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RESEARCH AND OBSERVATORY CATCHMENTS: THE LEGACY AND THE FUTURE

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Sources of variability in springwater chemistry in Fool Creek, a high-elevation catchment of the Rocky Mountains, Colorado, USA

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Abstract

Springs are the point of origin for most headwater streams and are important regulators of their chemical composition. We analysed solute concentrations of water emerging from 57 springs within the 3 km^2 Fool Creek catchment at the Fraser Experimental Forest and considered sources of spatial variation among them and their influence on the chemical composition of downstream water. On average, calcium and acid neutralizing capacity (bicarbonate-ANC) comprised 50 and 90% of the cation and anion charge respectively, in both spring and stream water. Variation in inorganic chemical composition among springs reflected distinct groundwater sources and catchment geology. Springs emerging through glacial deposits in the upper portion of the catchment were the most dilute and similar to snowmelt, whereas lower elevation springs were more concentrated in cations and ANC. Water emerging from a handful of springs in a geologically faulted portion of the catchment were more concentrated than all others and had a predominant effect on downstream ion concentrations. Chemical similarity indicated that these springs were linked along surface and subsurface flowpaths. This survey shows that springwater chemistry is influenced at nested spatial scales including broad geologic conditions, elevational and spatial attributes and isolated local features. Our results highlight the role of overlapping factors on solute export from headwater catchments.

KEYWORDS
groundwater-dependent ecosystems, seeps, springs, subalpine forests, wetland biogeochemistry

1 | INTRODUCTION

High-elevation headwater streams are generated by a combination of snow or glacial meltwater, rainfall, and water that emerges from shallow subsurface flowpaths or deeper groundwater reservoirs (Sueker et al., 2000; Winter, 2007). In Rocky Mountain subalpine forests, >95% of water accumulated as snow first infiltrates into soils and fractured bedrock and passes along shallow flowpaths before reaching stream channels (Frisbee et al., 2011; Troendle & Reuss, 1997). The amount of water contained in the snowpack, synoptic meteorology and antecedent soil moisture determines peak and total annual runoff of headwater catchments. Water that percolates through soils or fractured bedrock recharges groundwater sources and sustains late-season streamflow (Golden et al., 2017). Interactions within the soil profile and underlying saprolite influence the chemistry and temperature of water routed along near-surface pathways (Constantz, 1998; Fields & Dethier, 2019; Scheliga et al., 2017). Characteristics of emergent groundwater may be useful for identifying source water, differentiating shallow from deep flowpaths and confirming linkages between subsurface and surface water (Barbera & Andreo, 2017; Soulsby et al., 1999; US EPA, 2015).

The chemistry of emergent groundwater responds to subtle differences in bedrock composition, degree of alteration and distinct mixtures of source water (Fields & Dethier, 2019; Horton et al., 1999; Valett et al., 1996). For example, an evaluation of groundwater-fed Colorado wetlands demonstrated that the chemical composition of wetland porewater and adjacent streams were sensitive to relatively minor differences in bedrock type (LaPerriere Nelson et al., 2011). Weatherable minerals originating from a small band of sedimentary rock (Eppinger et al., 1985) were sufficient to alter the pH, Ca^{2+}, Mg^{2+}, K^+ and ANC of emergent groundwater compared to the low ionic strength surface waters associated with the resistant metamorphic rock that predominates the region (Kellogg et al., 2008; Turk & Spahr, 1991). Similarly, weathering of trace amounts of calcite was found to contribute 51% of the streamwater Ca^{2+} in a catchment comprised primarily of granitic and metamorphic bedrock (Clow et al., 1997). In the Scottish Highlands, springwater chemistry reflected broad differences in groundwater provenance and catchment lithology as well as local variability attributed to flowpaths, residence time and subsurface biogeochemical processes (Soulsby et al., 2007). However, most geologic maps do not report bedrock chemistry at scales adequate for predicting surface water chemistry (Olson & Hawkins, 2012).

Mountain wetlands that form where groundwater emerges can serve as conduits for carbon (C) delivery to headwater streams and sinks for atmospheric nitrogen (N) inputs (LaPerriere Nelson et al., 2011; Stevens, Schenk, & Springer, 2020). The saturated soils in these wetlands create an environment where incomplete oxidation of organic matter leads to C accumulation and release to streams (Creed et al., 2003; Pallud et al., 2020) and gaseous release of N (Spoelstra et al., 2010). Spring density is known to be high in portions of Colorado's subalpine forests (Alstatt & Miles, 1983; Retzer, 1962) but owing to the small size of openings in the forest canopy, it is often difficult to remotely locate their sources and evaluate their biogeochemical influence within subalpine catchments (Stevens, Jenness, & Ledbetter, 2020). The vegetation and water quality of groundwater-dependent ecosystems are vulnerable to changes in climate, atmospheric deposition and human disturbance (Earman & Dettinger, 2011; Junk et al., 2013; Stevens, Jenness, & Ledbetter, 2020; Stevens, Schenk, & Springer, 2020). Awareness that increasing deposition of N, metals, microplastics and other trace elements may be impairing aquatic resources not only in agricultural areas (Golden et al., 2017; Szczucińska, 2016), but also in high-elevation forest catchments (Brahney et al., 2020; Fenn et al., 2003) highlights the importance of biogeochemical links between emergent groundwater and surface water (Covino, 2017).

Protection of clean water supply from headwater catchments requires greater understanding of hydrologic and biogeochemical connectivity between emergent groundwater and streams. The overall objective of this study was to characterize sources of spatial variability in the chemistry of emergent springs, and as such, we compared spring chemistry across distinct catchment zones, elevational gradients and unique site conditions within a high-elevation forest catchment. Headwater streams represent the vast majority of total stream network length and their sources determine the chemical composition of the downstream network (Abbott et al., 2017; Nadeau & Rains, 2007; US EPA, 2015), so chemical variability among emergent springs has implications for downstream water quality, aquatic habitat condition and numerous other uses.

2 | METHODS

2.1 | Site description

Work was conducted at the Fraser Experimental Forest (FEF), 137 km west of Denver on the western edge of the Front Range of the Colorado Rockies. Saint Louis Creek drains the 93 km^2 research area and joins the Fraser River, a major tributary to the Colorado River. Water from FEF is also diverted through a transcontinental tunnel that supplies municipal and agricultural users along Colorado's eastern Front Range. The climate is temperate and continental with long cold winters and short cool summers. Mean annual temperature at FEF is 1°C with January and July average temperatures of −10 and 12°C, respectively at 2740 m a.s.l. (Elder, 2005, 2006). Total annual precipitation averages 600 mm with 64% comprised of snowfall received between October and May. Peak snowpack accumulation occurs at the beginning of April and peak runoff occurs in early June.

This study was conducted in Fool Creek, a 2.9 km^2 subalpine catchment that extends from 2926 to 3487 m a.s.l. elevation. The Fool Creek catchment is located just below treeline and is covered by forests comprised of subalpine fir (*Abies lasiocarpa*), Engelmann spruce (*Picea engelmannii*) and lodgepole pine (*Pinus contorta).* Like much of the Front Range, the catchment is underlain by metamorphosed Paleoproterozoic rock (Kellogg et al., 2008; Shroba et al., 2010). Biotite and calc-silicate gneiss, schist, granite and granodiorite are the predominant rock groups (Figure 1). The bedrock is fractured by faults associated with brecciated granodiorite, mylonite and migmatite. Foliated granodiorite dikes occur as exposed outcrops within the faulted East flank of the catchment. A 3–4 m layer of unconsolidated saprolite overlays the bedrock across much of the catchment, but deeper Quaternary glacial deposits are located in the Upper portion of the catchment.

2.2 | Emergent groundwater springs

A prior survey located 157 individual springs in the Fool Creek catchment (Retzer, 1953, 1962). Springs often emerge at the base of steep 1–10 m long slip faces or are located on uniform, lower gradient hillslopes. The density and spatial distribution of springs reflect distinct hydrogeologic zones within the catchment (Figure 1). In the Upper portion of the catchment, springs emerge through Quaternary deposits and are relatively evenly spaced. Those on the East flank

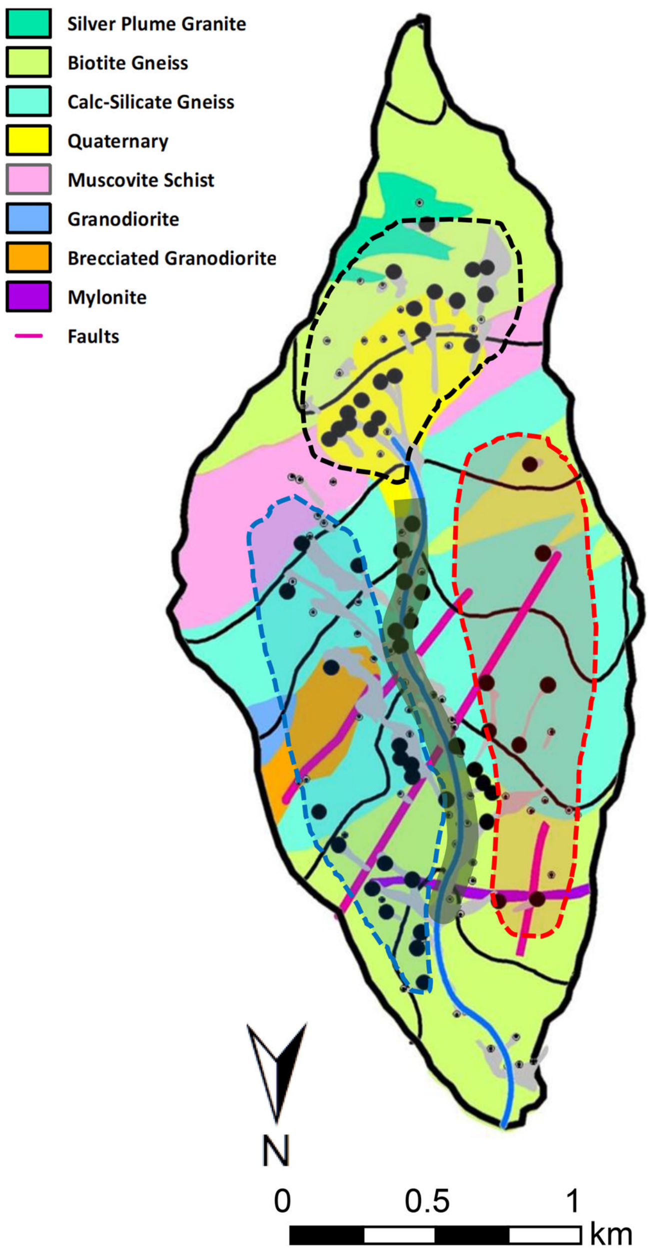

FIGURE 1 Geological map with emergent groundwater springs (dots) and associated wetlands (grey shading) in the Fool Creek catchment at the Fraser Experimental Forest, Colorado. The larger solid black dots were sampled in this study, the dashed lines and shaded areas delineate springs in the Upper (grey), East (blue) and West (red), and Riparian (green) zones. Black contour lines show 100 m intervals from 3000 to 3500 m above sea level. Geologic information from a digitally rasterized 1:100 000 scale map (Kellogg et al., 2008)

originate in faulted areas and are aligned along parallel drainages. Those on the West flank are isolated and relatively uncommon. Perennial streamflow of several Fool Creek tributaries begins as springs on the East flank of the catchment and create a network of hillslope wetlands. In contrast, owing to the scarcity of springs, wetlands and surface water, a historic forest road was constructed up the relatively dry West flank of the catchment (Figure S1).

Emergent groundwater springs create wetland openings that vary in size and plant species composition and maintain their saturated soil conditions (Ruddy & Williams, 1991). The plant communities associated with the emerging springs are typical of central Rocky Mountain wetlands underlain by metamorphosed, crystalline bedrock (Carsey et al., 2003; LaPerriere Nelson et al., 2011). Arrowleaf ragwort (*Senecio triangularis*), brook saxifrage (*Saxifraga odontoloma)* and various bryophytes are common. Bittercress (*Cardamine cordifolia*), five stamen miterwort *(Mitella petandra)*, woodrush (*Luzula parviflora)*, and water sedge (*Carex aquatilis)* are most abundant in small understory openings (e.g., <25 m^2) beneath the forest canopy. Dense willow clumps (*Salix planifolia*) differentiate larger openings (~2500 m^2) in sparse forests at upper elevations from forb-dominated communities within closed-canopy forests at lower elevations. Soils surrounding the springs are deep (>1 m), poorly drained Histic Cryoaquolls with surface peat layers (Alstatt & Miles, 1983; Daugherty et al., 2019). Organic layers average 20 cm deep but extend beyond 60 cm in some openings that are fed by multiple springs.

2.3 | Sample collection and analysis

To characterize variability among emergent springs, we sampled water at 57 springs distributed throughout Fool Creek in 2006 (Figure 1). Candidate springs were chosen at random from historic mapped locations (Retzer, 1962; Figure S1) within three subcatchment areas (Upper, East and West) and the near-stream Riparian zone. As described above, these zones correspond to distinct hydrogeomorphic conditions that influence spring abundance and distribution.

Sites were then selected for sampling based on the presence of springwater discharge and the absence of recent ungulate disturbance. To evaluate seasonal fluctuations, we compared samples collected during spring snowmelt (June 19) and during late summer at the onset of baseflow (August 22). We compared emergent springwater with streamwater collected weekly at Upper (3213 m.a.s.l.) and Lower (2926 m.a.s.l.) stream monitoring stations and collected once at 100 m intervals along Fool Creek and at confluences with principal tributaries (August 25). For general comparison with surface water samples, we analysed soil solution leachate concentrations sampled in five old-growth forest plots in the Fool Creek catchment (Hubbard et al., 2005). Leachate was sampled at the base of the rooting zone, using porous cup, falling-head tension lysimeters (Soil Moisture Corp, Goleta, CA) inserted to a depth of 20–30 cm (n = 50) and collected four times from late May through early July.

To characterize the chemical composition of surface water and soil solution samples we collected and analysed dominant cations and anions and dissolved carbon and nitrogen species. Spring and stream waters were collected after triple-rinsing bottles in sample water. Samples for anion and cation analyses were collected in opaque HDPE plastic bottles, those for dissolved organic carbon (DOC) and nitrogen (TDN) analyses were collected in amber borosilicate glass bottles. Prior to use, plastic sample bottles were triple washed with deionized water (SC < 1.0 μS/cm), and glass bottles were combusted for 1 hr at

500°C in a muffle furnace. Samples were refrigerated after collection, then ion chemistry samples were filtered through 0.45 μm mesh membrane filters (Durapore PVDF, Millipore Corporation, Billerica, MA) and DOC and TDN samples were filtered through 0.7 μm mesh glass fibre pre-filters (Millipore Corporation, Billerica, MA).

Anion and cation concentrations were determined by ion chromatography (Waters Co., Milford, MA) and conductivity detection with a Dionex AS12A Anion-Exchange column, an AG12A guard column and Waters IC-Pak Cation M/D column; APHA 1998a using EZChrom Elite Software (Scientific Software Inc., Pleasanton, CA). Samples were analysed within 72 hr of collection. Detection limits were 0.01 mg/L for K^+, Na^+, NH_4^+, Cl^- and NO_3^-, and 0.02 mg/L for Ca^{2+}, SO_4^{2-}, and Mg^{2+}. Acid neutralizing capacity (ANC) was measured on unfiltered subsamples by Gran titration. Specific conductivity and pH were analysed automatically with PC Titrate sensors (Man-Tech Co., Guelph, ONT, CA). Both DOC and TDN were determined by high-temperature combustion catalytic oxidation using a Shimadzu TOC-V_{CPN} total organic carbon analyser with a TNM-1 total nitrogen detection unit (Shimadzu Corporation Columbia, MD). Detection limits for DOC and TDN were 0.05 mg/L.

Water temperature was measured for a subset of springs (n = 12) at 30-min intervals using Hobo Pendant data loggers (UA-002; Onset Corp, Pocasset, MA; sensor resolution 0.1°C). Springwater discharge was measured at a prominent channel near the point of emergence by measuring the time required to fill a fixed volume.

2.4 | Data analyses

We compared the chemical attributes of springs located in four zones of the Fool Creek catchment (e.g., Upper, East, West, Riparian) and tested the influence of elevation, season and discharge on springwater. Differences in springwater between zones and discharge classes were determined using one-way analysis of variance and Tukey's multiple range means separation test (SPSS Inc., V. 22 IBM, Chicago, IL). Data were checked for homogeneity of variance and log transformed as necessary. Significance is reported at α = 0.05 critical value unless noted otherwise. The contribution of dominant anion and cations to spring, stream and soil solution chemistry, representing the relative stoichiometry of the various water sources, was compared graphically (Grapher V. 16.2.354; Golden Software LLC, Golden, CO). Early and late summer springwater chemistry was compared using paired t tests. To approximate the flowpath length above each spring, we estimated the upslope accumulating area (UAA) and the distance from the catchment boundary to the point of springwater emergence (ESRI 2020, ArcGIS Desktop: Release 10.7.1. Redlands, CA). We compared these flowpath metrics and elevation to chemical concentrations for each spring using least-squares linear regression. We used a two-pool end-member-mixing approach using the dominant ions ANC and Ca as tracers to estimate the contribution of several individual springs and the tributaries they generate to the concentration of streamwater at the lower Fool Creek gauge. The analysis used discrete spring tributary and streamwater ANC and Ca^{2+} concentrations from our June and August sample collections.

3 | RESULTS

The 2006 water year was relatively normal compared to mean values for streamflow and snowpack in Fool Creek. Snow accumulation throughout the catchment was 121% of the 30-year average. Fool Creek mean daily flow was 97% and peak flow was 89% of 30-year average values. The discrepancy between the moderately high snow accumulation and average streamflow can be explained by the previous year's (2005) low snow accumulation (72%) and relatively low streamflow (83%) and highlights the dependence of annual flow on antecedent soil moisture. These average hydrologic conditions likely produced average spring and stream hydrochemistry during the study period.

Emergent springwater had a mean pH of 7.0 (range: 6.2–7.9) and mean SC of 45 μS/cm (range 16–105 μS/cm; Table 1). Calcium and ANC (predominantly HCO_3^-) are the dominant cation and anion species in Fool Creek springwater (Figure 2). About half the cation charge originates from Ca^{2+} (53%), Mg^{2+} and Na^+ both contribute 20%, and K^+ represents the remainder (Figure 2). ANC dominates the anionic charge (90%) and SO_4^{2-} and Cl^- contribute 9 and 1%, respectively.

The concentrations of most springwater constituents fell between those of streamwater measured at the Upper and Lower Fool Creek gauge sites (Table 1). Streamwater concentrations increased or were uniform downstream. Calcium, Mg^{2+}, ANC and SC were 1.6 to 1.8 times higher at the Lower gauge, and K^+, Cl^-, SO_4^{2-}, and DOC increased by about 30% downstream. Nitrate was the only constituent that declined appreciably downstream (~80%). Springwater ANC, SC, pH and most dominant cations were higher than soil solution (Table 1). Anions, DOC, K^+ and total dissolved N (TDN) were lower in springwater than in soil solution. Specifically, soil leachate contained 5 and 20-times more TDN and DOC than springwater. The higher DOC and associated organic acids in the rooting zone neutralized alkalinity (ANC) and decreased soil solution pH.

Emergent springwater chemistry differed among catchment zones (Table 2 and Figure 1). Those located in the Upper zone had the lowest concentrations of most inorganic analytes. On average, springs emerging from the East flank had significantly higher levels of Ca^{2+}, Mg^{2+}, and SO_4^{2-} than those on the West and were approximately twice those of the Upper zone. Concentrations of springs emerging from the Riparian zone were often intermediate to those of the catchment flanks.

Four individual springs emerging from a faulted portion of the East flank had notably high ANC (Figure 3) and cation concentrations, and these springs generated two significant tributaries to Fool Creek. Concentrations of ANC, Ca^{2+}, and Mg^{2+} in these springs were more than double, and other constituents (K^+, Na^+, Cl^-, SO_4^{2-}) were significantly higher than all other Fool Creek Springs. Conversely, both NO_3^- and TDN were lower in this subset of springs. Despite differences in springwater concentrations across zones (Table 2), the contribution of individual analytes to the ion budget was relatively consistent (Figure 2). ANC

TABLE 1 Dissolved instantaneous ion concentrations in emergent springwater, streamwater, and soil solution leachate in the Fool Creek catchment at the Fraser Experimental Forest, Colorado

		Springwater		Upper Fool Creek		Lower Fool Creek		Soil Solution	
		Mean	*SD*	Mean	*SD*	Mean	*SD*	Mean	*SD*
pH	—	7.0	0.4	7.0	0.5	7.3	0.5	6.0	0.4
ANC	μeq/L	380.1	185.9	310.9	76.7	506.3	112.6	87.5	33.7
SC	μS/cm	44.7	19.9	34.0	5.2	53.3	12.5	26.3	12.5
Ca^{2+}	mg/L	4.9	2.8	3.7	0.5	6.4	1.3	2.9	1.6
Mg^{2+}	mg/L	1.1	0.5	0.8	0.1	1.4	0.3	0.7	0.5
Na^{+}	mg/L	2.6	0.5	2.4	0.3	2.7	0.3	0.8	0.4
K^{+}	mg/L	0.8	0.3	0.7	0.1	0.9	0.1	1.7	3.2
SO_4^{2-}	mg/L	1.8	0.5	1.5	0.2	2.1	0.4	2.0	3.1
Cl^{-}	mg/L	0.2	0.05	0.2	0.1	0.2	0.1	0.7	2.3
NO_3-N	μg/L	6.7	16.2	9.4	15.6	2.0	3.7	2.2	9.4
NH_4-N	μg/L	8.3	16.2	40.1	33.2	41.3	32.3	7.8	20.9
TDN	μg/L	76.1	41.4	560.9	915.5	543.5	1016.1	389.9	168.0
DOC	mg/L	1.8	1.5	2.4	2.4	3.0	2.4	35.6	13.4

Note: Stream chemistry was averaged from weekly samples collected between May and September 2006. Soil solution leachate was collected in the rooting zone at 20–30 cm soil depth using tension lysimeters (*n* = 50).

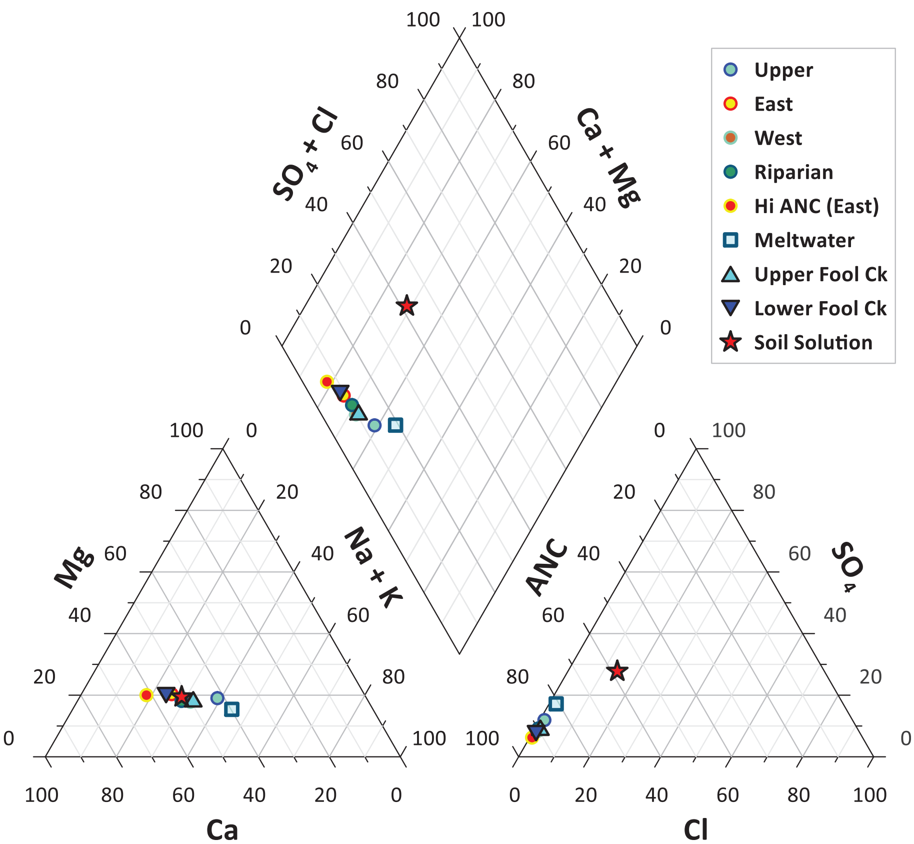

FIGURE 2 Chemical composition of emergent springwater, streamwater, and soil solution (leachate). The piper plots show the proportional contribution of cations or anions to combined sample composition. High ANC springs denote four springs emerging from the East zone (see Figure 3). All data sources were averaged throughout the summer period (June through August)

comprised 90% of the anions in Fool Creek spring across all zones (Figure 2), including the four springs with high ANC concentrations. The contribution of Ca^{2+} to springwater varied from 40% in the Upper zone to 60% in the 'High ANC' springs of the East flank. Soil solution had lower ANC and higher Cl^{-} but similar Ca^{2+} as spring and streamwater.

Stream discharge peaks in June and snowmelt dilutes concentrations of most ions in Fool Creek streamwater (Figure 4). Springwater ANC, Ca^{2+}, and Mg^{2+} concentrations and SC were 20–30% higher during late August across zones, though spring discharge was relatively constant (e.g., 0.31 vs. 0.29 L/s during June and August). Contrary to most other analytes, springwater DOC peaked concurrently

TABLE 2 Chemical composition (mean and *SE* of instantaneous concentrations) of 57 emergent springs in four zones of the Fool Creek catchment, Fraser Colorado for samples collected in June and August 2006

		Upper			East			West			Riparian				
		n = 14			*n* = 20			*n* = 13			*n* = 10			*F*	*p*
pH	—	6.7	0.04	a	7.1	0.05	b	7.1	0.05	b	7.1	0.05	b	27.0	<0.001
ANC	μeq/L	230.8	13.5	a	529.6	29.0	c	356.7	13.2	c	406.9	26.8	b	36.0	<0.001
SC	μS/cm	28.7	1.4	a	60.9	3.0	c	41.1	1.1	c	48.4	3.0	b	38.2	<0.001
Ca^{2+}	mg/L	2.6	0.16	a	7.1	0.45	c	4.6	0.18	b	5.6	0.46	b	36.1	<0.001
Mg^{2+}	mg/L	0.7	0.05	a	1.6	0.08	c	1.0	0.04	b	1.1	0.07	b	32.9	<0.001
Na^{+}	mg/L	2.2	0.06	a	2.8	0.09	b	2.8	0.07	b	2.7	0.07	b	16.6	<0.001
K^{+}	mg/L	0.6	0.03	a	1.0	0.03	c	0.9	0.02	c	0.9	0.05	b	37.2	<0.001
SO_4^{2-}	mg/L	1.4	0.05	a	2.1	0.07	c	1.6	0.05	a	1.9	0.09	b	30.6	<0.001
Cl^{-}	mg/L	0.1	0.01	a	0.2	0.01	c	0.2	0.01	c	0.1	0.01	b	31.4	<0.001
NO_3-N	μg/L	10.6	3.9	ab	1.7	0.8	a	4.8	2.5	a	12.1	3.1	b	3.6	0.015
NH_4-N	μg/L	6.3	1.7		11.1	2.9		5.4	2.8		9.3	3.0		1.0	0.389
TDN	μg/L	97.8	11.5	b	64.9	5.2	a	77.4	8.2	ab	64.4	6.3	a	3.9	0.012
DOC	mg/L	1.9	0.4		1.7	0.2		2.1	0.4		1.4	0.2		0.8	0.522

Note: Letters denote which zones differ at α = 0.05 (Tukey's pair-wise means separation test).

with stream discharge. Similarly, late-season NO_3^- was about 80% lower than that emerging from springs during the snowmelt period. Compared the other springs and streamwater, the ANC and Ca^{2+} concentrations of the High ANC springs were relatively unresponsive to seasonal changes (Figure S2). In general, across catchment zones, ion concentrations were lower in springs with higher discharge (Table 3). Major anion and cation constituents were diluted by as much as 27% in high compared to low flow springs, and ion concentration and discharge were linearly, though weakly related (r^2 = 0.03–0.11; p < 0.05). Concentrations of springwater DOC and the N species were unrelated to discharge in general, and for the four High ANC springs concentration and discharge were not related for any chemical constituent.

Springwater was generally cooler, and temperature fluctuated less on daily and seasonal timesteps relative to streamwater (Figure 5). For example, in July and August daily temperature fluctuated by <0.2°C in springs compared to 2.5°C in streamwater. The daily amplitude of streamwater temperature exceeded the average springwater temperature increase between late June and September.

3.1 | Geospatial relations with springwater

Concentrations of most chemical constituents in emergent springwater increased at lower elevations. Spring elevation explained 29–46% of the variability in ANC, SC, Ca^{2+}, Mg^{2+}, K^+, Na^+, and SO_4^{2-} concentrations (Figures 6 and S3). In contrast, TDN concentrations were consistently highest in Upper springs (Table 2), and there were no clear elevation trends for either NO_3^- (Figure 6) or DOC. Spring temperature minima increased 0.6°C with each 100 m descent in elevation (r^2 = 0.55; p < 0.001); elevation explained less variation in mean water temperature (r^2 = 0.27; p < 0.002) and was unrelated to temperature maxima.

The elevation patterns described for springs were similar to those of Fool Creek streamwater (Figures 6 and S3). Streamwater ion concentrations at the Upper Fool Creek site were similar to the springs that emerged in the nearby Upper zone. Streamwater at the Lower Fool Creek site was similar in composition to the East and Riparian zone springs. Stream ANC and Ca^{2+} (Figure 6) concentrations increased threefold over the 500 m elevation range (r^2 = 0.85 and 0.74, respectively). There were similar downstream patterns for K^+, Mg^{2+}, Na^+, SO_4^{2-} (Figure S3) and SC. Only Cl^-, DOC and the N species did not increase significantly downstream in Fool Creek.

Distance from the catchment perimeter to the point of emergence of springs in the Upper zone averaged 276 m compared to 604 m in the Riparian zone and about 345 m for both the East and West flanks. This distance was significantly and positively related to springwater ANC, SC and Ca^{2+} across all zones, but the relations were strongest for springs in the Riparian zone (p < 0.003; r^2 = 0.25–0.31). The UAA was also greatest for springs located in the Riparian zone, but UAA was a relatively poor predictor of springwater chemistry. The relation between NO_3^- and UAA was significant for Riparian zone springs (r^2 = 0.13; p = 0.029) and the relations between ANC, SC and Ca^{2+} were only significant in the Upper zone (r^2 = 0.12–0.15; p < 0.031).

4 | DISCUSSION

4.1 | Sources of variability in springwater chemistry

The chemical composition of surface water draining headwater areas reflects their underlying lithology (Fields & Dethier, 2019; Miller, 2002). The Fraser Experimental Forest is located north of the

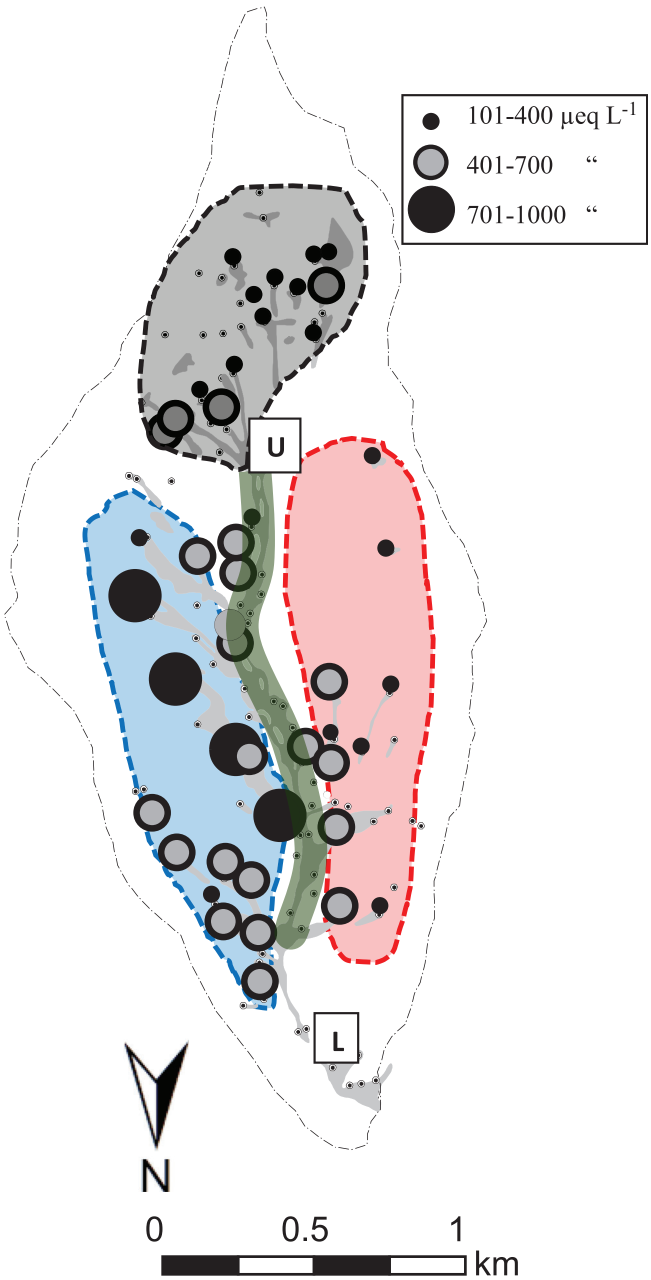

FIGURE 3 Variability in springwater ANC with special attention to connectivity between high ANC springs emerging in the faulted section of the East zone. Upper and Lower Fool Creek stream gauging stations are labelled with U and L. See Figures 1 and S1 for additional map details

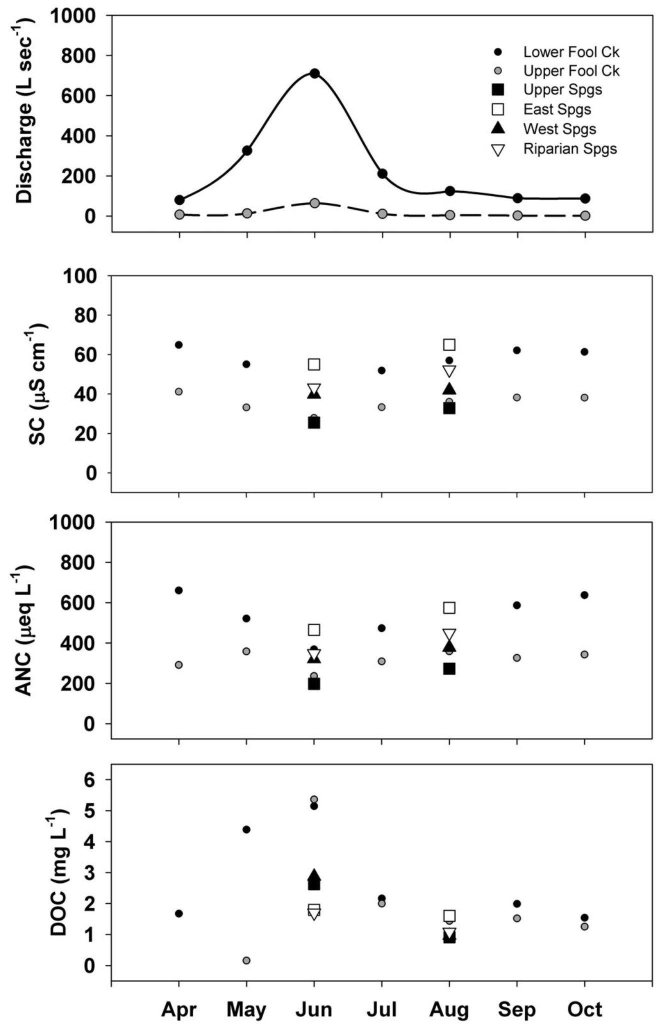

FIGURE 4 Seasonal discharge and chemistry at the Upper (3213 m.a.s.l.) and Lower (2926 m.a.s.l.) Fool Creek sites and for springwater chemistry in the catchment zones. The Upper and Lower Fool Creek gauges sample 66 and 289 ha contributing areas, respectively. Stream discharge are monthly means based on daily mean flow calculated from 10-min interval measurements and chemistry data are means of weekly samples during 2006

Colorado Mineral Belt, and the Ca^{2+} and ANC-dominated chemistry of Fool Creek spring and streamwater is consistent with weathering of intermediate to mafic mineral groups in the gneiss and schist bedrock common throughout the area (Wanty et al., 2009). The low Cl^{-} concentration we observed in Fool Creek springs and streamwater is typical of midcontinental snowmelt sources of precipitation (Covino & McGlynn, 2007). Ion concentrations were lower for springs draining the Quaternary deposits in the Upper zone and higher for those in the faulted portion of the East flank. However, as opposed to catchments draining contrasting lithology (Horton et al., 1999), the similar relative ionic composition of water emerging from springs across the Fool Creek zones (Figure 2) suggests that compositional differences in the underlying crystalline bedrock are minor. In contrast, nearby catchments at FEF with mixed sedimentary and crystalline lithology have threefold higher Ca^{2+}, Mg^{2+}, and ANC and twice the K^{+} concentrations in water draining hillslope wetlands as the Fool Creek springs (LaPerriere Nelson et al., 2011), including the High ANC springs on the East flank.

Differences in constituent concentrations among distinct zones and gradual changes across the catchment provide evidence of processes functioning at sub-catchment spatial scales (McGuire et al., 2014). Both spring and streamwater ion concentrations generally increased at lower elevation (Figure 6 and Table 1). Specifically, concentrations of most constituents were higher in springwater

TABLE 3 Chemistry and discharge class for Fool Creek springs

		Low		Moderate		High		p
pH	—	7.0	a	7.0	a	6.8	b	0.001
		(0.04)		(0.04)		(0.05)		
ANC	μeq/L	385.8	a	324.3	b	312.2	b	0.022
		(21.1)		(14.1)		(25.8)		
SC	μS/cm	45.3	a	38.8	ab	37.6	b	0.027
		(2.2)		(1.5)		(2.8)		
Ca^{2+}	mg/L	4.9	a	4.0	b	4.1	b	0.039
		(0.3)		(0.2)		(0.4)		
Mg^{2+}	mg/L	1.2	a	1.0	b	0.9	b	0.001
		(0.1)		(0.1)		(0.1)		
Na^{+}	mg/L	2.6		2.6		2.4		NS
		(0.1)		(0.1)		(0.1)		
K^{+}	mg/L	0.91	a	0.76	b	0.74	b	0.003
		(0.04)		(0.03)		(0.04)		
SO_4^{2-}	mg/L	1.80		1.62		1.64		NS
		(0.1)		(0.1)		(0.1)		
Cl^{-}	mg/L	0.17	a	0.14	b	0.13	b	<0.001
		(0.01)		(0.01)		(0.005)		

Note: Data are means and *SE* for all catchment zones, excluding four Hi ANC springs. Spring discharge classes as follows: Low < 0.2; Moderate 0.2–0.5; High > 0.5 L/s. Letters denote which classes differ ($\alpha = 0.05$; Tukey's pair-wise means separation test).

emerging in the Riparian zone compared to the Upper zone (Table 2). Springs emerging in the Riparian zone had a greater UAA and distance to catchment boundary than those emerging in the Upper zone or catchment flanks. Mirroring spring elevation, distance to the catchment boundary was positively correlated to springwater ANC, SC, and Ca^{2+} concentrations. The increased concentrations of weatherable minerals at lower elevation and distance from the catchment edge were consistent with greater chemical exchange along longer flowpaths and contact times (Zimmer et al., 2013). Conversely, the down-gradient decline in springwater TDN and NO_3^- likely reflects cumulative N uptake by upland vegetation and gaseous N loss (e.g., denitrification) from riparian soils (McClain et al., 2003; Vidon et al., 2010).

In addition to the broader geologic and spatial determinants of springwater composition within the catchment, several springs that emerged within the faulted East flank contributed another source of variability (Figure 3). High concentrations of ANC and dominant cations suggests that these springs originate from distinct or more highly altered bedrock, and their low N concentrations are consistent with deeper groundwater supply. The limited seasonal change in ion concentrations (Figure S2) and their insensitivity to discharge are additional evidence that they emerge from a deeper groundwater source. The high ANC springs originate within a faulted section of brecciated granodiorite dikes and exposed outcrops that is more fractured than the surrounding gneiss and schist bedrock, and where increased surface area and contact time with bedrock contributes to higher springwater ion concentrations. Elsewhere, unmapped local geologic features rather than broader landscape factors determined variability in groundwater and stream chemistry for 11 Swiss catchments (Floriancic et al., 2019). Similarly, high alkalinity and SC emerged from springs in the Scottish Highlands adjacent to small calcareous outcrops (Scheliga et al., 2017). At other Colorado Front Range sites, divergence between measured springwater Ca^{2+} concentrations and stoichiometric predictions based on bedrock weathering were attributed to release from unmapped calcite veins and aeolian dust inputs (Clow et al., 2016; Fields & Dethier, 2019). These unmapped factors are also known to influence soil, snowpack and emergent groundwater chemistry (Bergstrom et al., 2018; LaPerriere Nelson et al., 2011; Retzer, 1962; Rhoades et al., 2010) in numerous catchments at and around FEF. However, the similarity in the chemical composition of the Fool Creek springs indicates that there are no significant, unmapped lithologic changes within the catchment. Our work and earlier studies demonstrate the consequences of local features on emergent groundwater chemistry and underscore that this variability cannot be readily assessed a priori from existing data or landscape characteristics (Floriancic et al., 2019).

4.2 | The influence of springwater on streamwater

Fool Creek streamwater chemistry reflects the mixture of groundwater sources that emerge from different portions of the catchment. For example, the ion composition and concentrations of springs in the

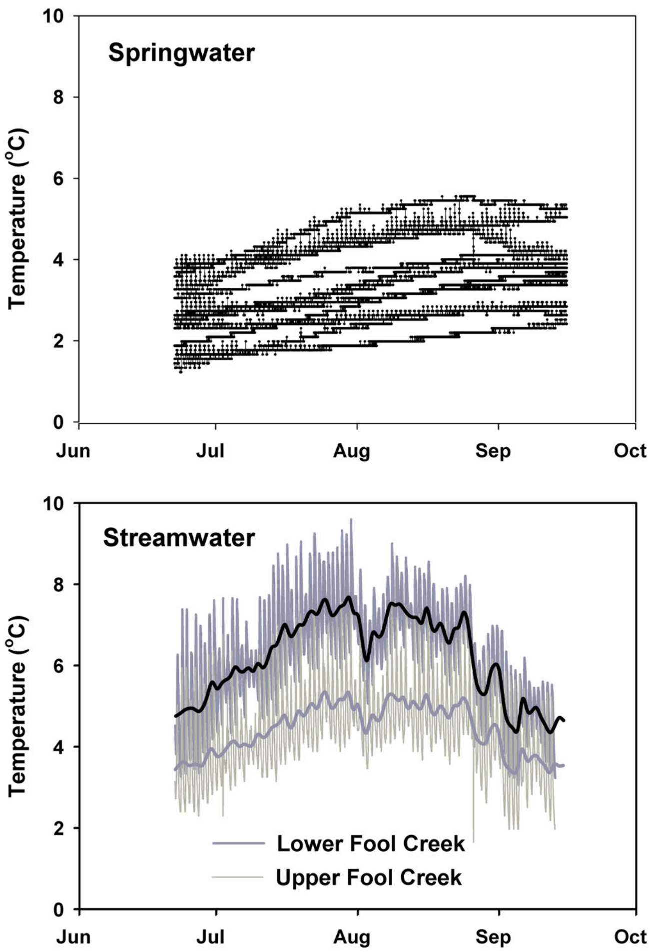

FIGURE 5 Diurnal and seasonal patterns in springwater (n = 12 springs) and streamwater temperature at the Upper (3213 m) and Lower (2910 m) Fool Creek sites. Temperature was logged every 30 min. Darker lines are mean daily temperature for stream sites

Upper zone are similar to snowmelt water (Figure 2) and contribute to the dilute character of streamwater at the Upper Fool Creek gauge station. Fool Creek streamwater changes gradually downstream, but the increase is more appreciable below the confluence with tributaries draining the concentrated springs in the East zone (Figures 3 and 6). An end-member mixing-model approach estimated that roughly half the concentration of Ca^{2+} and ANC in streamwater at the onset of baseflow conditions and a quarter of that during spring snowmelt originated from these springs (Table 4). Using a similar approach, more than half of the streamwater base cations were determined to originate from springs on Niwot Ridge (Fields & Dethier, 2019), a nearby site directly east of our study site. Since these two Fool Creek spring-derived tributaries contribute <1% to late-season stream discharge (i.e., springs: <1 L/s vs. lower Fool Creek ~100 L/s; Figure 4), their influence on stream chemistry is disproportionately large relative to the amount of water they contribute. Our findings indicate that a few springs can alter the aggregate streamwater chemistry of an entire catchment (Floriancic et al., 2019; Kaur et al., 2016).

4.3 | Susceptibility to change

Shallow groundwater is coupled to near-surface conditions, so changing climate, inputs and ecosystem disturbance have the potential to influence emergent springwater and downstream water quality (Earman & Dettinger, 2011; Junk et al., 2013; Stevens, Jenness, & Ledbetter, 2020; Stevens, Schenk, & Springer, 2020; Tetzlaff et al., 2010). Nitrate release from emergent groundwater is a concern not only in agricultural areas (Angier & McCarty, 2008) but also in forested headwaters (Kaur et al., 2016; O'Driscoll & DeWalle, 2010) especially where atmospheric N deposition is chronically elevated (Burns et al., 1998; West et al., 2001). Uptake by vegetation and denitrification in C-rich, saturated wetland soils has been shown to mitigate NO_3^- discharge from seeps in N-saturated forests in New York (Burns et al., 1998) but these retention processes do not fully compensate for N inputs and prevent excess N export to streams (Schiff et al., 2002). Catchment configuration and forest species composition influence general patterns in NO_3^- release from headwater springs (West et al., 2001), but individual springs have been shown to create critical areas that contribute the bulk of NO_3^- load to surface water (Angier & McCarty, 2008; McClain et al., 2003; Morley et al., 2011). Nitrogen deposition remains relatively low at Fraser (<5 kg N ha /yr; Rhoades et al., 2017), but chronically elevated inputs near the urban and agricultural centres along the eastern slope of the Front Range have altered catchment N cycling and export (Baron et al., 2000; Wegener et al., 2018). The shorter, shallower flowpaths contributing to the Upper Fool Creek springs are likely to be the most sensitive to continued increases in N deposition and other inputs (Brahney et al., 2020; Fenn et al., 2003; Tetzlaff et al., 2010).

Spring and streamwater in Fool Creek are both oligotrophic with NO_3^- concentrations consistently near analytical detection limits (Tables 1 and 2). We observed decreased down-gradient NO_3^- concentrations in both spring and streamwater (Figure 6 and Table 1) and TDN was also highest in the Upper zone springs (Table 2). Fraser catchments in general, and Fool Creek specifically, release little N even after forest dieback (Rhoades et al., 2017) or logging (Rhoades et al., 2020). The decline in N at lower elevations is consistent with the high plant N demand typical of subalpine forests (Fahey & Knight, 1986), as shown by low soil solution NO_3^- exported from the rooting zone (Table 1). Riparian zones are characterized by high N and C delivery from hillslopes that intersect subsurface flowpaths and anoxic soils to limit NO_3^- release to surface water (Pinay et al., 1993; Vidon et al., 2010). However, NO_3^- emerging from Riparian zone springs was equal or higher than elsewhere in Fool Creek, and spatial and temporal variability in subsurface hydrology (Lessels et al., 2016) and the exchange between N sources and sinks likely influence N retention within this biogeochemical hotspot (McClain et al., 2003).

Emergent springs maintain the hydrology of hillslope and riparian wetlands (Carsey et al., 2003; LaPerriere Nelson et al., 2011; Ruddy & Williams, 1991) and the rich biodiversity of these groundwater-dependent ecosystems within high-elevation subalpine forest ecosystems (Stevens, Jenness, & Ledbetter, 2020; Stevens, Schenk, &

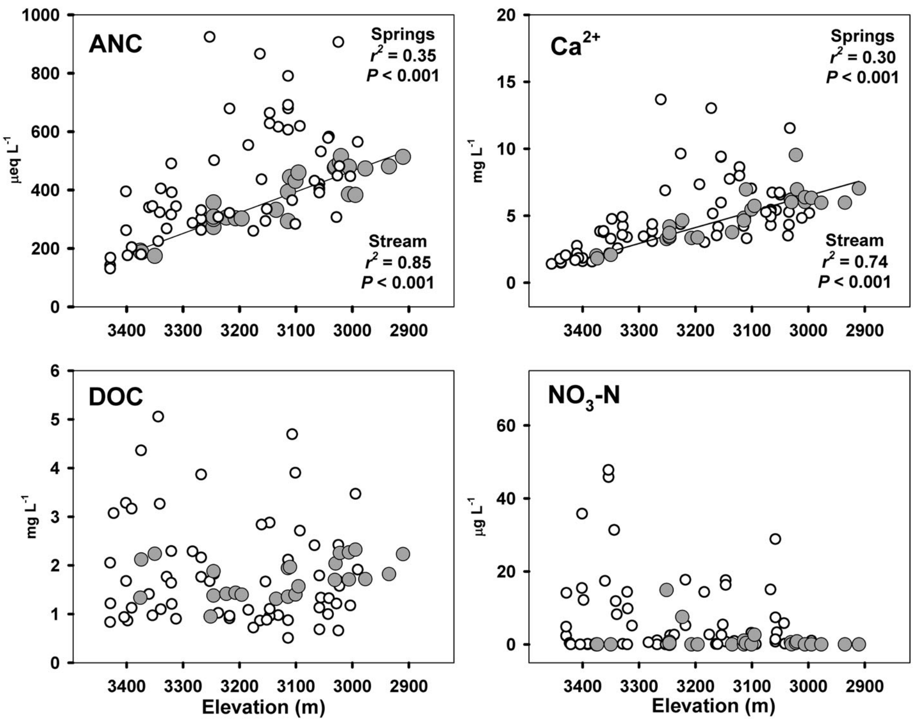

FIGURE 6 Relation between elevation and constituent concentration of spring and streamwater. Symbols indicate springs (hollow circles) and streamwater (filled circles). Least-squares linear relations fitted for streamwater samples. The elevation axis is displayed in reverse, so fitted slopes are negative

TABLE 4 Concentrations of ANC and Ca^{2+} in tributaries draining two high ANC springs (#43 and #51) and their fractional contribution to Fool Creek streamwater

Season	Type	Site	ANC (ueq/L)	Contribution from spring tributary[a] (%)	Calcium (mg/L)	Contribution from spring tributary[a] (%)
Snowmelt (June)	Stream	Upper Fool Creek	189.7		2.7	
		Lower Fool Creek	287.5		4.5	
	Spring tributary	Spg #43	483.9	33.2	8.1	32.2
		Spg #51	599.2	23.9	10.0	23.5
Late summer (August)	Stream	Upper Fool Creek	296.1		3.8	
		Lower Fool Creek	528.1		7.4	
	Spring tributary	Spg #43	670.2	62.0	10.0	58.6
		Spg #51	855.6	41.5	11.7	45.9

Note: The fractional contribution from each spring to streamwater ANC and Ca^{2+} concentrations at the lower Fool Creek gauge was compared during snowmelt (June) and late summer (August) flow seasons.

[a]Fraction of ANC or Ca^{2+} concentrations (C) from spring tributaries (Sprg) from end-member mixing-model analysis where: $\text{Fraction}_{Sprg} = (C_{Lower\ Fool} - C_{Upper\ Fool})/(C_{Sprg} - C_{Upper\ Fool})$.

Springer, 2020). There is concern about the sensitivity of these ecosystems to projected warmer and drier climatic conditions (Foks et al., 2018), and the implications of potential changes on groundwater recharge, sustained streamflow and downstream water quality. Though the critical role of these headwater ecosystems for maintaining clean water supply and aquatic biota and habitat is well known (Hauer et al., 2007; Nadeau & Rains, 2007), debate on the jurisdictional protection of headwater tributaries highlights the tenuous future of small, dispersed, and inconspicuous catchment features (Golden et al., 2017; Leibowitz et al., 2008). This study emphasizes the need to consider various scales of spatial variability to better understand and conserve the functional connectivity between emergent springs and the adjacent terrestrial landscapes that determine the chemical composition of water for downstream uses.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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