

THESIS

A CHARACTERIZATION OF COLORADO FRONT RANGE AND DENVER BASIN
AQUIFER SYSTEM WATER STABLE ISOTOPE SIGNATURES

Submitted by

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In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Summer 2024

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ABSTRACT

A CHARACTERIZATION OF COLORADO FRONT RANGE AND DENVER BASIN AQUIFER SYSTEM WATER STABLE ISOTOPE SIGNATURES

The Denver Basin Aquifer System (DBAS) is an important groundwater resource for Front Range communities and is currently experiencing increasing demand as populations grow and surface water supplies remain limited. It is necessary to better constrain aquifer recharge mechanisms to enable sustainable use of this resource. In other sedimentary basin aquifer systems, mountain front recharge has been shown to be a significant contributor to local basin groundwater recharge. In the DBAS, inputs from the mountain block are poorly understood, and previous numerical models have treated large segments of the mountain-front boundary as impermeable. However, there exist potential connections between the mountain block and the DBAS, either by direct contact of permeable units, which would facilitate underflow recharge into the basin, or by surface water infiltration to the aquifer units where they outcrop near the mountain front. To observe spatial and temporal relationships between mountain block water and DBAS water, we use water stable isotopes and characterize the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of monthly precipitation, seasonal surface waters, and groundwaters in and around the Front Range and Denver Basin. The goal of this study is to determine if differences in the isotopic composition of waters across the Front Range permit the use of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ as tracers of water flow between Front Range streams and groundwater and the DBAS. We analyzed the unique signature of mountain-block water to compare with DBAS water stable isotope data collected from Castle Rock Water municipal wells. Stable isotope ratios varied spatially and temporally, with the greatest temporal variance observed in precipitation.

Streams showed great spatial variance, and less significant seasonal variance between the three seasonal sampling events conducted. Groundwaters showed very little temporal variance but had great spatial variance both between the aquifer units of the DBAS and between different locations within the mountain block crystalline aquifer. The lowest $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios were measured in winter precipitation, winter streams, and groundwater samples collected from the high-elevation Front Range. Samples of DBAS groundwaters with the lowest $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios indicate potential hydrogeologic connection to the mountain block. Interpreted mixing lines on a d-excess versus $\delta^{18}\text{O}$ plot support the potential DBAS-mountain block connection. The deepest aquifer units of the DBAS (Arapahoe and Laramie-Fox Hills) show the least relationship with meteoric or surface waters on both a $\delta^2\text{H}$ and $\delta^{18}\text{O}$ plot and the d-excess versus $\delta^{18}\text{O}$ plot and have higher $\delta^{18}\text{O}$ values than would be predicted based on their previously measured recharge ages and paleoclimate data from the region. Characterizing the spatial and temporal variations in water stable isotope signatures of the Front Range and DBAS region enhances understanding of the region's hydrology and hydrogeology. Additionally, these results help to better inform models of aquifer recharge and promote sustainable use of the DBAS resource.

ACKNOWLEDGEMENTS

I have so much gratitude for everyone who supported me through my Masters. First, I would like to thank Dr. Jeremy Rugenstein for being a wonderful advisor, mentor, and person. Starting from even before I was his graduate student he was generous with his advice and time, and I am so lucky to have had such an excellent teacher and guide throughout my project.

I would like to thank my committee member Dr. Mike Ronayne for insight, data, technical support, equipment and field experience. Thank you to my committee member Dr. Matthew Ross for insight, advice, and for teaching a great R language class.

Thank you to Dr. William (Bill) Sanford for lending me equipment, for helping procure equipment, and for teaching an excellent hydrogeology class.

This study was partially funded by a 2023 GSA Graduate Student Research Grant, the Lipman Award. Additional funds were supplied by a Colorado Water Conservation Board grant (CMS 185254) as well an NSF RAPID grant (AGS-2333172), both to my advisor, Jeremy Rugenstein. Lastly, funds for the installation of the ultra-deep monitoring well at the Mountain Campus, as well the necessary equipment to sample this well and for analysis of initial samples were provided by the CSU Mountain Campus Research and Education Fund.

Thank you to the CoCoRaHS volunteers Jeannie Reynolds, Jeff Geiger, David Weber, Kristi Gay, Shawn Graffiti, and Kevin Tobey for collecting valuable precipitation and groundwater samples for this project.

Thank you to lab-mate Gaby Sanchez-Ortiz for helping me through my R coding learning journey. Thanks to you, coding is no longer such an arduous task. Thanks to Adam Walsh for being a great field assistant, and for showing me the ropes of our group's monthly field work

responsibilities. Thanks also to Clara Gillam, Noah Dayton, Tucker Chapin, Victoria Arnold, Claire Pickerel, Pat Ronneau, and John Bryan for being wonderful field assistants. Thanks also to Dan Reuss for assistance in the laboratory and to EcoCore Analytical Services (RRID: SCR_011015) at Colorado State University for instrument access, training, and assistance with sample analysis.

Lastly, much love and appreciation for my friends who have been sunshine on my shoulders since moving to Colorado. Cassie, thank you for being my rock. My heart is filled with so much gratitude for my family's love and support through this journey. Kimberly, Stephen, Sharon, Gabrielle, Sabrina, and Barnabas, I love you all!

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INTRODUCTION

1.1 Background and Study Significance

Groundwater is a critical resource for many communities and ecosystems globally. In arid and semi-arid regions where local surface water and precipitation are limited, it becomes necessary to meet agricultural, industrial, and domestic water needs with groundwater. In many places, groundwater is a finite resource, where any potential recharge to the aquifer is either nonexistent, or at a flux far below the output flux. As global climate change threatens to change regional climates, groundwater resources may face changes in their recharge flux if average annual precipitation declines. Close study of groundwater resources is necessary to prevent the negative effects of overexploitation of deep groundwater such as the lowering of the potentiometric surface, land subsidence and degradation of water quality (Custodio 2002). For those living in the arid and semi-arid Front Range and Denver Basin region of Colorado (CO), the Denver Basin Aquifer System (DBAS) is their critical groundwater water resource.

The Denver Basin region has been inhabited for thousands of years, but groundwater wells were not first drilled until approximately 1883 (Robson, S. G., & Banta, E. R. 1995). Since Denver's establishment as a city in 1858 surface water has been utilized as the primary resource, supplying most of the city's municipal water needs. Denver suburbs and exurbs have been growing rapidly since the 1950s, with the population over-doubling from approximately 1.3 million in 1970 (Paschke 2011) to nearly 3.0 million in 2023 (U.S. Census Bureau). Groundwater is an important resource for these newer communities. To enable its sustainable use, it is necessary to further constrain the properties of the Denver Basin Aquifer System (DBAS).

1.1.1 Geologic and Hydrogeologic Background

The DBAS underlies an area of about 7,000 square miles underlying the Denver Metropolitan Area and is defined as four aquifer units (Figure 1-1). Deepest to shallowest, they are the Laramie–Fox Hills, Arapahoe, Denver, and Dawson aquifers. These units are Late Cretaceous to Tertiary-age sandstone bedrock aquifers with intervening claystone confining units that occur in the uppermost layers of the structural Denver Basin above the Cretaceous Pierre Shale confining layer. The Denver Basin has a synclinal structure, and the bedrock aquifers outcrop in a ring pattern with the deepest and oldest formation (Laramie–Fox Hills) outcropping on the outer perimeter of the basin and then inward concentrically with each younger formation with the newest formation (Dawson) outcropping nearest the center of the basin. Overlying the bedrock formations are alluvial sand, gravel, and clay deposits primarily along stream channels in the South Platte and Arkansas River basins, and these materials form an unconfined alluvial aquifer where saturated (Paschke 2011).

Contact between the alluvial aquifers and the bedrock formations has been identified as the primary source of recharge to the DBAS (Paschke 2011, Musgrove et al. 2014, Cognac and Ronayne 2020). Most recharge occurs in the highland area near the Palmer Divide between stream channels in the topographically higher southern part of the basin where precipitation is greater, and the permeable soils derived from the Dawson Arkose enable deep percolation (Robson, S. G., & Banta, E. R. 1995). Recent work has shown seasonal contact and flow between the alluvial aquifer and the Dawson in the Cherry Creek region of the basin (Cognac 2023).

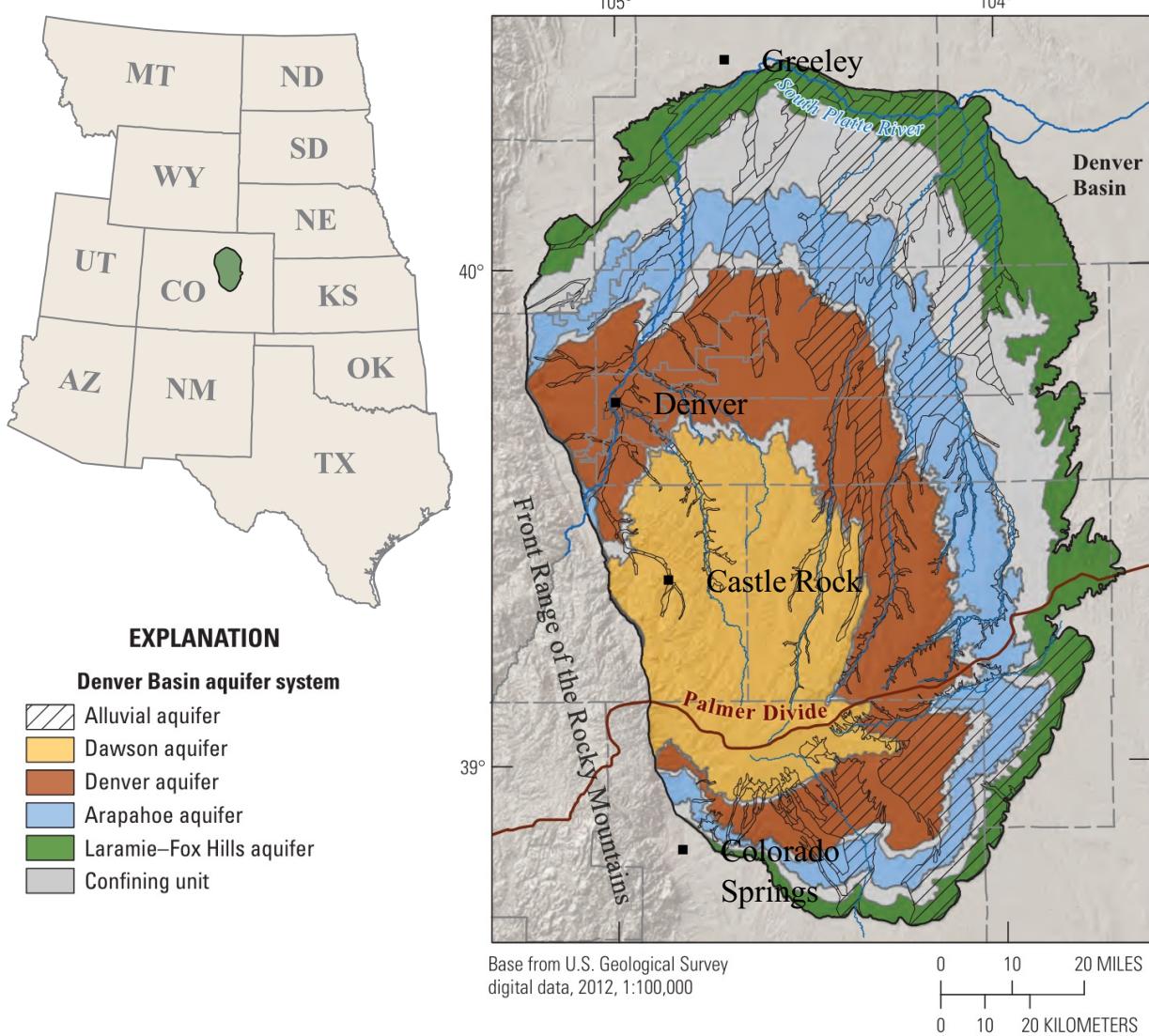


Figure 1-1. The Denver Basin Aquifer System is located to the east of the Colorado Rocky Mountains and consists of four aquifer units. Figure adapted from Bauch et al. 2014.

Previous literature (Novotny and Sanford 2004, Musgrove et al. 2014) has described the water in the DBAS as having groundwater ages of 10,000 to 30,000 years old. Deeper units of the DBAS have overall “older” water than the upper units (Musgrove et al. 2014). The first wells in the DBAS were artesian, having pressure sufficient to raise water 200 feet above the land surface. Existence of artesian conditions prior to pumping the DBAS shows that recharge from a higher

elevation could be taking place in recent geologic time. However, the USGS (Paschke 2011) modeled hydrogeologic maps of the DBAS currently show a no-flow boundary along the boundary of the Front Range and Denver Basin. Many similar mountain basins receive “mountain block recharge”, where there is subsurface inflow of groundwater to lowland aquifers from adjacent mountains (Markovich et al. 2019). The Colorado Geological Survey maps of the southwest region of the Denver Basin show many potential areas of direct contact between the DBAS sedimentary units and the crystalline bedrock of the Front Range, which could also indicate hydrogeologic interaction.

1.1.2 Mountain Block Recharge

In analogous mountain-basin aquifer systems, a commonly identified source of recharge flows directly from the mountain block aquifer to the adjacent basin aquifer units. Mountain-block recharge (MBR) has been detected and quantified in basins around the world, typically estimated to be 5–50% of basin-fill aquifer recharge (Markovich et al. 2019). Mountainous regions often receive much more precipitation than basins due to the orographic effect resulting in 85% of the annual runoff coming from 15% of the basin’s area in the mountain headwaters, such as in the case of the Colorado River Basin (Lukas and Payton 2020). Snowmelt is the primary source of annual runoff from the Front Range, as reflected in the prominent late-spring peaks in annual hydrographs (Liu et al. 2004). Not all snowmelt results in runoff into the basin; there is a significant contribution to mountain soils and groundwater. A study of infiltration and flow of snowmelt in the Front Range showed significant seasonal contributions to alpine and sub-alpine soils (Dethier et al. 2022). Mountain aquifers receive recharge from a combination of infiltration from rain, snowmelt, and glacier melt, as well as concentrated recharge beneath losing streams, or through fractures and swallow holes (Somers and McKenzie 2020).

Mountain bedrock aquifers can contribute to adjoining basin aquifers through deep fracture flow (Figure 1-2). Historically, this recharge has been difficult to quantify due to inaccessibility, costliness of wells, and the structural complexity of mountain bedrock aquifers (Manning and Solomon 2005). Within the last 20 years, the body of research surrounding MBR has grown as world demand on mountain-derived water resources continues to increase. Though recharge to the Dawson unit of the DBAS is understood to occur through the alluvial-Dawson aquifer contact and is apparent in the hydrogeologic models in Paschke's (2011) work with the USGS, some investigators have suggested the DBAS is being "mined" for water due to small or nonexistent rates of recharge to the other aquifer units as compared to their pumping rates (Moore et al. 2007).

In 1985, criteria for aquifer management set by Colorado Senate Bill 5 limited landowners'

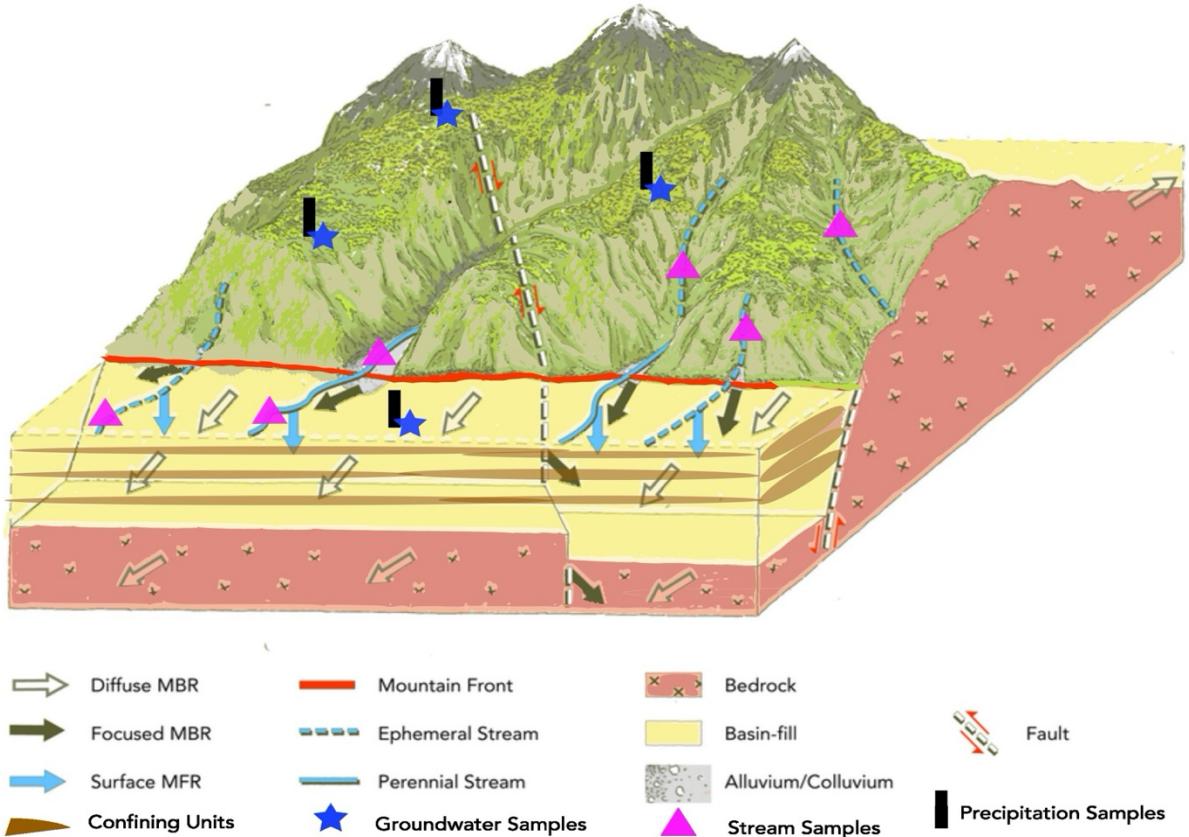


Figure 1-2. Conceptual diagram of Mountain Block Recharge, Mountain Front Recharge, and sampling location strategy adapted from Markovich et al. 2019. Diffuse MBR is shown with the clear arrows, and the contact between the DBAS and the Front Range Mountain block is shown by the yellow/brown and pink coloring.

groundwater usage to 1% of the calculated total recoverable water underlying the land per year. This policy was based around the arbitrarily set “100-year life” of the aquifer (Topper et al. 2003). These groundwater supplies were once thought by the CO State Engineer to be sufficient for 100 years but Moore et al. 2007 estimates they are only adequate for 10 to 15 years in areas on the west side of the basin. Now in 2024, we are 40 years into the “100-year” legislatively set aquifer lifetime, highlighting the criticality of understanding the inputs to this resource as demand continues to increase. In this study, we characterized the water stable isotope signatures of the Colorado Front Range and Denver Basin precipitation, surface waters, and groundwaters to allow for the investigation of potential sources of recharge to the Denver Basin Aquifer System.

1.2 Study Goals and Objectives

Characterizing groundwater inputs is a difficult task due to the variety of physical and chemical processes acting on waters before and after their entrance to an aquifer. Origins of groundwater recharge vary widely spatially and temporally. Water stable isotopes provide a cost-effective and simple method to characterize differences in waters seasonally and spatially. In the case of the Front Range and Denver Basin hydrologic system, the difference in elevation between the mountains and the basin allows for use of a well-known relationship between elevation and stable isotope composition to distinguish waters originating in the mountains versus waters originating from lower elevation and basinal sources (Poage and Chamberlain 2001). We performed a characterization of mountain and basin precipitation, surface water and groundwater to determine if water stable isotopes are a feasible method for distinguishing groundwater origins in the Front Range-DBAS system. Precipitation samplers in and around the Denver Basin provided temporal water stable isotope data on the water inputs to the system. Stream sampling events in the summer, fall, and winter provided temporal isotope data of Front Range surface

waters. We utilized municipal, residential, and research wells to collect spatially diverse water stable isotope data in the Front Range/Basin region. Analysis of this diverse collection of stable isotope data by origin, mean catchment elevation, season, and aquifer unit allows us to interpret the spatial and temporal relationship between the Front Range mountain block aquifer and the DBAS.

CHAPTER 2 - WATER STABLE ISOTOPES AS A GROUNDWATER TRACER

2.1 Water Stable Isotope Variability

The most abundant stable isotopes of hydrogen and oxygen, ^1H , ^2H , ^{16}O and ^{18}O have played an important role in the study of the hydrologic cycle. Study of the changes in isotopic ratios as water moves through the hydrologic system has improved understanding of water fluxes between stages of the cycle, and the Earth system properties that drive them. There are many drivers of variability in stable isotopes, with several of them relevant to hydrologic processes in the Front Range and Denver Basin.

These water isotopes fractionate in hydrological processes by mass. Water containing the heavy isotopes ^2H and ^{18}O are first to phase change to the liquid or solid state and the lighter isotopes are first to phase change to the gaseous phase. The water isotope composition of climatological air masses is progressively altered as they move across the surface of the earth gaining and losing moisture. Delta (δ) notation is used to report water stable isotope ratios as shown in Eq. 1:

$$\delta^{18}\text{O} (\text{\textperthousand}) = \left[\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}}} - 1 \right] * 1000 \quad (\text{Eq. 1})$$

where δ is reported in per mille (‰), “sample” is the quantity of interest, and “standard” is Vienna Standard Mean Ocean Water (VSMOW) defined as having a δ value of 0 ‰. To observe the relationship between the water isotope ratios, these values are plotted on a $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ graph. The GMWL is calculated from the relationship between $\delta^{18}\text{O}$ and δ at equilibrium conditions when taking natural meteoric water samples from globally distributed locations. Evaporation under non-equilibrium conditions is the predominate process for fractionating water isotopes and enriching

the sample in ^{18}O versus ^2H due to deuterated water having a 5% lower molecular mass than ^{18}O water. This enrichment in ^{18}O causes water subject to evaporation to plot below the meteoric water line. The global meteoric water line (GMWL) is often plotted with the sample data to observe how the data deviates from it. The general equation of the GMWL is defined in Equation 2:

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10 \quad (\text{Eq. 2})$$

In addition to $\delta^{18}\text{O}$ and $\delta^2\text{H}$ there is a second-order parameter useful for interpreting stable isotope data, deuterium excess (d-excess). Defined as $\text{d-excess} = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$ (Dansgaard, 1964), it can provide additional information about environmental conditions at the moisture source region and of potential moisture recycling during transport, notably evaporative processes affecting surface waters (Guan et al., 2013; Sun et al., 2019). The difference in the mass of deuterated water (^2H) versus water with ^{18}O is 1 amu, which allows for the preferential evaporation of the deuterated water, and therefore a depletion of d-excess. Low d-excess in samples is therefore an indicator that evaporative processes have taken place. Measuring $\delta^{18}\text{O}$ in precipitation samples can be an important indicator of the source of moisture and the relative effect of continuing precipitation and evapotranspiration on that moisture. As vapor condenses into the liquid phase and precipitates, ^{18}O -water preferentially “rains-out”. The rainout progresses as the moist air mass moves further inland, and the process of the decreasing $\delta^{18}\text{O}$ is often modeled by Rayleigh distillation, shown in Equation 3:

$$R = R_0 f^{(\alpha-1)} \quad (\text{Eq. 3})$$

Where R is the ratio of $^{18}\text{O}/^{16}\text{O}$ in precipitation, R_0 is the $^{18}\text{O}/^{16}\text{O}$ ratio in the initial precipitation, f is the fraction of moisture remaining in the storm, and α is the fractionation of ^{18}O between the liquid and solid phase. Concurrently with this rainout process, evaporation and transpiration (ET) return water to the atmosphere. About 65% of ET is transpiration, which is a process that does not

fractionate isotopes, resulting in Rayleigh distillation predicting lower $\delta^{18}\text{O}$ in a moist air-mass than is measured as it travels over the continental interior.

2.1.1 Spatial and Temporal Climate Variability and Precipitation Stable Isotope Ratios

Colorado resides in the mid-latitude region of the Northern Hemisphere, and experiences temporal variability in precipitation's location of origin. The primary atmospheric circulation system over North America can be traced by observing the isotopic effects of removal of moisture from the atmosphere via precipitation and return of moisture via ET. The Front Range sits at the nexus of moisture delivered from the Gulf of Mexico by the Great Plains Low-Level Jet (GPLLJ) and moisture delivered by westerly storms that originate in the Pacific (Helfand and Schubert 1995, Manser et al. 2024). These seasonal climate changes have been shown to have a strong relationship with stable isotope ratio variability globally (Bowen 2008). Precipitation isotopes in the Denver

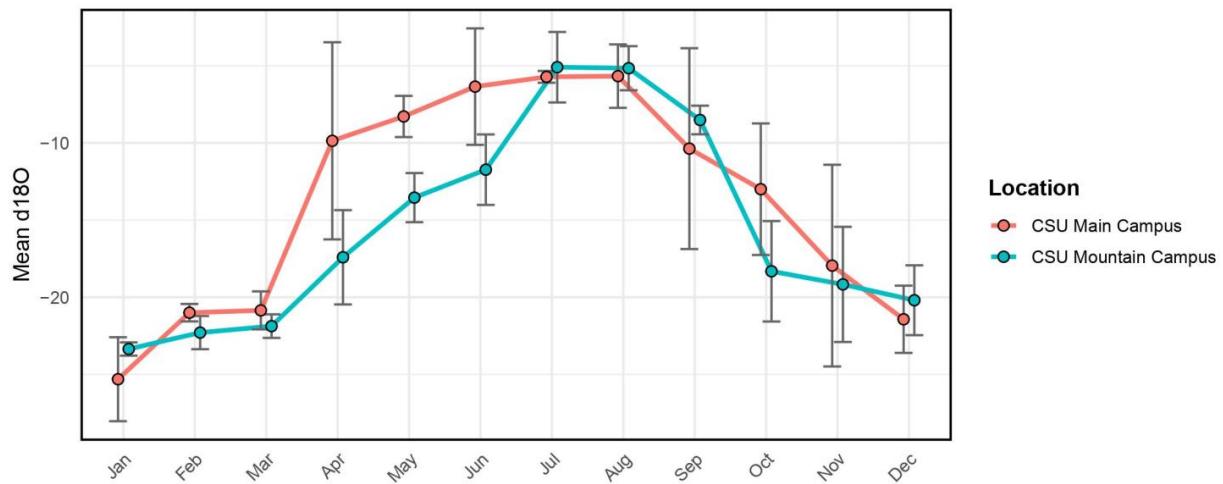


Figure 2-1. Monthly average precipitation $\delta^{18}\text{O}$ values for the CSU Main Campus in Fort Collins and the CSU Mountain Campus in Pingree Park. Error bars show 1 S.D. from the mean.

Basin have a characteristic annual cycle, where summer precipitation $\delta^{18}\text{O}$ (and δD) is high and winter precipitation $\delta^{18}\text{O}$ (and δD) is low. This characteristic cycle is also seen in other areas of the CO Front Range, including Fort Collins and in the mountains near the Colorado State University (CSU) Mountain Campus at Pingree Park (Figure 1). Westerly derived moisture must

traverse several mountain ranges before reaching the Denver Basin, and mountain ranges tend to increase the net loss of moisture from an air mass due to the orographic effect, decreasing the $\delta^{18}\text{O}$ of winter precipitation in this region (Poage and Chamberlain, 2001; Winnick et al., 2014; Kukla et al., 2019). GPLLJ derived moisture does not traverse any major topographic barriers on its way to CO and experiences a high degree of ET that replenishes the GPLLJ and is about 10 ‰ higher than equivalent westerly moisture (Mix et al. 2013). In addition to distinct spatial isotopic ratios of moisture, temporal variation in isotopic partitioning is significant. In summertime, the warmer atmosphere can hold more moisture and very active plant biosphere provides a high ET flux generally leading to high $\delta^{18}\text{O}$. In wintertime, lower atmospheric water content combined with typically very low ET fluxes leads to the opposite effect of low ^{18}O .

2.1.2 Variability in Isotopic Ratios in Surface and Groundwater

As water travels through the hydrologic system, there is an observed reduction in variability of the stable isotope ratios of surface waters and groundwaters. For arid and temperate climates such as the Denver Basin and the Front Range, research has shown that the groundwater recharge ratio is higher in the winter than in the summer, which results in groundwater stable isotope ratios more strongly resembling winter precipitation signatures (Jasechko et al. 2014). This reduction of variability in the stable isotope signal seen in surface and groundwaters can reveal unique and temporally stable signatures of spatially variable sample locations compared to precipitation stable isotope signatures (Hathaway et al. 2022). Identification of a unique isotopic ratio of different groundwaters allows stable isotopes to be a useful groundwater tracer.

2.2 Stable Isotopes as Tracers

Water stable isotopes have commonly been used as tracers of groundwater dynamics. Stable isotopes are a conservative tracer, and do not chemically react with the lithology or mineralogy of aquifers. This important property allows for comparison of waters over vast spatial and temporal scales. Stable isotopes have been used for a variety of tracer applications, including identifying the extent of mixing between water sources feeding into streams, identifying extent of surface water intrusion to shallow aquifer wells (Yapiyev et. al 2023), and for tracing groundwater recharge surrounding lakes (Li et. al 2022). They have also proven to be a valuable tracer for mountain block recharge (MBR) to basin aquifers from adjacent mountain ranges (Liu and Yamanaka 2012, Li et al. 2017, Eastoe and Wright 2019, Campbell et al 2021, Bouimouass et. al 2024). Studies examining MBR use the distinct signal of high elevation precipitation to distinguish MBR from direct recharge via precipitation in the basin. The use of water stable isotope data in the context of isotope altitude effects, isotope temporal variability, basin geology, and groundwater ages allows the interpretation of various mechanisms of recharge to basin aquifers.

CHAPTER 3: METHODS

3.1 Sample Location Strategy

Sampling locations are mapped in Figure 3-1, and sample location names, abbreviations, elevations, coordinates, and number of samples collected are all found in Appendix A. Locations for precipitation samplers were chosen in pursuit of measuring the unique water stable isotope signatures of the mountain block and the plains. Within these regions, CoCoRaHS volunteers were contacted, and a precipitation sampler was installed on each property.

Stream sampling strategy varied by sampling date. The June 28th/29th 2023 (summer) sampling event sampled high elevation streams flowing out of the mountain block and into the Castle Rock region. The October 7th/8th 2023 (fall) sampling event re-sampled many previous locations and included sampling streams flowing from the mountain block into the Denver Basin, starting as far south as the Castle Rock region and covering the Front Range moving northward to Loveland. The February 25th 2024 (winter) sampling event concentrated again on streams near the Castle Rock region, with a focus on sampling at the location of contact between the DBAS units and the mountain block.

Groundwater sampling locations were chosen to provide spatial variability in aquifer samples. Stable isotope data from the Musgrove et al. 2014 report were also utilized and provide our sole source of data for the Laramie-Fox Hills aquifer unit. Sampling groundwaters with wide spatial variability allows us to distinguish the unique signatures of the different aquifer units and the mountain block crystalline aquifer.

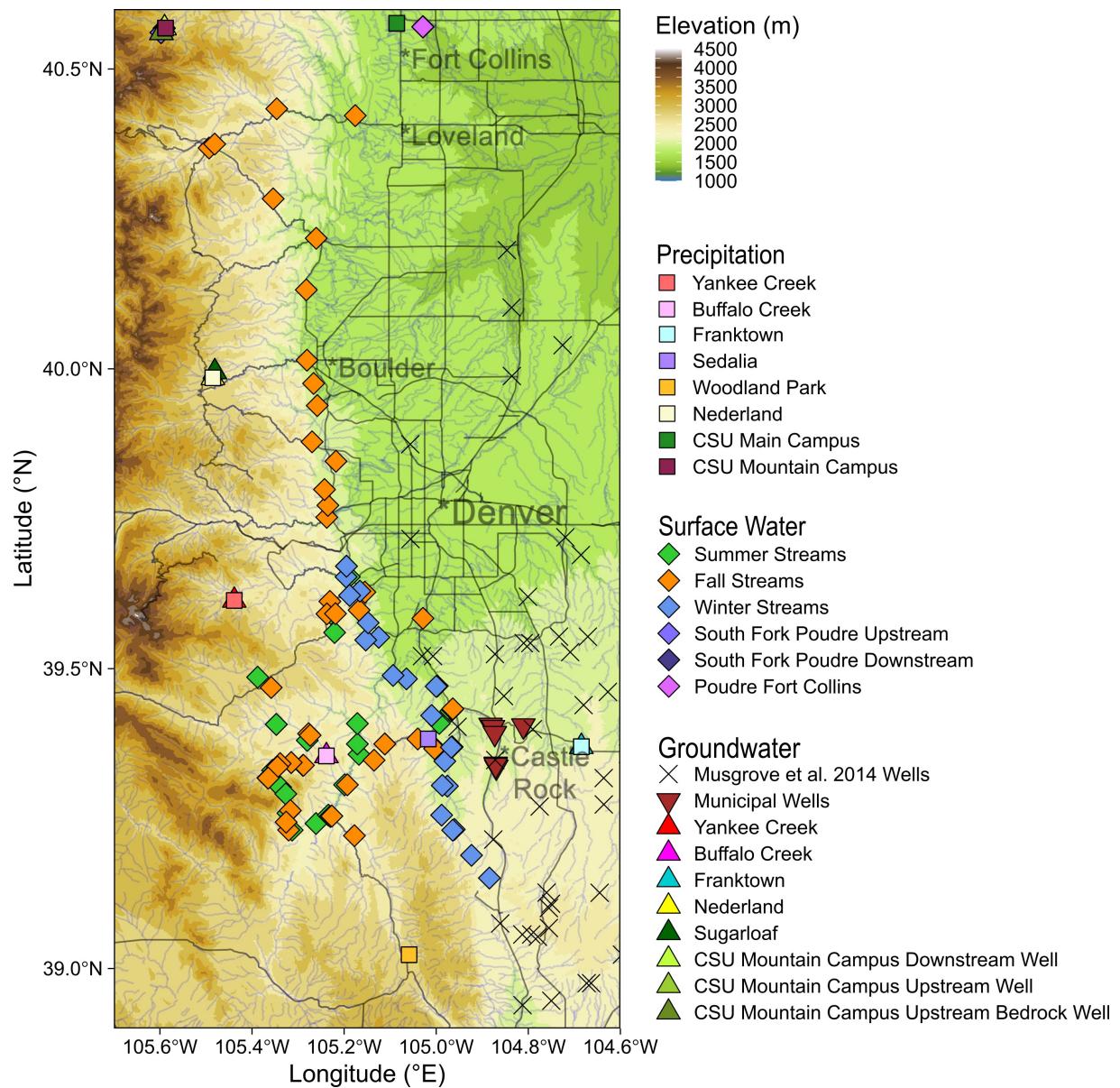


Figure 3-1. Map of sampling locations in the Denver Basin and adjacent Front Range regions. Municipal wells are all located in the Town of Castle Rock. The Yankee Creek sampling locations are both near the town of Evergreen, CO.

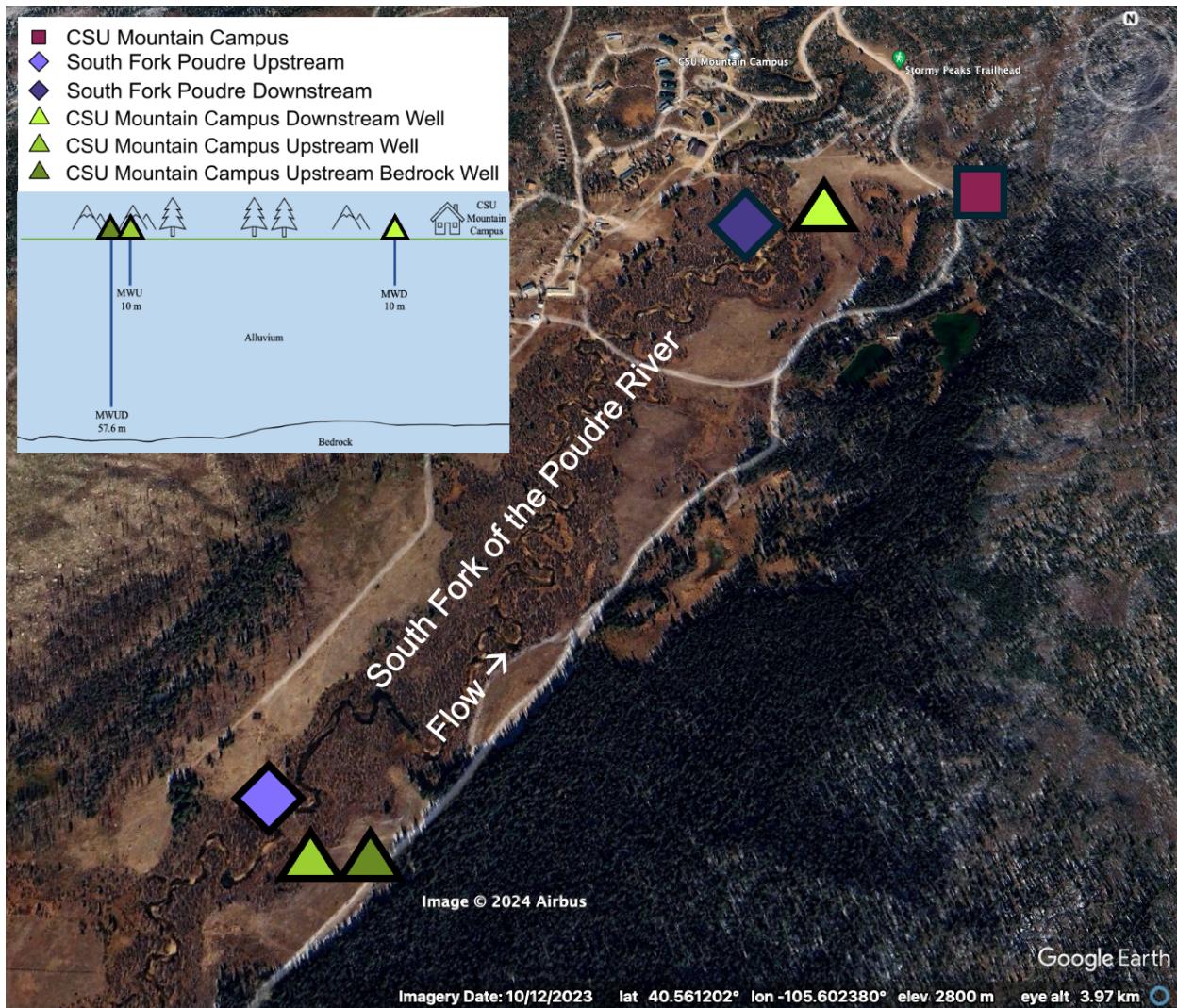


Figure 3-2. Detailed map of sampling locations at the CSU Mountain Campus. Satellite imagery was borrowed from Google Earth. Inset diagram shows relative depths of the observation wells used for groundwater sampling.

3.2 Sampling Instrumentation and Infrastructure

3.2.1 Instrumentation

This study benefited from previously installed precipitation collection stations at both the CSU Mountain Campus and the CSU Main Campus. These northernmost installations (Figure 3-

1) provide a useful characterization of Front Range and Plains precipitation with similar latitudes but differing elevations. All other precipitation installations and residential groundwater sampling wells were co-located with CoCoRaHS (Community Collaborative Rain, Hail, and Snow Network; <https://www.cocorahs.org>) stations, which are maintained by volunteers interested in weather and hydrology. CoCoRaHS was founded by CSU researchers in the late 1990s and there now exists a high density of volunteer observers in the Front Range and Urban Corridor. This partnership was and will continue to be beneficial for maintaining the samplers as well as engaging citizen scientists in ongoing research.

Precipitation samples were collected using an RS-1 sampling gauge (manufactured by the Palmex Corporation, Zagreb, Croatia) (Gröning et al. 2012), which was designed by the International Atomic Energy Agency (IAEA) to ensure consistent collection of precipitation samples for isotopic analysis. The IAEA runs the Global Network of Isotopes in Precipitation (GNIP), which provides monthly data on precipitation isotopes at more than 200 stations globally. The key feature of these samplers is that they are designed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis of cumulative precipitation samples and limit evaporative loss of sample, which can significantly alter its isotopic composition (Gröning et al., 2012; Putman et al., 2019). Each sampler required monthly maintenance—including cleaning of the sampling cone, tubes, and bottles—and this was facilitated by having these samplers under the care of a trained volunteer weather observer.

3.2.2 Infrastructure

Municipal well samples used in this study were collected with assistance from Town of Castle Rock Water. Details for the collection of other DBAS well samples included in this study are found in Musgrove et al. 2014.

This study benefitted from three previously installed observation wells at upstream and downstream locations of the South Fork of the Poudre River floodplain (Figure 3-2). The wells sampled along with their depths are MWD (10 m), MWU (10 m), and MWUD (57.6 m). Abbreviation explanations can be found in Appendix A.

3.3 Water Sampling Procedures

3.3.1 Precipitation Sampling

The CSU-MC and MT-CSU sites were sampled monthly. All other sampling stations were co-located with CoCoRaHS sites, and these volunteers completed monthly sampling. All samplers were sampled at approximately the 1st of the month. At the time of sampling, the sampler components were cleaned to remove dust and debris. Sampling was performed by removing the sample bottle, cleaning the water inlet, and replacing with a clean and dry bottle. The sample was then immediately measured with a graduated cylinder, the volume of precipitation recorded, and the sample collected in a HDPE bottle. Samples were wrapped in parafilm and stored in a cool, dark place until their analysis.

3.3.2 Stream Sampling

Monthly stream sampling was conducted at the CSU Mountain Campus at the upstream and downstream locations of the South Fork of the Cache la Poudre River. Monthly stream sampling also took place at the Poudre in Fort Collins and at Spring Creek in Fort Collins. Stream sampling of the Colorado Front Range took place on three events: The 28th-29th of June (summer), the 7th-8th of October (fall), and the 25th of February (winter). Samples were all collected using plastic syringes and filtered with a 0.23 micron disposable (material) filter into a polypropylene sample bottle or 2 mL glass vial. Syringes were re-used on the same sampling event and were rinsed three times with sample before collection. New filters were used for each sample. Samples

not tested within 2 weeks of collection were wrapped with parafilm and stored in a cool dark place to prevent any evaporation before analysis.

3.3.3 Groundwater Sampling

Groundwater at the CSU Mountain Campus located in Pingree Park, CO was sampled monthly at the MWU and MWD well locations using a whale pump and marine battery. Prior to sampling, three casing volumes of water were pumped from the well and measured using a 5-gallon bucket. The water sample was collected using the same protocol as for stream sampling, drawing directly from the 5-gallon bucket. Post-July 2023, a low-flow pump and lithium-ion battery were used to sample both wells named “MWU” and “MWD” which are both water table monitoring wells, and the “MWUD” well that was installed at the CSU Mountain Campus in October 2022. The low flow pump was adjusted to a flow rate less than 500 mL/minute, and the sample was taken directly from a large collection beaker using the syringe and filter method mentioned previously. In the upstream region of the valley, the MWU well is screened 2.7-10.4 meters below ground level and MWD is screened 5.8-10.4 meters below ground level. The more recently completed MWUD well is screened from 53.7-56.7 meters serving as a piezometer for this its location the aquifer, and accesses water in the Pingree Park valley aquifer near the contact of the valley fill and the mountain bedrock.

Groundwater samples from Castle Rock municipal wells were collected in two sampling events in June and November of 2023. These wells were pumped for either 5 minutes before sampling, or long enough for the water to run clear. Water was then sampled with the same procedure as stream sampling.

Groundwater samples from residential wells were sampled on the same day precipitation samples were collected by the volunteers. Sampling protocol was to run the tap for at least 1

minute before filling the sample bottle. Groundwater samples were wrapped with parafilm and stored in a cool, dark place prior to analysis.

3.4 Stable Isotope Measurements

The isotopic compositions of all samples were measured at the CSU Natural Resources Ecology Laboratory (NREL) EcoCore Analytical Facility using a Picarro L-2130i laser water isotope analyzer coupled to a High Precision Vaporizer. Prior to measurement, 2 ml of precipitation sample is filtered using a 0.23 micron filter to eliminate gross particles. The isotopic composition was then measured using the Picarro's cavity-ring spectrometer with typical precisions of $<0.1\text{\textperthousand}$ for $\delta^{18}\text{O}$ and $<0.5\text{\textperthousand}$ for $\delta^2\text{H}$. Approximately 1.8 microliters were injected seven times; results are the average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for the last four injections. Absolute $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were corrected based upon measurements of USGS standards 45, 46, and 47.

3.5 Data Analysis

Certain samples were removed from our analyses to clarify results. Stream samples that were determined to be evaporative—defined as a zero or negative d-excess value—were filtered out from the dataset prior to any calculations (Figure 4-4).

3.5.1 USGS Stream Stats

Data was pulled from the USGS Stream Stats online tool to determine the maximum elevations, basin outlet elevations, and mean hypsometric elevations of the catchment for each stream sampling location.

CHAPTER 4 - RESULTS

The stable isotopic compositions, volumetric data and geographic data (latitude, longitude, and elevation) of samples from this study are available in Supplementary Files.

4.1 Water Stable Isotope Composition in Precipitation

Annual mean $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are reported as a monthly volumetrically weighted mean and are found in Table 4-1. Not all sampling locations have a complete year of data (Figure 4-1) and means for the monthly stable isotope data may not represent a yearly average composition.

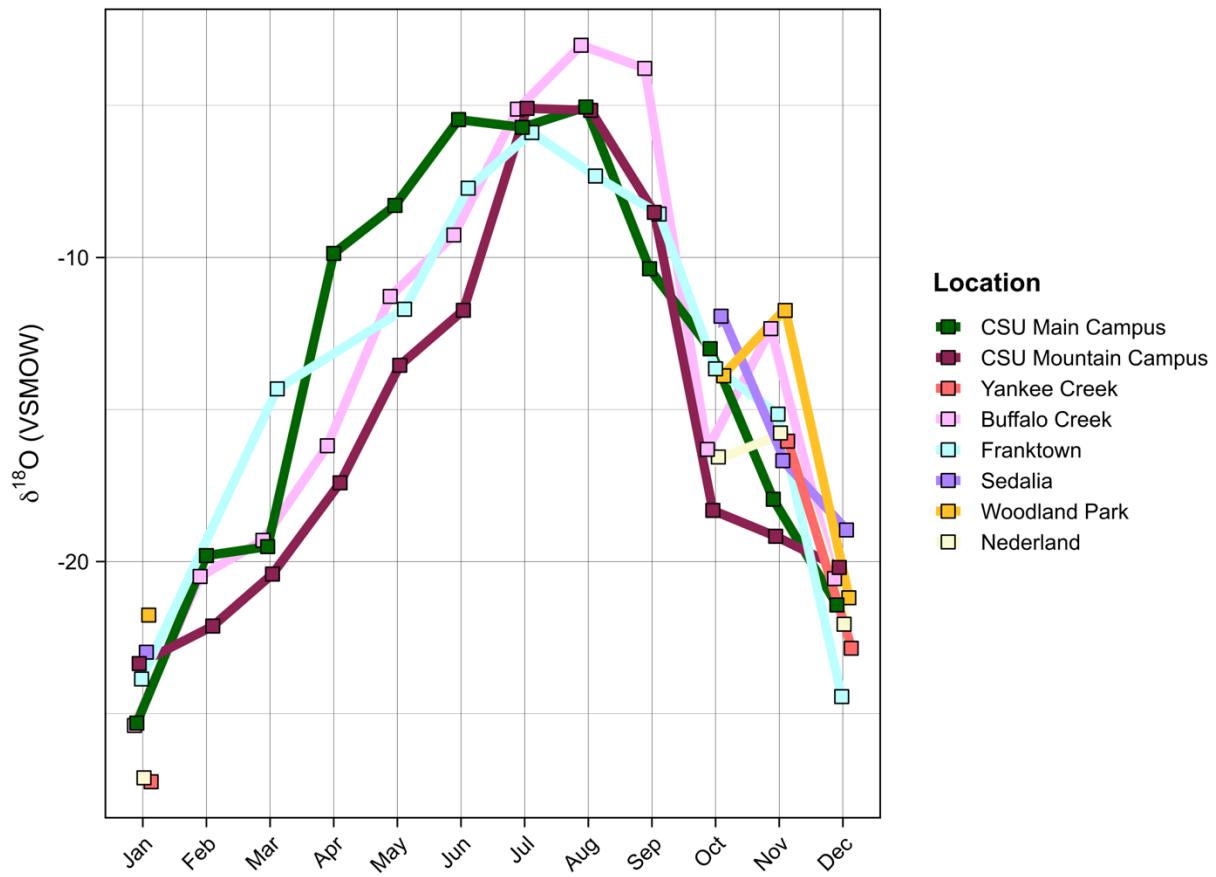


Figure 4-1. Precipitation mean $\delta^{18}\text{O}$ values for all sampling locations. $\delta^{18}\text{O}$ are highest in the summer and lower in the winter for all locations.

Table 4-1. Compilation of water stable isotope data statistics for all precipitation samplers reported in ‰. If there are multiple years of data for each sampling months, values were averaged before calculating the weighted average by precipitation amount. The ‘n’ column indicates the number of samples collected per location as of the completion of this manuscript.

Location	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$ min	$\delta^{18}\text{O}$ max	$\delta^2\text{H}$	$\delta^2\text{H}$ min	$\delta^2\text{H}$ max	n	Elevation (m)
CSU Main Campus	-10.17	-25.31	-5.05	-75.69	-197.38	-34.47	31	1523
Sedalia, CO	-17.34	-22.98	-11.93	-127.36	-177.55	-78.15	4	1966
Franktown, CO	-10.84	-24.44	-5.89	-72.58	-184.45	-33.87	11	2049
Buffalo Creek, CO	-12.00	-25.39	-3.02	-86.55	-196.49	-25.66	12	2295
Yankee Creek, CO	-23.47	-27.24	-16.04	-178.92	-212.51	-115.63	3	2466
Sugarloaf, CO	-20.93	-27.11	-15.77	-158.44	-214.89	-111.48	4	2548
Woodland Park, CO	-17.10	-21.76	-11.74	-123.83	-166.74	-76.06	4	2576
CSU Mountain Campus	-14.64	-23.35	-5.10	-107.66	-183.43	-29.65	30	2758

The Sedalia, Franktown, Buffalo Creek, Evergreen, Sugarloaf, and Woodland Park sampling locations are part of the CoCoRaHS volunteer network. Also included in this table are the precipitation samples collected at the CSU Main Campus and the CSU Mountain Campus which provide a useful characterization of Front Range and Plains precipitation with similar latitudes but differing elevations. These locations are in the Front Range north of the Denver Basin, but geographically close enough to provide insightful mountain block water data. Over two years’ worth of data have been collected at these two CSU locations, and values are averaged by month of collection, weighted by precipitation amount, then averaged for a yearly “mean” value. Sampling locations with n < 10 show bias to the season of precipitation collection of the available, which is October to January. The mean $\delta^{18}\text{O}$ values of these locations correspond to the typically lower winter precipitation values in the region. Considering only samples with n > 10, a trend of decreasing $\delta^{18}\text{O}$ with increasing elevation is observed (Figure 4-2).

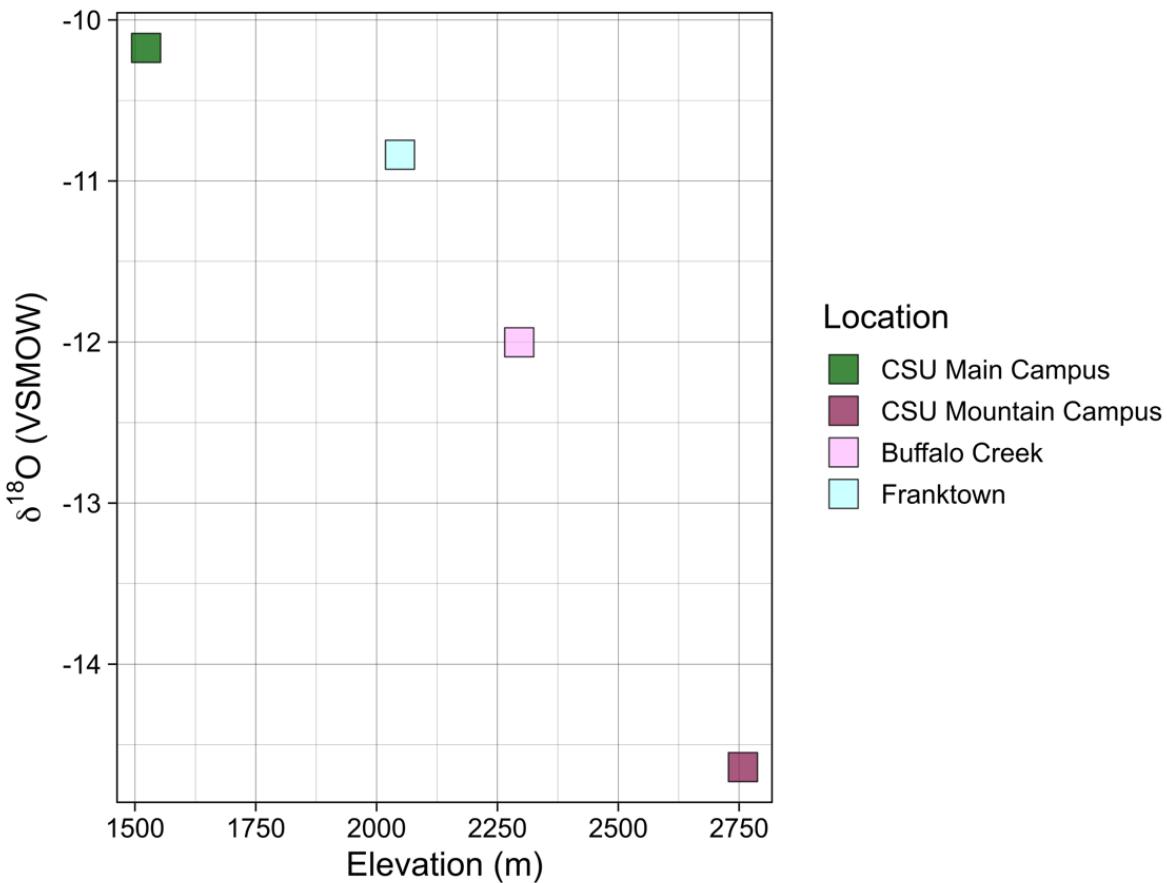


Figure 4-2. Amount weighted precipitation mean $\delta^{18}\text{O}$ values of locations with $n > 10$ samples plotted with elevation of sampling location. $\delta^{18}\text{O}$ decreases with increasing elevation.

4.2 Water Stable Isotope Composition in Surface Waters of the Colorado Front Range and Denver Basin

4.2.1 Front Range Stream Sampling Events

Stream samples were determined to be evaporative if their calculated d-excess was less than 3‰ and were then removed from the calculated statistics (Figure 4-4). All referenced sampling areas for each event can be observed in Figure 3-1. The June 28th, 2023 summer stream sampling event had measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ means of $-13.55 \pm 1.05\text{‰}$ and $-101.20 \pm 7.65\text{‰}$ respectively. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ samples from the October 7, 2023 (fall) sampling event had $\delta^{18}\text{O}$ and $\delta^2\text{H}$ means of $-13.32 \pm 0.99\text{‰}$ and $-100.54 \pm 7.08\text{‰}$ respectively. These samples were located in

the same geographic area as the summer sampling event. The October 8, 2023 (fall) sampling event had measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of $-14.67 \pm 1.12\text{\textperthousand}$ and $-109.82 \pm 7.99\text{\textperthousand}$ respectively. These values are slightly lower than the previous day's sampling, showing a distinct signature due to the difference in geographic location of sampling, with the water coming from further north in the Front Range where there are higher elevation catchments. The February 25, 2024 (winter) sampling event had $\delta^{18}\text{O}$ and $\delta^2\text{H}$ means of $-14.54 \pm 0.47\text{\textperthousand}$ and $-109.79 \pm 3.63\text{\textperthousand}$ respectively. Of the three seasonal stream sampling events, the winter sampling event had the lowest $\delta^{18}\text{O}$ values, followed by fall, then summer. When splitting the two fall sampling days into separate events due to their difference in geographic sampling location, the October 8th, 2023 event had the lowest $\delta^{18}\text{O}$ of all events (Table 4-2). Figure 4-3 shows the stream sampling events along with the time series of data from the Cache la Poudre in Fort Collins and the two sampling locations of the South Fork of the Poudre. The $\delta^{18}\text{O}$ values from the Poudre in Fort Collins lie within the spread of data from each seasonal sampling event. The Poudre originates in the Northern Colorado Rockies which receives similar precipitation to the Central Colorado Rockies indicated by the precipitation stable isotope data for both regions (Figure 4-1).

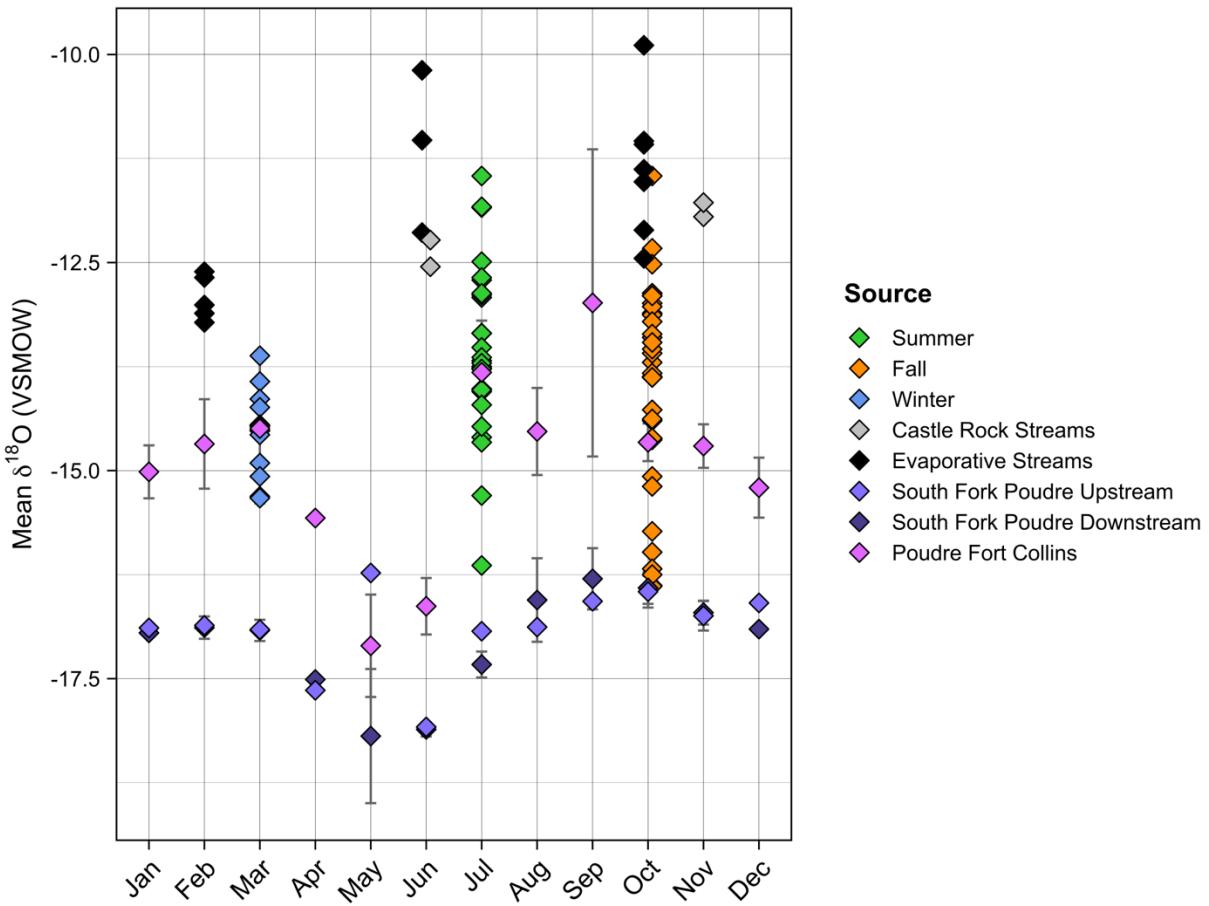


Figure 4-3. Time-series of stream data. Locations with $n > 1$ for a sampling month show error bars of 1σ .

4.2.2 Castle Rock and CSU Mountain Campus Stream Data

Streams sampled over two sampling events in the Town of Castle Rock, Colorado had measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values with means of $-12.13 \pm 0.34\text{\textperthousand}$ and $-91.23 \pm 1.01\text{\textperthousand}$ respectively, possibly indicating evaporative enrichment of these waters as they plot higher than most stream samples from every other seasonal sampling event. Further north in the Front Range west of Fort Collins, samples were collected at the CSU Mountain Campus in the upstream (SFPU) and downstream (SFPD) sections of the South Fork of the Poudre River. The SFPU and SFPD samples

had the lowest measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and were also collected at the highest elevation (Figure 4-3, Figure 4-4, Appendix A Table 1).

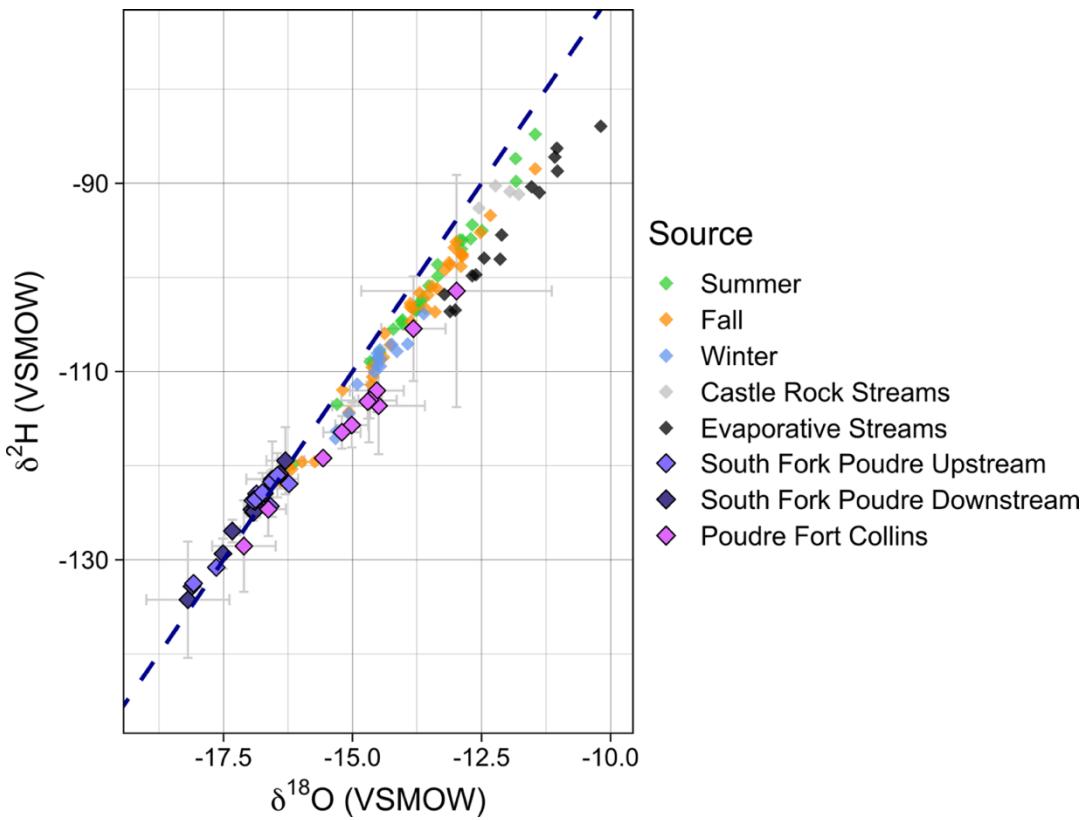


Figure 4-4. Stable isotope plot of stream data. Locations with $n > 1$ for a sampling month show error bars of 1σ .

Table 4-2. Compilation of water stable isotope data statistics for Castle Rock stream sampling (Cognac 2023) and CSU Mountain Campus monthly stream sampling reported in ‰. Two years of data were collected for the SFPD site, and one year of data were collected for the SFPU site as of the completion of this manuscript.

Sampling Event	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$ min	$\delta^{18}\text{O}$ max	$\delta^2\text{H}$	$\delta^2\text{H}$ min	$\delta^2\text{H}$ max	n
June 28th, 2023	-13.30	-16.14	-10.19	-13.30	-16.14	-10.19	30
October 07th/08th, 2023	-13.57	-16.39	-9.89	-13.57	-16.39	-9.89	43
October 07th, 2023	-13.32	-15.98	-11.46	-100.54	-119.60	-88.47	20
October 08th, 2023	-14.67	-16.39	-13.21	-109.82	-121.66	-99.19	23
February 25th, 2024	-14.54	-15.33	-13.62	-109.79	-117.11	-103.86	20
Castle Rock Streams	-12.13	-12.55	-11.78	-91.23	-92.63	-90.26	4
South Fork Poudre Downstream	-17.02	-18.76	-16.04	-125.24	-138.61	-116.95	14
South Fork Poudre Upstream	-16.86	-18.08	-16.23	-124.05	-132.50	-119.36	28
Poudre Fort Collins	-14.90	-17.50	-11.70	-114.00	-132.00	-92.70	23

4.3 Water Stable Isotope Composition of Colorado Front Range and Denver Basin Groundwaters

Stable isotope data for each DBAS unit were collected according to procedures listed in Cognac 2023 and Musgrove et al. 2014. Dates of collection, well depths, and aquifer units of the Castle Rock and Denver municipal well samples, residential well samples, and CSU Mountain Campus wells are included in Supplementary Materials. Municipal well, residential well, and stream sampling $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data are plotted together in Figure 4-6 and Figure 4-7.

4.3.1 Town of Castle Rock Municipal Wells

Samples for the Alluvial aquifer include wells categorized as “Alluvial” and “Shallow Alluvial”, and “Urban Water Table” in Supplementary Materials. Mean values for stable isotope values of the different aquifer units are calculated by combining Castle Rock municipal well data and data published by Musgrove et. al 2014. Alluvial well samples had a mean measured $\delta^{18}\text{O}$ that was the second highest compared to all aquifer units, with the highest $\delta^{18}\text{O}$ found in the Laramie-Fox Hills (LFH) aquifer unit (Table 4-3). The lowest $\delta^{18}\text{O}$ values measured were in the Dawson, with mean $\delta^{18}\text{O}$ steadily increasing with depth in the DBAS, from the Dawson to the Denver to the Arapahoe to the LFH. Standard deviations of $\delta^{18}\text{O}$ data also increase with depth in the DBAS, with the largest σ calculated for the LFH.

4.3.2 Residential Wells

Residential well sampling locations do not have a complete year of data; therefore, monthly stable isotope means do not represent a yearly average. However, for these groundwater samples, monthly fluctuation was minimal and standard deviations are all less than 2% of the mean, so a single well sample may be a yearly representative sample for residential locations. The lowest

Table 4-3. Compilation of stable isotope data for groundwater samples reported in ‰. Data was collected from Castle Rock and Denver municipal wells (Cognac 2023, Musgrove et al. 2014), residential wells, and observation wells at the CSU Mountain Campus. Standard deviations reported are 1σ . Number of samples for each sample group are listed in column ‘n’.

Castle Rock Municipal Wells									
DBAS Aquifer Unit	$\delta^{18}\text{O}$	$\delta^{18}\text{O} \sigma$	$\delta^{18}\text{O min}$	$\delta^{18}\text{O max}$	$\delta^2\text{H}$	$\delta^2\text{H} \sigma$	$\delta^2\text{H min}$	$\delta^2\text{H max}$	n
Alluvial	-13.33	0.39	-14.20	-12.88	-101.24	3.18	-109.00	-97.51	10
Dawson	-14.11	0.98	-15.18	-10.30	-106.50	7.17	-114.00	-78.80	21
Denver	-13.52	0.83	-14.38	-11.04	-100.66	6.18	-109.00	-83.70	17
Arapahoe	-13.35	1.29	-15.06	-10.19	-98.27	10.35	-110.00	-75.10	17
Laramie-Fox Hills	-12.28	1.63	-14.95	-9.61	-90.83	13.67	-114.00	-71.30	10
Residential Wells									
Well Location	$\delta^{18}\text{O}$	$\delta^{18}\text{O} \sigma$	$\delta^{18}\text{O min}$	$\delta^{18}\text{O max}$	$\delta^2\text{H}$	$\delta^2\text{H} \sigma$	$\delta^2\text{H min}$	$\delta^2\text{H max}$	n
Franktown	-13.41	0.13	-13.59	-13.28	-99.78	0.92	-101.08	-98.65	9
Evergreen	-14.56	0.06	-14.62	-14.50	-110.83	0.57	-111.44	-110.30	3
Nederland	-16.22	0.09	-16.33	-16.16	-122.78	1.24	-124.20	-121.95	3
Buffalo Creek	-14.44	0.03	-14.51	-14.39	-109.76	0.34	-110.34	-109.10	9
Sugarloaf	-16.30	0.11	-16.40	-16.16	-123.98	0.49	-124.41	-123.46	4
CSU Mountain Campus Wells									
Location	$\delta^{18}\text{O}$	$\delta^{18}\text{O} \sigma$	$\delta^{18}\text{O min}$	$\delta^{18}\text{O max}$	$\delta^2\text{H}$	$\delta^2\text{H} \sigma$	$\delta^2\text{H min}$	$\delta^2\text{H max}$	n
Downstream Well	-12.89	0.30	-13.76	-12.46	-96.44	2.27	-103.00	-93.30	15
Upstream Well	-16.54	0.90	-18.74	-16.04	-124.29	5.97	-138.26	-120.18	8
Upstream Deep Well	-16.98	0.08	-17.06	-16.85	-127.13	0.64	-127.57	-126.02	5

$\delta^{18}\text{O}$ values for all residential locations were found at the Sugarloaf and Nederland locations (Figure 4-5). These residential wells were drilled directly into the mountain bedrock, so this low $\delta^{18}\text{O}$ signal is representative of mountain block crystalline aquifer waters. The Evergreen (Yankee Creek) and Buffalo Creek locations are also known to be drilled into the mountain block crystalline aquifer and have slightly higher $\delta^{18}\text{O}$ means and they represent a different location within the Front Range, which has overall lower peak elevations than the Sugarloaf and Nederland region. Due to the similarities between the signals of the Evergreen/Buffalo Creek sites and the Nederland/Sugarloaf sites (Figure 4-5), they are later averaged and plotted together as the South Mountain Block Aquifer and the North Mountain Block Aquifer respectively (Figure 4-6, Figure

4-7). The Franktown well had the highest $\delta^{18}\text{O}$ mean and is screened in the Dawson unit of the DBAS.

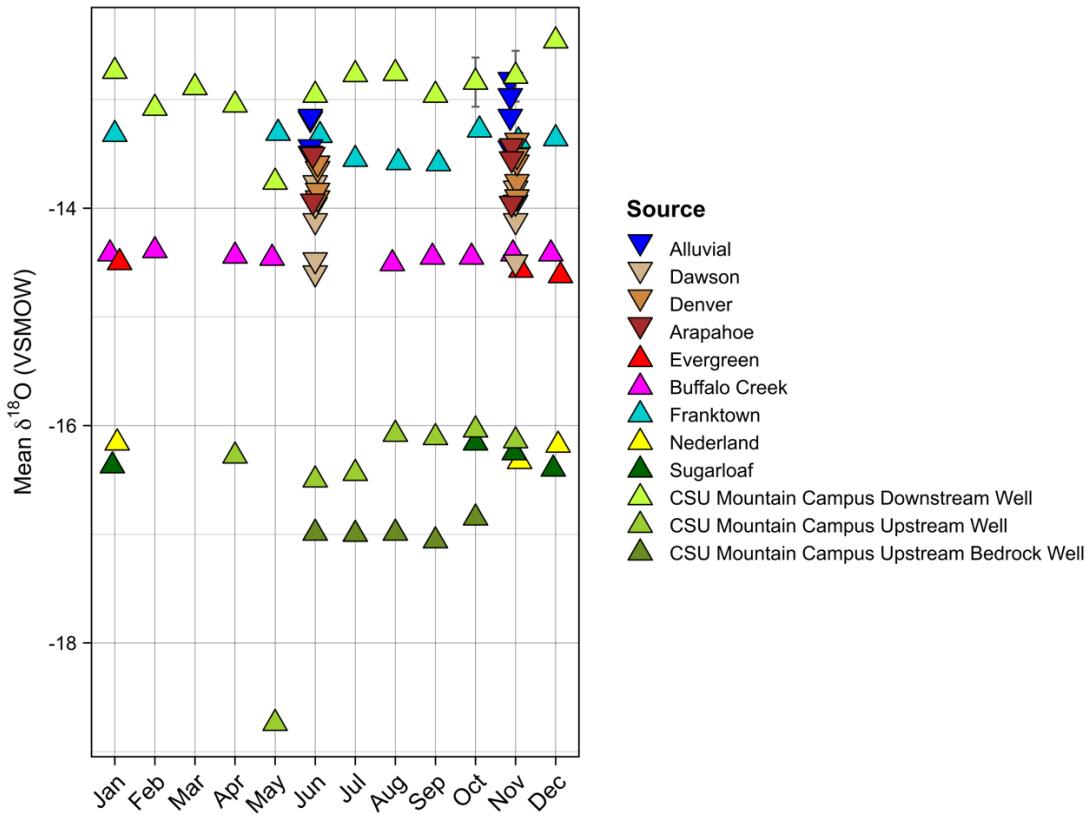


Figure 4-5. Time-series of groundwater data from residential wells, Castle Rock Water municipal wells, and CSU Mountain Campus wells. Locations with $n > 1$ for a sampling month show error bars of 1σ .

4.3.3 CSU Mountain Campus Wells

Stable isotope data for CSU Mountain Campus wells are included as an example of Front Range Mountain Block water signatures. Locations for sampling are mapped in Figure 3-2. Not all sampling locations have a complete year of data and means for the monthly stable isotope data may not represent a yearly average. For groundwater samples at this location, monthly fluctuation was minimal with all standard deviations less than 5% of the calculated mean value, so a single well sample may be a yearly representative sample. See Appendix A for sample name abbreviation

description. The upstream wells MWU and MWUD have the lowest mean $\delta^{18}\text{O}$ values of the valley, and the shallower MWU well has a signature very close to that of the near-bedrock MWUD well. The MWD well has a higher mean $\delta^{18}\text{O}$ value, and this is consistent with previous work indicating that the lower part of the valley receives recharge from evaporatively affected wetlands in the area (Doebley 2022).

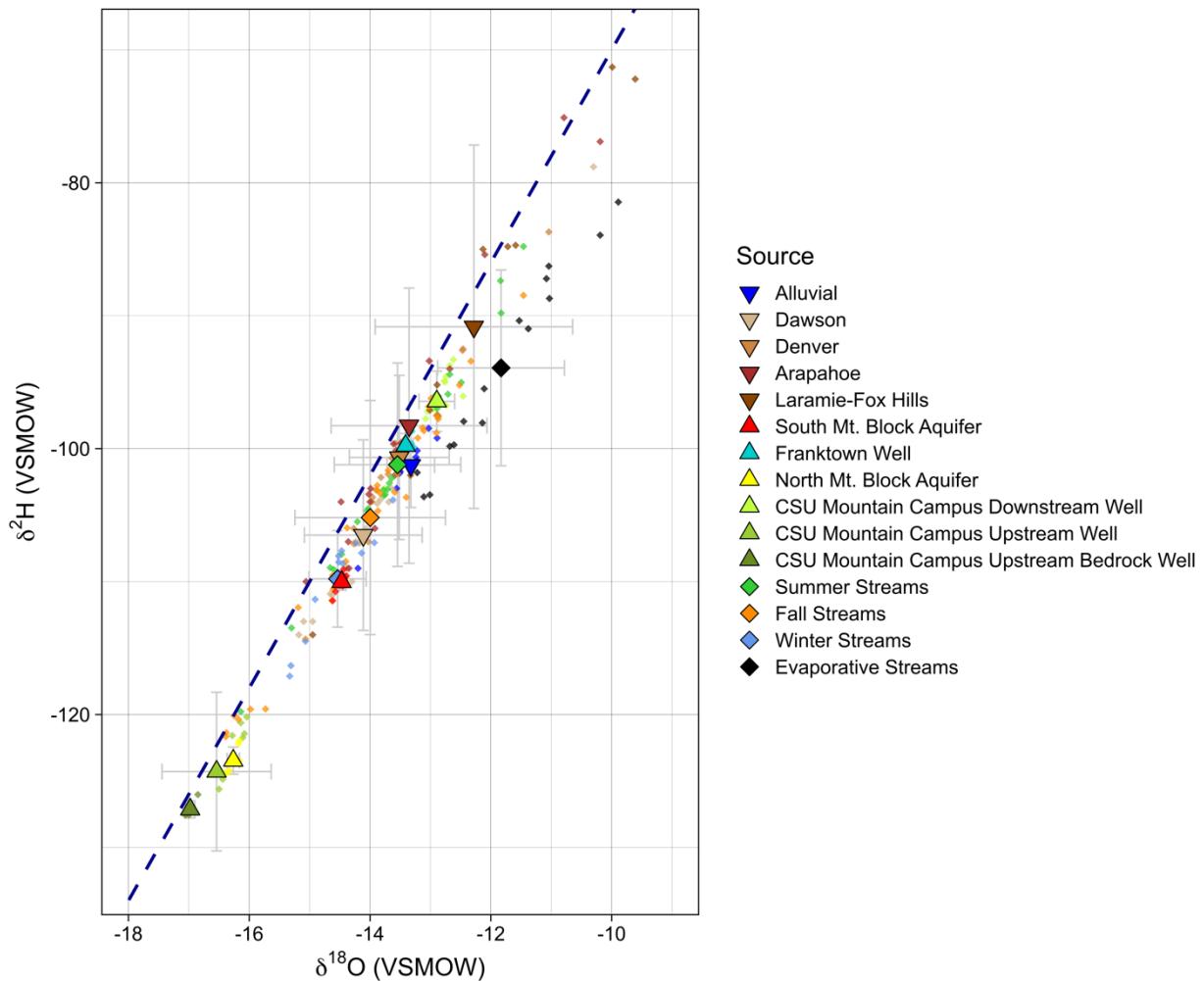


Figure 4-6. Plot of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ showing all Town of Castle Rock municipal wells, residential wells, CSU Mountain Campus wells, and stream sampling events. The south mountain block crystalline aquifer is an average of the Evergreen and Buffalo Creek residential wells, and the north mountain block aquifer is an average of the Nederland and Sugarloaf residential wells. Error bars indicate 1σ .

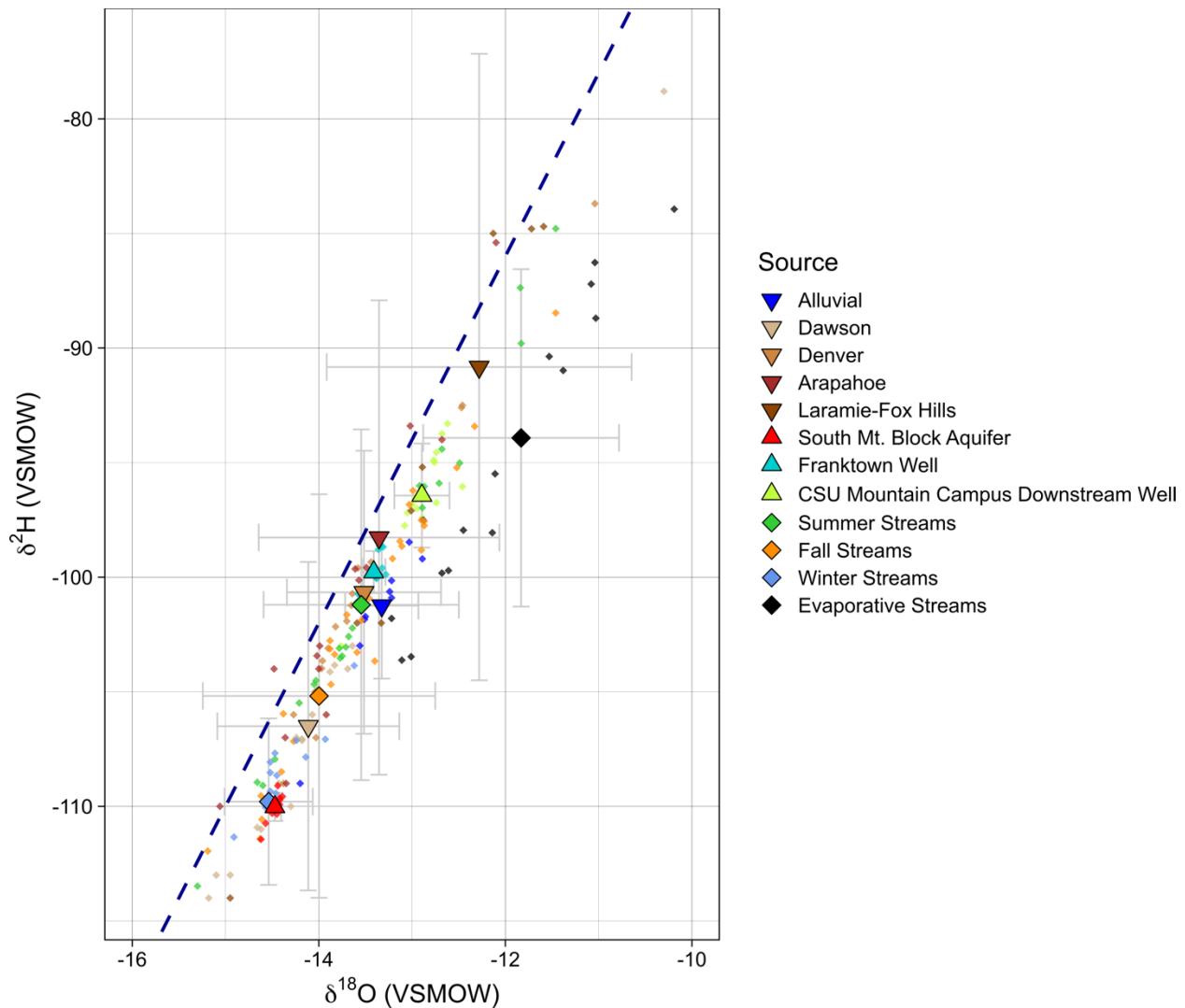


Figure 4-7. Plot of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ showing a zoomed view of all Town of Castle Rock municipal wells, residential wells, CSU Mountain Campus Downstream well, and stream sampling events. The north mountain block aquifer (an average of the Nederland and Sugarloaf residential wells) and the CSU Mountain Campus upstream wells are no longer visible in this figure. Error bars indicate 1σ .

4.4 Water Stable Isotopes and Average Catchment Elevation

Plotting mean catchment elevation vs. $\delta^{18}\text{O}$ and maximum catchment elevation vs. $\delta^{18}\text{O}$ reveal seasonal variations in this relationship. Figure 4-8 shows a negative linear correlation between mean and maximum catchment elevation and $\delta^{18}\text{O}$ for the summer and fall sampling events. A weak positive linear correlation between mean and maximum catchment elevation and

$\delta^{18}\text{O}$ for the winter sampling event is observed. The temporal variability of streams' source waters could explain the change in relationship between catchment elevation and $\delta^{18}\text{O}$. The October streams source primarily from baseflow, as inputs from snowmelt are no longer present. Fall is the time of lowest Q for Front Range streams (Peterson et al. 2024).

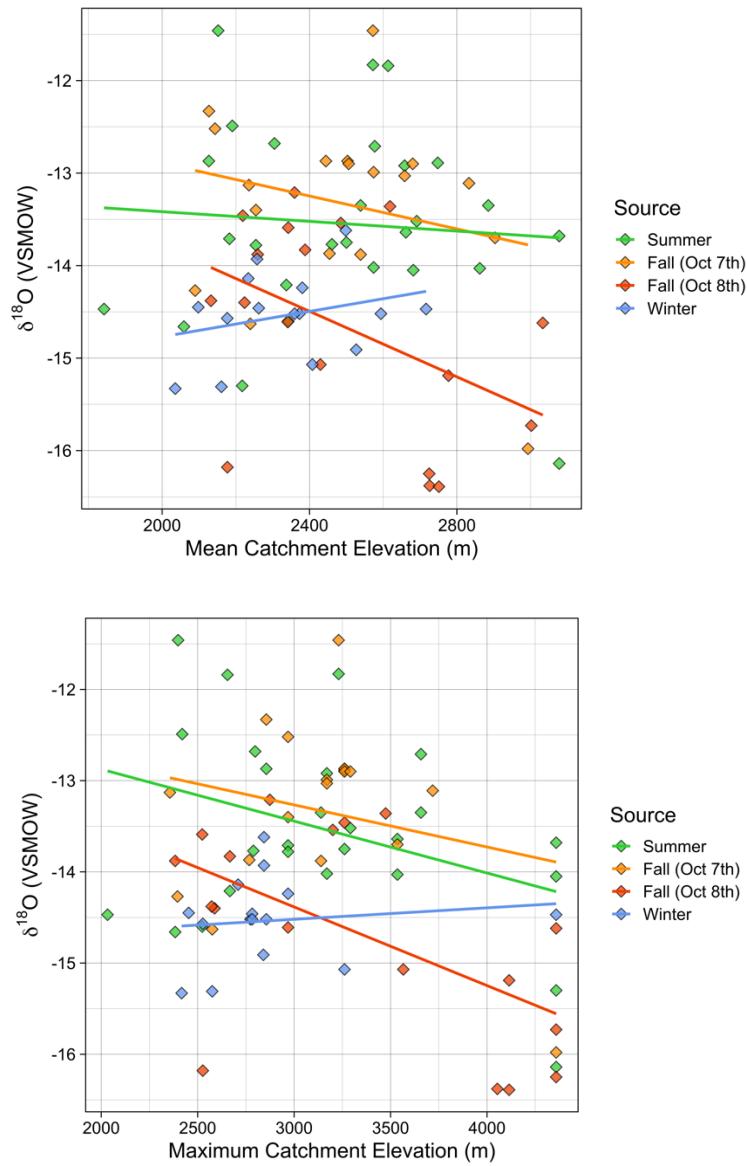


Figure 4-8. Plots of $\delta^{18}\text{O}$ vs. mean catchment elevation and $\delta^{18}\text{O}$ vs. maximum catchment elevation for stream samples plotted by seasonal sampling event. The two days of sampling form the October event are plotted separately to show the influence of maximum catchment elevation on resultant $\delta^{18}\text{O}$ values for stream samples.

4.5 Water Stable Isotopes t-tests

Welch two-sided t-tests were performed to determine statistical similarities between the measured $\delta^{18}\text{O}$ values of seasonal stream sampling events, residential wells, and the different aquifer units of the Denver Basin Aquifer System. Stream samples were determined to be evaporative by falling far off the GMWL when plotted in $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ space (Figure 4-4) and were removed from the calculated statistics. The t-test results are compiled in Appendix B. The p-values highlighted in the table show statistical similarity between the two datasets, indicating potential relationships between these various water sources when combined with geologic context.

Statistical similarity was calculated between the Alluvial aquifers of the DBAS and the Denver, Arapahoe, and summer streams. The t-test between the Alluvial aquifer and the Laramie Fox-Hills (LFH) had a calculated p-value of 0.08, just above the threshold of being considered statistically distinct. The Dawson unit of the DBAS was shown to be most like fall streams and the Buffalo Creek well, with a smaller similarity to winter streams. The Denver showed similarity to the Arapahoe, summer streams, and the Franktown well, with a smaller similarity to fall streams. The Arapahoe showed the greatest statistical similarity to summer streams and the Franktown well, and a smaller similarity to the LFH and fall streams. The LFH showed similarity to the Castle Rock Streams, and a smaller similarity to the Franktown well. Summer streams showed great similarity to the Franktown well, and a smaller similarity to fall streams. Lastly, the winter streams showed similarity to the Evergreen well and the Buffalo Creek well, which both access mountain block crystalline aquifer.

CHAPTER 5 – DISCUSSION

5.1 Water Stable Isotope Variability in the Front Range

5.1.1 Drivers of Precipitation Stable Isotope Variability

Seasonal changes in atmospheric dynamics and moisture transport across the Denver Basin and Front Range are the source of the major variability in precipitation stable isotope signatures in the region. $\delta^{18}\text{O}$ values reach a maximum in the summertime, and a minimum in the wintertime for Franktown, Buffalo Creek, CSU Main Campus, and the CSU Mountain Campus (Figure 4-1). Precipitation $\delta^{18}\text{O}$ from the CSU Main Campus increases earlier than the other sites, with higher $\delta^{18}\text{O}$ moisture from the Gulf of Mexico likely arriving earlier in the Plains than in the high-elevation Front Range.

Elevation was shown to be another key factor affecting the $\delta^{18}\text{O}$ of precipitation. In Figure 4-2, elevation is negatively correlated with the mean $\delta^{18}\text{O}$ of each collection site. This elevation dependence means that Mountain Block water can be distinguished due its lower $\delta^{18}\text{O}$ value (Clark and Fritz 1997). This relationship weakens in resultant surface waters (Figure 4-8) due to spatial variability of $\delta^{18}\text{O}$ of waters entering streams. Mountain groundwater retains the low $\delta^{18}\text{O}$ signal of high elevation precipitation, likely due to the majority of mountain block water receiving recharge from winter moisture (Jasechko et al. 2014).

5.1.2 Drivers of Surface Water Stable Isotope Variability

Surface waters are supplied by a mix of precipitation in the form of direct runoff and by groundwater as baseflow. Front Range streams showed seasonal variability, with the lowest average values coming from the winter stream samples and the fall stream samples collected along the westernmost border of the Front Range and DBAS. It must be noted that when data from the three stream sampling events is considered, the variability may be due to spatial differences in sources of streamflow, and not exclusively from temporal variation due to low sampling frequency. The low $\delta^{18}\text{O}$ of winter streams can be attributed partially to snowmelt, which will have the lowest $\delta^{18}\text{O}$ values due to being derived from winter precipitation (Figure 4-1). Winter streams have the smallest variability in stable isotope signatures, suggesting major contributions to the stream flow from a source with little variability, such as snowmelt and groundwater. Support for winter streams being derived from snowmelt with low $\delta^{18}\text{O}$ values can be found in the more complete time-series of stream sampling data from the CSU Mountain Campus, the SFPD and SFPU sites (Figure 4-3). Monthly stream sampling showed the lowest $\delta^{18}\text{O}$ values during the snowmelt season of April to June. Fall streams sampled on October 8th 2023, have overall higher maximum catchment elevations than the streams sampled on October 7th 2023, therefore the difference in $\delta^{18}\text{O}$ between these two sampling days can be attributed to spatial variation in baseflow isotopic signatures. This variation indicates differences in mean catchment elevation and maximum catchment elevation between the two fall sampling regions. Figure 4-8 displays a temporally variable relationship between $\delta^{18}\text{O}$ and mean/max catchment elevation. Summer and fall stream samples echoed precipitation sample's negative correlation between $\delta^{18}\text{O}$ and mean/max elevation, while winter stream samples show a weak positive correlation between these variables. Winter stream samples with high $\delta^{18}\text{O}$ but with high mean and maximum catchment elevations can be

attributed to input from reservoirs along the flow path, such as with the South Platte River. It is also possible the small standard deviation of winter stream samples is due to a pulse of precipitation from a large storm over the Front Range near the date of sampling.

Welch two-sided t-tests of $\delta^{18}\text{O}$ values between sampling events found no statistically significant difference between the summer streams and the fall streams, despite summer streams being dominated by snowmelt and fall streams being dominated by baseflow (Peterson et al. 2024). This supports previous work that shows the spring and summer seasons as the critical time for recharge in the mid-latitude arid and montane climates (Jasechko et al. 2014), resulting in baseflow-dominated fall streams reflecting the $\delta^{18}\text{O}$ of snowmelt-dominated summer streams.

5.1.3 Drivers of Groundwater Stable Isotope Variability

Groundwater stable isotope ratios showed very little temporal variability across municipal wells and residential wells (Figure 4-5). The stability of $\delta^{18}\text{O}$ values for these sampling locations has several potential explanations, including a narrow time interval of groundwater recharge, no recharge, or thorough mixing of resident groundwater with recent recharge. Previous studies have found little change in groundwater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values worldwide on interannual and interdecadal time scales, which along with the observed stability of monthly groundwater samples at each residential location in this study allows interpretation of well data with low sample frequency as a representative sample (Jasechko et al. 2014). The largest change in $\delta^{18}\text{O}$ of monthly groundwater samples was observed in the May sampling event for the MWD and MWU sites at MT-CSU and might be attributed to the influx of recharge from the melting snowpack in late April into May (Doebley 2022). Samples from the DBAS were sampled on two separate events and do not provide an adequate dataset for temporal variation analysis.

Spatial variability in stable isotope ratios between groundwater sampling locations was significant, with the highest values found in the deepest aquifers of the DBAS (Arapahoe and LFH) and the MWD well at MT-CSU (Figure 4-6). The high mean $\delta^{18}\text{O}$ of MWD is attributed to recharge from nearby evaporative wetlands in the mountain valley that contribute high $\delta^{18}\text{O}$ water to groundwater in the downstream portion of the valley (Doebley 2022). Origins of the high $\delta^{18}\text{O}$ of the water in the Arapahoe and LFH units of the DBAS are not well understood. It has been suggested that the high $\delta^{18}\text{O}$ of the deepest and oldest DBAS units are result of different climatic patterns during the LGM, resulting in overall higher stable isotope signatures of precipitation during the recharge period (Dutton 1994). However, Musgrove (et al. 2014) compared stable isotope values for the bedrock aquifers with age tracer results such as adjusted ^{14}C ages and ^3H values, and their lack of correlation indicated that the high $\delta^{18}\text{O}$ values are not representative of recharge during different climatic conditions. Most of their samples with heavier stable isotope values were from the southern part of the DBAS along the Palmer Divide, which suggests recharge to this basin region potentially being sourced from lower elevations or from the precipitation falling on the Palmer divide region, which had the second highest volumetrically weighted mean $\delta^{18}\text{O}$ of all precipitation sampling locations (Table 4-1).

The lowest mean $\delta^{18}\text{O}$ values of groundwater samples were found in the North Mountain Block Aquifer (Nederland and Sugarloaf) and the MWU and MWUD wells at MT-CSU. Seasonally, precipitation $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were found to be the highest in the summer and lowest in the winter, and a volumetrically weighted annual mean of monthly precipitation indicates the potential signature of groundwater recharge. At the completion of this study, a full year's worth of data for the Nederland precipitation sampler was not available, so no comparison can be made between the location's precipitation $\delta^{18}\text{O}$ values and the groundwater data due to the

temporal variability in precipitation data. However, there is a full year's worth of data for the MT-CSU precipitation sampler and comparing the volumetrically weighted $\delta^{18}\text{O}$ of yearly precipitation (-14.64‰) with the mean $\delta^{18}\text{O}$ of MWU (-16.54‰) and MWUD (-16.98‰) reveals a bias towards recharge from winter precipitation. This is consistent with currently understood recharge seasonality for this region and climate (Jasechko et al. 2014).

5.2 Denver Basin Aquifer System Isotopic Signatures

Groundwater $\delta^{18}\text{O}$ values of the upper units of the DBAS showed little spatial and temporal variability, with $\sigma < 1\text{\textperthousand}$ for the Alluvial, Dawson, and Denver Aquifers. Greater variability was observed in $\delta^{18}\text{O}$ values of the Arapahoe ($\pm 1.29\text{\textperthousand}$) and LFH ($\pm 1.63\text{\textperthousand}$). $\delta^{18}\text{O}$ signatures of each DBAS unit showed no statistical difference between the Alluvial aquifer and the Denver, Arapahoe, and LFH; the Denver and the Arapahoe; and the Arapahoe and the LFH (Appendix B). Increased pumping to all aquifers has increased inter-aquifer flow despite significant confining units (Paschke 2011, Musgrove et al. 2014), which is supported by the stable isotope data in this study. The Dawson has a statistically unique signature from other units of the DBAS, plotting much lower in $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ space (Figure 4-7). Groundwater from the older and deeper Arapahoe and LFH units have higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, suggesting a difference in where and when these aquifer units were recharged. The Dawson and Denver have lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values than the deeper units of the DBAS which suggests that recharge to these aquifers is derived from a source with a lower isotopic composition.

5.3 Stable Isotope Relationships between Surface Waters and Groundwaters in the Front Range and Denver Basin

The known mechanism of recharge to the DBAS occurs primarily through recharge to the alluvial aquifer from streams that enter the Plains, and then subsequently to the Dawson through direct seasonal contact between the alluvial and the Dawson (Paschke 2011, Musgrove et al. 2014, Cognac and Ronayne 2023). Understanding DBAS water to be a mixture of resident groundwater with recent recharge enables comparison of each unit's water stable isotope signatures with potential recharge sources, such as direct recharge via losing streams on the bedrock aquifer outcrops or via mountain-block recharge (MBR). The alluvial aquifers in the Denver Basin receive recharge via stream seepage (Cognac and Ronayne 2023), and this relationship is observed in Figure 4-7 between the alluvial aquifer stable isotope data and the summer stream stable isotope data. Summer stream samples were taken around peak flow, which would have the greatest flux of water into the Denver Basin. The t-test in Appendix B between these two water sources confirms no statistical difference in the $\delta^{18}\text{O}$ values of the two datasets. Another close relationship is observed between the fall streams and the Dawson (Figure 4-7). This could be attributed to fall streams contributing to recharge via stream seepage to the alluvial aquifer, and then to the Dawson, or the similarity could be attribute to both fall streams and the Dawson being derived from a similar mix of mountain block water and evaporative water sources. The stable isotope values of the south mountain block aquifer (Evergreen and Buffalo Creek wells) water samples plot very closely with winter streams. This relationship could indicate either a late-winter/early-spring seasonality of recharge to the mountain block crystalline aquifer, or major contributions from mountain block baseflow to winter streams. The Dawson water stable isotope data plots the lowest of all the DBAS units, indicating significant connection to waters with lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

5.4 d-excess of Front Range Surface and Groundwaters

The calculated parameter of d-excess can be a useful way to quantify and interpret effects of evaporation on various water types, and to track the evaporative signature through the hydrologic system (Dansgaard 1964). In Figure 5-1, a plot of d-excess vs. $\delta^{18}\text{O}$ compares the DBAS units and other measured water sources by providing a closer look at evaporatively effected waters and groundwater $\delta^{18}\text{O}$ values. A prominent relationship appears between the Dawson, the north and south mountain block residential wells, the CSU Mountain Campus upstream wells, winter streams, and alluvial aquifers. Despite the geographic disconnection of the CSU Mountain Campus from the DBAS, these upstream wells allow us to measure one of the many types of deep groundwater that exist in the Front Range. A linear relationship is seen between these components, indicating a “mixing line” between the lower $\delta^{18}\text{O}$ and higher d-excess mountain block derived water, and the higher $\delta^{18}\text{O}$ and lower d-excess evaporatively affected waters of alluvial aquifers and other evaporative streams across all stream sampling events. The Dawson sits along this mixing line (superimposed in pink), between both sources which strongly indicates it receives recharge from both. This data is not enough to determine the flux from these sources to the Dawson, or the seasonality of the recharge, but presents potential future work.

The second mixing line (superimposed in purple) in Figure 5-1 shows a relationship between the Arapahoe and Denver units of the DBAS, summer streams, the Franktown well and the alluvial aquifers. These points lying along the same mixing line may indicate a relationship between these surface water sources to the Arapahoe and Denver aquifers. The Franktown well is known to be drilled into the Dawson, yet it has an isotopically distinct signature from all other Dawson samples, showing spatial variability in stable isotope signatures within the same aquifer

unit. This distinct signal could indicate significant contributions of recharge from summer streams to this region of the Dawson. For this mixing line the Arapahoe aquifer unit is the highest d-excess endmember potentially contributing to the signature of the Denver.

The Laramie-Fox Hills (LFH) aquifer unit, along with the CSU Mountain Campus downstream well and the evaporative stream samples plot distinctly higher in $\delta^{18}\text{O}$ than all other sample groups. The MWD well samples showed evaporative character as compared to the MWU and MWUD wells in the same valley, as evidenced by its higher $\delta^{18}\text{O}$ values and lower d-excess than the upstream wells. The LFH aquifer unit shows a distinct signature from the other DBAS units, plotting far off the potential mixing lines.

5.5 Potential Sources of Recharge to the Denver Basin Aquifer System

Each unit of the DBAS displays a distinct mean stable isotope signature, with mean $\delta^{18}\text{O}$ values increasing with depth (Figure 4-7). The Laramie-Fox Hills aquifer has the highest $\delta^{18}\text{O}$, but also the largest $\delta^{18}\text{O}$ σ . The large spatial variability in sampling locations for the LFH could explain the variance, but the origins of the distinctly high $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of this aquifer unit remain uncertain. Previous literature cautiously attributes the high values of this aquifer unit to different climatic patterns in effect during the 10,000- to 30,000-year-old window of groundwater age (Dutton 1994). This study by Dutton in 1994 investigating the recharge sources and groundwater ages of the aquifers of the U.S. High Plains corroborates the groundwater ages from Novotny and Sanford using stable isotope data obtained from the δD of cellulose from local tree fossils ^{14}C dated to the known window of groundwater ages. These samples show higher δD values that correspond with the higher $\delta^{18}\text{O}$ values of the oldest confined aquifers of the High Plains, which includes the Laramie-Fox Hills aquifer unit. Musgrove et al. 2014 also suggests different

climate patterns at the time of recharge as the potential source of the LFH water but mentions that there is little correlation between the stable isotope values and the age-tracer results, which indicates that the heavier isotopic signature cannot be attributed to recharge during different climatic conditions. Additionally, age tracer results for the LFH had large uncertainties, partially due to high alkalinity values which can affect the interpretation of ^{14}C ages. With such uncertainties in groundwater age, it is possible to attribute the heavier isotopic signature of this unit to recharge at a lower elevation, through areas where the sedimentary unit outcrops on the easternmost extent of the DBAS in the Colorado Plains. This hypothesis could be tested by sampling meteoric and surface waters in the outcrop areas to look for similarities in isotopic signatures between them and LFH waters. Recharge from this outcrop zone that ranges over a large geographic extent has the potential to explain the spatial variability of stable isotopes in the LFH.

The Arapahoe aquifer unit plots as the highest d-excess end member on the purple mixing line in Figure 5-1. It shows very similar $\delta^{18}\text{O}$ values to the Denver aquifer, the summer streams, and the alluvial aquifer. The high mean d-excess value indicates very little evaporative character, and similar mean $\delta^{18}\text{O}$ values to streams and alluvial aquifers derived from Front Range meteoric water point to recharge via direct infiltration from Front Range streams. Spatial variation in the Arapahoe can be attributed to regional differences in stream isotopic signatures that recharged the aquifer.

In Figure 5-1 the Denver has lower d-excess and therefore more evaporative character than the Arapahoe, but it plots with nearly identical mean $\delta^{18}\text{O}$ and sits along the interpreted mixing line drawn in purple. This difference in d-excess between the Arapahoe and Denver units indicates

recharge from more evaporatively affected sources, such as summer streams and alluvial aquifers in addition to the same source that recharged the Arapahoe. Unlike between the Arapahoe and the LFH, there is no confining unit that covers the extent of the basin between the Arapahoe and the Denver (Robson, S. G., & Banta, E. R. 1995), allowing for inter-aquifer flow and contributing to the similarity of isotopic signatures between the two aquifer units. The t-test performed between the two aquifer datasets showed no significant difference between the two (Appendix B).

The Dawson aquifer plots distinctly lower in $\delta^{18}\text{O}$ than the other aquifer units and has lower d-excess than any of the other units as well. This indicates significant recharge from low $\delta^{18}\text{O}$ sources and evaporative sources such as basinal streams. Recharge is known to take place through seepage from the alluvial aquifer to the Dawson (Cognac 2023), but if this was the only source of recharge the Dawson would have a less distinct signal from the alluvial aquifer as is seen in Figure 4-7. Both Figure 4-7 and Figure 5-1 indicate a relationship between the Dawson, winter streams and mountain block groundwater. The Dawson must receive recharge from either winter stream infiltration and/or direct MBR, but it is difficult to determine which source is primary. The difference in potential recharge flux between the winter streams which only have that isotopic signature for a small portion of the water year as evidenced by data from the other stream sampling events (Table 4-2), and the known direct contact between the Dawson and the Front Range mountain bedrock helps to suggest that there is constant recharge flux from the mountain block. The pink mixing line in Figure 5-1 shows the Dawson lying between the alluvial aquifer signature and the CSU Mountain Campus Deep Well, which accesses deeper alluvial aquifer water that may be in contact with the Front Range crystalline bedrock aquifer. Using this bedrock well data as representative of the Front Range mountain block crystalline aquifer stable isotope signature, the relationship between February streams and mountain block water is clear.

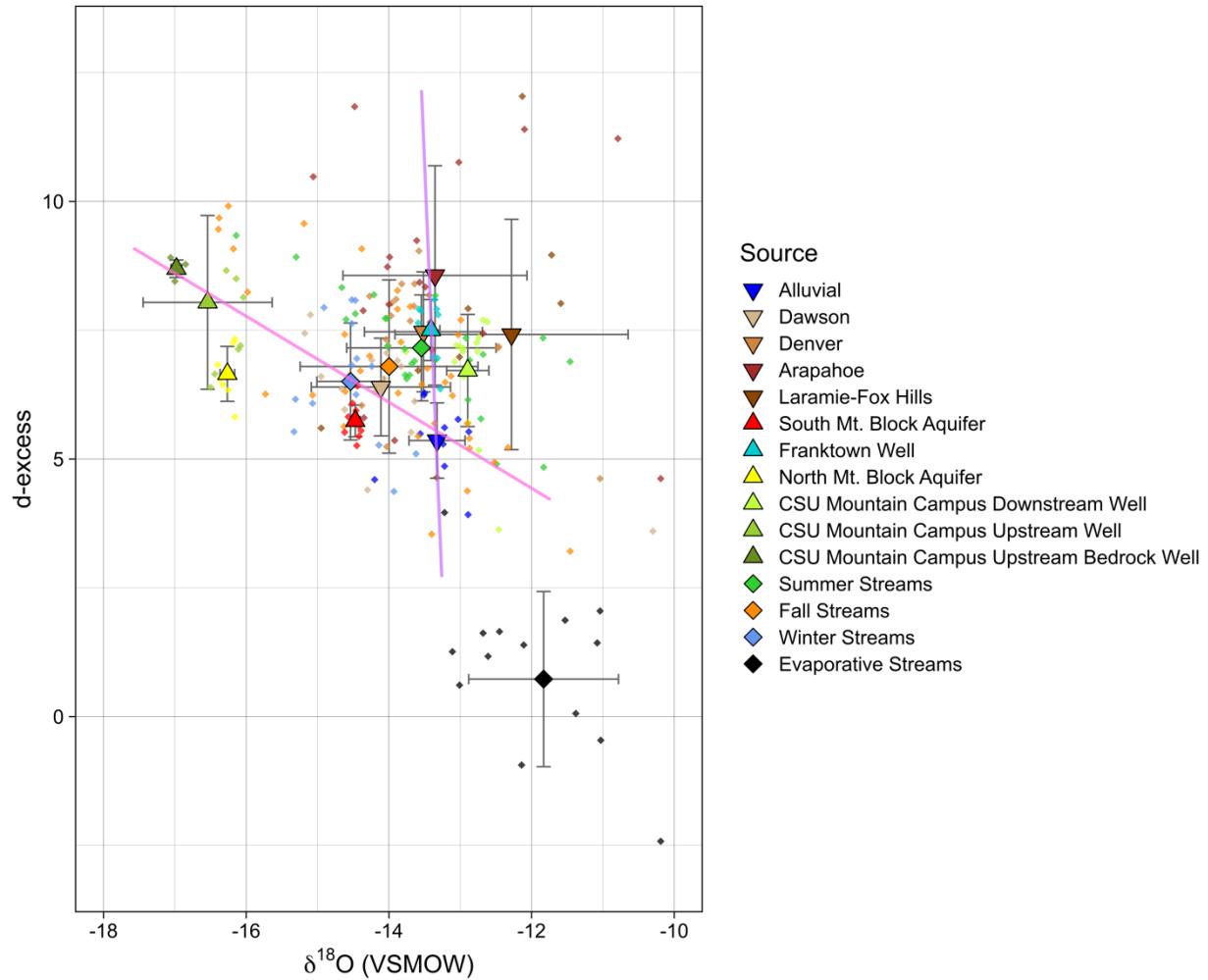


Figure 5-1. Plot of d-excess vs. $\delta^{18}\text{O}$ showing data from Town of Castle Rock municipal wells, residential wells, and all stream sampling events. The south mountain block crystalline aquifer is an average of the Evergreen and Buffalo Creek residential wells, and the north mountain block aquifer is an average of the Nederland and Sugarloaf residential wells. Error bars indicate 1σ . The superimposed pink and purple lines indicate potential mixing lines of mountain block water and evaporatively effected alluvial aquifer water within DBAS units.

CHAPTER 6 – CONCLUSIONS

6.1 Summary and Conclusions

This study collected and analyzed waters in the Front Range and Denver Basin Aquifer System (DBAS) for water stable isotope signatures of precipitation, surface waters, and groundwaters in the region. Sampling focused on the southwestern portion of the Denver Basin, around the Town of Castle Rock, where most municipal well DBAS samples were collected from. Monthly precipitation sampling at various locations in the mountains and basin allowed for observation and analysis of the spatial and temporal variability of precipitation in the region, and to determine its seasonal contributions to surface and groundwater through comparison of water stable isotope signatures. Characterizing primary sources of surface and groundwaters in the Denver Basin and Front Range is important for informing future water resource policy, such as surface water usage policy and future municipal well permitting and pumping limits.

Water stable isotope data were collected to characterize the spatial and temporal isotopic signatures of various geographic locations within the study region. Precipitation samplers were sampled monthly, with a total of four locations having $n > 10$ data points at the completion of this study. Three stream sampling events were completed, with one each in the summer, fall, and winter seasons. Catchment data was pulled from USGS Stream Stats for every stream sampling location. More stream sampling was completed concurrently with the Castle Rock Municipal well sampling. Sampling of the DBAS was enabled by collaboration with the Town of Castle Rock Water, sampling multiple municipal wells with spatial distribution around the Castle Rock region, and at various depths allowing characterization of the various units of the DBAS. Incorporation of data collected in the Musgrove et. al 2014 study of the DBAS was included in analyses to

increase the scope of data for the Alluvial, Dawson, Denver, and Arapahoe aquifer units, and as our singular source for water stable isotope data from the Laramie-Fox Hills aquifer unit.

Water stable isotope data from each sampling group were found to correlate in various ways temporally and spatially. Precipitation amount-weighted mean $\delta^{18}\text{O}$ values for collection sites with $n > 10$ showed a negative correlation with elevation, as predicted based on previous work establishing a decrease in $\delta^{18}\text{O}$ of precipitation as elevation increases. Precipitation $\delta^{18}\text{O}$ values for all sampling locations follow an annual cycle, with highest values collected in the summer and the lowest values collected in the winter. The signal of this effect is spatially variable, with collection locations at a higher elevation in the Front Range showing a delay in the increase of $\delta^{18}\text{O}$ values in precipitation in the summer months when compared to locations closer to the basin. Stream sampling events' $\delta^{18}\text{O}$ data show seasonal correlation with mean hypsometric catchment elevation and maximum catchment elevation, with the summer and fall sampling events showing a negative correlation and the winter sampling event showing weak positive correlation. Groundwater sample $\delta^{18}\text{O}$ data show correlation with geographic location and elevation with the lowest values appearing in mountain bedrock wells in the Fort Collins and Boulder areas of the Front Range, and the highest values appearing in the deepest parts of the DBAS, the Arapahoe and Laramie-Fox Hills aquifer units.

Water stable isotope data plotted in d-excess vs. $\delta^{18}\text{O}$ space plot along two interpreted linear mixing lines, the first showing the Dawson aquifer unit receiving recharge from the mountain block aquifer either by direct recharge or through winter stream seepage, and the evaporatively affected alluvial aquifer water, and the second showing the Denver aquifer and the Franktown well (southern region of the Dawson aquifer) receiving recharge from the summer streams and the alluvial aquifer. The Arapahoe aquifer unit plots the highest in d-excess along this

second (purple) mixing line. Potential sources of the higher d-excess water in the deeper aquifer units remain uncertain, with some previous research suggesting paleoclimatic atmospheric circulation patterns as the potential cause of higher $\delta^{18}\text{O}$. With previous work in the DBAS establishing groundwater ages of 10,000 to 30,000 years old and paleoclimate proxy data showing overall lower $\delta^{18}\text{O}$ values in precipitation from that time, further analysis is needed to determine the origins of these waters.

6.2 Recommendations for Future Work

Further sampling of the DBAS with an increase of spatial diversity would clarify findings in this study. With the established temporal stability of stable isotope data collected from residential wells, a sampling “survey” could be conducted of the entire basin and Front Range by obtaining single samples from many residential wells creating a robust data set for the DBAS and the mountain block aquifer, allowing for conclusions drawn in this study to be applied confidently throughout the region. Establishing a more extensive dataset for the Laramie-Fox Hills aquifer and collecting samples for geochemical analysis may reduce uncertainty in the groundwater age and origin. Longitudinal samples of streams in all four seasons would help enhance understanding of temporal variance in stream and alluvial aquifer dynamics, starting near the headwaters and following the stream until it joins with a major stem in the catchment. If feasible, a hydrogeological chemical tracer study would be useful in the geologic areas of direct contact between the mountain block bedrock aquifer and the Dawson aquifer, to confirm the connection seen in the d-excess vs. $\delta^{18}\text{O}$ plot.

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APPENDIX A
SAMPLING DATA

Table 1. List of sampling locations by water type with location information and number of samples.

Abbreviation	Location	Latitude	Longitude	Elevation (m)	# of Samples
Precipitation Samples					
CSU-MC	CSU Main Campus	40.576244	-105.085628	1523	31
MT-CSU	CSU Mountain Campus	40.568287	-105.587578	2758	30
FT	Franktown, CO	39.369981	-104.684299	2049	11
Buff_Crk	Buffalo Creek, CO	39.354490	-105.238397	2295	12
YankeeCreek-P	Evergreen, CO	39.614389	-105.437687	2466	3
Sedalia-P	Sedalia, CO	39.383326	-105.017628	1966	4
WPC-P	Woodland Park, CO	39.023004	-105.058892	2576	4
Reynolds-P	Sugarloaf Mountain, CO	39.993904	-105.485143	2548	4
Surface Water Samples					
PFC	Poudre, Fort Collins, CO	40.570249	-105.029064	1493	23
SC	Spring Creek, Fort Collins, CO	40.564492	-105.081900	1520	24
SFPD	South Fork of the Poudre Downstream	40.567840	-105.590687	2745	28
SFPU	South Fork of the Poudre Upstream	40.560663	-105.597772	2749	14
Groundwater Samples					
MWD/MW2	Mountain Campus Well Downstream	40.568028	-105.589964	2754	15
MWU/MW1	Mountain Campus Well Upstream	40.560273	-105.596831	2755	8
MWUD/MW1D	Mountain Campus Well Upstream Deep	40.560273	-105.596831	2755	5
FT_Well	Franktown, CO	39.369981	-104.684299	2049	9
BC_Well	Buffalo Creek, CO	39.354490	-105.238397	2295	9
YankeeCreek-G	Evergreen, CO	39.614389	-105.437687	2466	3
Cosper-G	Nederland, CO	39.993904	-105.485143	2548	4
Reynolds-G	Sugarloaf Mountain, CO	39.993904	-105.485143	2548	3

Table 2. List of number of groundwater samples by sampling event and aquifer.

Aquifer	# of Samples
Castle Rock Municipal Well Samples	
Alluvial	8
Dawson	9
Denver	9
Arapahoe	5
Musgrove et al. 2014 Samples	
Alluvial	2
Dawson	12
Denver	10
Arapahoe	12
Laramie-Fox Hills	10

APPENDIX B

WELCH TWO-SIDED T-TESTS

Table 1. Table of Welch two-sided t-tests, conducted in R. Each section indicates the comparison dataset, with the compared sets listed below each section. The highlighted p-values indicate statistical similarity between the two compared datasets. The lower the p-value, the greater the statistical significance of the observed difference. A p-value of 0.05 or lower is generally considered statistically significant.

Alluvial					
Water Samples	Estimate	Statistic	p-value	Low Conf. Int.	High Conf. Int.
Dawson	0.79	3.19	0.00	0.28	1.29
Denver	0.19	0.81	0.43	-0.30	0.68
Arapahoe	0.03	0.09	0.93	-0.67	0.73
Laramie-Fox Hills	-1.04	-1.96	0.08	-2.23	0.14
Summer Streams	0.22	0.93	0.36	-0.26	0.70
Fall Streams	0.67	2.78	0.01	0.18	1.16
Winter Streams	1.21	6.96	0.00	0.85	1.57
Castle Rock Streams	-1.20	-5.72	0.00	-1.70	-0.69
Franktown Well	0.09	0.66	0.52	-0.20	0.37
Buffalo Creek Well	1.12	8.94	0.00	0.83	1.40
Evergreen Well	1.24	9.60	0.00	0.95	1.53
Sugarloaf Well	2.97	21.83	0.00	2.67	3.27
Nederland Well	2.90	21.42	0.00	2.60	3.20
Dawson					
Water Samples	Estimate	Statistic	p-value	Low Conf. Int.	High Conf. Int.
Denver	-0.60	-2.04	0.05	-1.19	0.00
Arapahoe	-0.76	-2.00	0.05	-1.53	0.02
Laramie-Fox Hills	-1.83	-3.28	0.01	-3.05	-0.62
Summer Streams	-0.57	-1.94	0.06	-1.16	0.02
Fall Streams	-0.11	-0.39	0.70	-0.71	0.48
Winter Streams	0.42	1.73	0.09	-0.08	0.93
Castle Rock Streams	-1.98	-7.31	0.00	-2.57	-1.40
Franktown Well	-0.70	-3.23	0.00	-1.15	-0.25
Buffalo Creek Well	0.33	1.54	0.14	-0.12	0.77
Evergreen Well	0.45	2.09	0.05	0.00	0.90
Sugarloaf Well	2.18	9.92	0.00	1.73	2.64
Nederland Well	2.11	9.62	0.00	1.66	2.57
Denver					
Water Samples	Estimate	Statistic	p-value	Low Conf. Int.	High Conf. Int.
Arapahoe	-0.16	-0.44	0.67	-0.92	0.60
Laramie-Fox Hills	-1.23	-2.23	0.05	-2.45	-0.02
Summer Streams	0.03	0.10	0.92	-0.55	0.60
Fall Streams	0.48	1.67	0.10	-0.10	1.06
Winter Streams	1.02	4.35	0.00	0.54	1.50
Castle Rock Streams	-1.39	-5.30	0.00	-1.96	-0.82
Franktown Well	-0.10	-0.51	0.62	-0.54	0.33
Buffalo Creek Well	0.92	4.60	0.00	0.50	1.35
Evergreen Well	1.05	5.15	0.00	0.62	1.48
Sugarloaf Well	2.78	13.37	0.00	2.34	3.22
Nederland Well	2.71	13.05	0.00	2.27	3.14
Arapahoe					
Water Samples	Estimate	Statistic	p-value	Low Conf. Int.	High Conf. Int.

Laramie-Fox Hills	-1.07	-1.78	0.10	-2.36	0.21
Summer Streams	0.19	0.51	0.61	-0.57	0.95
Fall Streams	0.64	1.71	0.10	-0.12	1.41
Winter Streams	1.18	3.52	0.00	0.48	1.88
Castle Rock Streams	-1.23	-3.45	0.00	-1.97	-0.48
Franktown Well	0.06	0.18	0.86	-0.61	0.72
Buffalo Creek Well	1.09	3.47	0.00	0.42	1.75
Evergreen Well	1.21	3.84	0.00	0.54	1.88
Sugarloaf Well	2.94	9.26	0.00	2.27	3.61
Nederland Well	2.87	9.04	0.00	2.20	3.54

Laramie-Fox Hills					
Water Samples	Estimate	Statistic	p-value	Low Conf. Int.	High Conf. Int.
Summer Streams	1.26	2.28	0.04	0.05	2.47
Fall Streams	1.72	3.08	0.01	0.50	2.93
Winter Streams	2.26	4.25	0.00	1.07	3.44
Castle Rock Streams	-0.15	-0.28	0.78	-1.35	1.05
Franktown Well	1.13	2.18	0.06	-0.04	2.30
Buffalo Creek Well	2.16	4.18	0.00	0.99	3.33
Evergreen Well	2.28	4.41	0.00	1.11	3.45
Sugarloaf Well	4.01	7.72	0.00	2.84	5.19
Nederland Well	3.94	7.59	0.00	2.77	5.11

Summer Streams					
Water Samples	Estimate	Statistic	p-value	Low Conf. Int.	High Conf. Int.
Fall Streams	0.45	1.56	0.12	-0.13	1.03
Winter Streams	0.99	4.21	0.00	0.52	1.47
Castle Rock Streams	-1.42	-5.40	0.00	-1.98	-0.86
Franktown Well	-0.13	-0.65	0.52	-0.56	0.29
Buffalo Creek Well	0.89	4.43	0.00	0.48	1.31
Evergreen Well	1.02	4.98	0.00	0.60	1.44
Sugarloaf Well	2.75	13.16	0.00	2.32	3.18
Nederland Well	2.68	12.85	0.00	2.25	3.11

Fall Streams					
Water Samples	Estimate	Statistic	p-value	Low Conf. Int.	High Conf. Int.
Winter Streams	0.54	2.24	0.03	0.06	1.02
Castle Rock Streams	-1.87	-6.99	0.00	-2.44	-1.30
Franktown Well	-0.59	-2.77	0.01	-1.02	-0.16
Buffalo Creek Well	0.44	2.13	0.04	0.02	0.86
Evergreen Well	0.57	2.69	0.01	0.14	0.99
Sugarloaf Well	2.30	10.69	0.00	1.86	2.73
Nederland Well	2.23	10.38	0.00	1.79	2.66

Winter Streams					
Water Samples	Estimate	Statistic	p-value	Low Conf. Int.	High Conf. Int.
Castle Rock Streams	-2.41	-11.58	0.00	-2.91	-1.91
Franktown Well	-1.13	-8.73	0.00	-1.40	-0.85
Buffalo Creek Well	-0.10	-0.79	0.44	-0.36	0.16

Evergreen Well	0.03	0.20	0.84	-0.24	0.30
Sugarloaf Well	1.76	13.12	0.00	1.47	2.04
Nederland Well	1.69	12.65	0.00	1.40	1.97
Castle Rock Streams					
Water Samples	Estimate	Statistic	p-value	Low Conf. Int.	High Conf. Int.
Franktown Well	1.28	7.39	0.00	0.76	1.80
Buffalo Creek Well	2.31	13.68	0.00	1.78	2.85
Evergreen Well	2.44	14.15	0.00	1.91	2.96
Sugarloaf Well	4.17	23.48	0.00	3.65	4.68
Nederland Well	4.10	23.14	0.00	3.58	4.61