

Between May 2022–2023, the total annual precipitation at PRIMET (isotopic rain sampler) was 21% below the long-term average, receiving 1785 mm, compared to the average 2265 mm (1995–2022). Similarly, at the higher elevation UPLMET station was also below the long-term average data, receiving 2619 mm, compared to the average 2802 mm (1995–2022). This water deficit was mainly observed between the months December 2022 and May 2023, particularly at the lower elevation (Figure 3). Interestingly, when comparing precipitation inputs from May 2022 to 2023 there was an 87% increase (Figure 3). The median peak SWE during the water year 2023 was 1570 mm at the UPLMET station, which is the highest on record since at least the water year 1996. Furthermore, the previous water year (2022) recorded median peak SWE of 800 mm. Observations showed that SWE at this site has varied greatly with annual median peaks ranging 240 (2005) to 1570 (2023) mm, with a median peak SWE of 920 mm, over this 27 year period.

Similar to the precipitation, annual streamflow in the Lookout Creek (LO5) over the study period was also below the long-term (1950–2022) with a value of 3.12 m³/s compared to 3.43 m³/s, respectively. April through August were all months where the average stream discharge exceeded the long-term record (Figure 4). Seasonally, spring exhibited the highest average flows compared to the seasonal long-term (March–June, +70%), while winter showed the lowest values (December–March, -57%). On the other hand, winter flow (Nov-Feb) was lower than the long-term averages. High elevation snow melt that occurred during late spring likely triggered the high flows observed in May and June.

The average streamflow (Figure 5) for the gauged tributaries to Lookout Creek (CC, LC, and MC) varied between 0.08 and 0.35 m³/s with distinct monthly streamflow distribution. Like Lookout Creek (LO5), Mack Creek (MC) displayed similar patterns with maximum monthly streamflow in May 2022 (0.96 m³/s in MC and 8.20 m³/s in LO5) and minimum streamflow in September 2022 (0.03 m³/s in MC and 0.32 m³/s in LO5). These monthly streamflow distribution for Mack Creek and Lookout Creek may be indicative of streams in the transient snow-rain dominated zone where high streamflow occurs during the fall and winter (November, December, and January) associated to heavy rains events and in the spring (April and May) associated to the peak of the snowmelt processes (Elsner et al., 2010). In Cold and Longer Creek monthly

streamflow varies less than in Mack Creek and Lookout Creek at the gauging station hinting at relatively higher ground water contributions. Here cold Creek showed a highest discharge in May 2022 ($0.18 \text{ m}^3/\text{s}$) and lowest in February 2023 ($0.05 \text{ m}^3/\text{s}$), while in Longer Creek monthly streamflow was highest in May 2023 ($0.23 \text{ m}^3/\text{s}$) and lowest in October 2023 ($0.09 \text{ m}^3/\text{s}$).

Specific discharge was highest in Cold Creek with an annual mean specific discharge of 122 l/s/km^2 . Mack, Longer, and Lookout at the gauging station had an annual mean specific discharge between 50.6 and of 60.1 l/s/km^2 . Cold Creek had the highest total annual runoff (4197 mm), most of which was recorded in May 2022 (680 mm). The total runoff was lower in Mack Creek (2062 mm), Longer Creek (1870 mm), and Lookout Creek at the gauging station (1735 mm).

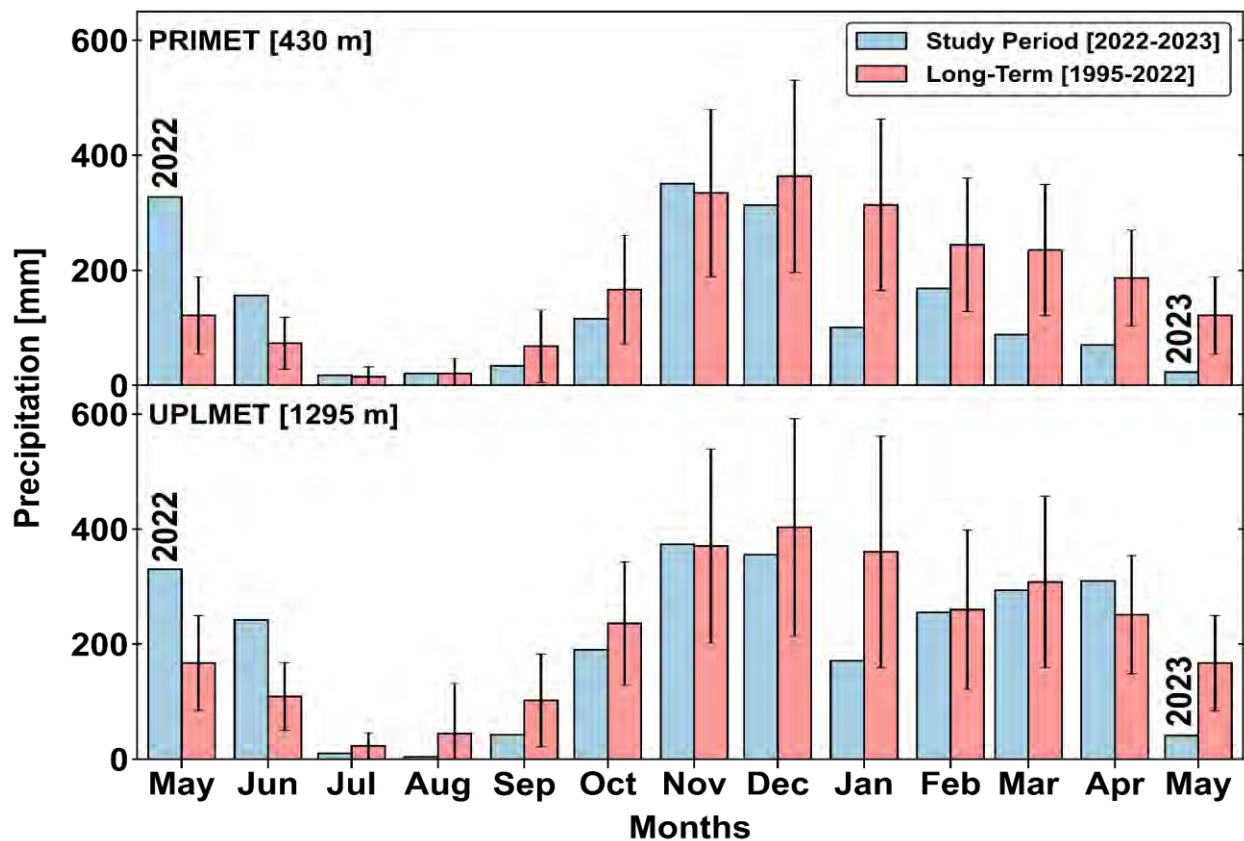


Figure 3. Monthly precipitation (A: PRIMET and UPLMET) distribution from the long-term data and study period. The error bars indicate the monthly standard deviation.

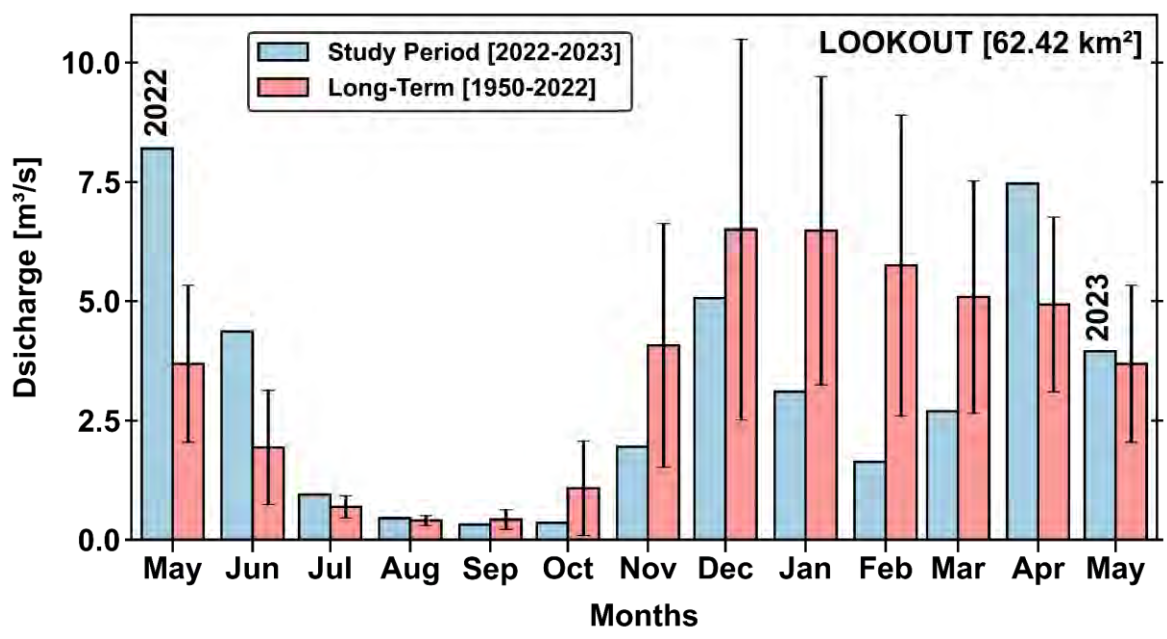


Figure 4. Monthly discharge (Lookout at the gauging station No. 14161500) distribution from the long-term data and study period. The error bars indicate the monthly standard deviation.

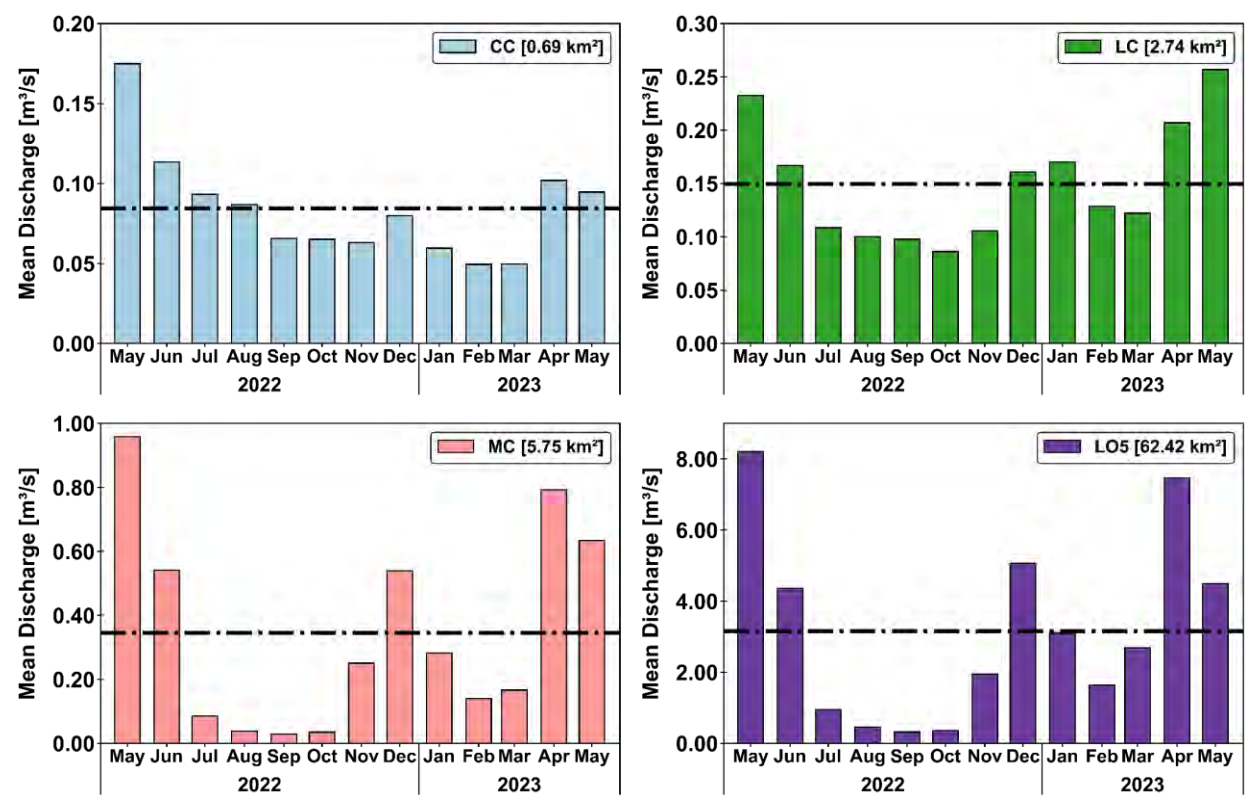


Figure 5. Streamflow distribution by gauged catchment (Cold, Longer, Mack Creeks, and Lookout Creek at Gauging station) during the study period (May 2022- May 2023).

2.2 Precipitation Chemistry

The weighted average precipitation chemistry was characterized by low solute concentrations (Figure 6A) throughout the study period, where $\text{Cl} > \text{SO}_4 > \text{Na} > \text{Ca} > \text{K} > \text{Mg} > \text{Si}$. Maximum individual precipitation sample concentration oscillated from 2.62 (Cl) to 0.01 (K and Mg) mg/l (Table 2). Compared to the long-term precipitation chemistry record at PRIMET where $\text{Cl} > \text{Na} > \text{Ca} > \text{K} = \text{SO}_4 > \text{Mg} > \text{Si}$ (Figure 6B), the study period showed similar weighted average cations concentrations (Table 2) compared to the long-term data, excluding Na, which was slightly lower than the long-term data. Conversely, anions concentration during the study period, were higher by 2 and almost 10 times for Cl and SO_4 than the long-term data. This discrepancy in the anions may be attributed to the burning of biomass related to the increased forest fire activity around the study area, specifically the Holiday Farm Fire in 2020. The strongest seasonal signal observed in the weighted precipitation chemistry was elevated anion and cation concentrations during the summer months (Figure 6A and 6B; particularly for the anions), while the winter season concentrations from the study deviated from the long-term pattern.

When we examined the solute concentration for each individual precipitation samples we observed no evident pattern across seasons, as illustrated by precipitation events with low and high concentrations occurring in the same season. Interestingly, Na and Cl showed a substantial variability (spread) between precipitation events (Figure 7), with higher concentrations of Na observed in fall and winter precipitation events, while Cl show elevated concentration events occurred in all season Ca, K and SO_4 showed moderate variability between precipitation events, with elevated concentration Ca and K observed most frequently in spring and summer, while SO_4 elevated concentrations occurred most in spring.

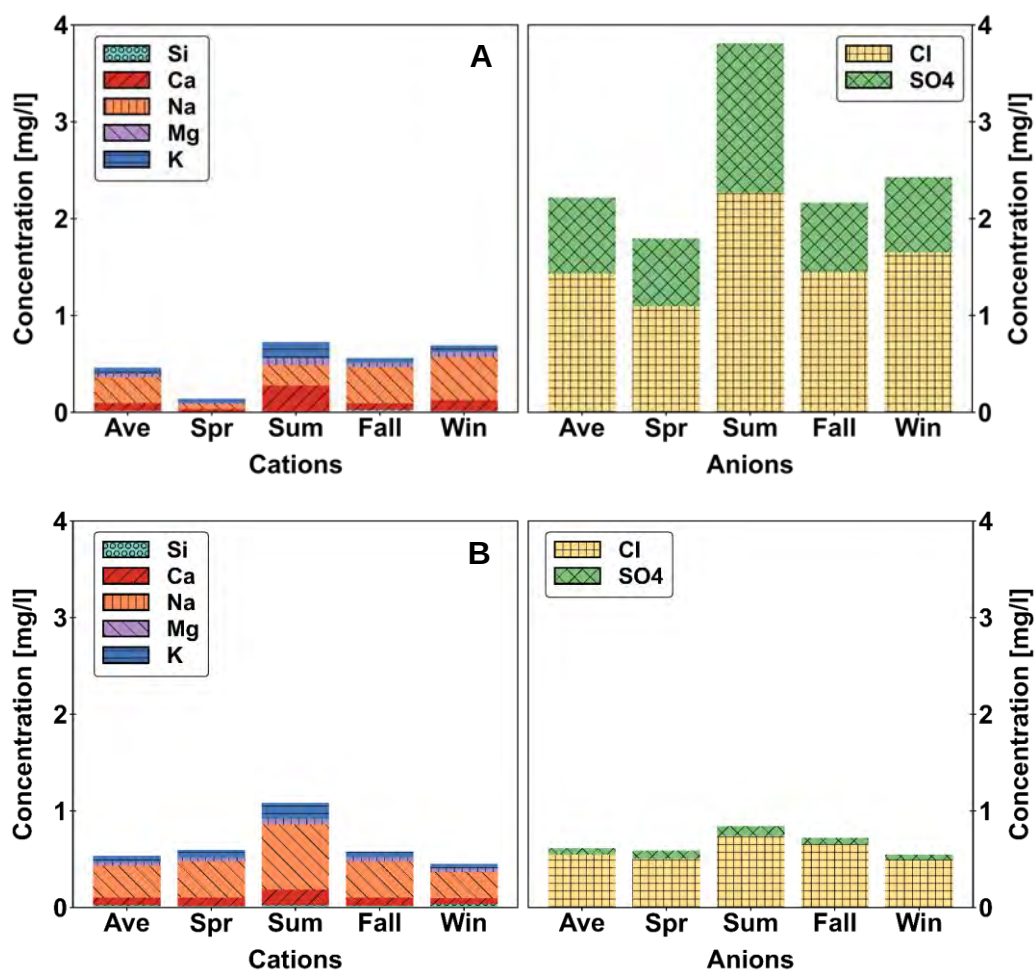


Figure 6. Weighted average solute concentrations (cations and anions) of the (A) study period and (B) long-term data (1978-2018) at PRIMET. Ave: weighted average, Spr: spring, Sum: summer, and Win: Winter.

Table 2. Weighted average precipitation solute concentration for the study period and long-term data from PRIMET (430 m).

Season		$\overline{\text{Ca}} \pm \sigma$	$\overline{\text{Mg}} \pm \sigma$	$\overline{\text{Na}} \pm \sigma$	$\overline{\text{K}} \pm \sigma$	$\overline{\text{Si}} \pm \sigma$	$\overline{\text{Cl}} \pm \sigma$	$\overline{\text{SO}_4} \pm \sigma$
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Study Period	Spring	0.03 ± 0.09	0.01 ± 0.04	0.05 ± 0.34	0.04 ± 0.06	<0.01 ± 0.02	1.10 ± 0.72	0.70 ± 0.45
	Summer	0.27 ± 0.21	0.07 ± 0.04	0.21 ± 0.26	0.17 ± 0.11	<0.01 ± 0.02	2.27 ± 1.07	1.54 ± 0.90
	Fall	0.07 ± 0.08	0.05 ± 0.03	0.37 ± 0.28	0.05 ± 0.06	0.03 ± 0.01	1.45 ± 0.63	0.71 ± 0.45
	Winter	0.12 ± 0.09	0.06 ± 0.03	0.44 ± 0.31	0.06 ± 0.06	0.01 ± 0.02	1.65 ± 0.67	0.78 ± 0.45
	Weigh. Ave.	0.08 ± 0.08	0.04 ± 0.03	0.27 ± 0.26	0.06 ± 0.06	0.01 ± 0.02	1.43 ± 0.63	0.78 ± 0.45
	Max - Min	1.55 - 0.00	0.34 - 0.00	1.01 - 0.02	1.22 - 0.01	0.42 - 0.01	4.70 - 1.05	3.43 - 0.60
Long Term	Spring	0.09 ± 0.09	0.04 ± 0.03	0.37 ± 0.29	0.08 ± 0.08	0.01 ± 0.06	0.5 ± 0.64	0.09 ± 0.06
	Summer	0.16 ± 0.12	0.05 ± 0.03	0.67 ± 0.45	0.17 ± 0.13	0.02 ± 0.06	0.74 ± 0.67	0.11 ± 0.07
	Fall	0.08 ± 0.09	0.04 ± 0.03	0.38 ± 0.29	0.06 ± 0.08	0.02 ± 0.06	0.65 ± 0.65	0.07 ± 0.06
	Winter	0.06 ± 0.09	0.04 ± 0.03	0.27 ± 0.3	0.05 ± 0.08	0.04 ± 0.06	0.49 ± 0.64	0.05 ± 0.06
	Weigh. Ave.	0.07 ± 0.08	0.04 ± 0.03	0.33 ± 0.29	0.06 ± 0.08	0.03 ± 0.06	0.55 ± 0.64	0.06 ± 0.06
	Max - Min	2.91 – 0.00	1.68 – 0.00	11.45 - 0.01	3.13 – 0.00	0.43 - 0.00	25.85 – 0.00	1.12 – 0.00

Max - min represents individual samples. Long-term data spans from 1968 to 2021.

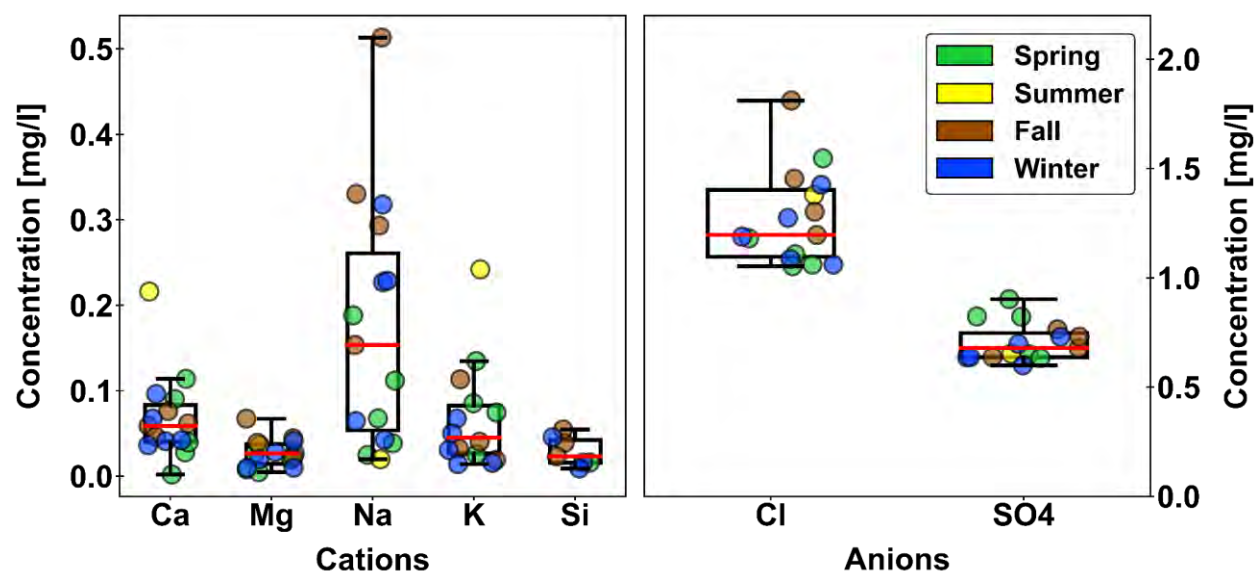


Figure 7. Box plot distribution of the precipitation chemistry (PRIMET) for the study period. Each scatter point represents an individual precipitation event. Significant outliers (individual samples) were intentionally omitted to prevent any distortion or reduction in the size of each box plot.

2.3 Stream Water Chemistry

2.3.1 Spatial Analysis

To understand the spatial trends along the main stem of Lookout Creek (LO1-LO5), we must first explore the chemical trends in the tributaries (Figure 9). Overall, starting from the most upstream (CC, 977 m) tributary to the most downstream (MR, 554 m) tributary catchment, the total concentration of cations measured generally decreased, with the exception of Mack Creek (MC, 757 m), which had among the lowest cation concentrations (Table 3, Figure 8). Spatial patterns were less evident in the anion concentrations, with concentrations differing by very little of Cl and SO₄ among the catchments (Table 3, Figure 8). In general, waters originating from Cold (CC, 977 m) and Longer (LC, 797 m) Creeks had K concentrations that were double that of the other tributaries. Downstream at Mack Creek (MC, 757 m) had among the lowest Ca and Mg concentrations, while Nostoc (NC, 672 m) had the highest average Na concentration (Table 3). Overall, these data hint at potential differences in mineralogy of the underlying bedrock.

Along the main stem of the Lookout Creek (LO1-LO5) changes in water chemistry often reflected contributions of tributary catchments from upstream to downstream. For example, concentrations of all solutes increased from LO1 downstream to LO2, here the main known source of incoming solute contribution is from Cold Creek, which had some of the highest solute concentrations observed across the entire study area. Cation concentrations, specifically for Ca,

Na, and Si, then tended to decline downstream (LO2-LO4) until reaching the outlet (LO5, lowest catchment), where concentrations increased again. Unlike Cold Creek, the Longer Creek which had a similar chemical makeup did not have the same impact on the main stem solute concentrations (LO3), which may be due to over-all lower discharge from this tributary compared to Cold Creek. By the time the main stem arrives at sampling site LO4 inputs from both Mack and Nostoc tributaries, which have generally higher solute concentration than the main stem, has occurred with only a light impact on average solute concentrations, specifically Si, Na, Cl and SO₄. At outlet (LO5) solute concentrations increase causing the stream water to become a strong mixture of inputs from McRae Creek and upstream water (LO4).

Only two long-term monitoring sites exactly overlapped with our study, the tributary catchment Mack Creek (MC) and the main stem outlet (LO5), both showed similar solute concentrations to those observed in our study (Table 4). Likewise, the solute concentrations we measured for McRae (MR) were similar to those in the long-term record for three upstream experimental catchments (WS06–WS08).

Table 3. Arithmetic mean stream solute concentration (mg/l) by catchments for the study period.

	Site	$\overline{\text{Ca}} \pm \sigma$	$\overline{\text{Mg}} \pm \sigma$	$\overline{\text{Na}} \pm \sigma$	$\overline{\text{K}} \pm \sigma$	$\overline{\text{Si}} \pm \sigma$	$\overline{\text{Cl}} \pm \sigma$	$\overline{\text{SO}_4} \pm \sigma$
Tributaries	CC	5.4 ± 3.1	1.6 ± 0.4	1.9 ± 0.4	1.1 ± 0.3	6.3 ± 3.7	1.5 ± 0.1	0.8 ± 0.1
	LC	5.3 ± 2.2	1.7 ± 0.2	2.0 ± 0.3	0.9 ± 0.2	6.7 ± 4.0	1.5 ± 0.1	0.8 ± 0.1
	MC	3.3 ± 1.7	1.0 ± 0.2	1.7 ± 0.4	0.4 ± 0.1	5.3 ± 2.0	1.6 ± 0.1	1.0 ± 0.4
	NC	4.2 ± 0.9	1.2 ± 0.2	2.4 ± 0.5	0.5 ± 0.1	5.7 ± 3.7	1.5 ± 0.1	0.8 ± 0.0
	MR	4.0 ± 3.4	0.7 ± 0.1	2.2 ± 0.3	0.3 ± 0.1	5.2 ± 1.8	1.6 ± 0.1	0.8 ± 0.0
	Ave	4.5 ± 2.6	1.2 ± 0.5	2.0 ± 0.4	0.6 ± 0.3	5.8 ± 3.2	1.5 ± 0.1	0.9 ± 0.2
	Max - Min	21.3 - 1.2	2.1 - 0.4	3.2 - 0.9	1.4 - 0.2	12.0 - 0.4	2.1 - 1.2	3.0 - 0.7
Main Stem	LO1	3.2 ± 4.7	0.5 ± 0.1	1.2 ± 0.3	0.2 ± 0.1	3.7 ± 1.1	1.4 ± 0.1	0.8 ± 0.1
	LO2	4.2 ± 3.4	1.2 ± 0.5	1.6 ± 0.4	0.7 ± 0.3	5.8 ± 3.0	1.5 ± 0.2	0.9 ± 0.2
	LO3	3.0 ± 0.8	1.1 ± 0.3	1.6 ± 0.3	0.5 ± 0.1	4.3 ± 2.8	1.6 ± 0.1	0.9 ± 0.0
	LO4	2.9 ± 0.7	1.0 ± 0.3	1.6 ± 0.3	0.4 ± 0.1	4.7 ± 2.5	1.6 ± 0.1	1.0 ± 0.0
	LO5	3.8 ± 2.3	0.9 ± 0.2	2.0 ± 0.3	0.4 ± 0.1	5.2 ± 2.4	1.7 ± 0.3	1.0 ± 0.2
	Ave	3.5 ± 3.1	0.9 ± 0.4	1.6 ± 0.4	0.5 ± 0.3	4.8 ± 2.5	1.5 ± 0.2	0.9 ± 0.2
	Max - Min	20.4 - 0.9	1.8 - 0.3	2.8 - 0.8	1.2 - 0.1	11.7 - 0.4	3.3 - 1.2	2.2 - 0.7

Table 4. Flow-weighted Monthly average stream water solute concentration long-term record from the established experimental catchments (nine) of the HJ Andrews.

Site	$\overline{\text{Ca}} \pm \sigma$	$\overline{\text{Mg}} \pm \sigma$	$\overline{\text{Na}} \pm \sigma$	$\overline{\text{K}} \pm \sigma$	$\overline{\text{Si}} \pm \sigma$	$\overline{\text{Cl}} \pm \sigma$	$\overline{\text{SO}_4} \pm \sigma$
LOOK	3.1 ± 0.5	0.9 ± 0.2	2.1 ± 0.3	0.4 ± 0.1	7.9 ± 0.8	0.7 ± 0.2	0.1 ± 0.0
MACK	2.6 ± 0.5	0.9 ± 0.5	1.6 ± 0.3	0.4 ± 0.1	7.0 ± 1.1	0.7 ± 0.5	0.1 ± 0.0
WS01	4.9 ± 1.2	1.1 ± 0.3	2.8 ± 0.6	0.2 ± 0.1	9.3 ± 0.7	0.9 ± 0.6	0.2 ± 0.0
WS02	3.8 ± 0.7	0.9 ± 0.5	2.7 ± 0.6	0.4 ± 0.1	9.1 ± 0.7	0.9 ± 0.2	0.1 ± 0.0
WS06	4.1 ± 0.2	1.0 ± 0.1	2.2 ± 0.2	0.4 ± 0.1	8.5 ± 0.7	0.7 ± 0.2	0.1 ± 0.0
WS07	4.5 ± 0.8	1.2 ± 0.3	2.4 ± 0.3	0.6 ± 0.1	9.9 ± 1.4	0.6 ± 0.2	0.1 ± 0.0
WS08	3.7 ± 0.6	0.7 ± 0.4	3.3 ± 0.9	0.5 ± 0.1	8.2 ± 0.8	0.8 ± 0.5	0.1 ± 0.0
WS09	5.4 ± 1.4	1.6 ± 0.8	2.9 ± 0.7	0.2 ± 0.0	9.4 ± 1.2	1.4 ± 0.4	0.2 ± 0.1
WS10	5.1 ± 1.7	1.3 ± 0.7	2.8 ± 0.9	0.2 ± 0.1	9.0 ± 0.9	2.0 ± 1.6	0.2 ± 0.1
Average	4.2 ± 1.4	1.1 ± 0.6	2.6 ± 0.8	0.4 ± 0.2	8.7 ± 1.3	1.0 ± 0.8	0.1 ± 0.1
Max - Min	$10.3 - 0.8$	$13.0 - 0.4$	$5.4 - 0.5$	$1.2 - 0.1$	12.6 ± 4.2	$9.5 - 0.2$	$0.5 - 0.0$

Max - min represents flow-weighted monthly average. Long-term data (water year) spanned for each catchment as follows: LOOK (2005-2018), MACK (1981-2018), WS01 (2003-2018), WS02 (1981-2018), WS06 (1972-2018), WS07 (1972-2018), WS08 (1972-2018), WS09 (1968-2018), and WS10 (1969-2018).

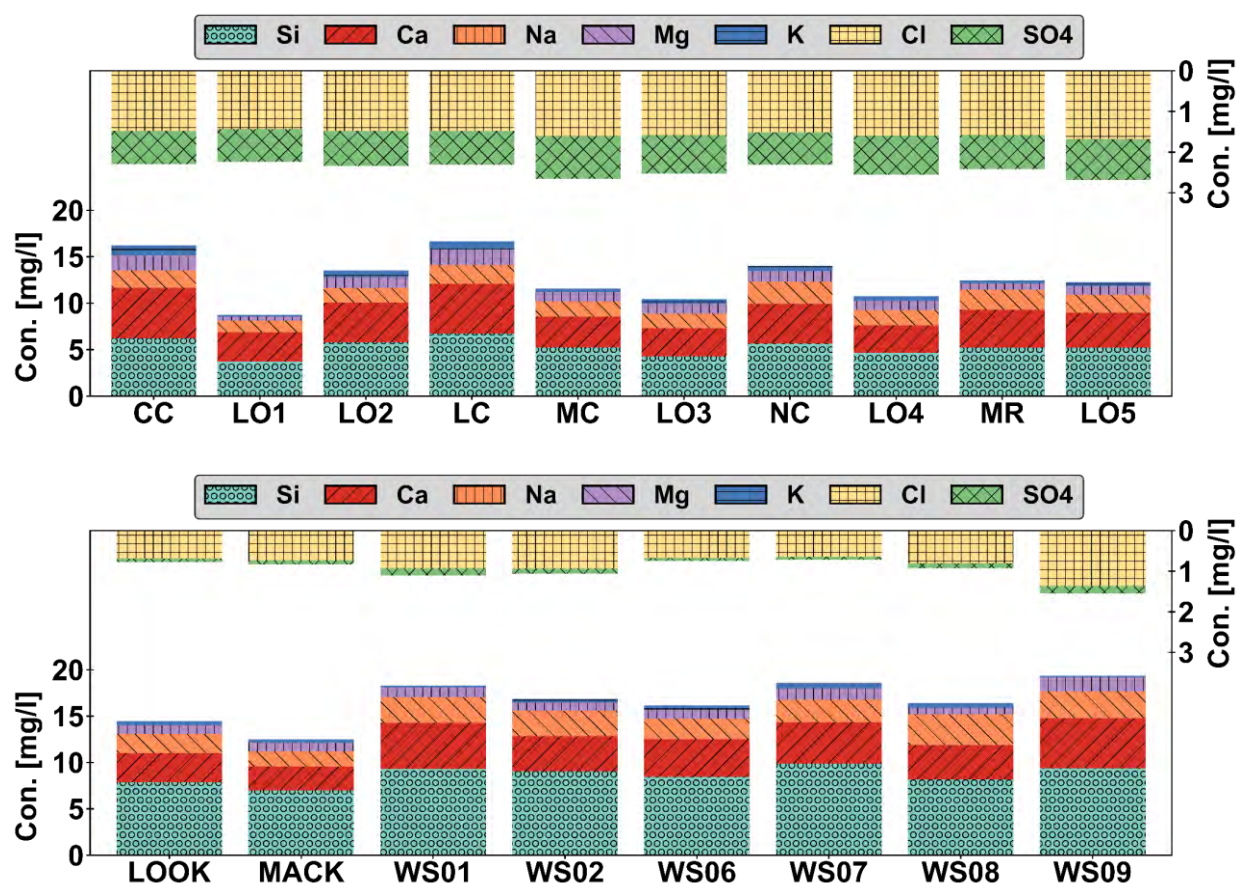
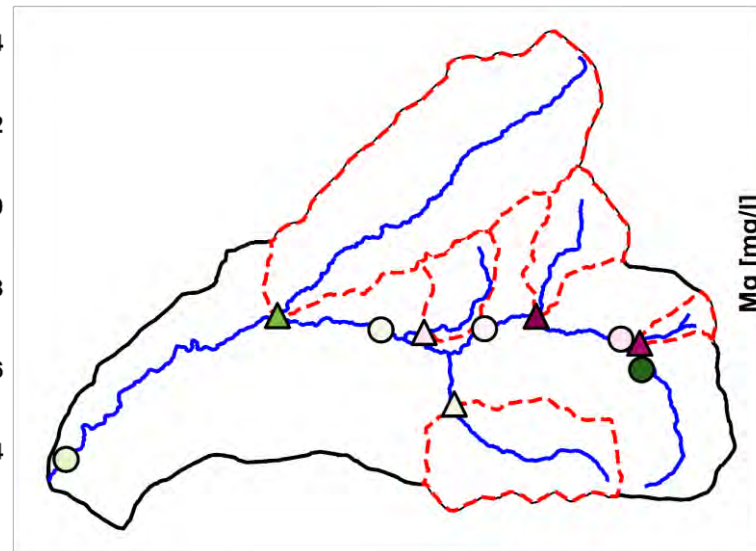
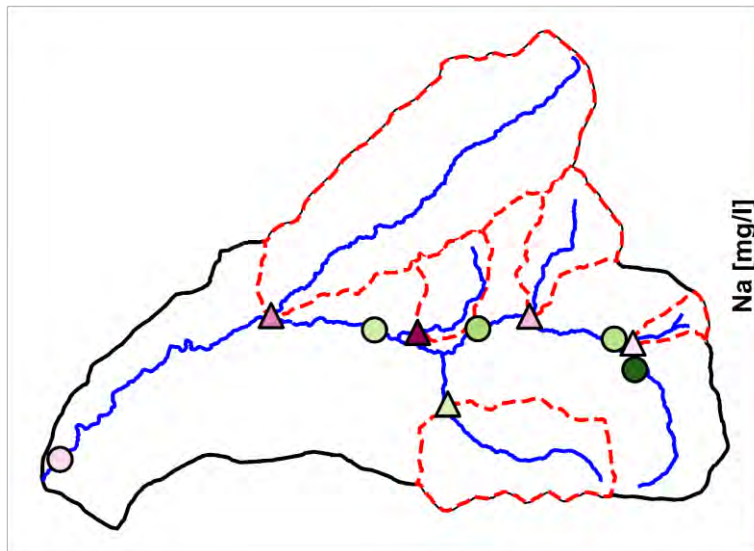
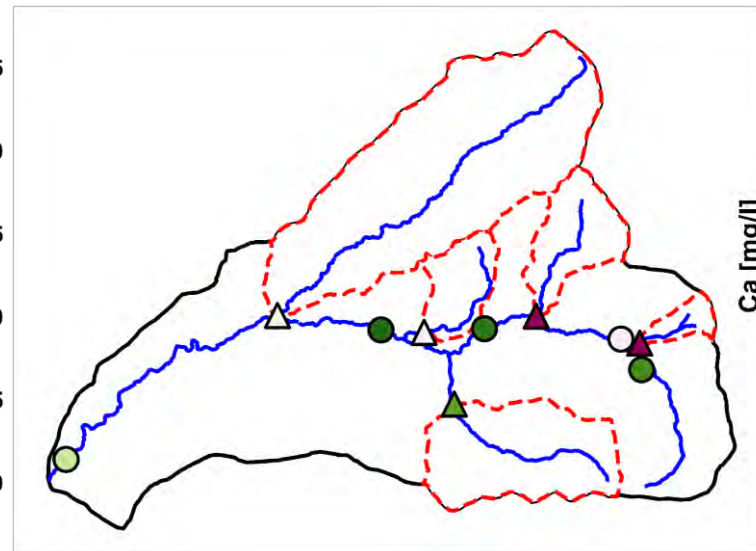
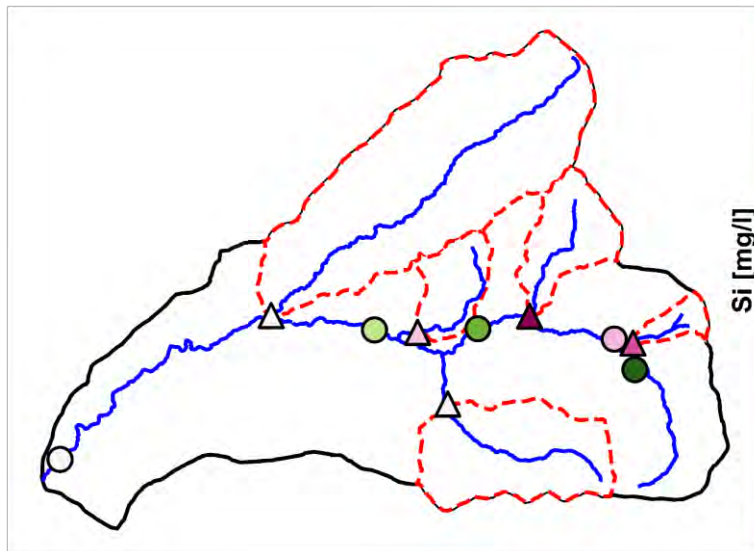


Figure 8. (A) Average stream solute concentration (grab samples) by study catchment for the study period and (B) flow weighted average monthly solute concentrations by experimental catchment for the long-term period (1968-2021) at the HJ Andrews. Lower bars represent cations and upper bars indicate anions.



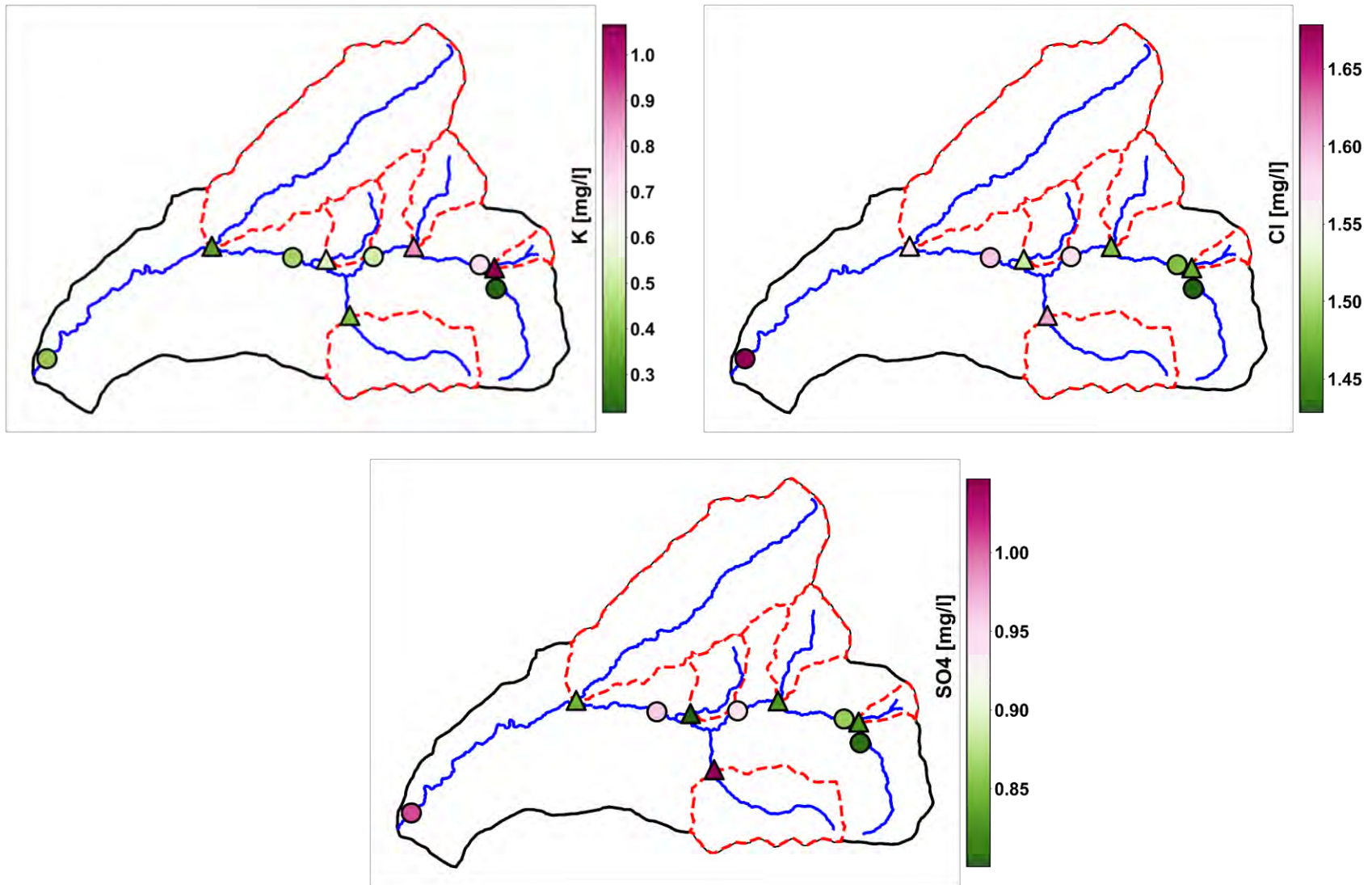


Figure 9. Spatial distribution of the average stream water solute concentrations (Ca, Mg, Na, K, Si, Cl, and SO4) during the study period. Triangles and circles represent tributaries and main stem catchments, respectively. Black and red line (dashed) are the HJ Andrews and catchments water divide.

2.3.2 Temporal Analysis

To understand temporal trends, we averaged our monthly chemistry into four seasons: fall (September–December), winter (December–March), spring (March–June) and summer (June–September), which captures the strong Mediterranean climate of Lookout Creek with wet winters and dry summers (Figure 3). Spring average solute concentrations—considering all study sites—were the lowest for all solutes except for Ca and Si. Conversely, all average solute concentrations across all sites were highest in summer except for Ca (Table 5).

Despite the overall seasonal variability across average solutes across sites, we observed no systematic variability in seasonal solute concentrations within each individual sampling site (Figure 9). The concentration of SO_4 varied little over time at most sites except at LC, MC, and LC. In MC and LC, SO_4 concentrations were highest in summer, though the other seasons didn't show the same concentration timing. There were a few solutes of note though (Figure 10): 1) Si whose concentrations were generally at their lowest in the fall across all tributaries and along the main stem, with the exception of LO1, 2) Ca whose concentrations tended to be highest in the summer at the upstream sites (LO1-O2; CC, LC) and near the outlet (LO5 and MR), 3) Na whose concentrations were higher during the summer and spring at the downstream catchments (NC, LO4, MR and LO5), 4) K concentrations were elevated in summer and fall, exclusively in upstream sampling sites (CC, LO2, and LC), and 5) Cl and SO_4 were higher in the fall, particularly in downstream catchments (MC, LO3, LO4, MR, and LO5).

Table 5. Summary of the average and flow weighted average concentrations (composite samples) of the study period and long-term data by sampled catchments and experimental catchments.

	Season	$\text{Ca} \pm \sigma$	$\text{Mg} \pm \sigma$	$\text{Na} \pm \sigma$	$\text{K} \pm \sigma$	$\text{Si} \pm \sigma$	$\text{Cl} \pm \sigma$	$\text{SO}_4 \pm \sigma$
Study Catchments	Spring	5.9 ± 5.5	0.8 ± 0.3	1.5 ± 0.4	0.4 ± 0.2	5.4 ± 2.0	1.5 ± 0.1	0.9 ± 0.1
	Summer	4.2 ± 1.8	1.2 ± 0.5	2.1 ± 0.5	0.7 ± 0.3	6.6 ± 3.0	1.5 ± 0.2	0.9 ± 0.3
	Fall	3.2 ± 1.2	1.1 ± 0.4	1.8 ± 0.5	0.6 ± 0.3	3.0 ± 2.3	1.6 ± 0.2	0.9 ± 0.2
	Winter	3.1 ± 1.0	1.0 ± 0.4	1.7 ± 0.4	0.5 ± 0.3	6.3 ± 2.4	1.5 ± 0.1	0.9 ± 0.1
	Ave	4.1 ± 2.9	1.1 ± 0.5	1.8 ± 0.5	0.6 ± 0.3	5.4 ± 2.9	1.5 ± 0.2	0.9 ± 0.2
	Max - Min	$21.3 - 0.9$	$2.1 - 0.3$	$3.2 - 0.8$	$1.4 - 0.1$	$12.0 - 0.4$	$3.3 - 1.2$	$3.0 - 0.7$
Experimental **	Spring	3.9 ± 1.1	1.0 ± 0.3	2.4 ± 0.6	0.3 ± 0.1	8.6 ± 1.2	0.8 ± 0.3	0.1 ± 0.1
	Summer	5.3 ± 1.6	1.4 ± 0.5	3.3 ± 0.8	0.4 ± 0.2	9.8 ± 1.0	1.3 ± 1.2	0.1 ± 0.1
	Fall	4.0 ± 1.1	1.0 ± 0.3	2.5 ± 0.8	0.4 ± 0.1	8.2 ± 1.1	1.2 ± 0.9	0.1 ± 0.1
	Winter	3.3 ± 0.7	0.9 ± 0.9	2.1 ± 0.4	0.3 ± 0.1	8.0 ± 1.0	0.8 ± 0.3	0.1 ± 0.0
	Ave	4.2 ± 1.4	1.1 ± 0.6	2.6 ± 0.8	0.4 ± 0.2	8.7 ± 1.3	1.0 ± 0.8	0.1 ± 0.1
	Max - Min	$10.3 - 0.8$	$13.0 - 0.4$	$5.4 - 0.5$	$1.2 - 0.1$	12.6 ± 4.2	$9.5 - 0.2$	$0.53 - 0.0$

* Spring: 03/20-06/20, summer: 06/21-09/22, fall: 09/23-12/20 and winter: 12/21-03/19.

** Flow weighted average concentrations.

Max - min represents individual samples.

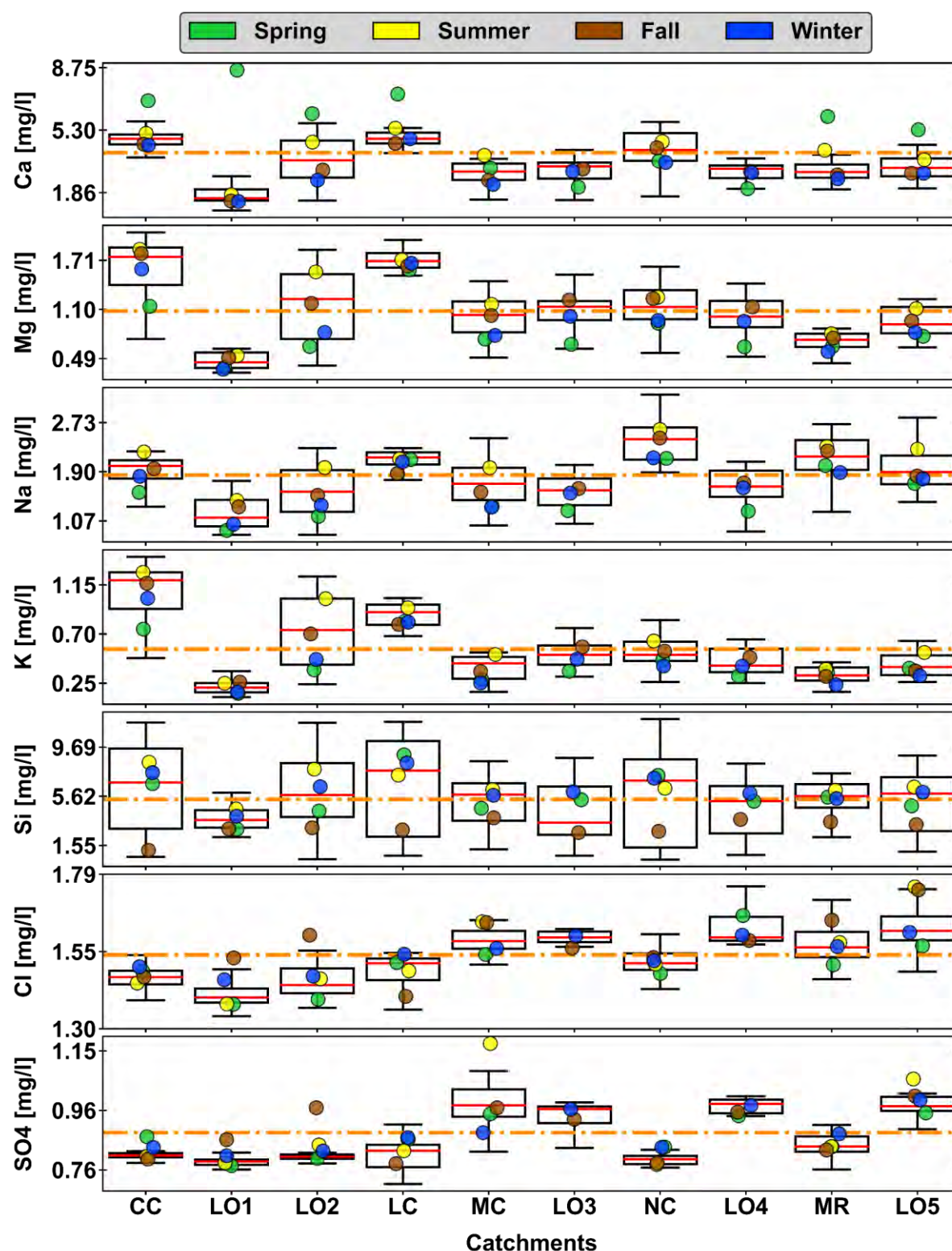


Figure 10. Box plot distribution of the stream water chemistry by catchments for the study period. Orange line represent the arithmetic average for all catchments. Each scatter point represents average seasonal stream solute concentrations. Significant outliers (individual samples) were intentionally omitted to prevent any distortion or reduction in the size of each box plot.

2.4 Solute Concentration and Yield Behavior with Discharge

The relationship between stream discharge and solute concentrations was not always self-consistent among solutes across the four gauged sites (CC, LC, MC, and LO5; Figure 12 and 13). In some instances, data showed strong linear relationships, while at other sites-solute pairs, such as Si for LO5, the linear relationship was weak, and the variability was high. Rarely were low concentrations observed at high discharge or high concentrations observed at low discharge. This heterogeneity in solute behavior with discharge across sites is indicative of variation in rock-water interaction times and thus, runoff generation processes. For example, we observed different concentrations for similar values of discharge, as discharge is highly seasonal these tended to occur at similar times of the year (e.g., May 2022 vs May 2023). October, November, April, and May were the months that depicted these discrepancies between concentrations and discharge. For Fall these discrepancies may be associated with the timing of the onset of precipitation following summer, while in the Spring shifts in snowmelt process may play a fundamental role in controlling solute concentrations. Cold (CC), Longer (LC) and Mack (MC) Creeks were the catchments more susceptible to those trends, particularly in Si and Ca. Unlike those catchments, systematic variability in the concentration discharge relationship emerged in hysteretic behavior at Lookout Creek (LO5) during low flow conditions, where concentrations were elevated as stream flow declined and were more diluted as stream flow increased (Figure 12 and 13).

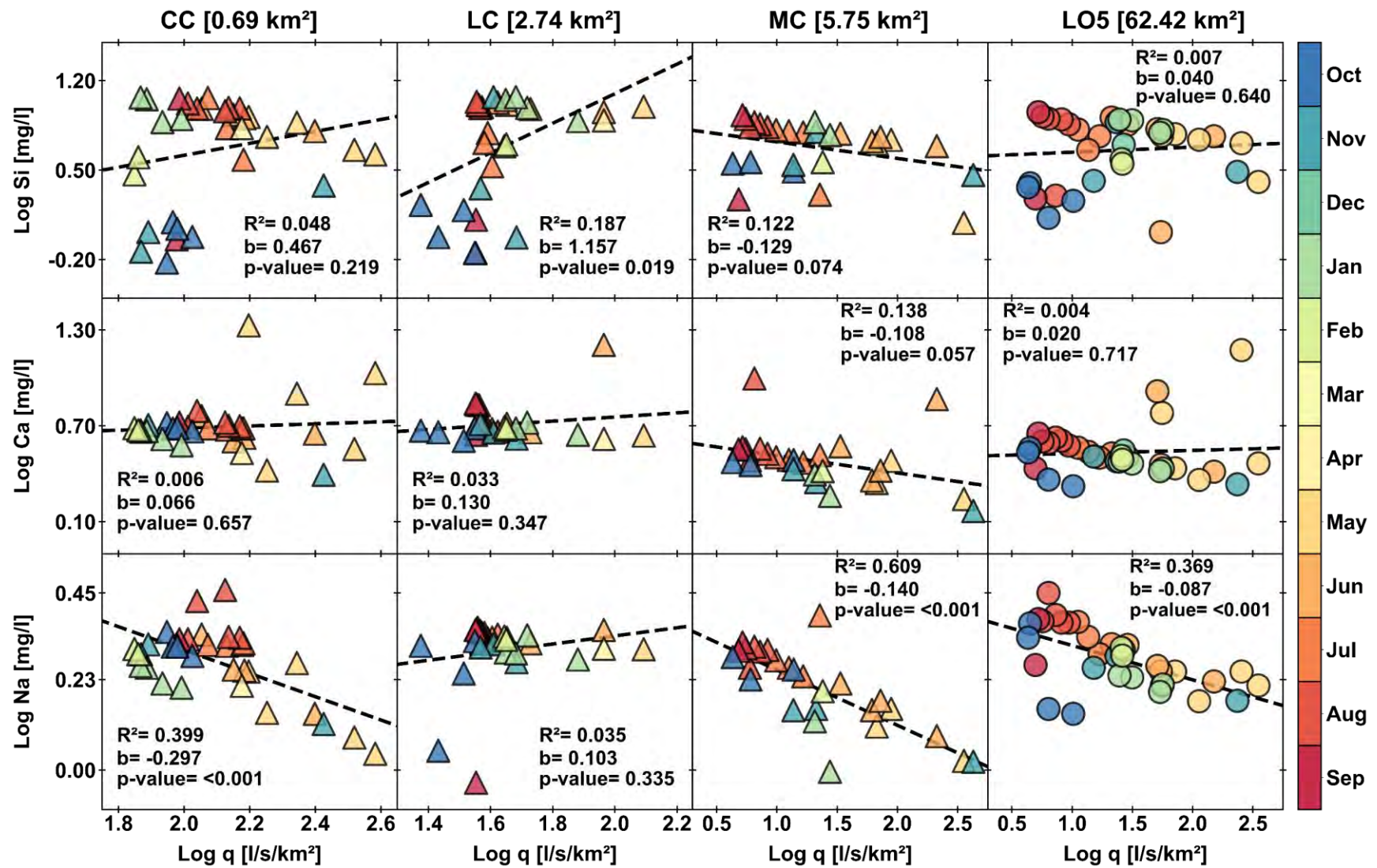


Figure 11. Concentration-discharge relationship of Si, Ca, and Na, (mg/l) at Cold (CC), Longer (LC), Mack Creeks (MC), and Lookout Creek at the gauging station (LO5). Black dashed lines depict the power law relationship with a slope of b and the p -value indicating the significance of the regressions.

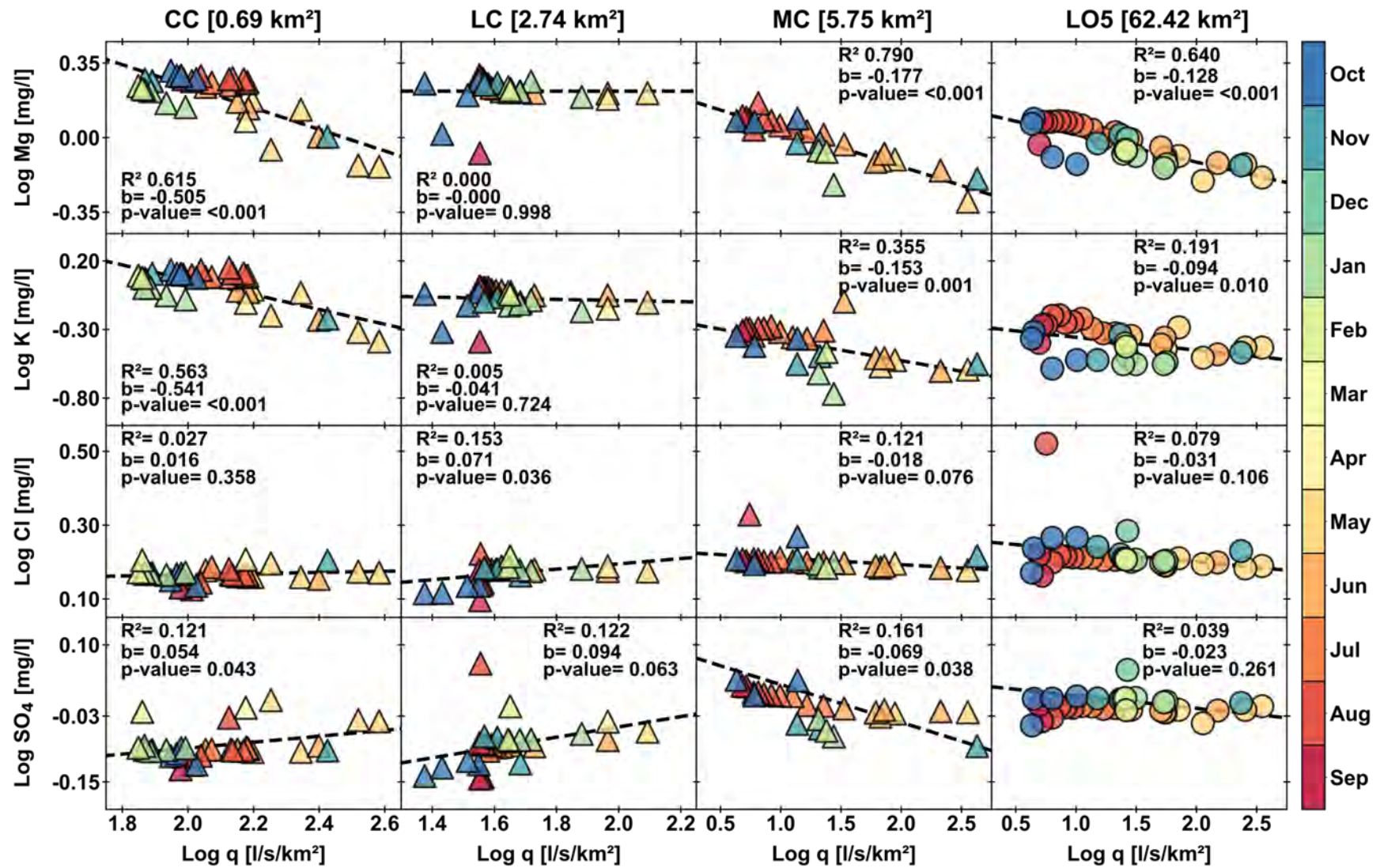


Figure 12. Concentration-discharge relationship of Mg, K, Cl, and SO₄ (mg/l) at Cold (CC), Longer (LC), Mack Creeks (MC), and Lookout Creek at the gauging station (LO5). Black dashed lines depict the power law relationship with a slope of b and the p-value indicating the significance of the regressions.

2.4.1 C-Q Relationship Behavior

Across the four gauged catchments (CC, LC, MC, and LO5), we assessed the concentration-discharge (C-Q) relationship using the slope (b) of a power-law function and the ratio of the coefficient of variation of concentration to discharge (Cv_c/Cv_Q). For slopes of the lines can be interpreted in terms of export pattern (dilution, chemostatic, or flushing) and Cv_c/Cv_Q regime can be simplified into chemostatic or chemodynamic. Overall, the slopes of the seven solutes at all four sites ranged from depleted at -0.54 (CC-K) to enriched at 1.16 (LC-Si), though many solute-site combinations showed chemostatic behavior ($-0.1 < b < 0.1$; Table 6; Figure 11). Overall, Si and Ca exhibited the most pronounced positive slope trends indicative of flushing. Conversely, Mg, Na, and K displayed predominantly negative slope patterns, suggesting a tendency towards dilution. Cl and SO₄ consistently showed slopes consistent with chemostatic behavior across catchments.

Based on the slope of the power-law functions we can group the general solute behavior of each catchment (Table 6, Figure 11-13). Starting at the outlet, Lookout Creek at the Gauging station (LO5) was dominated by chemostatic behavior (except Mg), Mack Creek showed mainly dilution behavior (except Cl and SO₄), Longer Creek showed a mixture of flushing (Ca, Na, Si) and chemostatic behavior, while Cold Creek exhibited all three behaviors: flushing (Si), dilution (Mg, Na, K) and chemostatic conditions. Furthermore, Cv_c/Cv_Q indicated chemostatic behavior for most of the solutes across catchments (Figure 11). Mack Creek and Lookout Creek at the Gauging station showed chemostatic behavior across all solutes. Longer and Cold Creeks also showed similar tendency but for fewer solutes (LC: Mg, Na, and K; CC: Na) compared to MC and LO5. Cold and Longer Creeks portrayed chemodynamic behavior, specifically in Ca, Mg, K, pointing out Si as the highest ratios across catchments. Cl and SO₄ had the lowest ratios oscillating from 0.04 (MC) to 0.23 (LC), matching with slopes $\sim$ zero for the concentration-discharge relationships. Contrarily, Si and Ca exhibited the highest ratios from 0.21 (MC) to 1.11 (CC), coinciding with slopes $\neq$ 0 in the concentration-discharges relationship (Table 6).

Table 6. Statistics summary of discharge and stream water chemistry on the four catchments.

Catchment	Constituent	Mean	STD	CV	Cv_c/Cv_Q	Slope (b)	R ²	Export Pattern	Regime
CC	Q [l/s/km ²]	139.2	73.5	0.53	-	-	-	-	-
	Ca [mg/l]	5.4	3.1	0.59	1.11	0.066	0.029	Const	CHD
	Mg [mg/l]	1.6	0.4	0.23	0.44	-0.505	0.653	Dilut	CHS
	Na [mg/l]	1.9	0.4	0.19	0.37	-0.297	0.417	Dilut	CHS
	K [mg/l]	1.1	0.3	0.26	0.48	-0.541	0.590	Dilut	CHS
	Si [mg/l]	6.3	3.7	0.60	1.13	0.467	0.003	Flush	CHD
	Cl [mg/l]	1.5	0.1	0.04	0.08	0.016	0.032	Const	CHS
	SO ₄ [mg/l]	0.8	0.1	0.07	0.14	0.054	0.139	Const	CHS
LC	Q [l/s/km ²]	47.4	21.8	0.46	-	-	-	-	-
	Ca [mg/l]	5.3	2.2	0.41	0.89	0.130	0.076	Flush	CHD
	Mg [mg/l]	1.7	0.2	0.14	0.30	0.000	0.011	Const	CHS
	Na [mg/l]	2.0	0.3	0.15	0.33	0.103	0.010	Flush	CHS
	K [mg/l]	0.9	0.2	0.18	0.39	-0.041	0.032	Const	CHS
	Si [mg/l]	6.7	4.0	0.60	1.30	1.157	0.107	Flush	CHD
	Cl [mg/l]	1.5	0.1	0.06	0.14	0.071	0.073	Const	CHS
	SO ₄ [mg/l]	0.8	0.1	0.10	0.23	0.094	0.068	Const	CHS
MC	Q [l/s/km ²]	57.6	105.7	1.84	-	-	-	-	-
	Ca [mg/l]	3.3	1.7	0.52	0.28	-0.108	0.022	Dilut	CHS
	Mg [mg/l]	1.0	0.2	0.24	0.13	-0.177	0.459	Dilut	CHS
	Na [mg/l]	1.7	0.4	0.23	0.12	-0.140	0.379	Dilut	CHS
	K [mg/l]	0.4	0.1	0.33	0.18	-0.153	0.174	Dilut	CHS
	Si [mg/l]	5.3	2.0	0.38	0.21	-0.129	0.197	Dilut	CHS
	Cl [mg/l]	1.6	0.1	0.08	0.04	-0.018	0.027	Const	CHS
	SO ₄ [mg/l]	1.0	0.4	0.37	0.20	-0.069	0.033	Const	CHS
LO5	Q [l/s/km ²]	52.5	80.1	1.53	-	-	-	-	-
	Ca [mg/l]	3.8	2.3	0.61	0.40	0.020	0.087	Const	CHS
	Mg [mg/l]	0.9	0.2	0.19	0.13	-0.128	0.373	Dilut	CHS
	Na [mg/l]	2.0	0.3	0.18	0.12	-0.087	0.202	Const	CHS
	K [mg/l]	0.4	0.1	0.26	0.17	-0.094	0.090	Const	CHS
	Si [mg/l]	5.2	2.4	0.46	0.30	0.040	0.029	Const	CHS
	Cl [mg/l]	1.7	0.3	0.18	0.12	-0.031	0.030	Const	CHS
	SO ₄ [mg/l]	1.0	0.2	0.21	0.14	-0.023	0.014	Const	CHS

Q: discharge, CV: coefficient of variation, slope: power law slope. Const: constant, Dilut: dilution, and Flush: flushing. CC: Cold Creek, LC: Longer Creek, MC: Mack Creek, and LO5: Lookout Creek at the Gauging station.

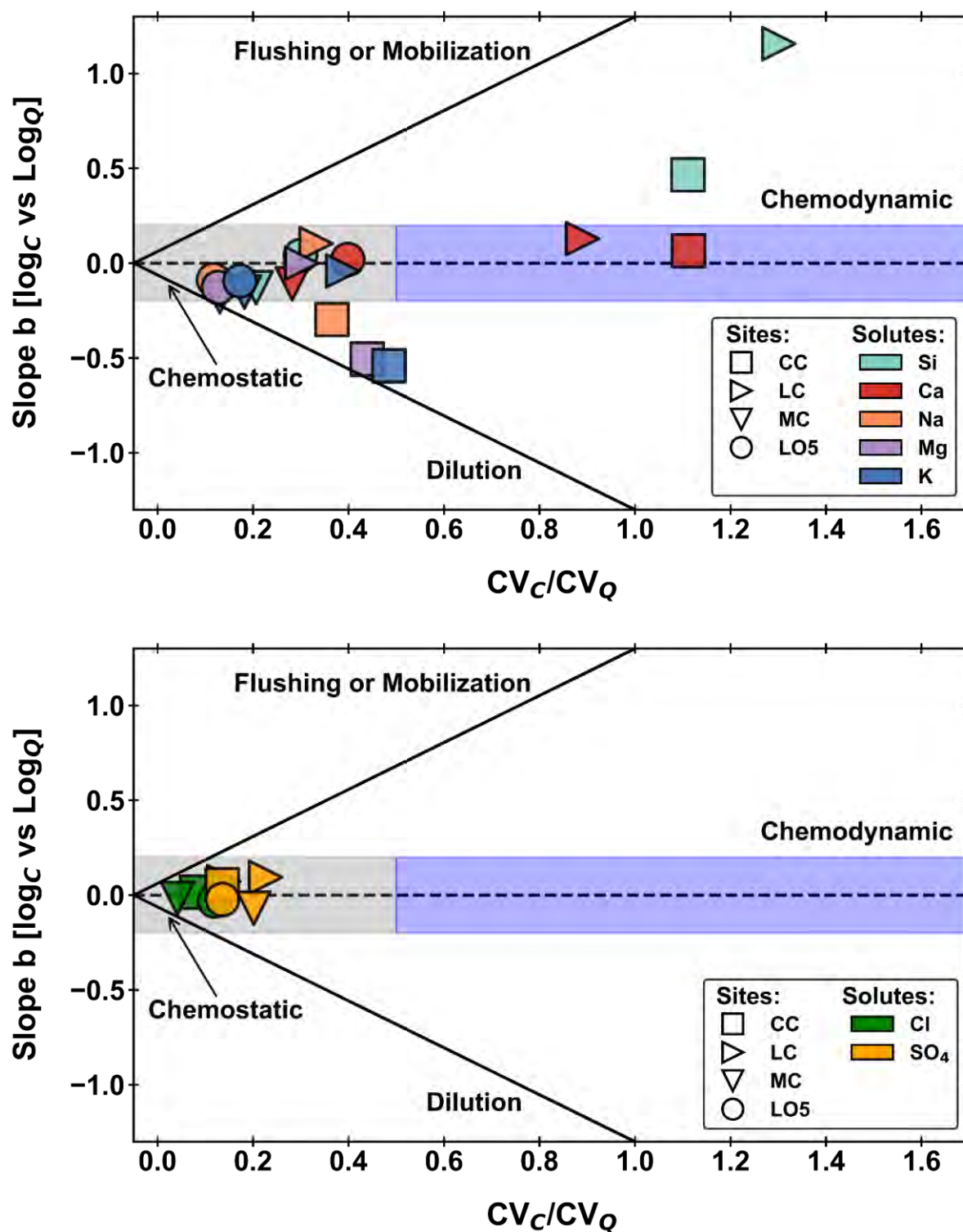


Figure 11. Slope (b) of the stream water concentration-discharge (C-Q) relationship compared to the ratio of the concentration and discharge coefficient of variation (CV_C/CV_Q) for solutes measured (A: cations and B: anions) at Cold (CC), Longer (LC), Mack (MC) Creeks, and Lookout Creek at the gauging station (LO5). Shaded field denotes chemostatic ($-0.2 \leq b \leq 0.2$) or chemodynamic ($-0.2 \geq b \geq 0.2$) behavior.

2.4.2 Solute Load and Yield Analysis

To reveal which solute had the most elevated load (tons/year) and yield (tons/year/km²) during the analyzed study period, total dissolved solutes (TDS) were calculated using daily discharge and solutes concentrations across gauged catchments. TDS yield values considerably varied across sites during the study period (Table 7), oscillating from 0.6 (K, MC) to 20 (Si, CC) ton/year/km². Si showed the highest unit area loads, followed by Ca and Na. In Contrast, K and SO₄ exhibited the lowest unit area loads throughout sites. The two most upstream catchments, Cold and Longer Creeks, presented the highest unit area loads across solutes, while Mack Creek and Lookout Creek at the Gauging station had the lowest loads. Load differences per unit area were up to four times greater at the highest elevation site (CC) compared to the lowest (LO5), specifically in Mg and K (Figure 14A).

On the other hand, the total dissolved solutes load indicated an opposite tendency compared to TDS yield across catchments. The most downstream catchment, Lookout Creek at the Gauging station (LO5), showed the maximum total loads across sites with amounts ranging from 513 (Si) to 38 (K) tons/year. Cold Creek (CC), the most upstream catchment, had the lowest total loads with values, oscillating from 13 (Si and Na) to 2 (K and SO₄) tons/year. Longer and Mack Creeks showed similar total loads throughout solutes, with Si and Na registering the highest amounts (Figure 14B).

The effective discharge across sites was characterized by the highest discharge of 12.17 m³/s and TDS load of 42.94 ton/year (Si) at the most downstream catchment (LO5) compared to the most upstream site, Cold Creek, with the lowest discharge of 0.07 m³/s and TDS load of 0.18 ton/year (SO₄). Mack and Longer Creeks had an effective discharge of 1.13 and 0.25 m³/s with a TDS load varying from 3.87 (Si) to 0.29 (K) for Longer and from 3.23 (Si) to 0.48 (SO₄) for Mack (Table 7).

These metrics and results all together revealed a substantial variability in solutes concentrations and discharges, particularly during fall storm and spring snowmelt events, where similar discharges transported different solute concentrations. The slope of a power-law relationship and coefficient of variation between solute concentration and discharge, showed that Si and Ca were the most chemodynamic solutes with flushing or dilution trends, while chemostatic behavior ($b \sim 0$) was observed for Cl and SO₄ across all sites. Chemostatic behavior was observed in Mack Creek

and Lookout Creek at the Gauging station, while non-chemostatic pattern was identified in Cold and Longer Creeks. The solute load and yield analysis demonstrated variations in Total Dissolved Solutes (TDS) yield across sites, with Si showing the highest unit area loads. The most upstream catchments (Cold and Longer Creeks) presented the highest unit area loads, while the most downstream catchment (Lookout Creek at the Gauging station) exhibited the maximum total loads. Effective discharge and TDS load values varied across sites, with the most downstream catchment having the highest discharge and TDS load.

Table 7. Summary of solutes load and yield, and solute rating equations for the study catchments and solutes.

Catchment	Constituent	TDS tons/day	TDS Yield tons/day/km ²	Equation	R ²
Cold Creek (CC)	Ca	13.82	20.02	$Q_s = 0.500Q^{1.066}$	0.623
	Mg	13.74	19.91	$Q_s = 0.039Q^{0.495}$	0.721
	Na	5.09	7.37	$Q_s = 0.079Q^{0.703}$	0.915
	K	4.16	6.03	$Q_s = 0.024Q^{0.459}$	0.917
	Si	2.74	3.97	$Q_s = 1.242Q^{1.467}$	0.604
	Cl	4.07	5.89	$Q_s = 0.132Q^{1.016}$	0.814
	SO ₄	2.30	3.33	$Q_s = 0.081Q^{1.054}$	0.988
Longer Creek (LC)	Ca	41.10	15.00	$Q_s = 0.582Q^{1.130}$	0.988
	Mg	26.18	9.56	$Q_s = 0.143Q^{1.000}$	0.789
	Na	10.20	3.72	$Q_s = 0.217Q^{1.103}$	0.803
	K	8.05	2.94	$Q_s = 0.067Q^{0.959}$	0.983
	Si	4.06	1.48	$Q_s = 4.855Q^{2.157}$	0.985
	Cl	7.40	2.70	$Q_s = 0.148Q^{1.071}$	0.481
	SO ₄	4.17	1.52	$Q_s = 0.087Q^{1.094}$	0.722
Mack Creek (MC)	Ca	45.47	7.91	$Q_s = 0.207Q^{0.892}$	0.944
	Mg	29.67	5.16	$Q_s = 0.057Q^{0.823}$	0.957
	Na	15.09	2.62	$Q_s = 0.104Q^{0.860}$	0.334
	K	8.46	1.47	$Q_s = 0.024Q^{0.847}$	0.444
	Si	3.45	0.60	$Q_s = 0.315Q^{0.871}$	0.863
	Cl	18.49	3.22	$Q_s = 0.133Q^{0.982}$	0.825
	SO ₄	10.67	1.86	$Q_s = 0.076Q^{0.931}$	0.991
Lookout Creek at the gauging station (LO5)	Ca	513.16	8.22	$Q_s = 0.294Q^{1.020}$	0.976
	Mg	377.54	6.05	$Q_s = 0.084Q^{0.872}$	0.998
	Na	184.32	2.95	$Q_s = 0.172Q^{0.913}$	0.988
	K	84.06	1.35	$Q_s = 0.036Q^{0.906}$	0.981
	Si	38.57	0.62	$Q_s = 0.385Q^{1.040}$	0.950
	Cl	171.17	2.74	$Q_s = 0.145Q^{0.969}$	0.972
	SO ₄	103.82	1.66	$Q_s = 0.087Q^{0.977}$	0.986

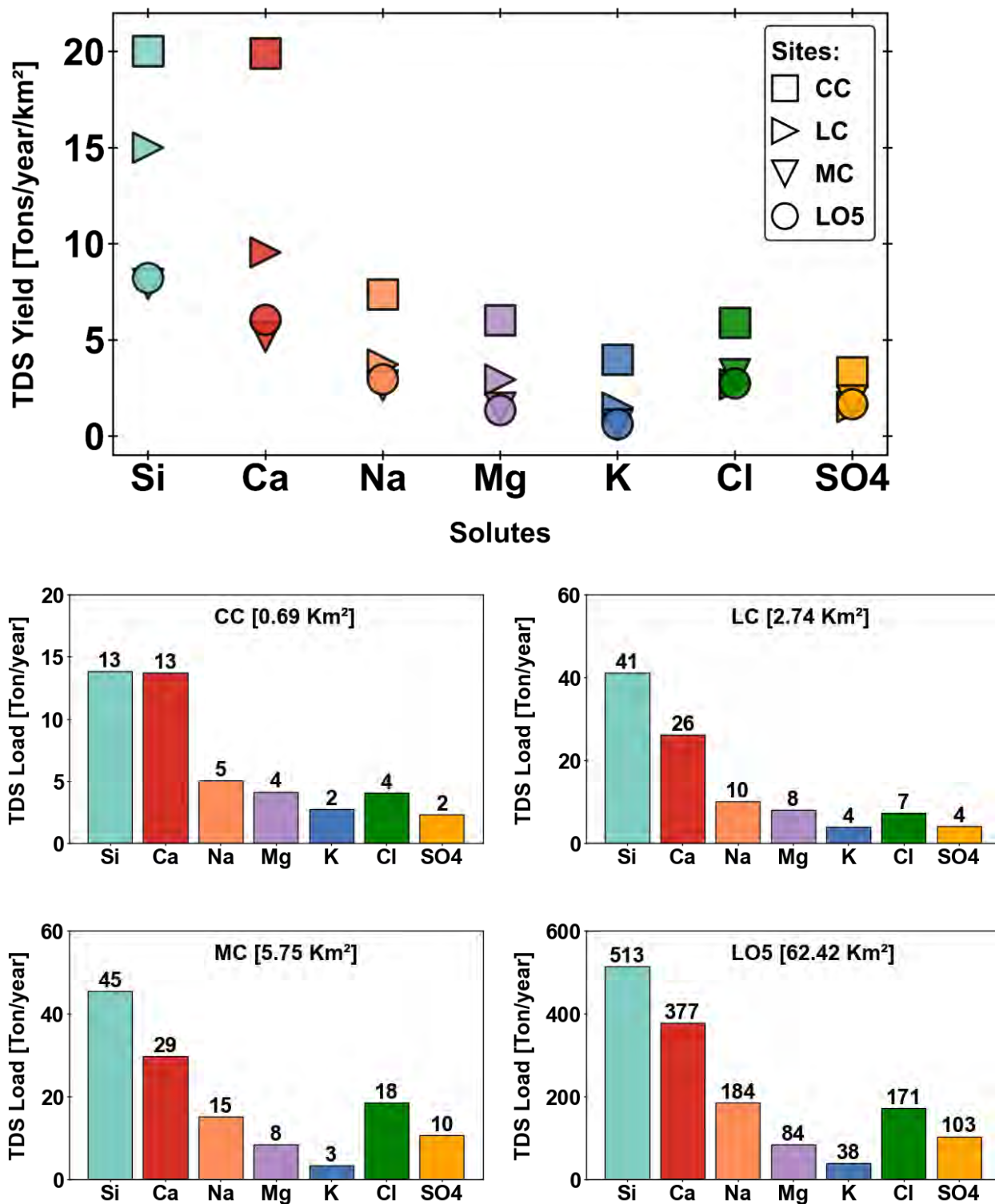


Figure 14. Total dissolved solute (TDS) yield (A) and load (B) by study catchment.

2.5 End-Member Mixing Analysis

2.5.1 Molar Ratios

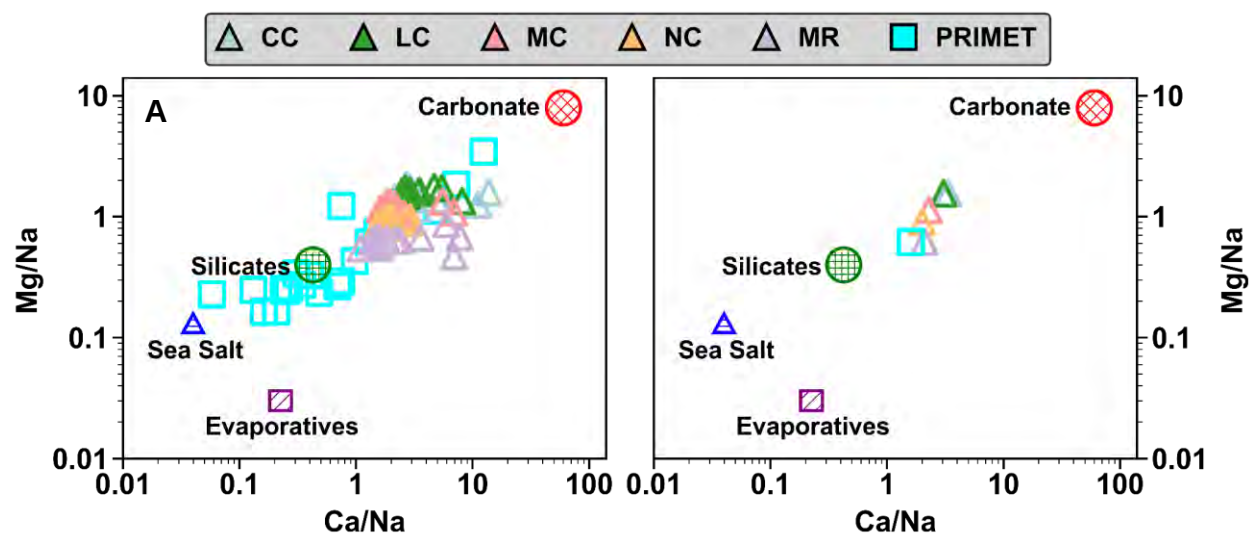
To illustrate clustering behavior between catchments to preliminary identify potential water sources and underlying geology, average Na-normalized ratios were calculated, fluctuating from 0.2 (SO_4/Na) to 3.5 (Ca/Na) across catchments (Table 8), excluding precipitation chemistry with ratios oscillating from 0.6 (Mg/Na) to 9.6 (Cl/Na). Throughout catchments, molar ratios exhibited the following ranking: $\text{Ca}/\text{Na} > \text{Mg}/\text{Na} > \text{Cl}/\text{Na} > \text{K}/\text{Na} = \text{SO}_4/\text{Na}$. On the other hand, precipitation chemistry displayed a different order with $\text{Cl}/\text{Na} > \text{SO}_4/\text{Na} > \text{Ca}/\text{Na} > \text{K}/\text{Na} > \text{Mg}/\text{Na}$. Most of ratios showed that the farthest upstream catchment, Cold Creek, had the highest molar ratios across catchments, pointing out Ca/Na and Mg/Na , followed by Longer Creek. The lowest ratios were exhibited by the most downstream tributaries, Nostoc and McRae Creeks. Main stem catchments presented similar upstream-downstream pattern for Ca/Na and Mg/Na ; however, the rest of ratios lacked an identical trend. This variability can be attributed to the integration of diverse chemical signatures originating from various tributaries along the watercourse or atmospheric inputs such as precipitation.

Building upon the findings of Gaillardet et al. (1999), the utilization of elemental ratios, specifically Ca/Na and Mg/Na , highlighted the presence of two primary water types, carbonate and silicate draining streams incorporating sea salt as a proxy of the ocean. Based on this frame, we found that all study catchments (tributaries and main stem) had averages Ca/Na and Mg/Na ratios (Figure 15) slightly oriented towards silicates, indicating their origin from silicate-dominated rock with presumably the presence of disseminated material (carbonate sedimentary rocks) with higher concentration of Ca. McRae Creek, and Cold and Longer Creek were the catchment with lowest and highest elemental ratios, aligned to silicate and carbonate. Certain individual ratios associated Cold, Mack, McRae, and Upper Lookout Creeks 1, 2, 5; were out of the boundaries between silicate and carbonates reservoirs, indicating the presence of a missing end-member. Precipitation chemistry ratios spanned a wide range of mixing space with some individual ratios influenced by seawater and others aligned between silicate and carbonate.

Table 8. Summary of molar ratios normalized by Na in precipitation and stream water from the study catchments.

	Site	Ca/Na	Mg/Na	K/Na	Cl/Na	SO ₄ /Na
Tributaries	CC	3.3 ± 2.4	1.6 ± 0.2	0.3 ± 0.0	0.5 ± 0.1	0.2 ± 0.1
	LC	3.1 ± 1.2	1.6 ± 0.1	0.2 ± 0.0	0.5 ± 0.1	0.2 ± 0.0
	MC	2.3 ± 1.2	1.1 ± 0.1	0.1 ± 0.0	0.7 ± 0.2	0.3 ± 0.1
	NC	2.0 ± 0.3	0.9 ± 0.1	0.1 ± 0.0	0.4 ± 0.1	0.2 ± 0.0
	MR	2.1 ± 1.6	0.6 ± 0.1	0.1 ± 0.0	0.5 ± 0.1	0.2 ± 0.0
	Average	2.6 ± 1.6	1.2 ± 0.4	0.2 ± 0.1	0.5 ± 0.1	0.2 ± 0.1
	Max - Min	13.7 - 1.1	1.8 - 0.5	0.4 - 0.1	1.0 - 0.3	0.7 - 0.1
Main Stem	LO1	3.5 ± 6.0	0.7 ± 0.1	0.1 ± 0.0	0.8 ± 0.2	0.3 ± 0.1
	LO2	3.2 ± 3.2	1.3 ± 0.3	0.3 ± 0.1	0.6 ± 0.2	0.3 ± 0.1
	LO3	2.2 ± 0.2	1.3 ± 0.2	0.2 ± 0.0	0.7 ± 0.2	0.3 ± 0.1
	LO4	2.0 ± 0.2	1.2 ± 0.1	0.2 ± 0.0	0.7 ± 0.2	0.3 ± 0.1
	LO5	2.2 ± 1.5	0.9 ± 0.1	0.1 ± 0.0	0.6 ± 0.1	0.3 ± 0.1
	Average	2.8 ± 3.5	1.0 ± 0.3	0.2 ± 0.1	0.7 ± 0.2	0.3 ± 0.1
	Max - Min	25.1 - 1.0	1.7 - 0.5	0.3 - 0.1	1.3 - 0.4	0.5 - 0.2
Rain	PRIMET	1.6 ± 3.0	0.6 ± 0.8	0.9 ± 1.7	9.6 ± 10.9	4.1 ± 4.2
	Max - Min	12.4 - 0.1	3.4 - 0.2	7.1 - 0.0	44.8 - 1.4	15.7 - 0.4

Max-min represent individual ration associated with a specific sample.



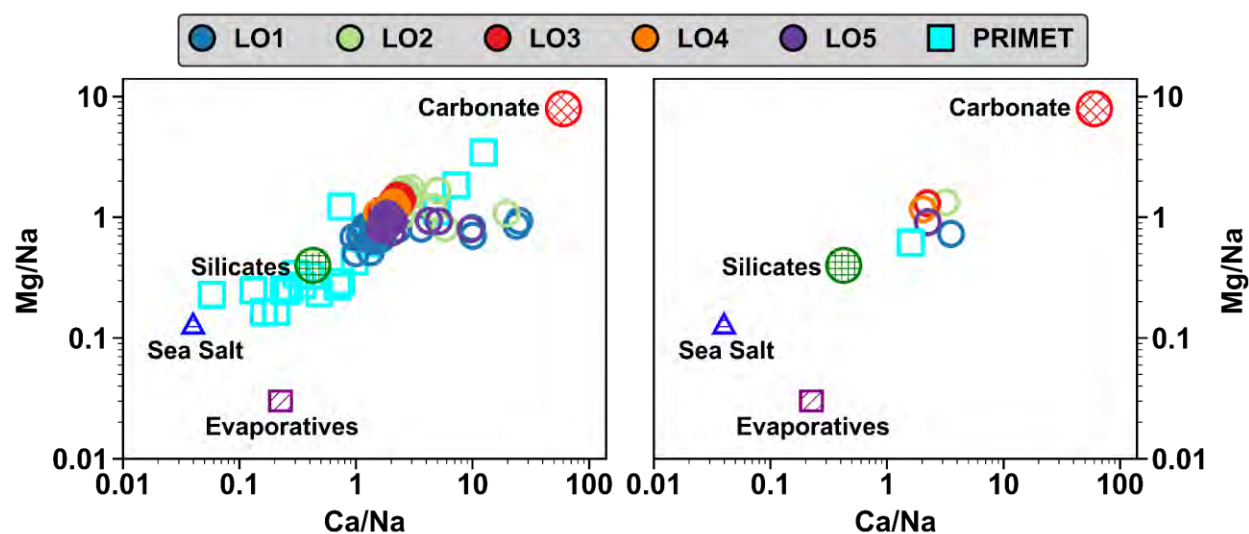


Figure 15. Molar ratios (Ca/Na Vs Mg/Na) of tributaries (A), main stem (B) catchments by individual samples (left panel) and average (right panel). End-member mixing reservoirs of carbonate, silicate, and evaporite lithologies have been illustrated based on the work of Stewart et al. (2022), utilizing data obtained from Gaillardet et al. (1999). Additionally, information regarding sea salt composition is derived from the findings of Schlesinger et al. (1982).

2.5.2 Principal Component Analysis (PCA)

To identify unknown potential end-members, circumscribing the projected stream chemistry data and solutes with higher loadings, scree plot criterion across sites (study catchments) indicated that two PCs were retained above the elbow, describing a total of 87% of variance. The first PC described 78% and the second PC described 9% of the variance (Figure 16A). Na, Cl, Ca, Si, and K were the most significant on PC1, with the strongest positive loading on Na (0.43) and Cl (0.43), and strongest negative loading on K (-0.01); suggesting that PC1 is mainly controlled by subsurface flow (water-rock interaction) and precipitation inputs. Mg, K, Cl, and SO_4 were the most significant on PC2, with the strongest positive loading on K (0.82) and strongest negative loading on SO_4 (-0.19); indicating that PC2 is dominated by soil water contributions and precipitation inputs (Table 9). An individual mixing space dimensionality analysis was performed for tributaries and main stem catchments, indicating a slightly higher variances compared to the study catchments. Overall, this revealed that approximately 91% and 90% of the total variance were accounted for by the first and second PCs, respectively. The first two PCs of the tributaries and main stem catchments appear to be described by the same solutes that drive the variability across all catchments, being the most representative Ca, Na, Si, and Cl for the first PC; and Mg and K for the second PC (Table 9).

Along PC1, the stream water chemistry showed a higher degree of spread, circumscribed by the precipitation end-member and a potential groundwater source (missing end-member). Tributaries displayed a notable variability, with Cold Creek identified as the farthest right catchment, closely associated with this potential missing end-member. Additionally, Upper Lookout Creek-1 and McRae were found to be the farthest left sites, exhibiting proximity to the precipitation end-member. Along PC2, the stream water chemistry was not as spread as compared to PC1, indicating a lower degree of variability between sites; however, soil water and precipitation chemistry were highly variable.

In average terms (Figure 16B), tributaries displayed a higher degree of variability than the main stem catchments, indicating different water sources contributions (groundwater vs precipitation) across sites. McRae (most down-stream catchment) and Mack Creek showed evidence of overlapping, illustrating similar water chemistry, and streamflow dependence on precipitation events. In contrast, Cold, Longer, and Nostoc Creeks, showed no signs of overlapping, suggesting different water chemistry associated with different runoff generation responses. Main stems catchments showed a lower extent of variability due to a less susceptibility in stream chemistry changes associated with a lower groundwater input along its path downstream. LO1, LO3, LO4, and LO5 exhibited evidence of overlapping, oriented to the precipitation reservoir; however, LO2 was apparent of this trend because of the water chemistry influenced of Cold Creek.

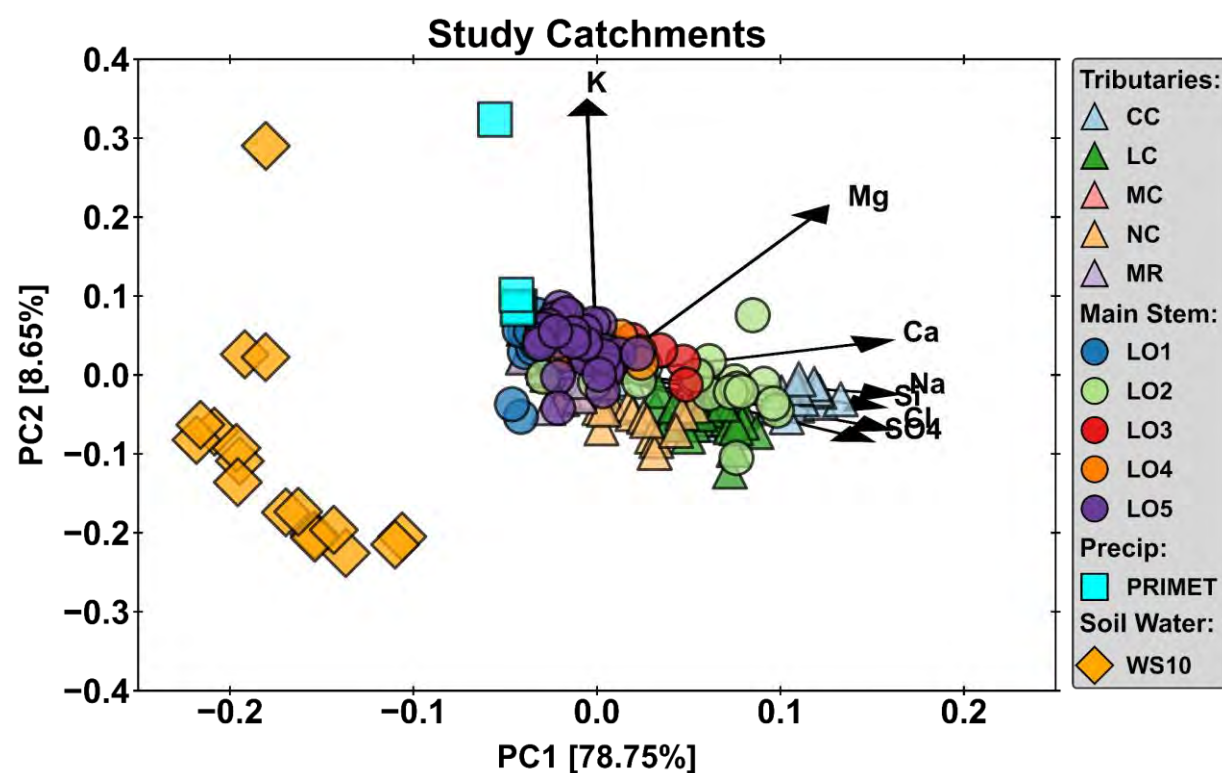
Tracer selection through a bivariate plot applied to the whole stream water chemistry dataset (Si^{4+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , and SO_4^{2-}) and maximum loadings obtained in PC1 and PC2 from the study catchments PCA, unveiled a strong and significant relationships ($R^2 > 0.5$, $p < 0.01$) for Na, Mg and K (Table 10). Solutes pair such as Na-K, Mg-Na, and Mg-K showed R^2 oscillating between 0.72 (LO5) to 0.93 (CC, MC, NC, and LO2); 0.50 (LC) to 0.95 (NC); and 0.53 (LC) to 0.98 (LO2). Additionally, when assessing the relationship of solutes in each individual catchment, it was observed that most catchments were characterized by the presence of Na, Mg, and K. However, Longer Creek stood out by exhibiting a robust correlation with Na, K, Cl, and SO_4 .

Table 9. Loadings on the first two principal components (PC1 and PC2) for all study sites, tributaries, and main stem catchments.

Solute	Study Catchments		Tributaries		Main Stem	
	PC1	PC2	PC1	PC2	PC1	PC2
Ca	0.42	0.10	0.42	0.12	0.41	0.05
Mg	0.35	0.49	0.34	0.51	0.39	0.36
Na	0.43	-0.05	0.43	-0.05	0.42	-0.04
K	-0.01	0.82	-0.09	0.83	-0.04	0.92
Si	0.41	-0.09	0.41	-0.08	0.41	-0.06
Cl	0.43	-0.15	0.42	-0.10	0.42	-0.12
SO ₄	0.40	-0.19	0.40	-0.13	0.40	-0.09

Table 10. Solute pair combination with the highest Coefficient of determination (R^2) throughout study catchments.

Tributaries	Solute Pair	R^2	Main Stem	Solute Pair	R^2
CC	Na-K, Mg-K	0.93, 0.93	LO1	Na-K, Mg-Na	0.89, 0.89
LC	Na-K, Cl-SO ₄	0.76, 0.74	LO2	Na-K, Mg-K	0.93, 0.98
MC	Na-K, Mg-Na	0.93, 0.91	LO3	Na-K, Mg-K	0.90, 0.91
NC	Na-K, Mg-Na	0.93, 0.95	LO4	Na-K, Mg-Na	0.90, 0.88
MR	Mg-Na, Mg-K	0.92, 0.79	LO5	Na-K, Mg-Na	0.72, 0.88



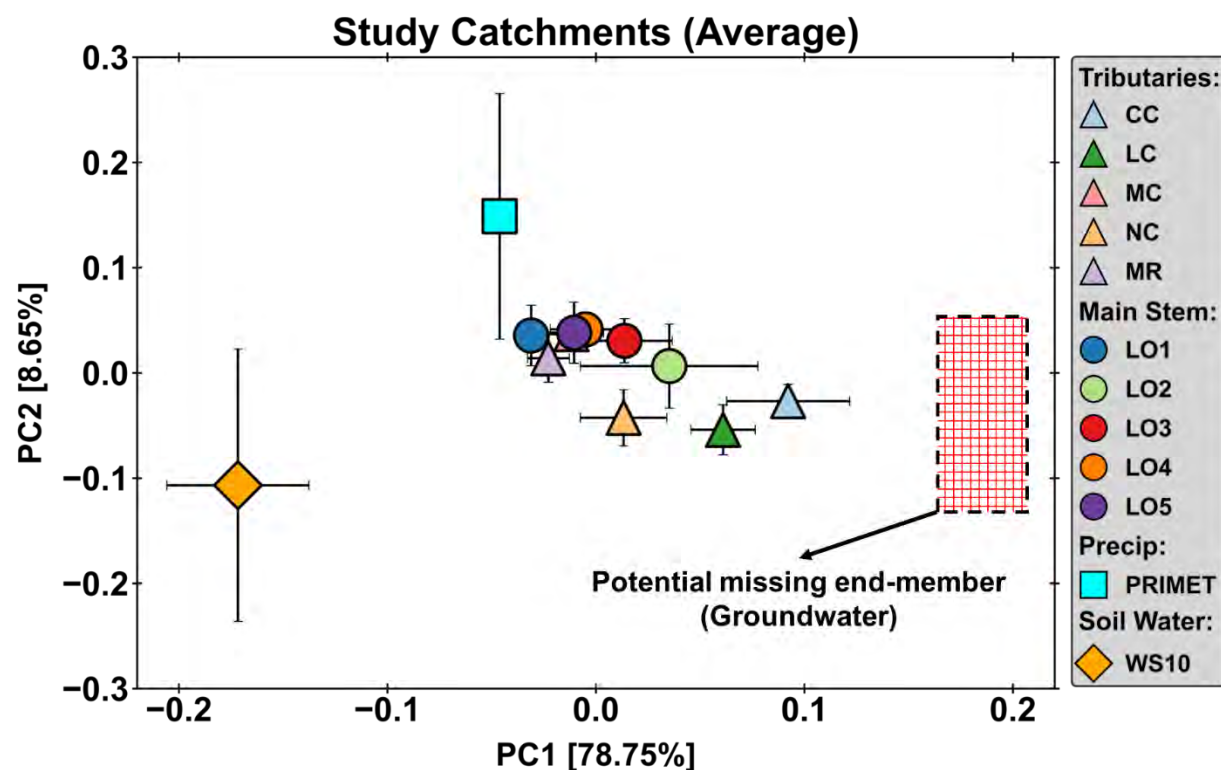


Figure 16. Principal Component Analysis (PCA) of the study catchments (tributaries and main stem). Individual samples and average are represented by sites in the mixing space and error bars represent standard deviation.

2.5.3 Hydrograph Separation based on PCA

End-member mixing analysis based on the projected stream water chemistry samples in a mixing space (PCs) was performed by independent dimensionality analysis for each defined cluster to assess the relative streamflow contribution and most influential water chemistry signature in the mixture or outlet (target site). Among the four clusters under analysis, clusters 1 and 3 necessitated a two-end-member configuration, while cluster 2 involved three end-members arranged linearly. The final group, cluster 4, required three end-members arranged in a triangular alignment. The range in total percentage explained by the first and second principal component (PC1 and PC2) for clusters with two-end member oscillated from 91 to 93%, while the only cluster with three-end member had 91%

Cluster No.1 was best explained by a chemistry mixture of CC and LO1, highlighting target individual samples of summer months (Jul, Aug, Sep, and Oct) align closely with Cold Creek, while those from winter and late spring exhibit characteristics more in line with Upper Lookout-1 Creek. Cluster No.2 was described by a combination of PRIMET, LO2, and LC reservoirs.

Individual samples from October demonstrated a pronounced alignment with LC, while those from December exhibited characteristics more closely associated with PRIMET. Furthermore, samples from November and February were notably indicative of Upper Lookout-2 Creek. Cluster No.3 was characterized by chemistry mixture of PRIMET and LO3, pointing out most of the individual sample were oriented to LO3 end-member. Lastly, Cluster No.4 was best explained by a chemistry mixture of WS10, PRIMET, and CC (proxy of groundwater), underscoring that most of samples were influenced by the precipitation reservoir.

Relative runoff contribution across clusters indicated a substantial input from the precipitation end-member, as elevation decreases and drainage area increases until the outlet (LO5) of the Lookout Creek catchment (Figure 17). Tributaries such as Longer, Nostoc, Mack and McRae Creeks showed a negligible relative contribution across clusters, excluding cluster No. 1 where Cold Creek supplied on average 49% of the flow. Furthermore, soil water chemistry was only relevant in cluster 4, supplying around 16% of the total runoff.

Cluster No. 1 (target site: LO2, 6.32 km²) was principally characterized by supplies of LO1 (5.53 km², 51%) and CC (0.69 km², 49%) on average basis (Table 11). During low flow conditions (July-October 2022), Cold Creek contributed more than 80% of the runoff, being August 2022 the highest month. Contrarily, Upper Lookout-1 Creek supplied much of the flow during the rest of the study period with values from 69 (January 2023) to 87% (May 2022) (Figure 18A and 18B). Additionally, 93% of the projected water chemistry samples from the target site, was described by the end-members, meaning that 2 out of 27 samples were not represented in the mixing domain. Cluster No.2 (target LO3, 15.63 km²) was dominated by the runoff contribution of Longer Creek (2.74 km², 6%), PRIMET (430 m, 27%), and LO2 (6.32 km², 67%). Longer Creek¹ played a limited role in the runoff, contributing only 24% in October, with negligible input in the remaining months. In contrast, LO2 emerged as the predominant source of flow, accounting for 75% in October 2022, 69% in November 2022, and a substantial 79% in February 2023. PRIMET exhibited higher influence solely in January 2023, contributing 55% of the runoff during that period (Figure 18C and 18D).

¹ The October Longer Creek contribution was determined through a two end-member mixing analysis involving this catchment and LO2. This analysis was performed as two projected samples fell within the domain of these two catchments, and their composition was not influenced by PRIMET (precipitation).

Cluster No.3 (target site: LO4, 30.67 km²) was influenced by the contribution of Upper Lookout-3 Creek (61%) and PRIMET (39%). LO3 played a significant role in contributing to the target site, particularly in November 2022 (69%), December 2022 (56%), and February 2023 (84%). PRIMET contribution was primarily observed in May 2023, accounting for 54%. Furthermore, 75% of the projected water chemistry samples from the target site were accurately described by the end-members, indicating that three out of the twelve samples were not adequately represented within the mixing domain (Figure 19A and 19B). Cluster No.4 (target site: LO5, 62.42 km) was described by the contribution of Cold Creek (36%, proxy of groundwater source), soil water chemistry (16%, WS10), and PRIMET (48%, precipitation). Groundwater source supplied on average 48% of the total runoff during summer months (July-September 2022). Precipitation contributed much of the flow during the rest of the study period with values from 43% (June 2022) to 59% (December 2022), and soil water contribution oscillated from 13% (May 2022) to 20% (January 2023) of the total runoff (Figure 19C and 19D).

A comparison between the observed and back-calculated stream solute concentration from each mixing scenarios using R^2 were consistent with values around 0.98 or 0.99 (Table 11). Traces such as K and Mg showed slopes close to one across clusters oscillating from 0.18 to 0.85, while Na displayed the highest slopes with values ranging from 3.05 to 3.50. These coefficients indicated the assumption of conservative mixing (co-linearity); however, the model could lead to under or over prediction in the observed solute concentrations based on slopes further from 1 (Bush et al., 2023; Hooper et al., 1990).

These data all together indicated the existence of some degree of heterogeneity across catchments. Molar ratios suggested that the study catchments lean slightly towards silicates, indicating their origin from silicate-dominated rocks, while meteoric precipitation demonstrate a wide mixing space, influenced by seawater and positioned between silicate and carbonate end-members. Principal Component Analysis (PCA) results revealed that tributaries showed a higher variability than main stem catchments, suggesting distinct water sources contributions and a potentially missing end-member (groundwater). Additionally, Na, Mg, and K were identified as the solutes with the strongest relationships and loadings in PCs, suggesting their convenience as tracers. The Hydrograph Separation based on PCA demonstrates that four clusters of stream water chemistry exhibit distinct end-member contributions to runoff. The relative streamflow

contribution across clusters indicated a substantial input from the precipitation end-member, particularly as elevation decreases and drainage area increases.

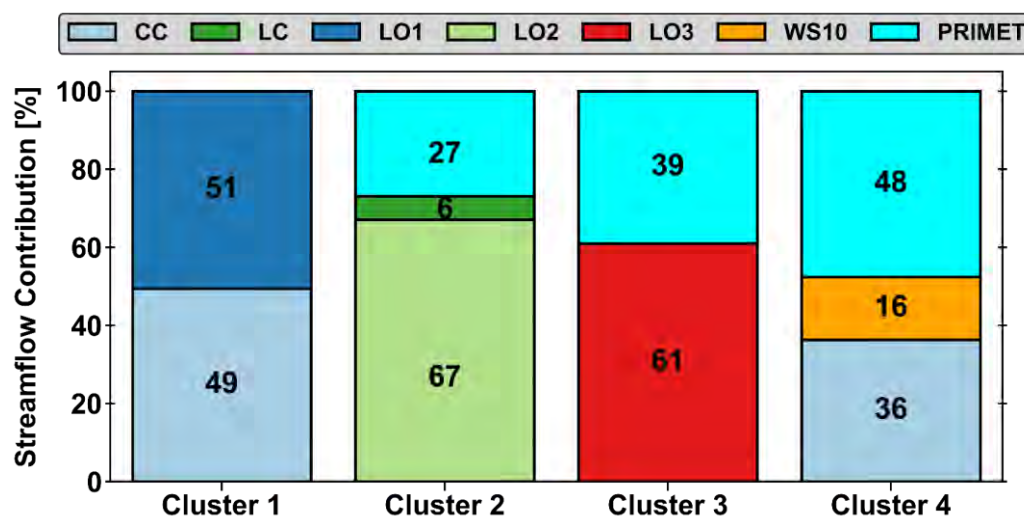


Figure 17. Average relative streamflow contribution for each end-member by mixing scenario (Cluster 1-4). CC: Cold Creek, LC: Longer Creek, LO1-3: Upper Lookout Creek, WS10: soil water, and PRIMET: meteoric precipitation.

Table 11. R^2 values and regression coefficients of simple linear regressions between observed stream solute concentrations (y) and back-calculated solute concentrations (x) from mixing model scenarios (clusters).

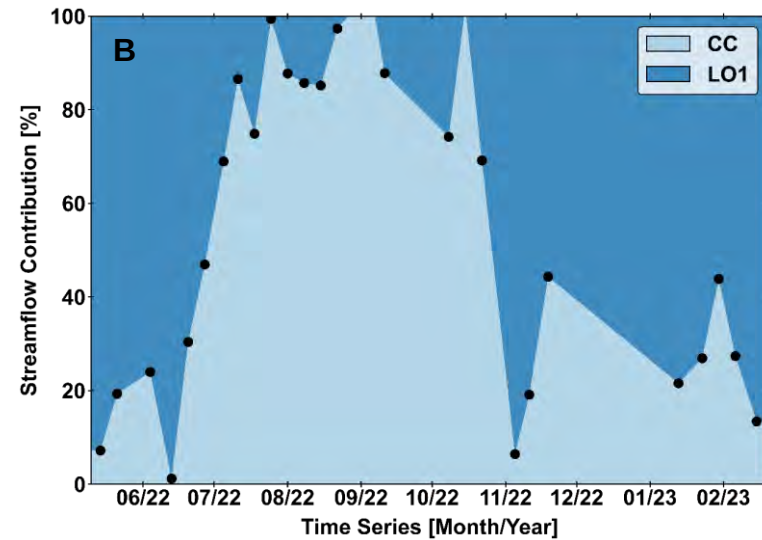
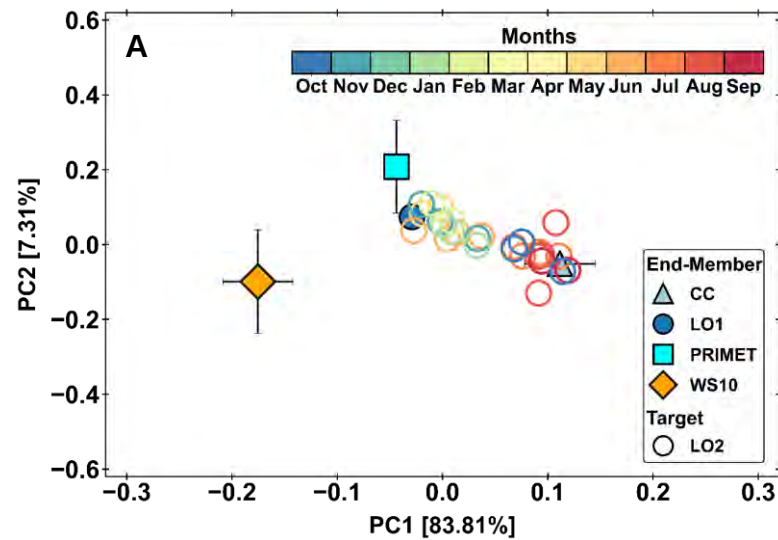
Cluster	End-Member	Tracer	Slope	Intercept	R^2
Cluster No. 1	CC	Na	3.425	3.057	0.98
	LO1	K	0.425	0.581	0.99
		Mg	0.848	1.316	0.99
Cluster No. 2	LO2	Na	3.500	3.398	0.99
	LC	K	0.322	0.621	0.99
	PRIMET	Mg	0.744	1.544	0.98
Cluster No. 3	LO3	Na	3.436	3.465	0.98
	PRIMET	K	0.177	0.418	0.99
		Mg	0.731	1.324	0.99
Cluster No. 4	CC	Na	3.048	3.115	0.98
	PRIMET	K	0.344	0.503	0.99
	WS10	Mg	0.734	1.251	0.99

Table 12. Monthly average relative streamflow contributions for each end-member each by mixing scenario (Cluster 1-4).

Cluster	End-members**	2022								2023				
		May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May
Cluster No. 1 [LO2]	CC	13	26	82	89	88*	72	23	-	31	20	-	-	-
	LO1	87	74	18	11	12*	28	77	-	69	80	-	-	-
Cluster No. 2 [LO3]	LO2	-	-	-	-	-	75	69	-	45	79	-	-	-
	LC	-	-	-	-	-	24	0	-	0	0	-	-	-
	PRIMET	-	-	-	-	-	1	31	-	55	21	-	-	-
Cluster No. 3 [LO4]	LO3	-	-	-	-	-	-	69	56	50	84*	-	-	46
	PRIMET	-	-	-	-	-	-	31	44	50	16*	-	-	54
Cluster No. 4 [LO5]	CC	35	38	46	53	46	33	33	25*	27	34*	-	-	29*
	PRIMET	51	43	39	33	35	52	52	59*	53	51*	-	-	55*
	WS10	13	19	15	14	19	15	15	16	20	15	-	-	16

* Values were based on a single measurement.

** End-members that explained most of the mixture in the projected space.
Catchments between brackets represent target sites (mixture or outtel).



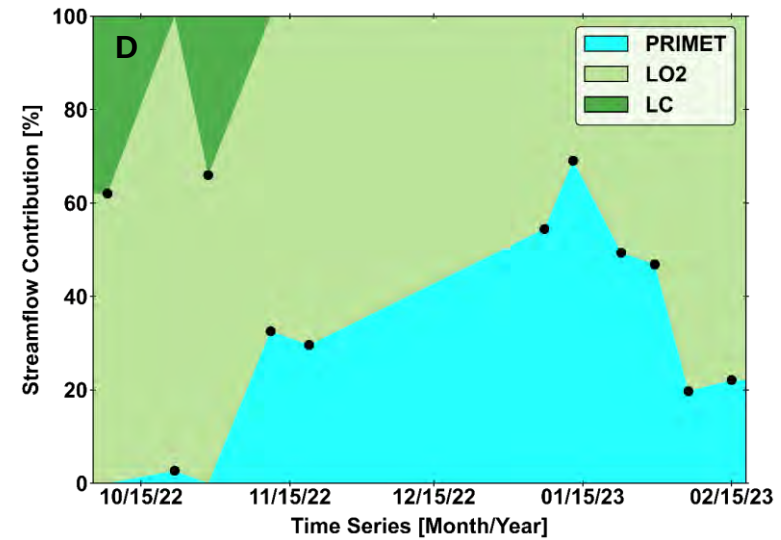
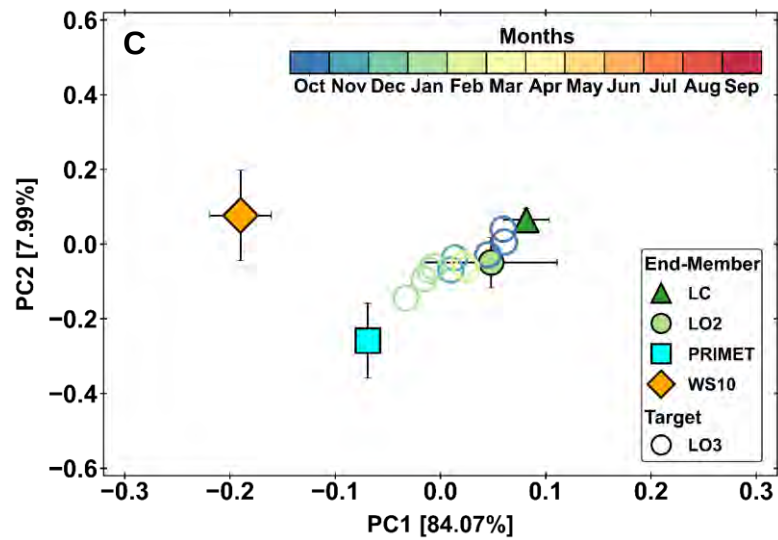
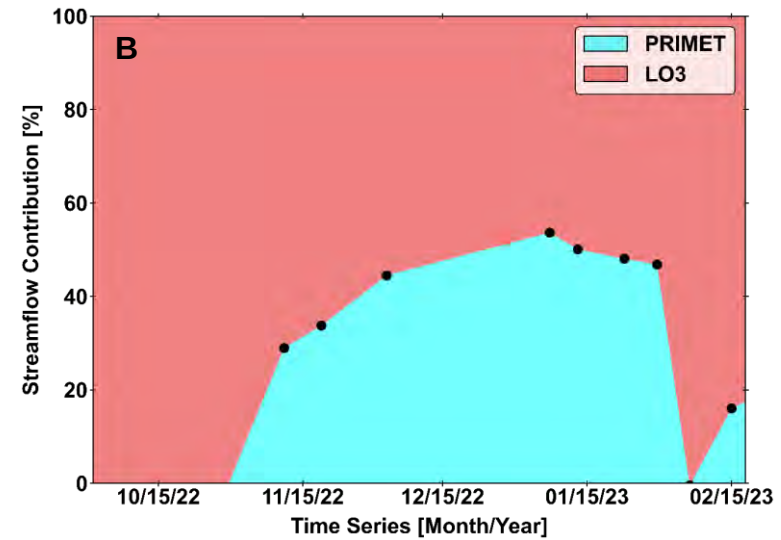
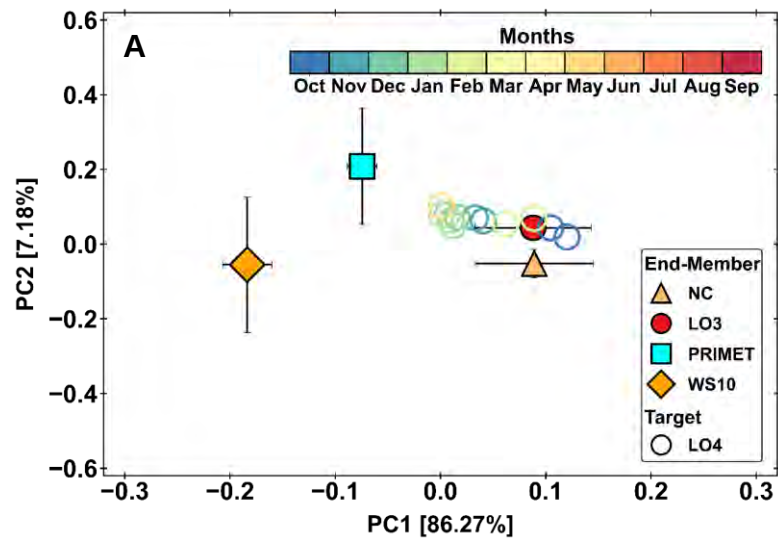


Figure 18. Two-dimensional principal component analysis (PCA) (A and C) results and their relative discharge contributions (B and D) for cluster 1 and 2, calculated in an End-Member Mixing analysis (EMMA). Error bars represent the standard deviation for each end-member in their corresponding mixing space.



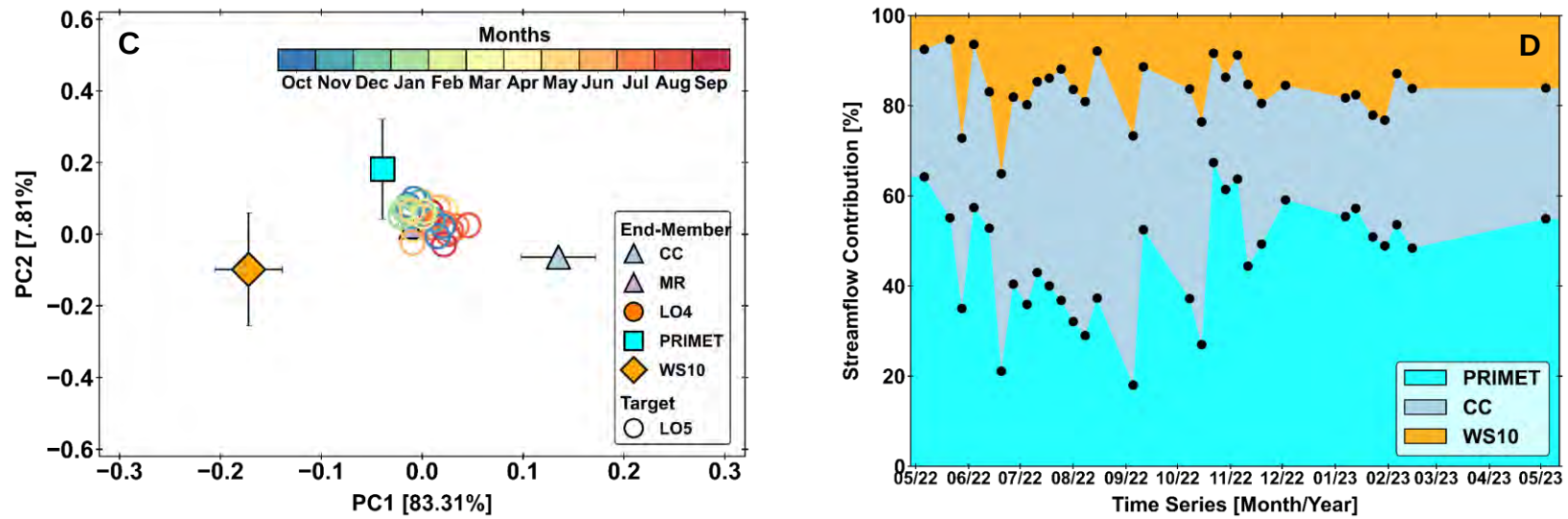


Figure 19. Two-dimensional principal component analysis (PCA) (A and C) results and their relative discharge contributions (B and D) for cluster 3 and 4, calculated in an End-Member Mixing analysis (EMMA). Error bars represent the standard deviation for each end-member in their corresponding mixing space.

