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Insights into Recharge Processes in Mountain-Block Hydrology Using Isotopic and Geochemical Characterization

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Insights into Recharge Processes in Mountain-Block Hydrology Using Isotopic and Geochemical Characterization

by

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Abstract

Mountain block hydrology, including mountain streamflow generation and aquifer recharge in both mountains and prairies, depends on the infiltration and transport of mountain precipitation. Yet these recharge processes are not yet fully understood, and the two dominant paradigms regarding mountain recharge appear to be in conflict – Mountain Block Recharge (MBR) suggests adjacent prairie aquifers are recharged by deep flowpaths from mountain blocks, while alpine recharge suggests local flowpaths generate most mountain streams, which then recharge prairie aquifers at the mountain front. This thesis investigates this apparent dichotomy by analysing mountain recharge, aquifer storage, and streamflow generation using water geochemistry and isotopes in the upper (unregulated) reach of the Elbow River, an eastern slopes watershed. Water isotopes in precipitation and streamflow demonstrate that the young water fraction (Fyw) methodology is not well suited to areas with overwinter snowpack, but that average water isotope composition of winter baseflow shows ~20% of streamflow is derived from the previous year’s precipitation, suggesting rapid infiltration and throughflow. Silica and sulfate in streamflow and groundwater samples, along with sulfate isotopes, show that siliciclastic and carbonate aquifers contribute water equally to the Elbow River despite greater carbonate volume in the watershed, and that aquifer residence times are less than 10 years. Finally, analyzing the same geochemical components in late October baseflow along the length of the Little Elbow shows that high, cold precipitation infiltrates and is transported along intermediate and deep flowpaths before becoming streamflow at low elevations. Together, these findings suggest that the dominant paradigms are really two aspects of the highly dynamic and interconnected nature of mountain block hydrology.
Preface

Chapter 1 (Introduction) is original, independent work by ÉMS Campbell.

Chapter 2 has been published as Campbell EMS, Pavlovskii I, Ryan MC. 2020. Snowpack disrupts relationship between young water fraction and isotope amplitude ratio; approximately one fifth of mountain streamflow less than one year old. Hydrological Processes. DOI: 10.1002/hyp.13914

ÉMS Campbell designed the study, collected and analysed the data, and wrote and edited the manuscript. I Pavlovskii modelled the data and provided feedback on the manuscript. MC Ryan supervised the study, provided detailed feedback, and edited the manuscript.

Chapter 3 has been published as Campbell EMS, Lagasca PA, Stanic S, Zhang Y, Ryan MC. 2021. Insight into watershed hydrodynamics using silica, sulfate, and tritium: source aquifers and water age in a mountain river. Applied Geochemistry. DOI: 10.1016/j.apgeochem.2021.105070

ÉMS Campbell designed the study, collected and analysed the data, co-wrote the three end-member model and silica equations, and wrote and edited the manuscript. PA Lagasca co-wrote the three-end-member model and provided feedback on the manuscript. S Stanic collected 2017 data and co-wrote the silica age equations. Y Zhang collected and analysed 2017 sulfate data and provided feedback on the manuscript. MC Ryan supervised the study, provided detailed feedback, and edited the manuscript.

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ÉMS Campbell co-designed the study, collected and analyzed the data, and wrote and edited the manuscript. MC Ryan co-designed the study, provided detailed feedback, and edited the manuscript.

Chapter 5 (Conclusion) is original, independent work by ÉMS Campbell.
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May they find ways to leave the world a better place and create happiness for themselves along the way.
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A drop of water, if it could write out its own history, would explain the universe to us.

- Lucy Larcom
Chapter 1: Introduction

Almost every drop of the Elbow River is groundwater, and each drop has a story to tell. This thesis presents three of those myriad possible stories, the findings from three years of research (2016-2018) in the Elbow River watershed. The chemistry of the water tells us that the rain and snow that fall do not run directly into the river. Instead, they are mixed and stored in the sandstones and shales of the front ranges and foothills, the majestic limestone cliffs of the headwaters, and even the soils and gravels of the river valleys before becoming the waters of the Elbow River. This collection of papers illustrates how the composition of the water in the Elbow River changes through the days, the seasons, and the years, and what these changes tell us about how the water moves through the watershed, where and how long it is stored, and how the changing climate will change the river itself.

This thesis employs the 435km² Upper Elbow Watershed (Figure 1-1) as a case study, using streamflow water chemistry and isotope composition to provide clues about how precipitation that infiltrates in the mountain block is transported through the rock units to become groundwater and streamflow. This watershed is ideally suited to such a purpose as it is relatively undeveloped yet very accessible, only 45 min by car from the city of Calgary with well-maintained road access from May to November. Understanding the watershed dynamics in this mountain block has more than academic interest – more than 80% of streamflow in the Elbow River is generated in this watershed and a small portion of the Middle Elbow Watershed upstream of Bragg Creek (Manwell and Ryan 2006). The Elbow River supplies rural and municipal water needs to residents of the Elbow River Watershed upstream of Calgary, and the Glenmore Reservoir, 10km upstream of the Elbow’s mouth, provides household water to over 500,000 people (Sturgess 2019). Thus, the hydrodynamics of the Upper Elbow mountain block directly impact a vast number of Albertans.

The 120km long Elbow River has relatively low average streamflow (∼4m³/s in winter to ∼40m³/s after spring rain events, though it can be up to 1700m³/s in severe
flood events (Alberta Environment and Sustainable Resource Development 2019)). Hudson (1983) describes its geological characteristics and fluvial geomorphology. The predominantly single-channel Elbow drains NE-SW tributary valleys into the main W-E channel, frequently switching to braided sections through the coarse gravels and cobbles of its alluvial aquifer. The alluvial aquifer varies from 5-25 km wide (Van Everdingen et al. 2009) and in the Middle and Lower Elbow Watersheds, throughflow from this aquifer is much more important in maintaining streamflow than minor bedrock contributions (Manwell and Ryan 2006). Yet where does the throughflow come from? Grasby et al. (2000) demonstrated that essentially all water in Front Ranges rivers spends time as groundwater before entering streamflow, and approximately 80% of the streamflow in the Lower Elbow Watershed is generated in the Upper Watershed (Manwell and Ryan 2006). Therefore there must be significant groundwater contribution to the Upper Elbow River. This thesis attempts to shed light on that connection.
Previous work on recharge and streamflow in the Rocky Mountains front ranges can be classified into two broad categories; water chemistry and hydrological modelling, though of course the two frequently overlap. The first category includes theses by Grasby (1997), Katvala (2008), and Chao (2011), which respectively investigated controls on major ion chemistry, precipitation sources and seasonality of water isotope composition, and sulfate and nitrate isotope compositions in the Bow River. Katvala demonstrated that winter precipitation is a major component in streamflow, but that snowpack and groundwater storage alter the isotopic composition of the input precipitation before it becomes streamflow. Chao showed that sulfate and
nitrate isotopes in streamflow are useful in determining streamflow sources, a finding supported by Nightingale and Mayer (2012), who used sulfate isotope to identify sources and processes in the sulfur cycle at Canyon Creek, an Elbow River tributary. Grasby’s thesis work laid the foundation for two subsequent papers about the relationships between groundwater and streamflow (i.e. Grasby et al. 1999a; 2000), highlighting that TDS and activity ratios indicate all streamflow spends time as groundwater, and that carbonate and evaporite rock aquifers strongly influence streamflow chemistry. Academic publications on Elbow River streamflow chemistry are fewer and farther between, with Manwell and Ryan’s (2006) investigation of chloride as a tracer for throughflow and point sources standing out as the major contribution.

However, there are several unpublished undergraduate theses and research reports (Leung 2018) that point out important areas for further investigation, highlighting the importance of such work. Professional reports cataloging major ion chemistry and contaminants for water quality assessment (summarized by WQ Consulting Services (2016)), and a published paper by Sosiak and Dixon (2006) demonstrating water quality deterioration in the Elbow have been used to inform municipal decisions on Elbow River management, but do not address questions about water provenance or recharge processes.

Hydrological modelling studies focused on streamflow generation in the Rocky Mountain front ranges have focused on infiltration and outflow alpine catchments (i.e. Hood et al. 2006; Hood and Hayashi 2015; Harrington et al. 2018; Christensen et al. 2020; Fang and W. Pomeroy 2020), and show the critical importance of alpine groundwater aquifer storage to maintaining overwinter baseflow in headwater streams. Paznekas and Hayashi (2016) demonstrated that winter baseflow, while low, tends to be consistent year to year, and is controlled by long-term annual precipitation and both age and type of bedrock. Glacial melt studies (i.e. Chernos et al. 2020a; Bash and Marshall 2020) indicate that glacial meltwater is a minor contribution to streamflow overall (3-6%) but sustain higher summer flows in August. No studies currently exist that link streamflow supply in the Middle and Lower Elbow (and by logical extension,
most eastern slopes rivers in the Rocky Mountains) explicitly to headwater streamflow generation.

One of the current “big picture” questions in mountain block hydrology is the relationship between infiltration, recharge, and nested flow systems. Mountain Block Recharge (MBR) has been investigated for more than 20 years (i.e. Wilson and Guan 2004; Markovich et al. 2019a), but the focus of the field has largely been how water from the mountain block recharges adjacent plains aquifers. Mountain aquifer recharge has been considered in various contexts (Winter 2007; Smerdon et al. 2009a), and Markovich et al. (2019a) suggest this phrase as the term for infiltrated water that becomes mountain streamflow, but studies in this area are often framed in terms of groundwater/surface water interaction or streamflow supply (i.e. Käser and Hunkeler 2016; Cochand et al. 2019) rather than a separate framework in the way MBR has been. Hayashi’s (2020) comprehensive review of alpine headwaters suggests that local flow systems are the primary recharge mechanism in mountain blocks due to decreasing porosity and permeability with depth, and that mountain streams encountering fractures near the mountain front are the primary recharge mechanism for adjacent prairie basin aquifers. Some recent studies focused on groundwater mixing and flowpaths within the mountain block itself support the dominance of alpine headwater storage and shallow, local flowpaths supplying the majority of mountain streamflow (i.e. Scheliga et al. 2017; Manning et al. 2021). While challenging the regional flowpath paradigm for prairie basin aquifer recharge in MBR, these papers do not explicitly assess the effects of highly fractured mountain aquifers such as those in the Upper Elbow watershed, dominated by repeating thrust faults (Evers and Thorpe 1975; Hudson 1983; Prior et al. 2013) or that of karstic porosity in the carbonate units (Ford 1971; Drake and Ford 1976) which can result in considerable connectivity (Ford 1983). In particular, the prevalence of springs in the Upper Elbow and other eastern slopes watersheds suggests a greater role for intermediate and regional flow systems (Grasby and Hutcheon 2001) than these studies indicate.
The papers in this thesis examine several aspects of mountain streamflow generation, such as the effects of snow storage versus immediate infiltration and the effects of rock type on aquifer storage and transmission (via streamflow chemistry) to examine the concept of mountain block recharge, mountain aquifer recharge and transmission, and nested flow systems within the Upper Elbow mountain block. To do so, the first paper (chapter 2) inspects the relative timing of infiltration and streamflow generation using precipitation and streamflow water isotope compositions with the “young water fraction” methodology, and evaluates the suitability of this methodology for watersheds that host overwinter snowpack. The second (chapter 3) uses streamflow water chemistry in a three end-member model, sulfur isotope compositions, and tritium measurements to identify groundwater aquifer types, their respective contributions to streamflow, and to estimate transport times in the Upper Elbow Watershed. The third paper pulls these methodologies together to further delineate aquifer contributions in early winter baseflow along the length of the Little Elbow, helping illustrate the distinctions and interconnectedness of local, intermediate, and regional flowpaths. These investigations shed light on some of the questions raised by conflicts between MBR and alpine hydrology paradigms.
Chapter 2: Snowpack disrupts relationship between young water fraction and isotope amplitude ratio; approximately one fifth of mountain streamflow less than one year old

Key Points:

- Snowpack accumulation disrupts the relationship between isotopic amplitude ratio and young water fraction ($F_{yw}$) and therefore constrains the two-compartment model in the estimation of young water fraction ($F_{yw}$);
- Incorporating snowpack in ‘precipitation’ input in the model improved the prediction of both discharge and mean monthly $d^{18}$O streamflow composition and produced a range for ($F_{yw}$);
- The improved model $F_{yw}$ estimate ranges (7 to 23% ‘young’ water) for the study catchment compared well with an independent estimation that 20% of winter baseflow came from the previous year’s precipitation.

Abstract

Previous “fraction of young water” ($F_{yw}$) estimates based on relative annual isotopic amplitudes in precipitation ($A_p$) and streamflow ($A_s$) produced low $F_{yw}$ values in mountain catchments, which is contrary to extensive research that reports rapid water transmission in mountains. This study investigated this discrepancy by testing the effect of snow accumulation on the model that underpins the $F_{yw}$ method. A Monte Carlo analysis of simulations for 20,000 randomly-generated catchment model configurations used 10 years of precipitation inputs for the Upper Elbow River catchment in the Rocky Mountains (Alberta, Canada) to model discharge with and without snowpack storage of winter precipitation. Neither direct nor modified precipitation input produced a 1:1 relationship between $A_s/A_p$ and $F_{yw}$, undermining
the applicability of the original $F_{yw}$ method in mountain watersheds with large seasonal snow accumulation. With snowpack-modified input a given $A_s/A_P$ ratio corresponds to a range of $F_{yw}$ values, which can still provide semi-quantitative information. In the small (435 km$^2$) Elbow River catchment a $F_{yw}$ range of 7-23% supports previous findings of rapid transmission in mountain catchments. Further analysis showed that the improved discharge prediction (Nash-Sutcliffe efficiency $> 0.9$) correlates with higher $F_{yw}$ values and demonstrated that the interannual shifts in $\delta^{18}O$ can be used to estimate new water (<1 year) fraction in winter streamflow, and the estimate of 20% for the Elbow River further supports rapid transmission in mountain catchments.

Introduction

Around the world, mountain catchments act as "water towers" for adjacent low-lying regions with their outsized contributions to river flow (Viviroli et al., 2007). Overwinter snowpack is often a dominant contribution to river flow (Viviroli et al., 2007). In these environments, the speed and pathways by which rain and snow in a watershed become streamflow is a critical element of water resource management, not only to mitigate flood and drought but also to understand land-use impacts and pollutant transport. For example, water sourced from the eastern slopes of the Rocky Mountains drives flow in major rivers of the semi-arid southern portion of the Canadian Plain (Ferguson et al., 2007), where there is increasing urban development pressure on the adjacent river-connected alluvial aquifers (Cantafio and Ryan, 2014). Knowing how much of the rain and snow in given year will become streamflow in the following year would improve water use planning and land use planning, and better inform pollutant and nutrient transport models.

The role of groundwater aquifers in storing and transmitting precipitation and snowmelt is crucial to understanding mountain streamflow generation (i.e. Käser and Hunkeler 2016; Paznekas and Hayashi 2016). Stable water isotopes have long been used to calculate water residence times and provide information about streamflow sources
on a watershed scale (Sklash and Farvolden 1979; McDonnell 1990; Botter et al. 2011; Tetzlaff et al. 2015)(e.g. Sklash and Farvolden, 1979; McDonnell, 1990; Botter et al., 2011; Tetzlaff et al., 2015). Unlike conventional age tracers such as CFCs, SF$_6$, and tritium, which can provide a direct age estimate, seasonal and interannual variability in stable isotope ratios in water can be used to estimate older and younger water fractions. However, these estimates do not correspond to specific ages and vary between different studies (e.g. McGuire & McDonnell, 2006; Manning et al., 2012). The “fraction of young water” ($F_{yw}$) approach (Kirchner, 2016a, b) does specify the age of a old/young boundary - young water is defined as river flow that has fallen as precipitation in the previous $10 \pm 3.0$ weeks ($2.3 \pm 0.7$ months) and can be calculated based on the relative seasonal changes in the $\delta^{18}$O precipitation and river water (Kirchner, 2016a, b). A particular advantage of the $F_{yw}$ approach is that it is not biased in spatially heterogeneous catchments comprising nested systems with different mean transit times. This approach assumes that the precipitation infiltrates at the time at which it falls, which is clearly violated in regions where overwinter snowpack accumulation occurs (without infiltration) for six months or more, however no accommodation is made for snowpack storage in the age of input water.

The $F_{yw}$ method has been applied in catchments throughout the world (Jasechko et al., 2016; Lutz et al., 2018; Song et al., 2017; von Freyberg et al., 2018) and indicates that $F_{yw}$ is lower in mountainous regions compared to plains. These low $F_{yw}$ values in mountainous regions contrast with the previously observed inverse correlation between transit times and topographic gradients found in previous studies (i.e. Tetzlaff et al., 2009; McGuire et al., 2005). Changes in precipitation isotopes are reflected rapidly in catchment discharge due to fast water transmission through small mountain catchments, implying high $F_{yw}$ (e.g. Cowie et al. 2017; Harrington et al. 2018). These conflicting findings create uncertainty about the general applicability of the $F_{yw}$ method.
in catchments with overwinter snowpack, and the associated interpretations of hydrological processes.

One possible explanation for the discrepancy is that the \( F_{yw} \) method does not accommodate for snowpack. However, there is conflicting evidence on the role of snowpack. Tetzlaff et al. (2009) did not explicitly adjust for snowpack in their model inputs, while McGuire et al. (2005) did, but both reported an inverse correlation between transit times and topographic gradients. Furthermore, von Freyberg et al. (2018) showed that incorporating snowpack accumulation into the evaluation of \( \delta^{18}O \) amplitude of inputs does delay cycle phases but does not have significant effect on the apparent \( F_{yw} \) in any but the most snow-dominated catchments. Thus, the discrepancy between low calculated \( F_{yw} \) and apparent rapid transmission in mountain catchments requires further investigation.

Seasonal changes in \( \delta^{18}O \) values in precipitation are characteristically significant at mid to high latitudes (Rozanski et al., 1993; Gat, 1996). Low \( F_{yw} \) values reflect a muted seasonal amplitude in river water \( \delta^{18}O \) relative to that of precipitation. Interannual variations in the mean \( \delta^{18}O \) value of precipitation also occur, and reflect changes to atmospheric circulation, including vapor sources, vapor transport and the prevailing meteorology (Vuille & Werner, 2005; Sodemann et al., 2008; Yamanaka et al., 2007). This large seasonal amplitude in precipitation is dampened in streamflow in midsize to large catchments, which is consistent with observations that catchments act as signal dampening filters for most solutes (Kirchner et al., 2001; Botter & Rinaldo, 2003; Mallard et al., 2014; Scheliga et al., 2017; Hensley et al., 2018). Jasechko et al. (2016) hypothesized that the muted streamflow \( \delta^{18}O \) signal mountainous regions compared with the precipitation signal reflected longer flowpaths than previously assumed, perhaps due to groundwater residence times in river-connected alluvial aquifers in
river valleys and/or within fractured bedrock units (i.e. Cantafio & Ryan, 2014; Voekler et al., 2014; Kaser & Hunkeler, 2015). Alternately, seasonal streamflow isotopic signal damping could be due to the snowpack homogenization of precipitation δ¹⁸O values in snowmelt (Taylor et al., 2002, 2001; Lee et al., 2010). In that case, snowpack accumulation homogenizes seasonal variation of precipitation δ¹⁸O values in the model input, and also violates the model assumption that precipitation infiltrates immediately. Thus for the purposes of FYW calculations, snowpack homogenization dissociates the age of precipitation and age of input water.

This study hence seeks to shed light on the discrepancy between low calculated FYW and apparent rapid transmission in mountain catchments. We evaluated whether FYW estimates are valid in catchments with significant snow accumulation by evaluating the effect of modifying the model input to account for overwinter snowpack accumulation (and isotopic homogenization of snowpack) on modelled FYW estimates. We also took advantage of an observed interannual variation in precipitation δ¹⁸O to provide further insight into the speed at which recent precipitation is transmitted to river flow.

**Study area**

The present study uses data collected in the 435 km² Upper Elbow River catchment located in the eastern slopes of the Rocky Mountains, Alberta, Canada (Figure 2-1). The Upper Elbow River catchment (defined here as the reach upstream of the Elbow Falls sample collection point), supplies the majority of total Elbow River discharge; ~80% of the discharge is generated upstream of Bragg Creek (Manwell & Ryan, 2006; Valeo et al., 2007). Elevation in the Upper Elbow River catchment ranges from 1500 to 3200 m.a.s.l. and the average surface slope is 25°. As elevation increases, vegetation includes forested montane, transitional sub-alpine, and treeless alpine ecoregions covering 5, 56,
and 39% of the catchment area respectively (Alberta Environment and Sustainable Resource Development 2005; Valeo et al. 2007). Most of the catchment is underlain by dolomites and limestones of Devonian and Carboniferous age (Prior et al. 2013). With the exception of the valley floors, unconsolidated sediments and soil thickness is generally less than a few meters.

The Upper Elbow catchment is characterised by a temperate humid climate. The average annual precipitation (1981-2010; not corrected for snow under-catch) was 665, 639, and 568 mm at Elbow RS, Kananaskis, and Pocaterra stations respectively (Environment Canada, 2019; Figure 2-1). Snow accumulation generally starts in November with snow water equivalent normally peaking in late March and decreasing during May and June as snowmelt occurs. Maximum daily discharge typically occurs in June due to the combination of snowmelt and high rainfall (Valeo et al., 2007; Farjad et al., 2016). Snowmelt occurs over a much shorter interval than snow accumulation, thus overwinter snow storage is a major factor in streamflow generation of the Elbow River, despite the fact that the majority of annual precipitation occurs during the spring and summer months.
Figure 2-1. Study site location showing the 435 km² Upper Elbow Watershed, the location of three weather stations, and the precipitation and Elbow River sampling locations.

**Methods**

*Data sources*

*River water sampling*
River water grab samples were collected at Elbow Falls (50°52'2.39" N 114°46'26.39" W; Figure 2-1), where a bedrock constriction forces shallow groundwater from the river-connected alluvial aquifer (Manwell & Ryan, 2006) into the river. Thus, samples at Elbow Falls represent an integrated isotopic sample of river and shallow groundwater from the upper Elbow catchment.

River water sampling was conducted between May 2016 and October 2018, with weekly samples collected during the ice-free season (mid-April to November) and monthly samples during the remainder of the year. Grab samples were collected approximately 30 cm from the stream bank at approximately 60% depth in 60 mL syringes and field-filtered through 0.45µm syringe filters (Pall Laboratory, Acrodisc) into 20ml polyethylene vials for δ¹⁸O analyses.

Precipitation sampling

The monthly means of precipitation stable isotopic composition for January 2009 – August 2018 dataset were produced by aggregating the results of daily precipitation sampling at the Barrier Lake sampling location (Figure 2-1).

Monthly precipitation amounts for January 2009 – August 2018 were summed from daily values measured at a long-term weather station in Kananaskis (Figure 2-1) operated by Environment Canada (Government of Canada, 2018). The weather station uses a copper Nipher gauge for snow collection and measures the snow-water equivalent (mm) of the melted snow samples. Rain is measured by both a funnel collector and a tipping bucket collector, with the funnel collector values as default. The data were used without adjustment for the snow undercatch, which is expected to have negligible effect on precipitation amounts given the forested setting (i.e. Pan et al. 2016). The elevation of the collection station is 1480 m.a.s.l., but the isotopic composition of
precipitation was not corrected for elevation due to high uncertainty and variability of the altitudinal effects on isotopic composition of the precipitation in the study area. A previous study approximately 35 kilometers west of the Upper Elbow Watershed (Moran et al. 2007) found that altitudinal gradients of the snowfall isotopic composition have high temporal variability, and varied from negative to positive.

**Isotopic analysis (δ^{18}O in water)**

Stable isotopic ratios of oxygen in streamflow and precipitation samples were determined by laser spectroscopy using an Isotopic Water Analyser (LosGatosResearch, DLT-100) in the University of Calgary Isotope Science Laboratory (ISL). Sample \(^{18}O/^{16}O\) ratios are reported relative to Vienna Standard Mean Ocean Water (VSMOW) in standard delta notation (\(\delta^{18}O = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \cdot 1000\%\)). Analytical uncertainty is ±0.2‰ for \(\delta^{18}O\).

Stable isotopes of hydrogen in river water and precipitation samples were also measured, but because river water samples do not deviate from the local meteoric water line defined by precipitation samples (see Figure 2-2) on isotopic by-plot (data not shown), only \(^{18}O\) data were used for analysis in this study. The full dataset (including \(^2\)H data) is available in Supporting Information C at Hydroshare.

**Discharge measurements**

Since the Elbow Falls gauging station was discontinued in 1995, monthly Elbow River discharge values for January 2009 – August 2018 were estimated from measured Elbow River at Bragg Creek values based on linear correlation (\(r^2= 0.92\)) of the historical discharge data and are adjusted for average monthly differences between the stations
(Campbell et al. 2019). The use of proxy discharge data from the Elbow River at Bragg Creek is not expected to introduce significant error to the modelling as the ratio of monthly discharge between the two stations are consistent through the period of available record (1968-1995).

Daily flow data (January 2009 – August 2018) for the Elbow River at Bragg Creek Gauging Station (ID 05BJ004; Government of Alberta) (Figure 2-1) were used, including quality checked data for 2009-2015 (Water Survey of Canada, 2018), and provisional data for 2016-2018 (Government of Alberta, 2018). Catchment-normalized discharge amounts (mm) for model input were calculated by dividing monthly discharge values by the area of Elbow River catchment at Bragg Creek gauging station (791 km²).
Figure 2-2. Two-compartment numerical, processed based model (after Kirchner, 2016b) details, including (a) conceptual model; (b) conceptual diagram how precipitation inputs were modified to consider snowpack storage; (c) example of linear relationship between precipitation and discharge\(^1\) used to estimate evapotranspiration.

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\( Q = 0.773 \cdot P - 127.21 \)

\(^1\) Correction: The amount of water reported in 2-2c is runoff (mm) rather than discharge (m³/s). Runoff was converted to discharge by linear routing based on catchment area.
Data analysis

Discharge, $\delta^{18}O$ in Streamflow, and $F_{yw}$ Modelling

Model Background and Description

Streamflow and $\delta^{18}O$ composition of streamflow modelling in this study uses and modifies a numerical conceptual\(^2\) model based on the two-compartment catchment characterization scheme developed by Kirchner (2016b; Figure 2-3a) and briefly outlined here. In the original conceptual model, streamflow generation is approximated by describing the catchment as two storage compartments, designated as an ‘upper’ compartment with relatively fast transmission time ($S_u$), and a ‘lower’ storage compartment with a longer residence time ($S_l$). Catchment input $P$ (encompassing precipitation and snowmelt, in mm) enters the $S_u$, with an outflux of ‘leakage’ split into a contribution to $S_l$ and streamflow according to a partitioning constant, $\eta$ (Fig. 3a). One leakage pathway is directly from $S_u$ to streamflow (at a rate of $\eta L$). The remainder of the leakage (i.e. $(1-\eta)L$) is partitioned by a second pathway into the lower storage ($S_l$).

The leakage ($L$) and outflow from $S_l$ (designated $Q_l$) are modified by drainage constants ($b_u$ and $b_l$, respectively), and $\bar{P}$ is long-term precipitation average, where:

1. \[ L = \bar{P} \left( \frac{S_u}{S_{u,ref}} \right)^{b_u} \]
2. \[ Q_l = (1 - \eta) \bar{P} \left( \frac{S_l}{S_{l,ref}} \right)^{b_l} \]

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\(^2\)In the published manuscript this model is described as process-based, which is an error. It is a conceptual model.
and the reference upper \((S_{u, \text{ref}})\) and lower \((S_{l, \text{ref}})\) storage values were used as initial storage values (mm) for each time-series model run in addition to serving as model parameters.

Catchment input \((P)\) in the non-snowpack modified model is assumed to infiltrate immediately upon contact with the ground surface, and both storage units are assumed to be perfectly mixed. Kirchner (2016b) shows that this model is robust under non-stationarity (i.e. the modelled discharges are similar to measured discharges, even with varying precipitation input over time). The model output is mm/month (transformed to discharge values (m\(^3\)/s)) when the input value \((P)\) is catchment input amount (mm). Modelled \(\delta^{18}O\) values in streamflow are the same units as input values of precipitation \((P; \permil)\).

In this study the fraction of young water \((F_{yw})\) is calculated according to Kirchner (2016a), where “young water” is defined by a threshold age \((\tau_{yw}; \text{i.e. the streamflow water fell as precipitation within the period } \tau_{yw})\). Because this analysis is based in transit-time gamma distribution analysis, the threshold age itself is dependent on a shape factor \((\alpha, 0.2-2)\), resulting in the threshold age range \(\tau_{yw}\) of 1.37-3.1 months, or 2.3\(\pm\)0.7 months. Kirchner (2016a) further showed that the fraction of streamflow younger than this threshold age should be equal to the ratio of amplitudes of \(\delta^{18}O\) in streamflow and precipitation \((A_s/A_p)\). With this method (Figure 2-3), the \(F_{yw}\) is estimated by tracking the fraction of young water in each storage \((S_u \text{ and } S_l)\). The model calculates \(F_{yw}\) independently from the isotope amplitude ratio \((A_s/A_p)\), allowing us to compare the effects of snowpack modification on both values.
Chapter 2: Snowpack and $F_{yw}$

Figure 2-3. Cross plot of $\delta^2$H and $\delta^{18}$O in grab samples from the Elbow River at Elbow Falls (yellow symbols) and volume-weighted monthly mean values for precipitation (blue symbols). The local meteoric water line is taken from Peng et al. 2004.

**Model Setup**

The equations for the original models for discharge and $\delta^{18}$O in streamflow and $F_{yw}$ (Kirchner, 2016 a,b; Fig. 2) and were implemented in MatLab (Math Works 2014). The code is available in Hydroshare (Campbell et al. 2019).

For the initial conditions the volumes stored in both upper and lower storages ($S_u$ and $S_l$, respectively; Fig. 2a) were set to reference values (20–500 mm range for $S_{u,ref}$, 500–10,000 mm range for $S_{l,ref}$ as detailed by Kirchner (2016b); Fig 2a). The initial isotopic composition of water in both storages was set to the precipitation-weighted
mean of measured isotopic composition of precipitation (-18.7‰) for the period of record (2010-2017).

Precipitation amounts (mm) from Kananaskis were used as input for discharge modelling between January 2009 and August 2018. Volume-weighted monthly values (see next section) for δ¹⁸O in precipitation (available between November 2014 and August 2018) were used to model δ¹⁸O in river flow for those time periods.

Since the model does not account for evapotranspiration, an observed linear relationship (Figure 2-3c) was used to adjust annual precipitation to annual discharge. The average annual flow reduction attributed to evapotranspiration was calculated separately for each hydrological year and distributed to monthly timesteps proportional to measured monthly precipitation.

A ‘hydrologic year’ (HY) that begins on November 1ˢᵗ (when annual snowpack accumulation begins), and ends on October 31ˢᵗ (Paznekas and Hayashi 2016) is used here to allow the entire winter snowpack from a single cold season to be accounted for in streamflow within the same year-long period. Since sample collection ceased before the end of HY2018, the HY2018 denotes the period from November 2017 to August 2018.

**Snowpack modification of model**

The effect of snowpack on streamflow modelling (i.e. ‘snowpack modified’, as opposed to ‘unmodified’ modelling) was tested using monthly time-steps to accommodate the scale of the catchment (435 km²); finer timesteps would require widespread snowmelt observations over several years that were beyond the scope of

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3 The published version contains a grammatical error that is corrected here.
the completed fieldwork. Snow in the Upper Elbow River watershed elevations is known to accumulate between November and April, and melt in May and June. This is also consistent with field observations and studies of nearby basins in the Alberta Rockies, although the exact fraction of melt in each of the two months can vary year to year (e.g.: DeBeer and Pomeroy 2010; Harrington et al. 2017; He and Hayashi 2019). To account for this variability in melt timing, a simple sensitivity analysis was performed by conducting additional snowpack-modified model runs with 75% of snowmelt weighted either in May or June, respectively (Figure 2-3b; Table 2-1).

Table 2-1. Summary of Nash Sutcliffe efficiencies (NS) from modelling sets with and without snowpack-modified input, including the mean, median and maximum NS values, and the number of 20,000 runs for each set that were greater than 0.7 and 0.9, included for snowpack modified input where snowpack was variably distributed between May and June.

<table>
<thead>
<tr>
<th>Model set</th>
<th>May/June Snowmelt</th>
<th>NS</th>
<th>NS</th>
<th>NS</th>
<th>NS</th>
<th>NS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>Mean</td>
<td>Median</td>
<td>Max</td>
<td>&gt;0.7</td>
<td>&gt;0.9</td>
</tr>
<tr>
<td>Unmodified</td>
<td>-</td>
<td>0.49</td>
<td>0.52</td>
<td>0.79</td>
<td>2,551</td>
<td>0</td>
</tr>
<tr>
<td>Snowpack modified</td>
<td>50/50</td>
<td>0.70</td>
<td>0.78</td>
<td>0.94</td>
<td>12,289</td>
<td>4,238</td>
</tr>
<tr>
<td></td>
<td>75/25</td>
<td>0.67</td>
<td>0.75</td>
<td>0.94</td>
<td>6832</td>
<td>1070</td>
</tr>
<tr>
<td></td>
<td>25/75</td>
<td>0.66</td>
<td>0.74</td>
<td>0.89</td>
<td>7650</td>
<td>0</td>
</tr>
</tbody>
</table>
Snowpack-modified model runs assumed complete isotopic homogenization of the snowpack (Taylor et al., 2002, 2001; Lee et al., 2010) and attributed the volume-weighted $\delta^{18}O$ value of the aggregated precipitation between November and April to snowmelt in May and June. While it is expected that the melt water at the beginning of the first month would have a more depleted isotopic composition relative to the end of the second month, Taylor et al. (2002) state that when looking at an entire melt event the error in assigning mean isotopic composition of snowmelt ($\delta^{18}O_{ave}$) is small, and that the errors at the beginning and end of the melt tend to cancel. Further, the total $\delta^{18}O$ evolution in a melting snowpack tends to be small (i.e. approximately 4‰ (range of 2-6‰; Taylor et al., 2002) relative to the range of $\delta^{18}O$ values observed in precipitation (see below). Half of the difference in isotopic melt composition (i.e. approximately 2‰) would occur before the midpoint and half afterward, and the midpoint of the melt season would have a value equal to $\delta^{18}O_{ave}$ (Taylor et al., 2002). Given the aggregating assumptions already included in the monthly time steps $\delta^{18}O_{ave}$ was applied for both months.

**F\textsubscript{yw} estimation**

Given the monthly time resolution of the model, $F_{yw}$ in the modelling was defined as fraction of inputs ≤ 3 months old instead of the variable threshold $\tau_{yw}$ of 2.3 ±0.7 months used by Kirchner (2016b) and subsequent studies (e.g. Jasechko et al., 2016).

For snowpack-modified runs the age of precipitation in the $F_{yw}$ calculation is not based on the timing of the precipitation (i.e. the month in which it fell), but on the month that it was melted. For example, precipitation that falls as snow in November is therefore seven months old before it is input into the snowpack-modified model as ‘new’ water. The November to April precipitation was aggregated and released in
equal parts as meltwater in May and June in addition to precipitation during these months (Figure 2-3b). The modelled age of river flow in the Fyw calculation is based on date of input into the model; for example, snow that falls between November and April and is released as snowmelt in May is one month old if it becomes streamflow in June.

Model Application

The effect of snowpack accumulation and melt on the estimated Fyw was evaluated using a Monte-Carlo approach, where one set of 20,000 model runs was run for each of unmodified and snowpack-modified precipitation input data sets over the three hydrologic years. Both model sets were defined using the same randomly-generated synthetic catchment parameters, which were varied over realistic ranges: 1–20 for bu, 1–50 for bl, 0.1–0.9 for n, 20–500 mm for Su,ref, 500–10,000 mm for Sl,ref (Kirchner, 2016b) without any model calibration.

Nash-Sutcliffe efficiencies (NS) (Nash & Sutcliffe, 1970; McCuen et al., 2006) were calculated for the discharge values in the Monte Carlo sets. The parameter sets that produced NS > 0.9 (i.e. with good predictive ability for discharge characteristics) were then used to evaluate whether isotope amplitude ratios are representative of Fyw. The discharge-weighted mean of young water fraction (Fyw) was calculated for each of HY2016, 2017 and 2018 within each parameter set. Simultaneously, the model calculated amplitude ratio (As/Ap) by fitting a sine function with a period of one year (by minimizing the sum of squared residuals) to seasonal variations in d18O values to estimate the amplitude value for measured values of precipitation (Ap) and modelled streamflow values (As).

In addition to the Monte-Carlo simulations of the randomized parameter sets, a best-fit set of synthetic catchment parameters (bu, bl, n, Su,ref, Sl,ref) was obtained by
calibrating the modelled discharges to the discharge at Elbow Falls for HY2011–
HY2015, by maximizing the Nash-Sutcliffe efficiency (Nash & Sutcliffe, 1970; McCuen et
al., 2006). The calibration was repeated 1000 times with starting parameter values each
time randomly selected from the corresponding ranges. No calibration was performed
for the stable-isotopic composition of the streamflow to test the validity of the model.
Predictions were4 tested by comparing the isotopic composition of modelled and
observed streamflow for the period where observed data were available (i.e. November
2014 and August 2018).

**Estimation of preceding year precipitation fraction in baseflow from precipitation
isotopes**

The percentage of streamflow that is less than one year old can be estimated from
annual differences in volume-averaged δ18O in winter streamflow. A two-component
mixing model was used to calculate the fraction of HY 2018 winter discharge (Nov 2017 – Feb 2018) that was derived from the HY2017 precipitation inputs (Eq. 3), based on the
interannual variation in δ18O of precipitation during the observation period and the
measured shift in δ18O values of winter discharge between years. No winter discharge
samples were collected in HY2016, so the calculation is conducted only for HY2018
winter discharge. This approach is based on the assumption that no precipitation
infiltrates during the period of snow accumulation (November–February), and
streamflow is sourced from groundwater storage, and thus its δ18O value represents the
isotopic composition of the current storage.

\[
(3) \ F = \frac{B_{HY2018} - B_{HY2017}}{A_{HY2017} - B_{HY2017}}
\]

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4 Grammatical correction from published version
where $F$ is a fraction of HY2018 winter streamflow that was sourced from the HY2017 snowmelt and precipitation inputs, $A$ is the annual $\delta^{18}O$ mean value in precipitation and $B$ is the mean $\delta^{18}O$ value of winter discharge (representing storage).

**Results**

**Precipitation and river water $\delta^{18}O$ values**

The volume-weighted, mean monthly values for $\delta^{18}O$ in precipitation range over ~20‰, and plot along the local meteoric water line for Calgary (Peng et al., 2004), which is located around 60 km east of the sampling points. A distinct seasonal signal is observed, with intra-annual ranges in monthly precipitation averages varying between 10‰ (HY2015) and 18‰ (HY2017). The annual single-event maxima occur in summer and vary from -15.8‰ (HY2018) to -12.7‰ (HY2016). The annual single-event minima occur in winter and vary considerably year to year, ranging from -33.8‰ (HY2018) to -25.4‰ (HY2015). The volume-weighted mean of precipitation was -18.66‰ for HY2010-2016, -20.97‰ in HY2017, and -21.46‰ in HY2018.

The river water $\delta^{18}O$ values ranged from of -21.4 to -18.1‰, with the range within each individual HY <1.8‰ (Figure 2-5). Annual means of $\delta^{18}O$ values decrease over the HY2016-HY2017 period, with values of -18.8 ‰, -19.4‰, and -19.7‰ in HY2016, HY2017, and HY2018 respectively. The $\delta^{18}O$ distributions vary significantly between years ($p < 0.05$ between each set, ANOVA single factor), with the caveat that 2016 is moderately skewed (0.9). The isotopically depleted river water samples in late May and early June 2017 (<-20‰; Figure 2-5) correspond to the period of maximum snowmelt. The less depleted samples (>19‰) were taken after rainfall events in an otherwise dry summer. The same pattern was repeated in HY2018 with $\delta^{18}O$ values
dropping in early May 2018, corresponding to the onset of snowmelt. δ\textsuperscript{18}O values then increased steadily through the remainder of HY2018 with a spike late June due to heavy rainfall. The mean monthly δ\textsuperscript{18}O values of precipitation and river water yielded measured amplitude ratios for the Upper Elbow catchment of, 0.026, 0.032, and 0.071 (in HY2016, HY2017, and HY2018, respectively).

Figure 2-4. Time series of volume-weighted monthly mean values of δ18O in precipitation (grey line). The annual means of δ18O in streamflow over three hydrologic years (dashed lines; blue HY2016, yellow HY2017, green HY2018) are also shown.
Figure 2-5. Time series of $\delta^{18}$O values in river water. Individual grab samples are smaller grey symbols. Monthly mean river water $\delta^{18}$O values for hydrologic years 2016 (blue circles), 2017 (yellow circles), and 2018 (green circles) are also shown. The mean winter (Nov to Feb) discharge $\delta^{18}$O values are shown as solid black horizontal lines for each of HY2017 and 2018.

**Comparison of modelled output to measured data records**

For the set of unmodified model runs, the median Nash Sutcliffe efficiency (NS) for discharge is 0.52, indicating only marginal matches to historical discharge (Table 2-1, Figure 2-6a). Furthermore, only 2,551 of 20,000 models runs produced a NS greater than 0.70, and none were greater than 0.79. In comparison, median NS for the set of model runs using snowpack-modified input (where snowmelt was distributed evenly between May and June) was 0.78; 12,289 of 20,000 model runs had NS values above 0.7; and 4,238 runs had NS values greater than 0.9 (Table 2-1; Figure 2-6b).
Distributing snowmelt variably between May and June did affect the mean, median, and maximum NS values of model outcomes considerably (Table 2-1), but the equal snowmelt distribution between May and June produced more high NS values (i.e. >0.7 and >0.9), indicating higher overall success at good reproduction of historic discharge. These results indicate that discharge and δ^{18}O are less sensitive to catchment parameterization than to appropriate precipitation input.

![Figure 2-6. Sample time series comparing measured discharge for the Elbow River (dashed line) with modelled discharge for a single parameter set using the (a) unmodified and (b) snowpack-modified model input, (snowmelt equally distributed between May and June). Both inputs produced above-median NS matches.](image)
Among the snowpack-modified model runs, those with high NS consistently had higher young water fractions (Figure 2-7), suggesting that high young water fractions are intrinsic in this catchment.

The observed seasonal variations in the monthly mean values of $\delta^{18}$O in river water were better predicted when the snowpack-modified model input was used (Figure 2-8). The prediction of the overall month-to-month variability was much better ($r^2 = 0.73$; Figure 2-8) with snowpack-modified input than with unmodified input ($r^2 = 0.10$).

![Figure 2-7](image.png)

Figure 2-7. Vertical bar chart showing the average young water fractions ($F_{yw}$) for the 20,000 synthetic catchments modelling sets with snow-pack modified input as a function of their Monte-Carlo NS efficiencies. Colours indicate hydrologic year (blue...
HY2016, yellow HY2017, green HY2018). Higher $F_{yw}$ generally correspond to higher NS efficiencies in all 3 years.
Figure 2-8. (a) Time series of river water $\delta^{18}O$ values comparing measured (symbols) and modelled mean monthly values. Modelled values are shown for both unmodified (dashed line) and snowpack-modified (dash-dot line) inputs. Scatterplots of measured vs. modelled monthly mean river water $\delta^{18}O$ values are shown for the (b) unmodified model input, and (c) snowpack-modified input model. The linear fit of the data is also shown. The symbol colours indicate hydrologic years (blue for 2016, yellow for 2017, and green for 2018).
Chapter 2: Snowpack and $F_{yw}$

**Relationship between seasonal $\delta^{18}O$ amplitude and young water fraction**

The two-compartment model directly calculates young water fraction ($F_{yw}$), and Kirchner (2016b) showed a 1:1 correlation between calculated $F_{yw}$ and measured amplitude ratios ($A_s/A_p$) (also directly and independently calculated within the model). In the Monte-Carlo model set with unmodified input, the predicted value for young water fraction ($F_{yw}$) and amplitude ratios ($A_s/A_p$) are reasonably-well linearly correlated, with slopes of approximately 0.77 throughout most of the data range ($r^2 = 0.98$) (Figure 2-9a). The offset from the 1:1 line is likely due to autocorrelation effects from evaporation and reprecipitation, which is expected in areas with seasonal low precipitation periods (Kirchner, 2016b). In contrast, the amplitude ratios, $F_{yw}$ values, and slopes (e.g. as low as 0.3 in HY 2016, $r^2=0.91$) tended to be lower Monte-Carlo model set with snowpack-modified input (Figure 2-9b). With snowpack-modified input, the amplitude ratios produced by the model were consistently below 0.2, reflecting the dampened precipitation amplitude in snowmelt (i.e. $A_p$) that would be expected to be caused by snowpack homogenization of $\delta^{18}O$.

The measured amplitude ratios for the Upper Elbow catchment of, 0.026, 0.032, and 0.071 (in HY2016, HY2017, and HY2018, respectively) correspond to modelled $F_{yw}$ ranges of 0.13 to 0.23 (HY2016), 0.07 to 0.09 (HY2017), and 0.16 to 0.21 respectively. In all three hydrologic years, the measured amplitude ratios are close to the low end of the modelled $F_{yw}$ values, suggesting that synthetic catchment parameter sets that produce $F_{yw}$ below ~30% may be more representative of the Upper Elbow watershed.
Figure 2-9. Amplitude ratios (Ar/Ap) cross plotted against the young water fraction (Fyw) for Monte-Carlo model sets using randomly-generated synthetic catchment parameter sets that produced historical discharge with a NS of 0.9 or higher using snowpack-modified input (n = 4,238). The Ar/Ap vs. Fyw values are shown for each of (a) snowpack-modified input (b) unmodified input. The symbol colours correspond to hydrologic year of precipitation inputs (blue HY2016, yellow HY2017, green HY2018).
Fraction of previous year’s precipitation in winter discharge

The two-component mixing model (Eq. 3) allowed estimation of the contribution of HY2017 precipitation to HY2018 winter discharge (i.e. Nov 2017-Feb 2018; Figure 2-5). Using δ¹⁸O values of HY2017 winter discharge (-18.87 ‰) and HY2017 precipitation (-20.97 ‰) as mixing components and HY2018 winter discharge (-19.26 ‰) as the output signal yields a HY2017 precipitation fraction in HY2018 winter discharge of ~20%; that is, ~80% of HY2018 winter discharge is from precipitation prior to HY2017.

Discussion

Our Monte-Carlo modelling highlights an important constraint in young water fraction ($F_{yw}$) estimation from streamflow and precipitation amplitude ratios in catchments with significant snow accumulation. The simulation, with 20000 synthetic catchments and three years of precipitation input, shows that there is not a 1:1 relationship between the isotope amplitude ratio $A_s/A_p$ and $F_{yw}$, but rather, the shape of the curve means that a given $A_s/A_p$ corresponds to a range of $F_{yw}$ values. This non-uniqueness limits the use of the $A_s/A_p$-based $F_{yw}$ estimates as a high level screening tool without accounting for watershed properties.

Storing precipitation as snowpack extensively alters the hydrological functioning of a catchment relative to one with constant infiltration and also alters the relationship between $A_s/A_p$ and $F_{yw}$. Discharge and δ¹⁸O modelling for the Upper Elbow catchment (Figure 2-6) demonstrate that to achieve appropriate output, the two-compartment model (Figure 2-3) (Kirchner, 2016b) requires snowmelt to be considered as a separate catchment input via snowpack-modified input, as indicated by consistently low Nash-Sutcliffe efficiencies in the unmodified model runs (Table 2-1). These results reflect the seasonal hydrological controls in the Elbow Valley and many mountain catchments
with overwinter snow storage; winter precipitation (Nov-May) falls as snow and cannot infiltrate into the subsurface or enter the river until it melts in May and June. This delay clarifies why $A_s/A_p$ and $F_{yw}$ do not correspond when there is overwinter snowpack; the “age” of winter precipitation becomes dissociated from the time at which it fell; rather than snow several months old, it instead enters the system as “young” isotopically homogenized\(^5\) snowmelt. Since the model uses the date of infiltration to calculate how much of the water in the system is less than three months old, dissociating the date of precipitation and infiltration undermines that calculation. That is, any given individual model run will still produce a single $F_{yw}$ for a given amplitude ratio, but varying the catchment configuration over several runs while keeping the same input will return a range of $F_{yw}$ values for a given $A_s/A_p$ value (Figure 2-9). Further investigation into these effects could clarify the reason for this range in values: for example, $F_{yw}$ is calculated by tracking the fraction of young water in each storage ($S_u$ and $S_l$), which is affected by the drainage exponents ($b_u$ and $b_l$, Equations 2 and 3), that change with different catchment configurations. With snowmelt modified input, the high volume of very “young” input in May and June (infiltrating with an age of zero or one months rather than time since precipitation) may increase the impact of the differences in drainage factors between catchment configurations, creating more finely discriminated values between catchments for $F_{yw}$ while at the same time reducing the differences in $A_s/A_p$ due to snowpack homogenization of winter precipitation. Such investigations were beyond the scope of this paper, but could provide further insights. The appeal of the original $F_{yw}$ and $A_s/A_p$ model is its simplicity – knowing the amplitude ratio, one can determine $F_{yw}$ regardless of the “true” catchment parameters. This study shows that

\(^5\) Note that this homogenization is a simplification based on the month-long time step; in real melt conditions isotopically lighter water will enter streamflow earlier in the season. Similarly, leakage coefficients would likely change throughout the melt season as volumetric drive increases and decreases. These parameters should be considered in more detailed timestep modelling.
snowpack complicates the process, but a Monte Carlo approach with randomized parameters can still provide semi-quantitative information by supplying a range for $F_{yw}$.

Measured $A_s/A_p$ for individual hydrological years in this study correspond to a range of young water fractions in the Upper Elbow watershed between 7-23%, which is considerably higher than previously published $F_{YW}$ estimates for catchments in the Alberta Rockies (Jasechko et al. 2016; 2017), but supports the concept of rapid transmission in such catchments (Cowie et al. 2017; Harrington et al. 2017) and rapid transit times in catchments with high topographic gradients (Tetzlaff et al., 2015; McGuire et al., 2005). Furthermore, the correlation between $F_{YW}$ and Nash-Sutcliffe efficiencies (Figure 2-7) suggests that relatively high $F_{YW}$ is an intrinsic feature of the Upper Elbow watershed, and the same may be true for other mountain catchments with overwinter snowpack. For example, the 7-23% range encompasses the delayed-input (snowpack modified, both flow-weighted and unweighted) $F_{yw}$ values for high mountain catchments in Switzerland (von Freyberg et al., 2018). If a Monte Carlo analysis of their inputs supplied a similar range, it could imply that young water fractions of ~10-30% are a common feature of snowmelt-dominated mountain catchments, supporting the rapid transmission suggested in previous studies. Larger young water fractions in mountain-sourced rivers with high-fraction of snowmelt has important implications for water use management. If discharge in a given year is more dependent on recent precipitation, long-term water supply will respond more rapidly to variable climatic conditions and both pollutants and nutrients will move through the watershed more quickly.

One consideration for future implementation of the snowpack-modified model is that we used a monthly timestep that ignores $\delta^{18}$O evolution of the snowpack (Taylor et
al., 2001, 2002) and spatio-temporal variability (Schmieder et al., 2016; Ala-aho et al., 2017) in snowmelt. These were practical choices given the large size of the catchment (435km²). However, the simple sensitivity analysis of altering timing of snowmelt release (Table 2-1) demonstrated that finer timesteps would offer further insights into snowmelt, precipitation, and stored groundwater mixing in streamflow. For example, although the annual δ¹⁸O means for river water match for HY2018, the month-long timestep does not allow the model to capture the observed positive δ¹⁸O excursion due to the heavy rainfall event in June 2018 (Figure 2-8). Similarly, altering the δ¹⁸O of weekly snowmelt according to the pattern of snowpack δ¹⁸O evolution could offer further insight into the details of mixing in streamflow. However, using a finer timestep or evolving snowpack δ¹⁸O would not resolve the disconnect between precipitation age and time of input, and Fyw would remain non-unique.

Although accounting for snowpack storage reduces the precision of the Fyw method, the interannual isotopic variation in precipitation and winter discharge does provide another way of estimating annual precipitation contributions to streamflow. The Elbow River δ¹⁸O value in winter discharge (Figure 2-2) shifts in response to the previous year’s precipitation inputs, indicating a portion of the groundwater storage that supplies winter discharge must contain relatively recently-recharged water. The binary mixing calculation (Eq.3) indicates that baseflow in winter 2017-2018 contains ~20% of water recharged in HY2017. This methodology is promising for calculating water age in mountain catchments, however, for this study the calculated “new water” fraction (< 1 year old; Manning et al., 2012) should be considered semi-quantitative due to relatively high variation of individual δ¹⁸O baseflow measurements, and future studies should sample baseflow more frequently. Nevertheless, that one fifth of streamflow comes from the previous year’s precipitation implies rapid transmission of water through the catchment, consistent with high Fyw ranges and previous studies.
Conclusions

This study evaluated the applicability of the young water fraction (F_{yw}) approach - estimating the fraction of young water from the ratio of precipitation and streamflow isotope amplitudes - in mountain catchments with overwinter snowpack. It also used interannual variations in precipitation isotopes to provide further insight into the speed of catchment transmission. Using the original two-compartment F_{yw} model, but applying a Monte-Carlo approach to input from a small mountain catchment, we showed that snow accumulation and snowmelt disrupts the relationship between the ratio of seasonal amplitudes of δ^{18}O in river water and precipitation (A_s/A_p) and F_{yw}. When snowpack is accounted for the relationship is non-unique and A_s/A_p corresponds to a range of F_{yw} values, which means care must be taken when applying the F_{yw} approach in catchments with overwinter snowpack. In the Upper Elbow Rocky Mountain catchment the measured A_s/A_p values corresponded to a F_{yw} range of 7-23%, corroborating previous findings of rapid water transmission in mountain catchments. The correlation between F_{yw} and Nash-Sutcliffe efficiency for the Monte-Carlo simulation suggests that high young water fraction is an intrinsic feature of the study watershed. These findings are further supported by the estimate of “new water” fraction of streamflow (<1 year old) of ~20% based on interannual differences in volume-averaged precipitation δ^{18}O and δ^{18}O in winter streamflow. Overwinter snowpack constrains the precision of the F_{yw} method, but a Monte-Carlo approach and support from the “new water” calculation suggest that approximately one-fifth of streamflow in mountain catchments may be derived from the previous year’s precipitation.
Chapter 3: Insight into watershed hydrodynamics using silica, sulfate, and tritium: source aquifers and water age in a mountain river

Key Points:

- Silica, sulfate, and sulfate isotopes are used to identify three source aquifers
- Streamflow has groundwater residence time of <5-10 years (from silica and tritium)
- Streamflow responds rapidly to seasonal and storm inputs and is therefore vulnerable to climatic change

Abstract

A clear concept of the recharge pathways for surface flow in mountain rivers is important for understanding the effects of climate change on streamflow in mountain block hydrology. In a mountain river in Alberta, Canada, three subsurface end-member sources were identified using silica, sulfate, and the isotopic composition of sulfate: interflow (water that has not undergone significant rock-water interaction), and groundwater derived from two types of hydrogeologic units (carbonate and siliciclastic fractured rock aquifers).

A three end-member mixing model was used to determine their relative contributions to river discharge and infer relative groundwater ages using silica dissolution kinetics and tritium.
In the three years of sampling, proportional contributions from subsurface end-members varied up to 25% within a given year while mean contributions between years varied as much as 19%. Interflow is the dominant source for the majority of the study period, contributing ~50% of river discharge during spring melt and 40-60% over the rest of the season. Siliciclastic and carbonate aquifer contributions varied interannually and seasonally. Although carbonate rocks comprise the majority of the watershed area, siliciclastic rocks contribute nearly equally to annual streamflow (~30% each), suggesting that siliciclastic aquifers transmit more water.

Silica- and tritium- based ages suggest residence times on the order of <5 to 10 years. The combination of short residence times and significant variability in streamflow provenance suggest streamflow in this river will be rapidly affected by climatic change.

Introduction

Despite their established importance to lowland populations (Viviroli et al. 2020), recharge pathways of groundwater that sustain surface water in mountain-sourced rivers are not yet well defined (DeBeer et al. 2016; Campbell et al. 2020a; i.e. Christensen et al. 2020). Somers and McKenzie (2020) emphasized the need for additional field-studies in mountain-block recharge while highlighting the importance of integrating new data and modelling techniques.
Mean travel time distributions (MTT) based on precipitation and streamflow water isotopes are a common tool for understanding water age and how water moves through watersheds (McGlynn and McDonnell 2003; Tromp-Van Meerveld and McDonnell 2006). However, dampening of the water isotope signal within the catchment reduces its ability to detect water older than 4 years (Stewart et al. 2010), and in higher-order streams the margin of error exceeds the value of MTT, making it unreliable (Kirchner 2016a). Sampling frequency and timing also substantially affect MTT estimates (i.e. Birkel et al. 2012; Schmieder et al. 2016). An alternate method using annual amplitudes of precipitation and streamflow water isotopes to estimate the fraction of water less than ~10 weeks old, “Fyw”, (Kirchner 2016a; 2016b) can seem to underestimate young water fractions when a watershed hosts overwinter snowpack (Jasechko et al. 2016; Campbell et al. 2020b). Other geochemical methods are therefore needed to investigate streamflow sources and storage.

Dissolved silica concentrations, tritium and sulfur and oxygen isotopes in sulfate are well-established geochemical tools used to provide information about streamflow residence time and sources respectively. Weathering studies, such as those by Clow and Mast (2010) and Maher (2011), indicate that dissolution of aluminosilicates is the primary control on dissolved silica in streamflow, while Burns et al. (2003) found dissolved silica concentrations correlated to apparent age of stream samples. This correlation was supported by Peters et al. (2014) when they combined tritium measurements and dissolved silica concentrations to estimate mean travel times. Benettin et al. (2015) calculated water residence time from silica concentrations using first-order kinetics supported by mean travel time calculations from water isotopes, and Marçais et al. (2018) found a linear relationship between mean residence time of watersheds and streamflow silica concentrations. These studies demonstrate the utility of applying multiple age-dating tools together.
In understanding streamflow dynamics in a watershed, determining the host aquifers that store and transmit streamflow is equally important as residence time. Sulfur and oxygen isotopes in sulfate are widely used to determine geological provenance (Dogramaci et al. 2001; i.e. Brenot et al. 2007; Shanley et al. 2013) and delineate waters separated by structural controls (i.e. Grasby and Hutcheon 2001). Combining the provenance information from sulfur and oxygen isotopes with the residence time of dissolved silica and tritium in streamflow is a promising tool for investigating where water is stored and transmitted in the watershed.

In this study we analyze where water is stored in the watershed prior to becoming streamflow in the Rocky Mountain Elbow River. We use dissolved silica and sulfate concentrations, along with the isotopic composition of the sulfate in streamflow, to identify contributions from siliciclastic and carbonate aquifers and interflow. Here we broadly define interflow to indicate groundwater that moves through surface and subsurface pathways where no substantial geochemical water-rock interaction occurs due to short residence time. We use a three end-member mixing model to estimate relative contributions to streamflow from groundwater and streamflow samples collected over three years of open water flow periods. We also use tritium and silica concentrations to estimate relative residence times in the siliciclastic and carbonate aquifers. These findings provide insight into where rain and snow are stored and how quickly they become streamflow in this watershed.

**Study area**

The 435 km² Upper Elbow River watershed, in the eastern slopes of the Rocky Mountains is defined here as the reach of the Elbow River upstream of Elbow Falls (Figure 3-1). This upper watershed supplies the majority of total Elbow River discharge;
~80% of the discharge is generated upstream of Bragg Creek (Manwell & Ryan, 2006; Valeo et al., 2007). The mountainous topography of the Upper Elbow watershed ranges in elevation from 1600 to 3200 meters above sea level with an average surface slope of 25°. Most of the watershed area is underlain by dolomites and limestones (carbonate aquifers) of Devonian and Carboniferous age (Prior et al. 2013), while Jurassic and Cretaceous sandstones and shales (siliciclastic aquifers) are exposed in the northeastern portion of the watershed (Figure 3-1). Forested montane, transitional sub-alpine, and treeless alpine ecoregions cover 5, 56, and 39% of the watershed area respectively, with a distinct distribution over the elevation range (Alberta Environment and Sustainable Resource Development 2005; Valeo et al. 2007). Unconsolidated sediment and soil depth is less than a few meters or absent except in valley floors, where it may be greater than 12 m.

The Upper Elbow watershed is characterised by a temperate humid climate; from 1981 to 2010 average annual precipitation (not corrected for snow under-catch) was 665, 639, and 568 mm at Elbow RS, Kananaskis, and Pocaterra stations, respectively (Environment Canada, 2019; Figure 3-1). Snow accumulation, representing approximately half of annual precipitation (Campbell et al. 2020c), generally starts in November with snow water equivalent normally peaking in late March, and decreasing during May and June as snowmelt occurs. Maximum daily discharge typically occurs in June due to the combination of snowmelt and high rainfall (Valeo et al., 2007; Farjad et al., 2016). Consequently, overwinter snow storage is a major factor in the hydrological functioning of the Elbow River, despite the fact that the majority of annual precipitation occurs during summer months (Campbell et al., 2020). Climate change projections for the region indicate intensifying wet and dry periods, with earlier snowmelt and earlier glacial discharge (St. Jacques et al. 2013; Farjad et al. 2016; Chernos et al. 2020b).
Previous Elbow River research has largely focused on water quality (Sosiak and Dixon 2006; WQ Consulting Services 2016) rather than water sources and storage. However, while investigating non-point-sources of chloride in the Elbow, Manwell and Ryan (2006) also demonstrated significant storage and throughflow in the Elbow’s extensive alluvial aquifer, and that at least 80% of baseflow is derived from sources above the town of Bragg Creek. The primary public perception is that the source of the Elbow River is the Rae Glacier above Elbow Lake (e.g. ERWP 2020), but recent studies of rivers in the Alberta Rockies indicate glaciers contribute only a fraction (3-6%) of annual flow (Marshall et al. 2011; Chernos et al. 2020b), with the majority of this contribution occurring in August and September. Sustained winter baseflow and peak spring streamflow in the Elbow must therefore have other sources.

Nightingale and Mayer (2012), used δ¹⁸O and δ³⁴S to investigate water sources in the Elbow River tributary Canyon Creek. They concluded the water was generally from shallow sources, dissolved gypsum in local carbonate rocks and dissolved pyrite in local sandstones and shales, and demonstrated the utility of δ³⁴S in distinguishing shallow water provenance in the area.
Figure 3-1 Upper Elbow watershed. a) Linear relief shading. Sample collection points are indicated with open circles (mainstem rivers), grey-filled circles (springs, tributaries), diamond (piezometers), and wells (triangles) at campgrounds with several handpumps completed at unknown depths). Sampling location abbreviations given in Table 2-1. b) Watershed bedrock types. Most of the watershed is carbonate rock (~73%), with siliciclastics in the north east (~27%) and small areas of carbonate and siliciclastic interbedded layering. Inset shows the upper, middle, and lower Elbow watersheds in relation to Calgary, Alberta and the location of the Kananaskis precipitation collection (PPTN).
Table 3-1 Sampling location names and designations. Locations indicated by abbreviations in Figure 3-1.

<table>
<thead>
<tr>
<th>Surface Water</th>
<th>Site Type</th>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>Elbow Falls</td>
<td>Outlet</td>
<td>O1</td>
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<tr>
<td>Elbow River at Beaver Flats</td>
<td>River</td>
<td>R3</td>
</tr>
<tr>
<td>Little Elbow</td>
<td>River</td>
<td>R2</td>
</tr>
<tr>
<td>Big Elbow</td>
<td>River</td>
<td>R1</td>
</tr>
<tr>
<td>Ford Creek</td>
<td>Tributary</td>
<td>T1</td>
</tr>
<tr>
<td>Forget-me-not Creek</td>
<td>Ephemeral tributary</td>
<td>T2</td>
</tr>
<tr>
<td>Forget-me-not Spring</td>
<td>Spring</td>
<td>S1</td>
</tr>
<tr>
<td>Beaver Flats Spring</td>
<td>Carbonate aquifer - spring</td>
<td>CA1</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Groundwater</th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Piezometer (Interflow)</td>
<td>Interflow - piezometer</td>
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</tr>
<tr>
<td>Little Elbow Campground</td>
<td>Siliciclastic aquifer - well</td>
<td>SA1</td>
</tr>
<tr>
<td>Little Elbow Campground</td>
<td>Siliciclastic aquifer - well</td>
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<tr>
<td>Little Elbow Campground</td>
<td>Siliciclastic aquifer - well</td>
<td>SA3</td>
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<tr>
<td>Beaver Flats Campground</td>
<td>Carbonate aquifer - well</td>
<td>CA2</td>
</tr>
</tbody>
</table>

Methods

Data sources

Streamflow sampling

Streamflow grab samples were collected at several points within the Upper Elbow watershed (Figure 3-1, Table 3-1). The Elbow River’s two large tributaries (knows as the Big and Little Elbow Rivers, R1 and R2) are here both designated as “mainstem” rivers above their confluence, as is the Elbow River downstream of the confluence (R3). At Elbow Falls a bedrock constriction forces shallow groundwater from the river-connected alluvial aquifer (Manwell & Ryan, 2006) into the river. Thus, samples at Elbow Falls (O1) represent an integrated sample of streamflow from the upper Elbow watershed. Tributary samples were collected about 30m above their
confluences with the mainstems. Grab samples for major ion analyses were collected approximately 30 cm from the stream bank at 60% depth in 60 mL syringes and field-filtered through 0.45µm syringe filters (Pall Laboratory, Acrodisc) into 20ml polyethylene vials. The headspace was eliminated by filling to form a positive meniscus before placing lids, which were sealed with electrical tape until analyses. Grab samples for δ³⁴S analysis were collected approximately 30 cm from the stream bank at 60% depth in 1L polyethylene vials and capped underwater. The bottles were sealed with electrical tape and kept in a cooler until arriving at the lab in the afternoon, where they were vacuum filtered using 0.7 µm glass-fibre filters and then acidified with 3M HCl to pH<2.

Streamflow grab samples were collected between May 2016 and October 2018, with weekly sampling mid-April to November. R3, T1 and T2 ceased to flow between August and October each year, so no samples were collected from dry-up to the following spring. R2, R1, and O1 continue to flow year-round, but access to the R2 and R3 sampling points are closed December-April so monthly winter samples were collected only at O1.

**Ground water sampling**

Groundwater samples from drilled wells fitted with handpumps for camper use in two areas Little Elbow Campground (SA1, SA2, SA3) and Beaver Flats Campground (CA 2) (Table 3-1). The handpumps are too close in proximity to show individually in Figure 3-1, but are spaced approximately 200m apart. Little Elbow Campground is located on siliciclastic units at surface, which also outcrop at the riverbank adjacent. Unfortunately, only limited drilling log information was available, which indicated that the wells were drilled and completed in various siliciclastic units. These wells, SA1-3, represent the siliciclastic end-member in the study. Beaver Flats campground is located
on alluvial aquifer gravels that sit on carbonate bedrock. Numerous springs originating in the carbonate bedrock have been landscaped by beavers into a series of pools and waterfalls on the cutbank side of the valley, creating the peninsula “flats” between the ponds and the Elbow River. Site CA1 is a small pool spring disconnected from the main series of pools and waterfalls, 5m from the handpump well CA2. Again, limited drilling information is available for CA2 so the completion interval is unknown, but the well likely intersects alluvial gravels (as do adjacent wells in the campground) which may affect the silica values in the samples. Thus CA2 sample values are not included in the carbonate end-member averaged value, which is represented by CA1. The final groundwater sampling site, P1, is a steel piezometer screened at 2m depth in unconsolidated soil/sediment at the base of Forget-me-not Mountain, placed 0.5m from the slope. Samples from this piezometer have silica (0.7mg/L) and sulfate (1.16 mg/L) values very close to those in precipitation samples from the area (0.2mg/L and 0.45 mg/L), suggesting that these waters have indeed had very little soil or water-rock interaction, and are used as the interflow end-member in the study. We note however that interflow may vary considerably across the watershed and additional interflow sampling sites would be a robust addition to follow-up investigations.

Campground wells with pumps were primed until water flowed freely for 30 seconds, an interval chosen based on stabilization of electrical conductivity in pumped water samples during initial field site scouting. For major ion analysis, 60 mL syringes were rinsed three times with the flowing water before filling the syringe again, then field-filtered through 0.45µm syringe filters (Pall Laboratory, Acrodisc) into 20ml polyethylene vials. Headspace was eliminated by filling to positive meniscus before placing lids, which were sealed with electrical tape until analysis. The piezometer was emptied using a handheld pneumatic pump, but refill rate in the piezometer is too slow
(approximately 3 days to refill) to allow purging and sampling on the same day so sample bottles were rinsed and filled with the single draw of water following the procedure above.

For δ³⁴S analysis, 1L polyethylene vials were rinsed three times with flowing water and then filled to a positive meniscus before placing lids. The bottles were sealed with electrical tape and kept in a cooler until arriving at the lab in the afternoon, where they were vacuum filtered using 0.7 µm glass-fibre filters and then acidified with 3M HCl to pH<2.

**Sampling for tritium analysis**

Samples from the wells and spring at Little Elbow Campground (SA1, SA2, SA3), Beaver Flats Campground (CA1, CA 2) (Table 3-1)), and Elbow Falls outlet (O1) were collected on July 18 2019 according to the procedure provided by AEL AMS Laboratory at University of Ottawa. For well samples, pumps were primed until water flowed freely for 30 seconds (as per section 3.1.2). A clean 4L widemouth polyethylene container was rinsed 3 times then filled, and a 500ml polyethylene vial submerged and capped underwater to ensure no headspace. For open water samples, the 500ml polyethylene vial was rinsed three times with water, submerged in the flowing water and capped underwater to ensure no headspace. The samples were sealed with electrical tape and shipped via courier to AEL AMS Laboratory for enrichment and TU count.

**Laboratory analysis**

Major ion concentrations were measured by ion chromatography with an Metrohm 930 Compact Ion Chromatography Flex system which has a measurement uncertainty less than ± 5% (Chao 2011). Dissolved silica and bicarbonate were measured using a ThermoFischer Gallery with analytical error of ±0.3mg/L.
Samples were prepared for δ\(^{34}\)S analysis by adding BaCl\(_2\) (10%) solution to induce precipitation of BaSO\(_4\) then filtered through 0.45 µm Millipore filters to collect the precipitate. δ\(^{34}\)S and δ\(^{18}\)O in SO\(_4\) analyses were conducted in an elemental analyzer. Analytical error for these procedures is ±0.2‰ for δ\(^{34}\)S in SO\(_4\) and ±1‰ for δ\(^{18}\)O in SO\(_4\). \(^{34}\)S is reported relative to Troilite from Canyon Diablo meteorite (CDT) and \(^{18}\)O/\(^{16}\)O ratios are reported relative to Vienna Standard Mean Ocean Water (VSMOW), both in standard delta notation.

**Discharge**

Daily discharge data (April 2016 – November 2018) are collected from the Elbow River at Bragg Creek Gauging Station (ID 05BJ004; Government of Alberta; Figure 3-1). The gauging station at Elbow Falls was discontinued in 1995, so Elbow at Bragg Creek station (Bragg Creek in Figure 3-1 inset) discharge values were used as a direct proxy for discharge at Elbow Falls based on linear correlation (\(r^2=0.92\)) of the historical discharge data (Campbell et al., 2019).

**End Member Mixing Model**

The end-member model was derived by first conducting correlation analysis that showed silica and sulfate to be the only components with significant variability between sampling sites. Cross-plotting all samples for silica and sulfate (Figure 3-3) indicated that geographic source end-members (i.e. siliciclastic and carbonate rock aquifers and precipitation/interflow) were appropriate. The discrimination between siliciclastic and carbonate aquifer sources for each sample were confirmed by measuring the stable isotope composition of sulfate (Figure 3-4).
The interflow end-member composition is the mean measured silica and sulfate in precipitation records (0.2mg/L Si, non-detect reported as one half the detection limit, and 0.45mg/L SO₄). The siliciclastic end-member is the arithmetic mean for SA1-3 of the median silica and sulfate of samples for each well, and the carbonate end-member is the median silica and sulfate concentration for the carbonate spring (CA1) samples.

These end-member concentrations were used in an End Member Mixing Model (EMMM), which is based on mass balances of dissolved silica and sulfate (i.e. the product of their concentration discharge). Known values in the EMMM included the assumed end-member concentrations, measured silica and sulfate concentrations ([Si]stream and [SO₄]stream), and the total stream flow, Qstream. The statistical programming and graphics program ‘R’ was used to perform matrix inversion to solve the three equations for three unknowns, including the flow from interflow (Qint), carbonate aquifers (Qcarb) and siliciclastic aquifers (Qsil) (full equation and output matrix in Supplementary Materials).

Eq (1) Si mass balance

\[ Q_{\text{int}} \times [\text{Si}]_{\text{int}} + Q_{\text{carb}} \times [\text{Si}]_{\text{carb}} + Q_{\text{sil}} \times [\text{Si}]_{\text{sil}} = Q_{\text{stream}} \times [\text{Si}]_{\text{stream}} \]

Eq (2) SO₄²⁻ mass balance

\[ Q_{\text{int}} \times [\text{SO}_4^2]_{\text{int}} + Q_{\text{carb}} \times [\text{SO}_4^2]_{\text{carb}} + Q_{\text{sil}} \times [\text{SO}_4^2]_{\text{sil}} = Q_{\text{stream}} \times [\text{SO}_4^2]_{\text{stream}} \]
Chapter 3: Si, SO₄, ³H Aquifers and Water Age

Eq (3) Discharge

\[ Q_{\text{int}} + Q_{\text{carb}} + Q_{\text{sil}} = Q_{\text{stream}} \]

Minimum residence time from Silica concentrations

Minimum Residence Time Calculation for Siliciclastic End Member

Eq (4) \[ t = \frac{\ln \left(1 - \frac{c(T)}{C_{\text{eq}}}\right)}{-k} \]

The approach for estimating a minimum residence time for water in a siliciclastic aquifer (Eq 4), adapted from Benettin et al. (2015) and Maher (2011), where \( t \) is minimum residence time and \( c(T) \) is measured silica concentration in the sample. \( C_{\text{eq}} \) is equilibrium concentration, corresponding to the highest silica concentration measured during baseflow conditions. The equilibrium constant is \( k \), in this study defined by the equation for amorphous silica dissolution by Rimstidt and Barnes (1980):

Eq (5) \[ \log k = 0.3380 - 7.889 \times 10^{-4}T - 840.1/T \]

where \( T \) is 274.15 kelvin (4⁰ Celsius, average groundwater temperature in the study area, corresponding to annual average air temperature), and therefore \( k = 1.14 \times 10^{-3} \). We chose the amorphous silica equation because silica cementation is common in these units (Mossop and Shetsen 1994) and because amorphous phyllosilicates, a major component of these units, tend to control silica content in streamflow (Clow and Mast 2010; Maher 2011). The equilibrium value (\( C_{\text{eq}} \)) for dissolved silica in the siliciclastic aquifer was designated as 8.79 mg/L, the highest value measured from any siliciclastic aquifer well in the sampling period. The siliciclastic aquifer end-member silica value is slightly lower, reflecting that not all water in the aquifer may have reached equilibrium:
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$c(T) = 8.1$ mg/L (median of mean values in SA1-3). This value was used to determine minimum residence time for the end-member (Eq 4).

**Water age estimates from tritium**

Water samples from the outlet (O1) and end-member sampling sites (SA and CA) were collected on July 18 2019 to measure tritium units for age estimates. This post-hoc analysis is not ideal – the samples would preferably have been collected during the 2016-2018 sampling period. However the tritium measurements in these water samples do serve to supplement the overall understanding of water age in the Elbow River Upper Watershed.

Water ages from tritium were estimated based on the long-term record of tritium in precipitation at measurement from Ottawa from 2010-2018 (International Atomic Energy Agency 2017) modified to account for regional variability (i.e. Michel et al. 2018) by comparing the Ottawa record with the fragmentary tritium in precipitation records nearest Elbow Falls collection point: Edmonton, Alberta (1960-68) and Wynard, Saskatchewan (1975-1982) (Supplementary Materials). Since the mean values for the two western sites were somewhat lower than the Ottawa mean values (86% of the Ottawa mean at Edmonton and 82% at Wynard), the tritium curves are scaled down 15% to create a “Southern Alberta” tritium curve (Figure 3-2). We also compared the Ottawa curve to that from Bismark, ND, the nearest North American station with a continuous record to ensure consistency (Supplementary Materials), and found no discrepancy beyond the lower overall magnitude in atmospheric tritium due to latitudinal variation (Michel et al. 2018).
Figure 3-2. Time series of tritium in precipitation and decayed tritium values. The Southern Alberta curve (dark blue solid line) is derived from the Ottawa curve (dark blue dotted line) where measurements are taken. Decayed tritium values are calculated using Eq 6 (Southern Alberta light blue solid; Ottawa light blue dotted). Grey dashed lines indicate modern (blue arrow), mixed (green arrow), and pre-modern (yellow arrow) threshold values for tritium in water samples. Figure follows conventions defined in Lindsay et al. 2019. Study samples (orange circles) were taken slightly after the most recent available tritium measurements.
From the Southern Alberta curve, tritium values were decayed to July 18 2019 using Equation 6, where $^3$H$_t$ is the measured tritium concentration at collection, and $^3$H$_0$ is the initial tritium concentration in precipitation.

$$Eq \ (6) \ t = -17.77 \ln \frac{^3H_t}{^3H_0}$$

The $^3$H$_0$ value was derived using the method defined in Lindsey et al. (2019) (Figure 3-2) and supported by Mann-Kendall analysis of trends over various time intervals (Table 3-2). Since the peak-bomb tritium period of 1952-1966, tritium levels in the atmosphere have declined both due to radioactive decay and atmosphere-ocean interactions (Clark 2015). Natural background levels of cosmogenic tritium were reached in the Southern Hemisphere in the early 2000s (Morgenstern et al. 2010) and appear to have stabilized in the Northern hemisphere in the last several years. To evaluate this stabilization we evaluated post-peak intervals of the Southern Alberta curve (solid dark blue line, Figure 3-2) from 1992, 1997, 2002, and 2010 to present for monotonic decline (following Morgenstern et al. (Morgenstern et al. 2010)) using the Mann-Kendall function in R. All periods exhibited monotonic decline (negative $\tau$ and 2-sided $p$value <0.05)(Table 3-2) except 2010-2018, where $p$=0.27, indicating no monotonic trend and a stabilization of atmospheric tritium at this North American monitoring station. We therefore set the mean tritium value for 2010-2018 as $^3$H$_0$ to represent background tritium concentration in 1952 and to apply the tritium decay function (Eq 6) to the Southern Alberta tritium curve (light blue line, Figure 3-2), using bi-yearly means to preserve inter and intra-annual variation while reducing the effects of outliers (Lindsey et al. 2019).
Table 3-2. Post-peak tritium curve periods evaluated for monotonic trends.

<table>
<thead>
<tr>
<th>Span for “Modern” Calculation</th>
<th>Average TU in Precipitation</th>
<th>Pre-modern threshold</th>
<th>Modern (min)</th>
<th>Modern (Post 1997)</th>
<th>Kendall τ</th>
<th>2-sided pvalue</th>
<th>Monotonic Trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Southern Alberta</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1992-2018</td>
<td>14.4</td>
<td>0.34</td>
<td></td>
<td></td>
<td>-0.308</td>
<td>2.22E-16</td>
<td>Y</td>
</tr>
<tr>
<td>1997-2018</td>
<td>14.0</td>
<td>0.33</td>
<td></td>
<td></td>
<td>-0.308</td>
<td>1.17E-13</td>
<td>Y</td>
</tr>
<tr>
<td>2002-2018</td>
<td>12.8</td>
<td>0.30</td>
<td></td>
<td></td>
<td>-0.225</td>
<td>1.93E-06</td>
<td>Y</td>
</tr>
<tr>
<td>2010-2018</td>
<td>11.0</td>
<td>0.26</td>
<td>3.1</td>
<td>3.7</td>
<td>-0.0772</td>
<td>0.26788</td>
<td>N</td>
</tr>
<tr>
<td>Ottawa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010-2018</td>
<td>13.2</td>
<td>0.31</td>
<td>3.7</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We also set threshold values for discriminating “modern” “mixed” and “pre-modern” waters using the procedure in Lindsay et al. (2019). The minimum post-peak value for the decayed tritium curve (light blue line, Figure 3-2) is defined as the modern water threshold (3.1). The prominent flattening between 1992-1996 suggests a possibly more likely minimum (3.7), so we included that threshold but this variation does not affect classification of the data points in the study. The pre-modern threshold is the 2010-2018 mean tritium value (11.0) decayed from 1952 to present (0.3).

Results and Discussion

Water Sample Composition and End-member Designations

Strong variation exists between sampling sites for dissolved silica (SiO$_2$$_{(aq)}$) and sulfate (SO$_4$$_{(aq)}$) concentrations (Figure 3-3), and δ$^{34}$S values of SO$_4$ (Figure 3-4). Variation in silica and sulfate concentrations in Rocky Mountain source waters was noted as early as 1974 by Drake and Ford, who used these dissolved components to delineate a two end-member mixing model describing seasonal variation in the Athabasca and North Saskatchewan River. Although they described a two end-member model, they explicitly
stated that these source waters mixed with “overland flow” to create the measured streamflow concentrations. Using water activity and smectite content, Grasby et al. (1999b) demonstrated that overland flow is not a significant component of streamflow in the Bow River, Alberta, and the processes they described can reasonably be generalized over the Front Ranges. The “overland flow” component described by Drake and Ford (1974a), therefore, can more realistically be described as interflow: water that has undergone limited water-rock interaction, likely passing through soil and/or alluvial aquifer sediments before becoming streamflow. Therefore, an end-member mixing model for the Front Ranges rivers should have three end-members; interflow, siliciclastic aquifer, and carbonate aquifer. Figure 3-3 shows that water samples from the Upper Elbow Watershed clearly define such a system. Furthermore, δ^{34}S values of SO_{4} in the water samples support the discernment of siliciclastic and carbonate sulfate sources (Figure 3-4). Therefore, this variation in dissolved silica and sulfate concentrations provides a clear delineation of end-members and mixed waters for the points sampled within the watershed. Given the size of the watershed (435 km²), it is likely that these sampling points do not encompass all the variability in the system and the end-members may need adjusting. We tested the fit of the end-member model with individual single-day samples taken from more widespread springs and streams within the watershed and found they fit well into the defined framework (Supplementary Materials), suggesting that this end-member mixing model is a fair general representation of the hydrogeochemical interactions in the watershed.

Interflow End Member: Precipitation collected at Barrier Research Station in Kananaskis (PPTN, Figure 3-1) in 2017 had both low dissolved silica and sulfate (0.2 and 0.45 mg/L), similar to low-concentration samples from piezometer P1 (diamond, Figures 3-1 and 3-3). The silica and sulfate concentrations from P1 were therefore used to represent the interflow end-member, that is, water that has not undergone significant
water-rock interaction within the system. No $^{34}$S values for the precipitation or piezometer samples were obtained due to insufficient sulfate concentrations.

*Siliciclastic End Member:* Samples collected from three wells completed in siliciclastic units (SA1-3, orange symbols Figures 1-3) had relatively high dissolved silica (mean value 8.1 mg/L) and low sulfate (mean value 13.6 mg/L respectively). The sulfate in these samples has $^{34}$S values between -19.4 and 1.6, indicating oxidation of sulfide as its source (Figure 3-4), signifying origins from weathering of siliciclastic sediments containing minerals such as pyrite (Krouse and Mayer 2000). The siliciclastic end-member values for dissolved silica and sulfate were therefore designated as the arithmetic mean for SA1-3. This designation is consistent with the assumption that the siliciclastic aquifer comprises numerous heterogeneous layers, with some variability in the ‘end member’ solute concentrations.

*Carbonate End Member:* Samples from the artesian spring CA1 consistently had the highest sulfate (162.8 mg/L) of all sampling points in the watershed, with relatively low dissolved silica (4.44 mg/L). The sulfate has $^{34}$S values between 21.7-22.5, indicating dissolution of evaporites as its source (Figure 3-4), from weathering of minerals such as gypsum in carbonates (Krouse and Meyer, 2000). The dissolved silica and sulfate values for the carbonate aquifer end-member were assigned as the mean values from this spring.

Framing the Upper Elbow Watershed hydrodynamic system with these three end-members provides a useful way to visualize sources and mixing within the system. For example, samples from tributaries and springs (T1-2, S1) that surface in siliciclastic rocks fall along the interflow-siliciclastic mixing line; that is, they have relatively high dissolved silica and low sulfate concentrations along with low $\delta^{34}$S values, indicating
interflow-siliciclastic end-member mixing (Figure 3-4). The Beaver Flats area (CA1-2) is in a syncline that exposes carbonate rocks at surface and the low dissolved silica, high sulfate and δ\textsuperscript{34}S water in CA1 suggest groundwater recharge occurs in that same rock unit. In contrast, CA2 is directly adjacent to CA1, but is drilled partly through gravels of the Elbow River alluvial aquifer. Its samples have high sulfate and δ\textsuperscript{34}S values similar those of the spring (CA1), but its higher average Si indicates some influence of siliciclastic/interflow contributions due to throughflow in the alluvial aquifer (Figure 3-3). Mainstem river samples from R1-3 fall centrally within the mixing space, indicating relatively equal contributions from all three end-members. We evaluated this inference from the two-dimensional end-member mixing diagram using a three-end member mixing model.
Figure 3-3. Crossplot of SO$_4$ and SiO$_2$ concentrations for mainstem (R1-3, O1), tributary (T1-2), spring (S1, CA1), and groundwater (SA1-3, CA2) samples. End member compositions used in the mixing model are indicated by filled squares. Mainstem river samples fall centrally within the space bounded by end-members. Tributaries and springs fall along the silicilastic-interflow mixing line greyed arrow) and their ages are calculated based on binary mixing. Mainstem river ages fall closer to those of interflow end-member than those of tributaries.
Figure 3-4. Cross plot of δ18O and δ34S in SO42-. The ranges that indicate the origin of SO4-2 are indicated by boxed areas. Samples from wells SA1-3, S1 spring, and tributaries (T1,T2) fall within the oxidation of sulfides origin area (siliciclastic). Samples from CA1-2 fall within the weathered from evaporites area (carbonate). River samples (R1-R3 and O1) fall along a mixing line between the two. Adapted from Krouse and Meyer, 2000.
Source Contributions from End-Member Mixing Model

Dissolved silica and sulfate values for river samples seem to indicate relatively equal contributions of water from interflow, siliciclastic aquifers, and carbonate aquifers, an assumption we tested with an end-member mixing model. Elbow Falls is the terminal outlet of the Upper Elbow Watershed, and its samples are therefore snapshots of the integration of water sources within the watershed. Frequent sampling in open-water season over three years (June to November 2016-2018) provided a comprehensive picture of watershed mixing dynamics. We evaluated the proportion of water at Elbow Falls derived from each of the three end-members identified in Figure 3-3, using the end-member mixing model.

Interflow comprised the largest proportion of streamflow, with an overall mean of 39% over most of the sampling period (Table 3-3; Figure 3-5) with the remaining contributions distributed approximately equally from siliciclastic (mean 30%) and carbonate (mean 32%) aquifers. However, seasonal and interannual contributions from each source vary considerably. Carbonate contributions are lowest during snowmelt and increase over the season, up to twice the spring minima by October. Siliciclastic contributions tend to be the highest during May-June snowmelt, up to three times higher than during October baseflow. Low snowpack corresponds to reduced overall streamflow and corresponds to reduced siliciclastic contributions in early and late open water season (i.e. 2016; Table 3-3), while rainfall events can produce siliciclastic peaks (August 2016, June 2018). The variability of siliciclastic contributions in response to seasonal and storm inputs suggests relatively rapid transmission in the siliciclastic aquifers. This rapidity could be due to higher porosity (8-25%) in the siliciclastic units (Stott et al. 1984; Varley 1984) compared to 7-9% in the carbonate units (Rupp 1969; Alley 1982). However it is more likely due to the very high permeabilities in some siliciclastic units, from 80 milidarcies in some of the lower porosity units up to 1 darcy
in some of the mixed conglomerates. In contrast, permeabilities in the carbonates are often less than 1 milidarcy, and up to only approximately 10 milidarcies. Mega-pore karst conduits are a common feature of the carbonate units, which can produce rapid and voluminous throughflow, but they can require threshold water levels to become connected (Worthington 1991; White 2016).

The high permeabilities in the siliciclastic units may also explain the decrease in relative contribution from interflow during rainfall events. While total volume of contributions from all three sources increases during rainfall events (Figure 3-5b), the relative contributions from carbonate and interflow often decrease while that from siliciclastic aquifers increases (Figure 3-5a). The decrease in relative interflow contribution is somewhat surprising as shallow flowpaths would be expected to accommodate much of the precipitation. However, high permeability in some siliciclastic units could lead them “capture” some of the infiltrating water especially if the storm cell is centered in higher elevation areas with no alluvial aquifer sediments and thin soil cover. Piston-style flow encouraged by high topographic gradient would then push water through the siliciclastic reservoirs, creating a relative surge that diminishes as the top-down drive subsides.
Table 3-3 Fraction of streamflow discharge (Q) from each of three end-members (interflow, siliciclastic aquifers, and carbonate aquifers) for all samples, and each of 2016-2018 sampling years.

<table>
<thead>
<tr>
<th></th>
<th>Interflow (%)</th>
<th>Siliciclastic (%)</th>
<th>Carbonate (%)</th>
<th>Max Snowpack at Little Elbow Summit (mm)</th>
<th>Q_{max} (m^3/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>range mean</td>
<td>mean</td>
<td>range</td>
<td>peak</td>
</tr>
<tr>
<td>All Years</td>
<td>60</td>
<td>39</td>
<td>21-52 30</td>
<td>9-58 32</td>
<td>17-46</td>
</tr>
<tr>
<td>2016</td>
<td>10</td>
<td>42</td>
<td>35-52 23</td>
<td>9-35 35</td>
<td>28-39 358</td>
</tr>
<tr>
<td>2017</td>
<td>23</td>
<td>38</td>
<td>31-49 30</td>
<td>31-49 32</td>
<td>21-43 510</td>
</tr>
<tr>
<td>2018</td>
<td>27</td>
<td>37</td>
<td>21-48 32</td>
<td>24-58 30</td>
<td>17-6 520</td>
</tr>
</tbody>
</table>
Figure 3-5. Timeseries of EMM-modelled relative discharge (Q) contributions from interflow (grey) and siliciclastic (orange) and carbonate (blue) aquifers for each of three sampling years. a) Percentage contributions. Interflow provides 40-60% of discharge throughout the season. Contributions from carbonate and siliciclastic reservoirs vary seasonally. b) As volumetric flow (m$^3$/s) Precipitation is shown as blue bars (mm). Note that the low overall streamflow and peak in 2016 reflects very low snowpack that year (Table 3-4).

More rapid transmission in siliciclastic reservoirs has important implications for resilience of the watershed’s water resources to climatic change in maintaining streamflow. Geographically, siliciclastic rocks comprise only ~27% of the watershed (Figure 3-1). Carbonate rocks underly the remaining 73% of the watershed but overall streamflow contributions from carbonate and siliciclastic aquifers are approximately
equal. This disparity occurs in part because large portions of the carbonate rock do not function as an aquifer – the sulfate rich portions and areas adjacent to fractures are preferentially dissolved, creating karst aquifers with preferential flow along fractures (Drake and Ford 1976; White 2002; White and White 2005). If variations in snowmelt volume and rainfall affect siliciclastic throughput more strongly, as the model outputs suggest (Figure 3-5), long-term changes to the precipitation regime will translate into changes in streamflow, with earlier snowmelt, causing earlier peak flows, and less frequent but more intense rainfall at different times of the year than historically, resulting in flashier, more volatile hydrographs. To further investigate the implications of this variability in siliciclastic inputs, we used silica concentrations to assess the minimum residence time for water in the siliciclastic aquifers.

**Minimum Residence Time from Silica and Tritium Age**

The minimum residence time for the siliciclastic end member was estimated using the median silica concentration of the end members samples (including three siliciclastic end-member wells (SA1-3); Figure 3-1) of 8.1 mg/L as 6.1 years (Eq 4). This minimum age corresponds well with the mean tritium age of 5.4 years measured from July 2019 samples from the SA wells (Table 3-4). Interestingly, the tritium age for the July 2019 carbonate end-member CA1 of 3.3 years suggests a similar residence time for carbonate waters in the watershed. However, silica provenance in these carbonate rocks was unclear, and a much lower maximum measured silica value from this source \((c(eq)=5.31\text{mg/L})\) prevented application of the dissolved silica methodology for the carbonate end-member.
Table 3-4. Mean values of $\text{H}^3$(TU) and Si used to estimate groundwater ages from Eq. 5 and 6

<table>
<thead>
<tr>
<th>Site</th>
<th>$d^{34}\text{S}$</th>
<th>$^3\text{H}$ (TU)</th>
<th>$^3\text{H}$ Age (y)</th>
<th>Minimum Age from Average [Si] (y)</th>
<th>Average [Si] (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siliciclastic Source</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA1</td>
<td>-12</td>
<td>9.1</td>
<td>3.8</td>
<td>5.3</td>
<td>7.84</td>
</tr>
<tr>
<td>SA2</td>
<td>-19.1</td>
<td>9.5</td>
<td>3.1</td>
<td>5.4</td>
<td>7.85</td>
</tr>
<tr>
<td>SA3</td>
<td>1.4</td>
<td>6.7</td>
<td>9.3</td>
<td>7.5</td>
<td>8.40</td>
</tr>
<tr>
<td>Carbonate Source</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA1</td>
<td>22.1</td>
<td>9.4</td>
<td>3.3</td>
<td>N/A</td>
<td>4.41</td>
</tr>
<tr>
<td>CA2</td>
<td>21.8</td>
<td>9.9</td>
<td>2.4</td>
<td>N/A</td>
<td>4.82</td>
</tr>
<tr>
<td>Mixed Source</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outlet</td>
<td>12.9</td>
<td>9.7</td>
<td>2.7</td>
<td>N/A</td>
<td>3.88</td>
</tr>
</tbody>
</table>

Given the good correspondence of silica-derived minimum residence time and tritium ages, the age of samples that plot on or near the interflow-siliciclastic line (Figure 3-3) can be calculated as a continuum between precipitation (0.2 mg/L SiO$_2$, 0 years) and siliciclastic aquifers (8.1 mg/L SiO$_2$, 6.1 years). Siliciclastic and interflow-sourced tributaries and springs therefore have intermediate ages of ~3.6 years. While carbonate end-member age could not be calculated from silica, the similar tritium
measurements suggest similar residence time as in siliciclastic aquifers, implying that relative position along the interflow-siliciclastic line provides an appropriate age estimate. The river samples from R1, R2, and at the outlet falls O1 have proportionately more contribution from interflow and therefore can generally be assumed to have composite ages of less than ~3.6 years, which again corresponds well with the O1 tritium measurement of 2.7 years.

Together, the seasonal variations (in any given year), the year-to-year variation of the end-member contributions to flow, and the relatively short silica and tritium-derived water ages paint a picture of a watershed that is responsive to short-term perturbations, and therefore vulnerable to long-term climatic change. The silica-derived minimum residence times and tritium ages suggest relatively rapid movement of water through the watershed, with much of the water stored in aquifers for less than 10 years before becoming streamflow. The end-member mixing model suggests that contributions from siliciclastic aquifers respond rapidly to changes in inputs, so the extended droughts and intense precipitation events predicted for the area (St. Jacques et al. 2013; Farjad et al. 2016; Chernos et al. 2020b) could quickly affect streamflow patterns. Perhaps more importantly, if the steadier carbonate aquifer contributions have similar residence times to the siliciclastic contributions, extended periods of drought could diminish streamflow significantly as both rock aquifers decrease throughput overall.

**Conclusions**

Silica and sulfate concentrations along with the isotopic composition of sulfate in streamflow were used to investigate sources and storage of streamflow in the Rocky Mountain Elbow River, identifying contributions from interflow and flow from
siliciclastic and carbonate aquifers. We used a three end-member mixing model to estimate their relative contributions to streamflow over time. We found that interflow comprises ~40% of annual flow while 60% comes from the siliciclastic and carbonate aquifers. The relative seasonal contributions from rock aquifers varied, with siliciclastic aquifers contributing higher proportions during spring melt in two of the three years, and carbonate aquifers contributing more in late summer and autumn. The relatively similar contribution of river discharge from the two rock aquifer types despite the geographic preponderance of carbonate rock aquifers (i.e., 73% of the watershed area) suggests that significantly more throughflow occurs in the siliciclastic aquifers.

Silica dissolution-based residence time estimates in the siliciclastic aquifers found a minimum residence time of ~6 years, which was supported by similar tritium-based estimates (<5-10 years). Similar tritium measurements for carbonate aquifers suggest that water at Elbow Falls has an overall residence time of <5 years, which has significant implications for long-term water management in the region. The low residence times (consistently less than ten years) combined with significant seasonal and interannual variations in the proportion of water originating in carbonate and siliciclastic aquifers suggest the watershed has little resilience to climatic changes.
Chapter 4: High elevation snowpack generates low elevation overwinter baseflow in a Rocky Mountain river

Key Points

- Nested flow systems convey higher elevation/colder precipitation to lower elevation river reaches
- Winter baseflow is generated mainly from carbonate aquifers
- Winter baseflow is generated mainly from winter precipitation

Graphical Abstract
Abstract

The majority of each year’s overwinter baseflow (i.e., winter streamflow) in a 3rd-order eastern slopes tributary is generated from annual melting of high-elevation snowpack which is transmitted through carbonate and siliciclastic aquifers. The Little Elbow River and its tributaries drain a bedrock system formed by repeated thrust faults that express as the same siliciclastic and carbonate aquifers in repeating outcrops. Longitudinal sampling over an 18 km reach was conducted at the beginning of the overwinter baseflow season to assess streamflow provenance. Baseflow contributions from each of the two primary aquifer types were apportioned using sulfate, $\delta^{34}$S$_{\text{SO}_4}$, and silica concentrations, while $\delta^{18}$O$_{\text{H}_2\text{O}}$ composition was used to evaluate relative temperature and/or elevation of the original precipitation. Baseflow in the upper reaches of the Little Elbow was generated from lower elevation and/or warmer precipitation primarily stored in siliciclastic units. Counterintuitively, baseflow generated in the lower elevation reaches originated from higher elevation and/or colder precipitation stored in carbonate units. These findings illustrate the role of nested flow systems in mountain block recharge: higher elevation snowmelt infiltrates through fracture systems in the cliff-forming - often higher elevation - carbonates, moving to the lower elevation valley through intermediate flow systems, while winter baseflow in local flow systems in the siliciclastic valleys is reflects more influence from warmer precipitation. The relatively fast climatic warming of higher elevations may alter snowmelt timing, leaving winter water supply vulnerable to climatic change.

Key Points:
- Nested flow systems convey higher-elevation/colder precipitation to lower-elevation river reaches;
- Winter baseflow is generated mainly from winter precipitation stored and transported through carbonate aquifers;
• Long flow pathways for high-elevation precipitation suggest little difference between intermediate and deep flow pathways and therefore between mountain aquifer and mountain block recharge;

• Dependence on winter precipitation leaves the river vulnerable to climate change.

Introduction

Mountain streamflow provides water to more than 1 billion people worldwide, with increasing demand expected in coming decades (Viviroli et al. 2020). Mountain catchments often receive much of their precipitation as snow (Somers and McKenzie 2020) and are warming faster than lowlands (Pepin et al. 2015) leaving them vulnerable to observed changes in snowfall and snowmelt (Musselman et al. 2021). Understanding how streamflow is generated is crucial to understanding how to manage climate change in these watersheds, particularly in the parts of the hydrologic year with the lowest streamflow (i.e., the baseflow season).

Mountain-block hydrology refers to recharge and streamflow generation processes in areas of high topographic relief (Wilson et al.). The term mountain block recharge (MBR) denotes water delivered from the mountain block to lowland aquifers by deep or regional flow systems rather than the processes of recharge within the mountain block itself (Wilson et al.; Markovich et al. 2019a) which Markovich et al. (2019a) suggest can be referred to as “mountain-aquifer recharge”. This distinction may be necessary because of the historical usage of the term MBR, but it is debatable whether there is any real differentiation in the processes of recharging local, intermediate, and regional flow systems within a mountain block. In mountain headwaters precipitation can be stored and released as streamflow from coarse deposits such as talus slopes, rock glaciers, and moraines (Christensen et al. 2020; Hayashi 2020) as well as alluvial aquifers (Käser and Hunkeler 2016). Though orders of magnitude less permeable, bedrock infiltration in these environments is also significant due to lack of soil in alpine regions, high topographic relief (Tóth 1963) and fracturing. Manning et al.(Manning et al. 2021) indicate that approximately 10% of
infiltrated water moves into deep or regional flow pathways, and along with previous modelling studies, suggest the majority of bedrock infiltration remains in the uppermost ~20 m with higher permeability, resurfacing as mountain streamflow (Smerdon et al. 2009b; Markovich et al. 2019a; Hayashi 2020). Somers and McKenzie (2020) list numerous studies identifying groundwater contributions to mountain streamflow was greater than 50% in many cases. These findings correspond to the results of previous hydrologic modelling in the Elbow River watershed where the provenance of up to 60% of spring and summer streamflow in the Elbow River was bedrock aquifers, and the remaining “interflow” contribution had relatively short residence times in coarse, shallow groundwater systems before becoming streamflow (Campbell et al. 2021). Thus, recharge processes in mountain-block hydrology deserve closer focus.

While groundwater contribution to mountain streamflow is well-established (Winter 2007; Markovich et al. 2019b; Somers and McKenzie 2020), a robust understanding of the seasonal variability and intricacies of streamflow generation in a given watershed is required when managing land-use and climate change. A good example is the part of the hydrologic year with the lowest streamflow. In the Rocky Mountains in western North America this period is overwinter baseflow, important where mountain and lowland populations alike rely year-round on mountain streamflow. In cold regions where winter precipitation falls as snow and does not contribute to streamflow in that same season, winter baseflow is necessarily groundwater generated. But which groundwater? Do all possible aquifers in the watershed contribute? How old is the winter baseflow water – did it fall as last year’s rain and snow, or that from a century ago? Manning et al. (Manning et al. 2021) demonstrated that low vertical permeability produces distinct stratification in mountain groundwaters, with the majority of younger circulation occurring in the upper 20 m. Paznekas and Hayashi (2016) showed that winter baseflow rate in several Rocky Mountain watersheds is not dependent on the volume of precipitation from the previous year, suggesting a “fill and spill” model for the aquifers, and Campbell et al. (2020c) demonstrated that in an eastern slopes Rocky Mountain river, up to 20% of winter baseflow is derived from the previous winter’s snowmelt, implying relatively rapid cycling through the hydrogeologic system.
Similarly, Campbell et al. (2021) found an average groundwater residence time of ~4 years for streamflow. Somers and McKenzie (2020) highlight the ‘buffering capacity’ that groundwater storage provides for streamflow in dry seasons and drought and suggest that it may provide some resilience to climate change. With mountain aquifer residence times of only a few years in some systems, this capacity may be limited.

To better understand the resilience of a given watershed it is ideal to understand where precipitation infiltrates, in which hydrogeologic units it is stored during groundwater transport, and becomes streamflow, and the time scales of each. Water isotopes in precipitation and streamflow have long been used as intrinsic tracers to estimate mean travel times for water through watersheds (see for example McGuire and McDonnell 2006; Klaus and McDonnell 2013), and also provide information about the relative temperature and/or elevation of the original precipitation (i.e. warmer, lower-elevation vs. colder, higher-elevation) (i.e. Feng et al. 2009; Jasechko et al. 2017; Beria et al. 2018). Dissolved ions within streamflow can provide information about the type(s) of rock-water interaction, and hence the aquifer(s) where the water was stored after infiltration and before discharge into rivers as groundwater baseflow. Dissolved silica has been used with water oxygen isotopes to evaluate transit times (Hoeg et al. 2000; Peters et al. 2014; Benettin et al. 2015) and can also provide insight about rock-water interaction and therefore host aquifers (Haines and Lloyd 1985; Clow and Mast 2010; Maher and Chamberlain 2014). Campbell et al. (2021) used silica and sulfate, along with sulfur isotopes in sulfate, to define a three-end-member mixing model that differentiated spring and summer aquifer contributions to the Elbow River. This method can be further applied to assess source-aquifer contributions to overwinter baseflow, and these findings used to assess resilience of the Elbow River watershed to climatic change.

Although aquifer types and average streamflow age have been evaluated for eastern slopes of the Rocky Mountain rivers, like the Elbow River, there is no work on determining the relative contributions of different aquifer transport pathways and recharge elevations during the critical seasonal period where streamflow is dominantly groundwater baseflow. To evaluate these
pathways for early winter baseflow, we conducted longitudinal streamflow sampling along a reach of the Elbow River (akin to a seepage run (Donato) but for sampling as opposed to discharge measurements) at the end of the open water season. Thirteen samples were collected over an 18 km reach, stretching from the mouth of the groundwater/surface water transition (i.e., headwater) of the Little Elbow to above its confluence with the Big Elbow, and collated the results from open water season streamflow sampling (July). All samples were analysed for silica and sulfate concentrations and water and sulfate isotope compositions. We demonstrate that winter baseflow in the Little Elbow is mainly generated from high elevation winter precipitation which is primarily stored in carbonate aquifers. High elevation regions are particularly susceptible to climate change (Musselman et al. 2021), which leaves winter streamflow vulnerable to changes in melt patterns and reduced snowfall.

Objectives:

1. Assess relative contributions of aquifer types to baseflow;

2. Assess relative temperature and elevation of precipitation contributing to baseflow along the length of the river;

3. Use these assessments to integrate conceptualization of local, intermediate, and deep flow pathways in mountain aquifer and mountain block recharge.

Materials and Methods

Study Area

The Little Elbow River is one of two mainstem rivers that join to form the Elbow River, an eastern-slopes Rockies river. Most of the Elbow River’s flow is generated in the 435 km² Upper Elbow River watershed (defined here as the reach of the Elbow River upstream of Elbow Falls,
Figure 4-2; Manwell & Ryan, 2006; Valeo et al., 2007). Open water season is typically April to October, with peak flow mid-May to late June due to snowmelt and seasonal rainfall. Overwinter precipitation (Nov-April) falls as snow and therefore does not contribute to streamflow in those months, thus overwinter streamflow (described hereafter as overwinter baseflow) is groundwater sourced. Despite the relatively long course of the Big Elbow (relative to the Little Elbow) tributary, the Big Elbow was observed to be ephemeral, with water levels dropping to more than 2m below ground surface in the stream bed by mid-September in 2016-2018 (data not shown). Thus, between October and May, streamflow in the Elbow River is principally supplied by the Little Elbow. This supply is important as the main end-use of the Elbow River municipal water supply for ~400,000 people in the City of Calgary in Alberta, Canada, as well as several smaller communities and rural uses. Elbow River streamflow is highly variable (< 5 to ~50 m$^3$/s, and up to 1800 m$^3$/s in major floods (Alberta Environment and Sustainable Resource Development 2019)), which necessitated construction of the Glenmore Dam and Reservoir in 1933 for steady overwinter water supply to the city.

The upper watershed is zoned as a multi-use recreation area and has had minimal development. Although recreation remains the primary use, usage is rapidly increasing, with a 35% increase in recreational visitors between 2019-2021, from ~4 million to 5.4 million. At the same time, development has continued along the Elbow River and its alluvial aquifer corridor, and development pressure in both the Upper Watershed and downstream is projected to increase in coming decades (Wijesekara et al. 2014; EPCOR Water Services Inc. 2018). At the same time, climate change projections for the region indicate intensifying wet and dry periods, with earlier snowmelt and earlier glacial discharge (St. Jacques et al. 2013; Farjad et al. 2016; Chernos et al. 2020).

The temperate humid climate of the Upper Elbow Watershed results from 1981-2010 average annual precipitation (1981-2010, not corrected for snow under-catch) of 665, 639, and 568 mm at three stations in and around the watershed: Elbow RS, Kananaskis, and Pocaterra stations respectively (Environment Canada, 2019). Approximately half this annual precipitation is snow
(Campbell et al. 2020), with accumulation beginning November and peaking in late March. The spring melt usually begins in May and is complete in late June. Seasonally high rainfall, often coincident with snowmelt, produces peak streamflows in June (Valeo et al., 2007; Farjad et al., 2016).

With an average topographic slope of 25°, the mountainous Upper Elbow watershed has a maximum elevation of 3200 m above sea level (asl) and minimum 1600 m asl. A series of thrust faults repeatedly superimpose Paleozoic age dolomite and limestone units (carbonates) over Mesozoic age sandstone and shale units (siliciclastics), creating alternating carbonate cliffs and siliciclastic valleys (Prior, G.J., Hathway, B., Glombick, P.M., Pana, D.I., Banks, C.J., Hay, D.C., Schneider, C.L., Grobe, M., Elgr, R. and Weiss 2013) (Figures 1 and 2). Vegetation follows a clear elevation gradient with three major ecoregions; forested montane (5%), transitional sub-alpine (56%), and treeless alpine ecoregions (39%) (Alberta Environment and Sustainable Resource Development 2005; Valeo et al. 2007). Valley floors may have deep deposits (>12m) of unconsolidated sediment and soil, while these deposits are less than a few meters or absent elsewhere.
Figure 4-1. Upper Elbow watershed. a) Linear relief shading. Sample collection points are indicated with black circles. b) Watershed bedrock types. Most of the Upper Elbow watershed (including the Little Elbow where sampling was conducted) is carbonate rock (~73%), with siliciclastics upper extremities (~27%) and small areas of carbonate and siliciclastic interbedded layering. Inset shows middle and lower Elbow watersheds in relation to Calgary, Alberta. Numbers indicate sampling locations (named in Table 4-1).
Figure 4-2. Schematic cross-section of the Upper Elbow Watershed (A-A’ on Figure 4-1) with Little Elbow River elevation profile projected (orange line). Numbers indicate the approximate location of sampling locations (yellow and blue dots (named in Table 4-1). Yellow units are the youngest (Mesozoic) siliciclastic rocks, medium blue units are younger (Upper Paleozoic) carbonates, dark blue are older (Lower Paleozoic) carbonates. Dashed lines indicate thrust faults and pink arrows illustrate illustrate some of the many possible conceptual local and intermediate flow pathways. Note the figure has significant vertical exaggeration. (Adapted from CSPG Field Guide(Evers and Thorpe 1975))

Figures 4-1 and 4-2 emphasize the alternating siliciclastic and carbonate rock units through which the Little Elbow flows. Krouse and Mayer (Krouse and Mayer 2000) demonstrated that paired $\delta^{34}$S$_{SO_4}$ and $\delta^{18}$O$_{SO_4}$ isotopes can be used to distinguish whether SO$_4$ was dissolved from siliciclastic or carbonate rock, and Campbell et al. (2021) used this characteristic, along with dissolved silica and sulfate concentrations, to confirm distinct water types in a three end-member mixing model for the Elbow River. The same approach, based on silica and sulphate concentrations, and dissolved sulphate isotopes are used in the present study to analyse aquifer contributions to streamflow.
Chapter 4: Flowpaths and Mountain Block Hydrology

Water isotopes in streamflow are used in this study to evaluate the relative elevation and temperature of precipitation before infiltration. Seasonal variability in the $\delta^{18}$O in precipitation is considerable at high latitudes (>40‰) and varies with elevation (Rozanski et al. 1993; Gat 1996a) such that lower $\delta^{18}$O indicates colder and/or higher elevation precipitation. While seasonal variability is strongly dampened and lagged in streamflow in the Elbow River (Campbell et al. 2020b) (~2‰ intra-annually), relative variations in $\delta^{18}$O$_{H2O}$ in spatially separated streamflow samples collected along a river reach under steady baseflow conditions can still provide evidence of different precipitation and infiltration regimes for source aquifers.

Sample Collection and Analysis

Stream Profile and Sample Points

Elbow Falls (Figure 4-2) is the outlet for the Upper Elbow Watershed where the river mainstem flows over bedrock falls stripped bare of alluvial gravels, which provides an integrated snapshot of the combined surface and alluvial groundwater in the watershed. Samples were collected at the mouth of the Little Elbow (sampling point 12; Figure 4-1) is 12 km upstream of the falls and ~100m upstream of the seasonal confluence with the Big Elbow, adjacent to a seasonally accessible public access point. On the Oct 26 sampling date, surface flow in the Big Elbow had not been observed for more than two months (in weekly sampling visits), and hence the flow at Elbow Falls was mainly from the Little Elbow tributary. The sample collection points above Little Elbow’s mouth (sampling point 12) were chosen based on river accessibility with a view to longitudinal distribution along the 18 km reach that was sampled. Vehicle access above Little Elbow is normally restricted to fire suppression, but single-day access along a fire-service road was granted to facilitate the longitudinal sampling program. The first sample (transition from groundwater to surface water; sampling point 1) was the first occurrence of surface water below the remnant of Tombstone glacier in the Little Elbow Valley, and was accessed by hiking approximately 1km from the end of the fire-service road.
The late-season October date was chosen as the latest part of the open water season (i.e. beginning of the overwinter baseflow season) with minimal likelihood of river ice formation. Sampling was conducted after seven days with no recorded precipitation. The relatively short days in late-October imposed additional time constrictions on field work, but twelve samples were collected over the 18 km length reach. At each sampling point location and elevation were recorded with a handheld GPS. The flow distance was estimated by detailed tracing in Google Earth Pro.

Sampling point 1 is the groundwater/surface water transition in the uppermost headwaters, where the stream first surfaces between rough, unrounded cobble blocks. Point 2 is 5 m downstream in similar material, chosen to determine how quickly water chemistry changes away from the transition zone. Point 3, designated “main creek” is 5 m further downstream, where the stream is wider and has developed a finer bedload. From there the stream meanders through marshy deposits to the change in valley slope at Point 4, is at a bridge crossing nearly 700 m downstream. The stream then enters a steep, inaccessible canyon for ~5 km where sampling was not possible. Point 5 is at the downstream base of the canyon, flowing over bare bedrock before moving out into a poorly defined channel in a coarse alluvial fan. Point 6 samples the stream in this rocky channel 100 m upstream of its confluence with Piper Paradise Fisher (PPF) Creek. This alluvial fan and the confluence with PPF creek create the transition between the second-order tributary of the upper Little Elbow and the Little Elbow itself. Point 7 samples PPF creek 100 m upstream of the same confluence, and point 8 samples the stream 10 m downstream of the confluence. Sampling points 9-10 were taken at accessible locations along the main valley, and point 11 sampled a tiny surface flow of Nahahi Creek tributary 10 m above its confluence with the Little Elbow river.

Streamflow sampling

Streamflow grab samples were collected mid-stream at 60% depth at all but the higher flow sampling points at Little Elbow and Elbow Falls (points 11 and 12; Figure 4-1), where they were collected approximately 30 cm from the stream bank for field safety concerns. One litre
polyethylene bottles were rinsed three times with streamflow then filled and capped underwater. The bottles were sealed with electrical tape around the caps and kept in a cooler for transportation. The following day the samples were vacuum filtered using 0.7 µm glass-fibre filters and then acidified with 3M HCl to pH<2. Samples for sulphate and silica analysis were collected and field-filtered in 60ml syringes with 0.45µm syringe filters (Pall Laboratory, Acrodisc) into 20ml polyethylene vials. Headspace was eliminated by filling to positive meniscus before placing lids, which were sealed with electrical tape until analysis.

The longitudinal streamflow samples were collated with the analytical results for tributary and summer samples collected in July 2017 and previously reported in Campbell et al (2021). At points 4, 6, and 8, water levels were high enough and field conditions safe enough to measure streamflow rate. The rate was calculated by measuring stream area and average velocity (discharge (m³/s) = average area (m²) x average velocity (m/s)). For a stream-section perpendicular to flow, the entire stream width was divided along a line into 10 equal sections/segments. At each segment, instantaneous discharge and stream depth were measured using a Son Tec® Flowtracker current-velocity metre and depth gauge. For each rectangular section, discharge was calculated, and streamflow was calculated as the average of all 10 sections. Discharge at point 13 (Elbow Falls) was taken from the gauging station at Bragg Creek at Elbow Falls based on linear interpolation between historical records at Elbow Falls and that station, r²=0.92 (Campbell et al. 2019). Discharge values for the remaining stations were then interpolated using a polynomial fit (y = 0.0043x² - 0.0001x - 0.0001, r² = 1).

**Laboratory analysis**

Major ion concentration for all samples was analysed with a Metrohm 930 Compact Ion Chromatography Flex system (measurement uncertainty less than ±5% (Chao 2011)), and dissolved silica and bicarbonate with a ThermoFischer Gallery (analytical error of ±0.3mg/L.) Charge balances for each sample were ≤±2.5%. Isotope concentrations of δ³⁴S and δ¹⁸O in SO₄ were analyzed after sulfate precipitation as BaSO₄ by addition of BaCl₂ (10%). Precipitate collected
on 0.45 μm Millipore filters was air dried for at least 24 hours, then weighed and analyzed in an a Thermo Finnigan Delta+ XL elemental analyzer (analytical error ±0.2‰ for δ³⁴S in SO₄ and ±1‰ for δ¹⁸O in SO₄). ³⁴S is reported relative to Troilite from Canyon Diablo meteorite (CDT) and ¹⁸O/¹⁶O ratios are reported relative to Vienna Standard Mean Ocean Water (VSMOW), both in standard delta notation.

Results and Discussion

Longitudinal samples collected revealed clear spatial patterns in streamflow chemistry and isotopic composition. As is typical for eastern slopes rivers (Grasby and Hutcheon 2000), total dissolved solids (TDS) generally increased with flow distance (from about 225 to as high as 350 mg/L; Table 4-1). However, silica concentrations did not follow this pattern, decreasing from 6.9 to as low as 3.68 mg/L. Conversely, sulfate concentrations increased (from 14 to >100 mg/L) along with δ³⁴S (from ~5 to ~20 ‰).
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<th>Distance km</th>
<th>TDS mg/L</th>
<th>δ¹⁸O H₂O %</th>
<th>δ²H H₂O ‰</th>
<th>δ³⁴S SO₄ ‰</th>
<th>Sulfate mg/L</th>
<th>SiO₂ mg/L</th>
<th>Q (Measured) m³/s</th>
<th>Q (Interpolated) m³/s</th>
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Water oxygen isotope values normally decrease with flow distance (and decreasing elevation) (Rozanski et al. 1993; Gibson et al. 2010). Like the silica concentrations, they also displayed a counterintuitive pattern in this study, decreasing from ~-19.4 to as low as -19.8 over more than 500 m of elevation (Table 4-1, Figure 4-3). These counterintuitive findings are interpreted in conjunction with the distribution of rock types provide insight into the relative recharge elevation and carbonate vs. siliciclastic pathways in the Little Elbow River mountain block hydrologic system.

Figure 4-3. Longitudinal sampling results, including the a) elevation profile of sampling points (orange) for Little Elbow and Elbow River, b) $\delta^{34}$S$_{SO_4}$ and c) $\delta^{18}$O$_{H_2O}$ plotted as a function of sampling distance from the headwaters (filled circles and triangle). Yellow symbols have $\delta^{34}$S/$\delta^{18}$O$_{SO_4}$ values that indicate derivation of sulfate from oxidation of
sulfides and blue have intermediate or evaporite derived ratios (see Figure 4-4). Sample point numbers (Table 4-1) are indicated, and the triangle symbol is for a single tributary sample. Open circles and triangle are samples from July 11 2017 to illustrate seasonal variation occurs but does not change overall trend.

The range in sulfur isotope values is attributed to relative composition of rock-water interaction representing end-member origins of the sulfate found in the source aquifer types (Figure 4-4). Sulfur isotope values in sulfate were smallest in the Little Elbow Valley samples (points 1-4) falling between -4 to -10 ‰, samples in the transition area from the Little Elbow Valley tributary to the Little Elbow River (points 5-8) measured between 0 and 11 ‰, and Little Elbow River samples (9-13) measured up to 20 ‰ (Figure 4-4). A similar trend (from smaller values of -14 ‰ to as high as 6 ‰) were observed for oxygen isotope values in sulfate (δ¹⁸O₅O₄)(Figure 4-4). These values indicate the primary provenance of sulfate in the streamflow shifts from siliciclastic-derived in the upper watershed to carbonate-derived along the length of the river, corresponding largely to the bedrock distribution, which is dominantly siliciclastics in the upper and carbonates in the lower watershed (Figures 1 and 3).
Figure 4.4. Cross plot of $\delta^{18}O_{SO_4}$ and $\delta^{34}S_{SO_4}$ for distance profile samples (filled circles and triangle). The isotopic composition of sulphate from samples collected in the open water season (July, 2017) at Elbow Falls and Little Elbow Main (open circles; Campbell et al., 2021) are included to show seasonal differences occur but do diverge from the two-end member mixing line. The origin of $SO_4$ indicated by the range of isotopic values are shown by boxed areas (adapted from Krouse and Mayer, 2000). Symbol colours indicate relative contribution from rock-water interaction in two end-member aquifers (yellow – siliciclastic; blue – carbonate; hatched yellow – intermediate or mixed).

Isotopes in sulfate indicate the origin of sulfate in the water samples, but the two-end-member mixing model implied by Figure 4-4 does not account for water with very little water-rock interaction. This third end-member was first identified as “overland flow” by Drake and Ford (1974b), but Grasby et al. (1999a) demonstrated that overland
flow is not a significant component of water in eastern-slopes rivers. An end-member assigned the silica and sulfate concentrations of precipitation in the region (i.e. SiO$_2$ <2 mg/L, SO$_4$ <8 mg/L) was termed “interflow” by Campbell et al. (2021) and incorporated into a three end-member model that encompasses the measured samples in the Little Elbow Watershed (Figure 4-5). In addition to interflow, the high silica (low sulfate) end-member reflects rock-water interaction in siliciclastic aquifers, while low silica (high sulfate) water is characteristic of carbonate aquifers. The model establishes the relative contribution from the two aquifer types and interflow from these silica and sulfate concentrations and can be used to better understand the interplay of water storage and streamflow within the system.

Silica and sulfate concentrations in the longitudinal streamflow samples varied inversely to each other, with higher silica and low sulfate in the highest elevation samples collected (points 1-4; sampling elevations ranging from 2142 to 2152 m asl; Table 4-1, Figures 3 and 5) compared to lower silica and high sulfate in the transition area and main valley (points 5-13; 1809 to 1405 m asl; Table 4-1, Figures 4-3 and 4-5). The samples collected in the highest part of the Little Elbow watershed (points 1-4) plot near the upper end of the siliciclastic-interflow mixing line, indicating a predominance of water (i.e. 60-90%; Table 4-1, Figure 4-5) from siliciclastic aquifers with the remainder supplied by interflow. The streamflow samples collected at in the transition area and the first Little Elbow River point (6 and 8) plot centrally but slightly toward the carbonate end member, reflecting mixing of siliciclastic-sourced water (~20%) from the Little Elbow valley with ~50% carbonate-sourced water. The remaining main valley points (9-12) plot toward the carbonate end-member (i.e. > 65% carbonate end member and <10% siliciclastic), signifying dominantly carbonate aquifer contributions. The Elbow Falls sample (point 13) plots more centrally, reflecting increased siliciclastic
contributions as the river flows through longer stretches of siliciclastic bedrock before reaching the falls (Figures 1-3).

Figure 4-5. Silica-Sulfate concentration crossplot illustrating the position of the samples collected in the current study within the three end-member mixing model previously developed for the Upper Elbow Watershed (from Campbell et al. 2021). Little Elbow Valley samples (yellow circles, points 1-4) plot toward the upper part of the siliciclastic-interflow mixing line. Samples from the transition area (hatched yellow circles, points 6 and 8) plot centrally but slightly toward carbonate end-member, and main Little Elbow River samples (blue circles, points 5, 7, 9-13) plot toward the carbonate aquifer source.
Open blue circles are previously published data at points 13 and 14 from Campbell et al. (2021).

The silica and sulfate concentrations and sulfate isotopes provide multiple lines of evidence to support interpretations of siliciclastic and carbonate aquifer contributions varying spatially in the Little Elbow mountain block. On their own, however, they do not paint a clear picture of how the water moves through the hydrologic system. The water isotopes in streamflow (i.e. $\delta^{18}O_{H2O}$ and $\delta^2H_{H2O}$) provide further insight in this regard.

In general, river water isotopes tend to increase as elevation decreases (Gibson et al. 2010), following global patterns of water isotopes in precipitation (Rozanski et al. 1993; Gat 1996b). Colder and higher elevation precipitation tends to enter rivers at higher elevations while warmer and lower elevation precipitation enters rivers at lower elevation. The $\delta^{18}O/ \delta^2H$ in precipitation for the Little Elbow system (Figure 4-6) highlights this pattern: average monthly water isotope values in precipitation for winter (Nov-Mar, Figure 4-5 blue squares) and summer (Apr-Sept, orange squares) are distinct and emphasize the difference in precipitation temperatures between the seasons. Water isotope values in Little Elbow streamflow are dampened due to mixing in groundwater storage and transport (i.e. Taylor et al. 2001; Campbell et al. 2020c), but separation between the siliciclastic-stored and carbonate-stored water is evident, with overlap for the intermediate or mixed-source samples (Figure 4-6, inset).
Figure 4-6. Cross plot of $\delta^{18}O$ and $\delta^2H$ in precipitation (filled squares; from Campbell et al., 2020) and longitudinal streamflow samples (circles). The global meteoric water line (solid grey) and local meteoric water line (dashed grey, from Peng et al., 2004) are shown. Colder and/or higher-elevation precipitation has lower $\delta^{18}O$ and $\delta^2H$ values (blue squares) and warmer and/or lower-elevation precipitation has higher values (orange squares). Siliciclastic-stored streamflow (yellow circles) falls in the warmer/lower elevation region and carbonate-stored streamflow (blue circles) in the colder/higher-elevation region. Inset shows details of streamflow samples.

However, these global patterns do not necessarily hold at smaller scales, and the deviations can provide valuable information. In the Little Elbow longitudinal streamflow samples, the water oxygen isotope values ($\delta^{18}O_{\text{H}_2\text{O}}$) in samples
counterintuitively decreased with decreasing streamflow sampling elevation (Figure 4-4), indicating that streamflow in the lower-elevation main valley is derived from colder or higher-elevation precipitation than that in its valley nearer the headwaters. These data introduce some nuance to the concepts that water infiltrating bedrock tends to stay within the upper 20m with only 20% entering deeper flow systems (Smerdon et al. 2009a; Manning et al. 2021), and that there is a functional distinction between recharge processes in local, intermediate, and regional pathways, or indeed between mountain aquifer recharge and MBR (Markovich et al. 2019a). There is ~450 m elevation difference between the upper Little Elbow valley sampling points and those in the main valley (i.e., between sampling points 1 and 8; Table 4-1), and typically >1000 m between the Elbow River and the adjacent carbonate mountain peaks. The streamflow sample at Point 12 highlights this point: although the sampling point is at 1605 m elevation, approximately 500 m lower than adjacent peaks, the δ¹⁸O of 19.8‰ indicates that the water is dominated by cold or high-elevation precipitation.

Water isotopes, silica concentrations, and sulfate concentrations in the longitudinal samples suggest that the colder, higher-elevation precipitation travels through intermediate and deep flow systems, falling as snow on the cliff-forming carbonate rocks and infiltrating as melt through their well-developed fracture systems down to the bedrock of the main valley before becoming streamflow. In contrast, more of the warmer, lower-elevation precipitation infiltrates in the siliciclastic valleys and surfaces as streamflow through local flow systems (Figures 1 and 4). The Graphical Abstract illustrates this process, with the warmer, lower-elevation precipitation infiltrating into the local flow systems in the upper valley, producing siliciclastic aquifer-hosted streamflow with low δ¹⁸O of approximately 19.2‰, and, colder, higher-elevation precipitation infiltrating into intermediate and regional flow systems, producing dominantly carbonate aquifer-hosted streamflow.
Details around infiltration in the carbonate units could fall within the current paradigm; for example, the majority of infiltration could remain in the upper 20m of the mountainside, with more oblique travel down the mountain than vertical. Future work using drilled groundwater wells in combination with hydrologic modelling, similar to Manning et al. (Manning et al. 2021), could help delineate these details. Nevertheless, it is clear that in the Little Elbow hydrologic system, the boundaries between mountain aquifer recharge and mountain block recharge are blurry. For investigating lowland recharge these distinctions can be useful, but when considering mountain block hydrology more generally, and the relationships between recharge and streamflow within the mountain block, they may introduce artificial divides because the same recharge processes that produce streams in the mountains must logically also produce deep mountain groundwater.

A final consideration highlighted by these longitudinal streamflow data is the effect of climate change on the Little Elbow hydrologic system. In this area, as elsewhere, warming temperatures are producing earlier snowmelt (Chernos et al. 2020b). The late season sampling date (Oct 26) for the longitudinal survey was chosen to sample streamflow as characteristic of winter baseflow as possible, to assess the relative contributions of aquifers in the hydrologic system. Low silica, high sulfate concentrations with high $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ in the main valley samples (points 9,10,12,13) indicate that the majority of overwinter baseflow in the Elbow River is supplied by carbonate aquifers (Figure 4-5). The relatively low values of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ indicates this water originates as cold/high elevation winter precipitation (Figure 6). This interpretation is supported by the July samples for Little Elbow and Elbow Falls sampling locations – both plot much further toward the interflow-siliciclastic mixing line than the late October samples, emphasizing the higher seasonal contribution from interflow and siliciclastic aquifers in summer (Figure 4-3). Thus, winter baseflow is
dependent on previous winters’ precipitation, and changes in the volume and timing of
snowfall and snowmelt may impact future winter baseflow.

Conclusions

In the Elbow River catchment, nested mountain aquifer flow systems convey
lower-elevation, warmer precipitation to headwater streams in siliciclastic-bedrock
valleys, while high-elevation, colder precipitation is conveyed to lower elevation river
reaches via snowmelt infiltration into cliff-forming carbonate bedrock. The large
elevation difference between infiltration areas and main valley streamflow suggests less
separation between intermediate and deep flow pathways, or mountain aquifer and
mountain block recharge, than previously thought. Longitudinal streamflow sampling
at the end of the open water season indicates that winter baseflow is generated mainly
from carbonate aquifers and mainly from high-elevation winter precipitation. This
dependence means winter streamflow in the Elbow River is vulnerable to changes in
winter precipitation volume and timing.

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Chapter 5: Conclusion

Together, the three papers in this thesis follow and illustrate the processes of infiltration, recharge, storage, transport, and streamflow generation in the mountain block of the Upper Elbow River watershed. They demonstrate the interconnection of the structural, physical, and chemical aspects of the watershed on its streamflow, and demonstrate that understanding the hydrodynamics of the mountain block is crucial to both academic concerns such as the paradigm of MBR and practical concerns such as overwinter river water supply to adjacent lowlands.

The first paper presents a simple solution to an intriguing conundrum. Steep topography in mountain blocks suggests rapid infiltration and transit times through aquifers to river (McGuire et al. 2005; Tetzlaff et al. 2009). Yet several studies (i.e. Jasechko et al. 2016; Lutz et al. 2018; von Freyberg et al. 2018) using the fraction of young water ($F_{yw}$) method (Kirchner 2016b) found very low young water fractions. That is, <5% of their stream water fell as precipitation less than 10 weeks earlier. The intuitive response to this contradiction is “snow!”, given that most mountainous regions store some precipitation as snow before it infiltrates, lengthening the time between water falling as precipitation and becoming streamflow. Although Jasechko et al. (2016) excluded watersheds where February snow-water equivalent made up more than 10% of annual precipitation and still found low $F_{yw}$ in mountainous areas, their analysis
used the Glob-Snow2 database, which does not include mountainous catchments. The intuitive snow storage idea therefore warranted further investigation.

We ran the $F_{yw}$ model using data from our study area, and it indeed produced very low (<5%) young water fractions. To investigate further, we ran the model using discharge data rather than isotope in streamflow and attempted to match historical discharge data, but found low Nash Sutcliffe efficiencies, which suggested the model was not doing a great job of reflecting processes in the watershed. We then modified the precipitation input for snowpack by storing all of the November-May precipitation as snow and releasing it to infiltrate in May and June. Without changing any further inputs or parameters, the Nash Sutcliffe efficiencies improved, with many above 90%. Keeping the precipitation modified for snowpack, we again ran the model for isotopes in streamflow and this time produced young water fractions between 7-30%, comparable with those in lowland rivers. This finding is important, as it indicates that snowpack dissociates the age of precipitation from the age of input water, which affects the apparent young water fraction and skews young water fractions much lower than they likely are. Further, we noted that modifying precipitation inputs to reflect snowpack alters the amplitude of the isotopes in the characteristic precipitation sine curve formed seasonally, affecting the ratio between that and curve amplitude for isotopes in streamflow. The altered ratio becomes non-unique for a given catchment, meaning the young water fraction could be within a range of values. While this range may still be informative, it is much less precise, and reduces the usefulness of the tool in
watersheds with overwinter snowpack. In this case, an apparent contradiction between two lines of investigation (the association between mean travel time and topography and young water fractions in mountainous areas) was resolved by re-considering the intuitive answer.

The findings in this first paper reflect the importance of recharge processes in mountain block hydrology. The $F_{yw}$ model does not consider a mechanism for infiltration – the water enters the system immediately in the same month it falls. Yet we can glean information from this direct input assumption; the very high Nash Sutcliffe values for discharge in the snowpack-modified model suggest that the large volume of snowmelt does indeed infiltrate rapidly in May and June, pushing water through aquifers to increase streamflow. This rapid infiltration and streamflow response are also reflected by the simple method we suggested to estimate the percentage of streamflow from the previous year’s precipitation. Shifts in average isotope value in winter baseflow show how much precipitation from that year must now be streamflow to change the average isotope value in baseflow. These measures of how quickly some water moves through the watershed begin to paint a picture of the connectivity and hydrological processes in the watershed, and correspond well to previous findings that storage capacity in alpine headwaters is quickly exceeded when inputs are high (Hayashi 2020). The success of the snowpack modified model also highlights the importance of considering how climatic controls in a given watershed (or other
important aspects of the system) may affect a standardized model, especially when the outputs don’t seem to fit prior understanding.

The second paper looks at recharge and streamflow generation processes in the Upper Elbow watershed from a different perspective, investigating the connections between stream water chemistry, groundwater chemistry, and aquifer rock. Groundwater wells, springs, and tributary streams in different parts of the watershed provide clues about the aquifers through which infiltrated water moves. Elbow Falls is the outlet for the upper watershed, where alluvial aquifer gravels give way to bedrock constriction, providing an integrated snapshot of how the elements of the watershed contribute to streamflow chemistry. Correlations between major ions in water samples showed distinct differences in silica and sulfate concentrations between sampling locations, providing a jumping off-point for more detailed investigations. Cross-plotted, silica and sulfate concentrations identified three distinct end-members for the system (silicate-hosted, carbonate-hosted, and interflow), with Elbow Falls showing seasonally-varying influences from each. We applied a three end-member model to tease out these influences and found that much of the water in the system is interflow – water that has had limited water-rock interaction. This finding suggests rapid transport in the shallow groundwater and hyporheic zone pathways.

The three end-member model also indicated that siliciclastic and carbonate aquifers contribute approximately equally to annual streamflow despite the preponderance of carbonate rock in the watershed, but that siliciclastic aquifer
contributions dominate during the snowmelt period and carbonate later in the season. Applying low-temperature silica dissolution calculations supported with tritium measurements, we estimated water residence times of ~4 years in siliciclastic aquifers, and tritium measurements alone suggest similar residence times for carbonate aquifers. These short residence times and variable relative contributions support the idea raised in the first paper, of rapid infiltration and transport within the watershed.

The first two papers focus on the connections between precipitation, recharge, storage, and streamflow generation within the watershed itself, illuminating a dynamic system that moves much of the water from precipitation to streamflow within 5 years. Yet more investigation is needed to understand the connections between mountain aquifer recharge and the deeper flow systems that move groundwater into the adjacent plains from this mountain block. The third paper looks more deeply at the implications of mountain recharge and infiltration by assessing the chemistry and isotopic composition of late fall baseflow along the length of the Little Elbow River. Distance sampling revealed distinct changes related to elevation and bedrock type at the sampling points. Sulfur and oxygen isotope compositions were key to identifying the provenance and seasonal influence of water in streamflow. The highest elevation sampling points in the Little Elbow tributary produced water from the warmest or lowest elevation precipitation, which had moved through siliciclastic aquifers. Together with the lowest total dissolved solids (TDS), these samples suggest short local flowpaths for the uppermost streamflow samples. In contrast, samples from the lower-
elevation sampling points in the Little Elbow valley had higher TDS, carbonate-sourced sulfate, and cold or high elevation water isotope composition. These samples suggest longer, intermediate or regional flowpaths, with more influence from precipitation stored as high mountain snowpack. The three end-member model developed in the second paper provides further insight here, showing little to no carbonate-sourced water in the uppermost tributary samples, and indeed even very little interflow in the first surface water. This balance reverses in the lower elevation main Little Elbow Valley, reflecting the dominance of long flowpaths and carbonate aquifers. These findings suggest that overwinter baseflow in the Little Elbow river is heavily dependent on snowmelt infiltration from high elevation snowpack, and that changes in precipitation and snowmelt timing due to climate change could have dramatic impacts on baseflow. The National Issues Report on Canada’s Changing Climate (2021) emphasizes these impacts; warmer, wetter winters could allow snow to infiltrate year round, and heavier spring rainfalls could move water through both siliciclastic and carbonate aquifers more quickly. The resulting variability in streamflow (higher peak spring flow, higher winter baseflow, possibly lower summer baseflow during periods of drought) will require careful water supply management for downstream users.

Another consideration suggested by these long flowpaths is that mountain aquifer and mountain block recharge are the same process. Snowpack that melts and infiltrates near the mountain peaks must travel down through more than a thousand meters of rock to reach the springs discharging into the river – while Manning et al.
(2021) demonstrate that most infiltrated water remains in the upper 20m of mountain rock units, oblique transport along mountain slopes and extensive fracture systems create long flowpaths for valley waters. There is no practical or logical division between water transported thousands of meters within aquifers in the mountain block that encounters an upward-oriented fracture and surfaces as a spring, and water that continues to travel obliquely down gradient toward the plains.

Taken together, these papers indicate that in the Upper Elbow watershed both local and intermediate flowpaths contribute to mountain streamflow, which suggests that there is no logical distinction between mountain aquifer recharge and mountain block recharge, and that these and mountain stream generation are the same processes. Thus, these papers answer the question initially put forth; if water in the Middle and Lower Elbow River is all groundwater, but almost no water is supplied by the underlying prairie aquifers, where does it come from? The mountain groundwater aquifers; alluvial, siliciclastic, and carbonate mountain aquifers supply the majority of Elbow River streamflow.

A concluding note on this research would be incomplete without mentioning the tremendous contribution of undergraduate researchers. Weekly for three years, every field excursion to the research site was accompanied or led by undergraduate students. Some were occasional volunteers who jumped at the chance to experience geohydrological field work, which was fun and beneficial for both the students and myself. Since field opportunities are unfortunately limited within undergraduate
programs at the moment, I strongly recommend supporting future graduate students so they can provide similar opportunities to undergraduate students. Several students were paid summer interns who not only provided integral support for my research goals, but developed and carried out their own research ideas alongside mine, following their internships with independent research studies in fall and winter. Some of these students are recognized as co-authors on Chapter 3, while others left excellent reports and data sets that can be built on by future students. This aspect of my thesis work was by far the most important and most rewarding. Mentoring undergraduate students with the support of a fabulous mentor of my own developed the skills most essential in managing and supervising a research group.

In light of the importance of undergraduate research to this project, a few suggestions for future work are framed in terms of projects with an appropriate scope for future students. I list them below, and hope that either myself or others can continue to build understanding of the hydrodynamics in the Elbow River watershed with the help of future student researchers.

1. *Evaluating spring locations and correlations with water geochemistry and isotope composition*

   There are numerous springs in the Elbow Watershed that were not included in this study. Taking water samples at these springs and assessing correlations between bedrock geology, alluvial/colluvial cover, elevation, temperature, etc. would provide a student with an excellent foundation in the complexities
introduced by spatial heterogeneity yet provide manageable research outcomes. It would also add to scientific understanding of flowpaths in the watershed.

2. *ISCO sampling of storm events to confirm siliciclastic contributions*

As part of her research, Sofia Stanic used ISCO autosamplers bi-hourly before, during, and after two large rain events, and her results hinted at rapidly shifting contributions from aquifer sources during these events. The data were not statistically significant with so few events to evaluate, but the trend was intriguing enough to beg for follow up. The sampling procedure was manageable and continuing this methodology would provide a future student with a strong understanding of streamflow variability and how to analyze water geochemistry and isotopes. This analysis would give a much more precise understanding of the differences in aquifer throughflow in response to rainfall events, an important contribution to scientific understanding.

3. *Correlation of Equisetum sp. and silica-rich waters (suggested by M.C. Ryan)*

Horsetail (*Equisetum sp.*) is a known biosilicifer, meaning that it bioaccumulates silica. Horsetail tea is consumed to support uptake of silica in the human body as a micronutrient, although as with many folk remedies its efficacy is unconfirmed. Conversational hints that horsetail may be more abundant near silica rich waters may be supported by Pearce and Cordes (Pearce and Cordes 1988), who observed their growth in silty alluvium in North West Territory, Canada. A student more interested in the relationships between bioecology and groundwater could use crowd-sourcing technologies (chat boards, Facebook groups, etc.) to ask people to record GPS locations of horsetail, and evaluate any correlation between plant abundance, springs and streams, and the silica concentration of these water sources. This project would contribute to scientific understanding of indicator species, since controls on the distribution of horsetail
are not yet well constrained, as well as possibly providing visual hints of silica-rich water.
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