

GEOLOGIC AND HYDROLOGIC CONTROLS ON SPRING, STREAM,
AND GROUND WATER CHEMISTRY IN THE BIG CHICO CREEK
WATERSHED AND BUTTE BASIN, CALIFORNIA

A Thesis

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Master of Science

in

Environmental Sciences

by

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Carol Lynn Perkins

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DEDICATION

I dedicate this project and resulting interim discoveries to the Big Chico Creek Ecological Reserve and the following individuals instrumental in key phases of this study.

Dr. Paul Maslin, field scientist extraordinaire – without your prior fieldwork this particular project would never have lifted off the ground. Paul’s knowledge of the natural environment at the Reserve is second to none. I’m indebted to you for discovering and making accessible the springs in the BCCER, hosting exhilarating field excursions and for your keen handling of the “Amphibian.” I appreciate your willingness to share your insights about the geology and hydrology of the Reserve and for your wisdom regarding everything in the canyon.

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ABSTRACT

GEOLOGIC AND HYDROLOGIC CONTROLS ON SPRING, STREAM, AND GROUND WATER CHEMISTRY IN THE BIG CHICO CREEK WATERSHED AND BUTTE BASIN, CALIFORNIA

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The foothill and mountain reaches of the Big Chico Creek watershed have experienced little impact from human activities. The watershed encompasses physical and hydrologic characteristics ideal for water resource studies. Big Chico Creek traverses deformed strata assumed to be the principal recharge zone for the Tuscan Aquifer system. These strata comprise formations of the Cascade Province and the much older Great Valley Sequence. Of primary interest are the Chico and Tuscan Formations of which the later is the principal host rock for Butte Basin ground water found in the valley reach of this watershed. The underlying Chico Formation is considered the base of fresh ground water in the Butte Basin. Big Chico Creek is a spring fed stream that travels 45 miles from Colby Mountain to its confluence with the Sacramento River. The stream is hydrologically connected to the strata it dissects exchanging water and nutrients its entire length: alternating as an effluent and influent stream contingent on the physical and hydraulic

parameters of the rock it encounters; stream flow; and the elevation of the water table surrounding the stream. The creek often dries late in the water year, long before its confluence having lost its flow to valley sediments as ground water recharge.

Over 30 springs have been mapped in the Big Chico Creek Ecological Reserve within the foothill region of this watershed. The study of spring water yields a small window into the exploration of interactions between ground water and rock without expensive, exploitive processes. Investigating the controls on the composition of water is essential toward understanding source, flow mechanisms, and interactions of waters within a watershed. Current methods described in the literature use hydrogeochemical data as a tool for advancing watershed science. Little hydrogeochemical data exist for water from the Tuscan and Chico Formations in regional literature. Springs in the Big Chico Creek Ecological Reserve offer a unique opportunity to examine ground water quality from various host rocks in a setting relevant to controls on creek and aquifer water quality and explore recharge processes and interactions between surface and ground water for the valley aquifer system.

Previous reconnaissance work by earlier field scientists led to the location of 37 springs and the development of a database. These early, informal observations included the measurement of field parameters of water temperature, electrical conductivity, and pH for 25 of the springs. These data were instrumental in the selection of springs emanating from the different lithologic strata of the watershed. Tuscan, Chico, and Lovejoy Formation springs were sampled for standard field hydrologic parameters and major ion analyses. Interpretations concerning hydrologic and geologic controls that affect the hydrochemistry

of the watershed are be made by comparing reported data for Big Chico Creek and ground water from near-creek wells to spring water chemistry data.

Water chemistry was interpreted through graphical modeling techniques and numerical modeling. Collected spring water chemistry shows significant variations corresponding to bedrock lithology but little seasonal variation. Little evidence exists for vertical hydrologic connectivity between the Tuscan and Chico Formations from the formation springs sampled. Lack of connectivity appears to indicate that Chico Formation springs are fed by perched water, near-surface seepage, seepage from crevices and fractures or other forms of preferential flow. Tuscan Formation spring water appears to be young leading to the assertion that these springs discharge perched water or seepage from crevices and fractures. The ground waters of these two formations within the middle reach of the watershed may also be separated by strata that function as aquitards.

Reported creek water chemistry shows seasonal variations with a strong meteoric component and lower concentrations at high discharge. During base flow, Big Chico Creek is a mixture of discharge from the Tuscan and Chico Formations. Additional processes, which have not been identified in this study, occur within the watershed affecting the chemistry of waters discharging to the stream. Additional water sources not identified in this study, discharge to the stream during runoff. Reported ground water chemistry is similar to the Tuscan Formation spring end member and shows influence from dilute creek water under runoff conditions. Some reported ground water samples indicate influence from the Chico Formation.

CHAPTER I

INTRODUCTION

Big Chico Creek Watershed

The foothill and mountain reaches of the Big Chico Creek watershed have experienced little impact from human activities. The valley reach of this watershed is a ground water dependent system fed in part by Big Chico Creek. For many reasons, the physical and hydrologic characteristics of the watershed provide an ideal environment for water resource studies. Consider the geologic setting. Big Chico Creek dissects the primary formations of the Cascade Province. The structure of the Big Chico Creek valley landscape changes in vertical profile, width, and longitudinal gradients as the creek incises the different formations. The Tuscan Formation forms the varied topography of the creek canyons; and the stratified, shear cliffs as well as the buttes of the region. The cliffs are evidence of the textural and compositional changes due to varying deposition of this formation. The volcanogenic sedimentary deposits of the Tuscan Formation encompass principal freshwater aquifers. The Lovejoy Basalt creates a gorge within the terraces of the Big Chico Creek canyon known locally as Iron Canyon. Down cutting by Big Chico Creek has exposed the marine sediments of the Chico Formation. The Chico Formation is also a principal aquifer formation, but it is believed to contain connate waters of poor quality (Dudley, 2005). The Tuscan Formation is the primary water-bearing unit for parts of Butte, Tehama, and Glenn counties in the Northern Sacramento Valley. Aquifers exploited in the

Tuscan Formation are collectively known as the Tuscan Aquifer and referred to in this study as Butte Basin ground water.

The Tuscan Formation is a broad, constructional plain that covers a significant portion of the eastern foothills from Red Bluff to Oroville. Lithologically the Tuscan Formation is a stratified rock of massive, unsorted volcanic lahars interbedded with sedimentary strata of volcanic detritus and sandstones. Presence and thickness of the strata vary regionally west of the source and with depth or age of the rock. The Tuscan Formation has been described as a volcanoclastic fan apron (Sullivan and Brunkal, 2004). The mountain and foothill geomorphic units consist of the proximal and medial extents of this apron. The Tuscan Formation dips below the alluvial sediments at the eastern margin of the Northern Sacramento Valley where the distal extents of the fan apron are located deep beneath the Sacramento River.

Traveling NE along the ridges of the upper reach of the Big Chico Creek watershed, the lahar layers thicken with corresponding decreases in the sedimentary strata. These proximal lahars are less resistant to weathering and contain a greater amount of poorly sorted clasts and less fines enabling continuous infiltration from the snowpack that resides on these ridges late into spring. Resulting snowmelt provides two functions: (1) a recharge source in the less confined strata, and (2) acts as the driving, reactive force in the weathering and soil formation processes (Feth et al. 1964b). In the valley, Tuscan Formation strata consist of 48 to 78% sedimentary interbedding, with increasing water-bearing capacity toward the Sacramento River (Doukas, 1983). The lahars of the Tuscan

Formation fine as the deposits were laid to rest, increasingly confining the water as it slowly migrates west (Doukas, 1983; CDM, 2001; Brunkal, 2004).

The Chico Formation is a unit of the Great Valley geomorphic province that comprises the compressional trough of the Central Valley. It lies unconformably beneath the Tuscan Formation and dips more steeply than the overlying rocks. The Chico Formation laps onto the metamorphic bedrock and Sierra Nevada basement rocks at the eastern boundary of this study area (Doukas, 1983). Where the creek has exposed the Chico Formation, the cross sectional profile of the creek valley broadens and is not as steep. The Chico Formation is thought to hold connate water; ancient seawater trapped in the pores as lithification of this formation began. As such, the Chico Formation is estimated to be the lower boundary of the fresh water aquifer system of the Butte Basin (Dudley, 2005).

Consider the hydrologic setting. Big Chico Creek watershed is home to a rich spectrum of springs and seeps. Considerable attention has been placed on locating and exploring the diverse spring environments found in the Big Chico Creek Ecological Reserve (BCCER). Informal field observations of 37 springs by earlier field scientists enabled this study. These springs offer a unique opportunity to examine ground water quality from various host rocks in a setting relevant to controls on creek and aquifer water quality and recharge processes for the Tuscan Aquifer system. The hydrochemical characteristics of these springs have not been previously studied in detail and little information about the springs has been published prior to this study.

Big Chico Creek is a spring fed, fourth order perennial stream (derived from the National Hydrography Dataset for the watershed and after Strahler's 1957, modified

Horton method for stream order). It is one of many tributaries along the eastern margin of the Sacramento River hydrologic region, which produces more than a third of the runoff on which Californians rely. Most of the streams entering the valley lose water to shallow aquifers as a source of recharge (Hull, 1984). The stream is a basin-scale marker; a hydrologic mixture of all processes and lithologies encountered throughout the watershed (Hooper et al., 1990; McGuire and McDonnell, 2010). In this study, precipitation in the form of rain and snow is referred to as meteoric water and carries a dilute chemical signature acquired in the atmosphere as well as from dry deposition. Meteoric water has not had time to react with rocks and soils.

Precipitation that falls on a watershed contacts the minerals of soil and parent rock and chemical weathering occurs. Chemical weathering is the dissolution of soil and rock minerals releasing major elements to the runoff and soil water through gas-water-rock interactions. Biological processes and organic constituents also play an important role in the resulting inorganic chemistry of water, but are ignored in this study. Weathering changes precipitation from water with a dilute chemical signature to water that carries a signature reflecting the geochemical composition of the drainage basin (Miller, 2002). This chemical signature depends on the path the water takes through soil and rock, how long the water resides in contact with the soil or rock, and the subsequent processes that may cause the chemistry to change. Seasonal variations in rainfall and runoff are reflected as temporal variations in the stream water chemistry and flow. In this study, runoff refers to the precipitation that has reacted with near surface environs including snowmelt and soil water contributions and has been enriched in the dissolved aqueous species $\text{CO}_{2(\text{aq})}$.

Within the conifer woodlands of the upper watershed, numerous first order channels are evidence of a deeply incised landscape that maintains hydrologic connectivity with the hillslope. Geomorphologic evolution of the watershed has given birth to many springs or surface expressions of ground water (Glynn and Plummer, 2005). Springs are evidence of the intersection of the ground surface with ground water. Ground water may be perched on rock that is impermeable or the expression at the water table of a regionally large body. Discharge occurs where the permeability of the rock changes (Feth, 1964a). Springs found at higher elevations should reflect young, dilute water (waters emerging from the Tuscan Formation, for example). Springs found at lower elevations may experience longer residence times and flow paths reflecting ground water that is older and more concentrated than most water in the watershed (Rademacher et al., 2001). Waters emerging from the Chico Formation might represent older ground water in the Big Chico Creek watershed. Reported flow data for Big Chico Creek is a combination of meteoric water, runoff, and spring discharge.

For this study, Butte Basin is described as the terminal basin of the Big Chico Creek watershed. Reported water chemistry records for 28 wells that tap this aquifer system with proximity to Big Chico Creek were assessed to explore possible connections between the creek, host rock, and ground water. Interpretations of geologic controls evidenced through formation water chemistry from springs and seasonal or hydrologic controls evidenced through creek water chemistry provide the context for interpretation of the interactions between stream and ground water.

Consider the hydrogeochemical setting. Exposures of the Chico and Tuscan Formations within the study reach of this project facilitate chemical characterization of the formation waters. The structure, mineralogy and extent of these formations are reflected in differences in their water chemistry, producing chemically distinct waters. Differences in ground water chemistry in the Sacramento Valley correlate strongly with the recharge waters of the different geomorphic units on the valley margins (Hull, 1984; Dawson, 2001). Springs provide access to the study of the hydrochemical nature specific to the rocks from which the springs emanate. However, spring water can represent a mixture of precipitation and soil water that has been in contact with the aquifer rock. The creek is a chemical marker for the entire watershed, reflecting changes in seasonal runoff patterns and base flow sources during the dry season. Butte Basin ground water provides further evidence of the evolution of water chemistry from dilute precipitation to waters that have reacted chemically with the gases and minerals in the surrounding soils and rocks.

Two Essential Supplies

Ground Water

Ground water is a significant water source for Californians meeting 40 to 60% of all domestic, industrial, and agricultural demands as well as water needs for managed ecosystems during dry years (DWR, 2012). In Butte County, California, approximately 80% of domestic needs are met by ground water. Globally, ground water comprises nearly 99% of all usable freshwater for human consumption (Gleick, 1993), but only a small fraction is accessible. Ground water is hidden in compacted and cemented sediments and rock. The type of rock and its physical characteristics as well as the geologic structure and

stratigraphy of a given location complicate our understanding of the extent and volume of a ground water body. Ground water sources and flow paths cannot readily be mapped similarly to that of surface water: rivers, streams and canals. Measuring the amount of precipitation and snowpack that infiltrates and percolates to feed ground water is a complex process with many variables. The hidden nature of ground water and the myriad physical, chemical, and biological factors and interactions create great research opportunities.

Snow

Recharge is the process by which surface water replenishes ground water. Natural recharge comes from streams, direct precipitation or snow melt. Some water infiltrates soil and rock and percolates to depth through the unsaturated zone; becoming ground water when it reaches the water table. A water table defines a subsurface region below which all pores and open space in soil and rock are filled with water. Water that remains at the surface evaporates, is taken up by plants, or becomes surface runoff eventually returning to the oceans. Ground water moves vertically and horizontally due to gravitational heads (or pressure) and follows a path of least resistance in response to lithologic and stratigraphic differences as well as antecedent water conditions. Recharge may occur locally at time scales of less than a year or regionally, where water may move great distances at depth below the water table to recharge a terminal basin at time scales of ten years to tens of thousands of years.

Recharge occurs across the geographical continuum of a watershed, from mountain regions to the basin. The mechanisms of recharge vary as the lithology, stratigraphy, and structure of the regional rock vary. The timing and type of source water

supplying recharge is also critical and varied. Several studies have shown that snowmelt constitutes a significant portion of ground water recharge in the western USA (Earman et al., 2006; Liu et al., 2004). California will experience changes to both surface and ground water supplies as climate change alters the distribution and volume of the Western snowpack (Earman and Dettinger, 2007). Understanding the recharge mechanisms of mountain and basin zones and how water moves through the watershed are critical components to protecting water quality and quantity. Natural recharge to the Northern Sacramento Valley ground water basin has not been estimated (Moran et al., 2005).

Ecological Importance of Big Chico Creek

The Big Chico Creek watershed is not only hydrologically and geologically extraordinary, the stream provides extraordinary habitat for many endemic species of the Central Valley. More than half the length of Big Chico Creek (24 miles) is home to several species that are themselves critical components of the hydrogeochemical system of this watershed. Anadromous Salmonidae spend more than half their lifecycle in the Pacific Ocean consuming and absorbing valuable nutrients. As these beneficial carriers return to their freshwater habitat – their nursery, spawning, and eventual burial grounds – these nutrients and hydrochemical markers are left to benefit the entire watershed. Big Chico Creek has historically been accessible to three vulnerable species: the Central Valley fall and spring run Chinook (the later is state and federally listed as threatened); the state and federally listed, endangered late-fall run Chinook; and the federally listed, threatened Central Valley steelhead (CDFW, 2013). Their numbers have plummeted by ten-fold since the mid 20th Century. Passage to the upper watershed was blocked in the early 1900's due

to natural disintegration of the Lovejoy Basalt in the Iron Canyon reach. Constrictions continue to plague fish passage especially during low flow (DWR 2005; Katz et al., 2012). As climate patterns change the timing, amount, and form of precipitation in this region, flow and water temperature changes will exacerbate threats to fishery populations in this stream.

Characterization – An Important First Step

This study characterized six springs based on elevation, distinct lithology, and water chemistry. The springs mapped for this study lie in the middle reach of Big Chico Creek Watershed, within the boundaries of the Big Chico Creek Ecological Reserve, California State University, Chico. The Reserve comprises 3950 acres surrounding 4.5 miles of the creek from ridge to canyon bottom. In prior work, field scientist mapped and sampled twenty-five springs in the Big Chico Creek watershed. Field parameter data collected includes temperature, pH, electrical conductivity, and oxidation-reduction potential. This study publishes the results of that earlier work.

Spring water and creek water chemistry was used to assess the reported chemistry of Big Chico Creek for seasonal variations and solute and base flow sources. Results were compared with reported chemistry of Butte Basin ground water to begin characterizing potential recharge mechanisms, sources and timing. Exploring the mechanisms that govern stream flow and the sources that contribute to this flow and understanding how streams may respond to various stresses – climate change, nutrient transport, and pollution – is an essential first step. Protection of surface and ground water resources depends in part on the degree to which these issues are understood.

Researchers have used the measurement of aqueous bulk chemistry for nearly a century to understand the source of constituents in natural waters as well as the source of water within a watershed. In their 1964 study, Feth, Roberson, and Polzer postulated that understanding the where, how, and why behind water quality was mandatory for the advancement of industry and technology dependent on water (Feth et al., 1964a). These prevalent questions remain today. Consider the questions of ‘where.’ From what place or source does water and the dissolved chemical constituents it carries come? Is water in the form of snow or rain? Consider the questions of ‘how.’ In what manner and by what means does water evolve as it moves from source to point of sampling? What flow paths does water follow? Does water infiltrate or run off? Consider the questions of ‘why.’ What are the phenomena and processes behind the presence of water and the chemical constituents it carries? What are the lithologic and hydrologic controls affecting water chemistry? What are the amounts and timing of new and existing water? What chemical reactions between water, minerals, and gas might take place?

Objectives of this Study

Investigating aqueous major ion chemistry permits a better understanding of source waters, water-rock interactions, and interactions between waters within a watershed. This is a study of the aqueous geochemistry of springs in the Big Chico Creek watershed and an interpretation of the relevant geologic and hydrologic controls on water quality and source. This study extends this information to explore connections between stream, springs, and ground water in the Tuscan aquifer system. This study addresses the questions raised

above and lays the groundwork for future projects where data limitations and constraints prevail.

Big Chico Creek is a perennial stream; therefore its hydrochemistry should reflect water that discharges to the stream (i.e., spring water) during base flow and a mixture of spring water and meteoric water over the remainder of the water year. If the principal aquifer system in the Tuscan Formation near Chico, California is locally recharged by Big Chico Creek, then Butte Basin ground water should reflect a mixture of creek water and host rock water. This study addresses: (1) characterization of Chico Formation and Tuscan Formation water as components of Big Chico Creek stream water and Butte Basin ground water; (2) speciation assessment, based on major ion chemistry and formation mineralogy of the watershed, that provides clues to the solutes released and adsorbed through contact with water; and (3) analysis of mixing relationships between host formation waters, stream, and ground water.

This study should lead to a better understanding of the origin and recharge processes of ground water with proximity to Big Chico Creek. Characterizing the hydrologic and geologic controls within this watershed provides an important analog to enhance water resource research for all other streams dissecting the Tuscan Formation along the eastern margin of the Northern Sacramento Valley.

CHAPTER II

BACKGROUND AND PHYSICAL SETTING

Literature Review

This study focuses on the geochemical characterization of the Chico and Tuscan Formation waters to identify and quantify differences in water chemistry due to varying lithologic and hydrologic controls. It begins the process of understanding ‘the where,’ ‘the how,’ and ‘the why’ behind the presence of water in the Big Chico Creek watershed, and more specifically the presence of inorganic chemical constituents in those waters.

Spring Water Studies

Feth et al. (1964a,b), early workers in the Sierra Nevada Mountain range, collected and analyzed compositional data of snow and spring water. Feth et al. (1964b) provide one of the first studies of snow chemistry in the western U. S. mountains in an effort to better understand ‘the where’ and to quantify baseline reserves in atmospheric water. The 1964b study remains the definitive characterization of snow in the Sierra Nevada. Feth et al. notes that the chemical signature of snow is regionally varied and hypothesized that constituent sources include the Pacific Ocean and continental dust. A greater understanding of where water comes from is a critical tool for resource protection as climate and land use changes play an ever-increasing role affecting source and timing within the hydrologic cycle.

Feth et al. (1964b) concluded that chemical diversity is lost to a great extent when snowmelt makes first contact with the lithosphere. The recorded snow and spring data Feth et al. (1964a,b) collected 1957–1958 provides a baseline for comparison of long-term changes due to various environmental and anthropogenic forcings. Erman and Erman (1992) collected spring data (1982 through 1990) before, during and after a 6-year drought for three watersheds in the northern Sierras to examine the physical and chemical relationships on species distributions and explore possible impacts from drought on distribution changes and species persistence. Based on published data and analysis from Feth et al., 1964a, Erman and Erman conclude that the 21 springs they measured are typical of Sierra Nevada spring water and provide additional data for long-term trend analysis. The variables of climate, preferential rock and mineral weathering along flow paths and stratigraphical differences between the western and eastern slope springs are evident. They note differences in response to changes in snowpack that highlights the complexities of assessing regional flow paths and recharge mechanisms.

Guler and Thyne (2004) used geochemical data from spring, surface, and well water collected in the southeastern Sierras over an eighty-year period to examine changes in water quality and determine processes affecting the chemistry of the water. The Guler and Thyne study examines the controls on water chemistry over a regional scale, similar to Feth's studies (1964a,b), and identifies the significance of characterizing local lithologic and hydrologic differences qualifying local processes and flow paths.

In the 1964a report, Feth et al. document results of their comprehensive hydrogeochemical study of 56 Sierra Nevada springs. The 1964a study combines their

analysis of snow and spring water as a first step to hypothesize hydrologic and geologic processes controlling the mineral content of snow water as it evolves after first contact with the lithosphere in granitic terrain. The Feth et al. (1964a) study considers the ‘how’ question by quantifying weathering and water-gas-rock interactions. In 1967 Garrels and Mackenzie generated the seminal work on the hydrologic and geologic controls on perennial and ephemeral spring chemistry through inverse mass-balance analysis of spring waters of the Sierra Nevada. Their study was a thorough examination of the ‘why’ made possible by the extensive dataset collected by Feth et al. (1964a,b), which includes both aqueous phase chemical composition for snow and springs and solid phase chemical composition of the soil and rock mineralogy. Garrels’ and Mackenzie’s work advanced Feth’s first steps and provides a greater understanding of the how and the why behind the presence of dissolved constituents in Sierra Nevada spring waters.

Stream Chemistry Studies

Holloway and Dahlgren (2001) studied event-based stream water chemistry of four small Sierra Nevada catchments with differing lithologies. They measured major ion chemistry for the streams, soil water, and bulk precipitation over a two-week sampling period. Chemical analysis of bulk precipitation includes dissolved constituents derived from wet deposition as well as dissolved loads derived from dry deposition. Holloway and Dahlgren hypothesized that Central Valley windblown dust was responsible for a significant chemical overprint over oceanic sourced constituents. They found all major ion measurements were enriched over reported precipitation-weighted mean concentrations from a sub-alpine meadow station in the Sierras as well as a station located on the western

margin of the Central Valley. Sodium and calcium measurements were significant even when compared against reported values from the National Atmospheric Deposition Program (NADP) site in Davis, CA. The increase in calcium concentrations that Holloway and Dahlgren (2001) measured matches a trend documented by Feth et al. (1964b) of calcium enrichment in precipitation as storm events progress eastward.

Major ion chemistry has been used to separate hydrographs to qualify stream water sources during precipitation or snowmelt events. The aqueous chemistry of streams is representative of watershed scale controls. Early researchers employed mixing models for hydrograph separation studies that relied on chemical signatures of two sources or end members: event water and pre-event water. Genereux et al. (2002) collected major element data of surface and shallow ground water from several sites in an effort to quantify interbasin water movement. Genereux's work focused on a number of small watersheds within the topographic boundaries of La Selva Biological Station, Costa Rica over a 4.5-year period. They sought a better understanding of interbasin transfers to improve water budget calculations throughout the water year. As such, they collected water samples during periods of the year when the stream was in base flow. Water samples collected defined two hydrologically and chemically distinct water sources. Local water source end members consisted of springs and shallow ground water. A deep bedrock ground water source from a spring outside of the La Selva watershed boundaries comprised the second source end member.

Examining contributing sources to stream flow alongside the hydrochemical properties of stream water provides additional insight into the processes and possible

timescales responsible for water and chemical movement within a catchment (Rademacher et al., 2005). In two separate papers, Christopherson et al. (1990) and Hooper et al. (1990) sought a greater understanding of the origin of pre-event water to improve data derived from hydrograph separation analysis for catchment scale acidification modeling. The authors of these studies coined the term End Member Mixing Analysis (EMMA) and found a minimum of three sources comprise the pre-event water that exhibits control of stream chemistry during events. Genereux et al. (2002) found two end members satisfactorily explained all variability in water samples they collected. The efforts of Christopherson et al. and Hooper et al. (1990) sought an improved understanding of ‘the where’ behind water and chemical constituents within the geographic regions of their respective studies; their work was also a commencement of modeling ‘the how.’

Local Ground Water Studies

Hull (1984) studied existing sets of data for 671 chemical analyses from wells throughout the Sacramento Valley collected at different times during the later half of the 1970’s. The original data were collected and analyzed by the Geological Survey (Fogelman, 1975, 1976; Fogelman and Rockwell, 1977) and California Department of Water Resources through unpublished efforts. Hull mapped the chemical signatures of the wells against water table elevations and the geomorphic units described by Olmsted and Davis (1961) to initially define six hydrochemical facies. Just as a geologic facies describes rock with specific characteristics and reflects conditions of formation such as environment and processes, hydrochemical facies define chemically distinct bodies of ground water. Differences in hydrochemical facies of the Northern Sacramento Valley reflect recharge

sources, differences in lithology and mineralogy of the host aquifer rock as well as the rock water encounters during movement. Prior to the characterization this thesis includes, control mechanisms on water chemistry due to geology and hydrology of the Butte Basin have not been explored. Glynn and Plummer (2005) indicate that recharge sources exhibit the primary hydrologic control on ground water chemistry. Hull (1984) divided Butte Basin waters into facies based on the perceived recharge source, stating in essence that recharge waters from the Cascade province are different than those of the northern extent of the Sierra Range. Dawson (2001) similarly concludes that recharge sources provide the greatest control on the resulting chemistry of Butte Basin ground water.

The Hydrogeologic Setting

The Big Chico Creek watershed is a large, 72.4 square mile (188 km²), elongated drainage basin that lies within the southern extent of the Cascade Province. The watershed consists of 8 sub-basins that form a parallel drainage pattern consistent with the sloped structure of the primary formations found in this watershed (Figure 1). The foothills of the Cascade Range lie east of the City of Chico. The Cascade Province overlies the basement rock of the Sierra Nevada batholiths. Big Chico Creek flows southwest 45 miles from headwaters that begin as a series of springs on the southwest slope of Colby Mountain (Tehama County). Colby Mountain is a NE trending ridge with an approximate elevation of 5400 feet at latitude 40.146° N and longitude 121.522° W.

Project Setting

The Big Chico Creek Ecological Reserve (BCCER) is located in the canyon of Big Chico Creek. To the west of the BCCER the Tuscan Formation comprises the principal

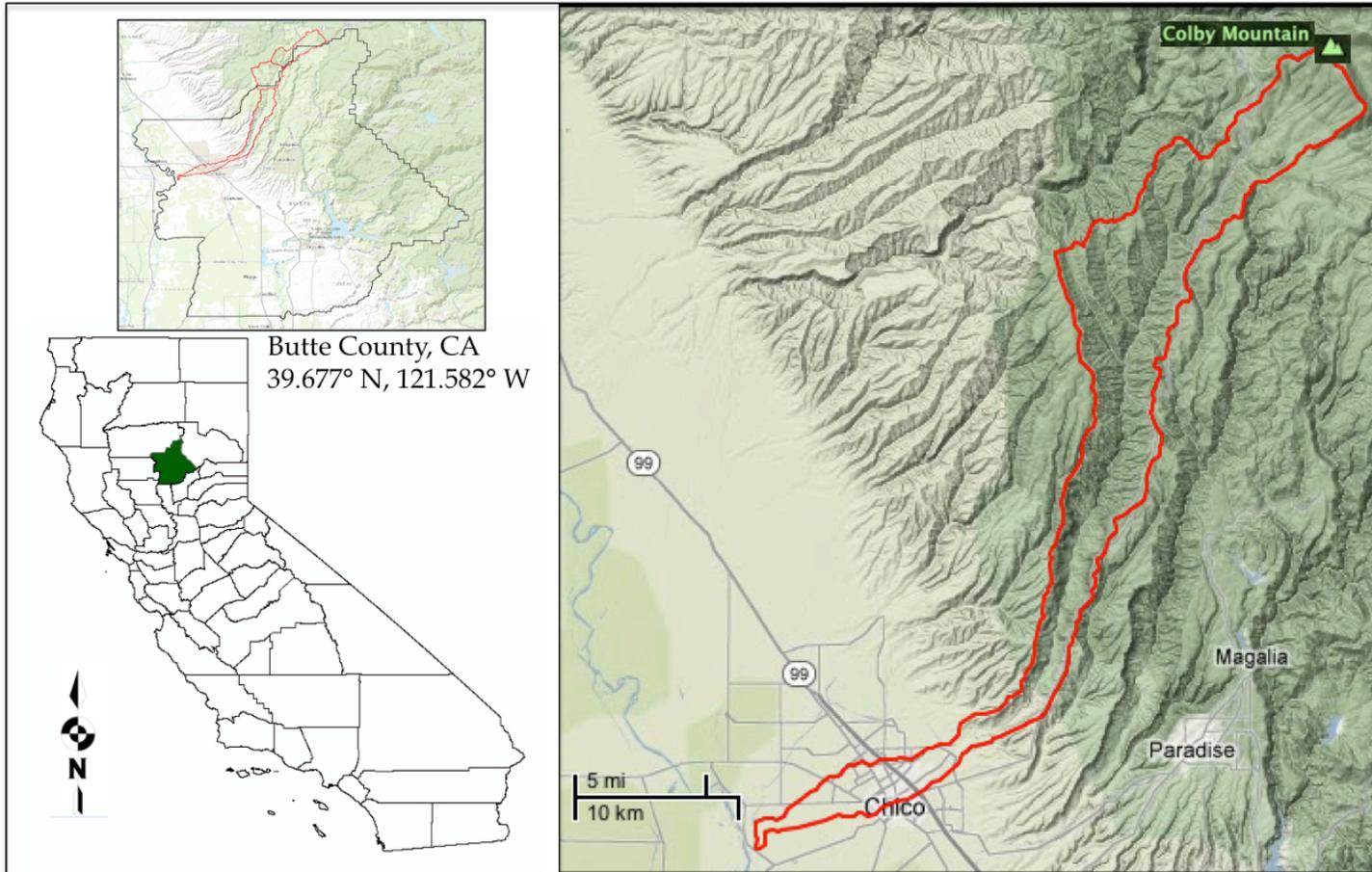


Figure 1. Big Chico Creek Watershed, Butte County, California. Source: Data sources for maps from Esri Base maps, 2013: Topographic and USA Topo Basemap; GeoSpatial Data Gateway, 2010, Watershed Boundary Dataset for HUC# 1802015705, CA: <http://datagateway.nrcs.usda.gov> (March 2013); Cal-Atlas, 2009, California and county boundaries: <http://www.atlas.ca.gov> (March 2013).

water supply aquifer in the Butte Basin. Headquarters for the Reserve are 10.5 miles NE of the City of Chico at latitude 39.847° N and longitude 121.713° W. West of the Reserve, Big Chico Creek flows past the only stream gage on the creek at elevation 274 feet, latitude 39.769° N and longitude 121.783° W. Flow data and some water quality data have been collected at this site since the early 1950's. The creek continues through the city of Chico to its confluence with the Sacramento River at an elevation of 120 feet.

Climate and Precipitation Patterns

The region experiences a Mediterranean climate with most precipitation occurring November through April. Precipitation ranges from approximately 80 inches falling annually in the mountain region to 24 inches of rain in the upland and valley reaches. Most precipitation in the mountainous upper reaches falls as snow (Maslin, n.d.).

Publically available precipitation data for this watershed was evaluated for three precipitation stations located in the middle reach of the watershed: Paradise Fire Station (PRD) located on the southern ridge of the watershed at 1750 feet elevation; DeSabra (DSB) on the southern ridge east of the PRD station at 2710 feet elevation, the highest station in the watershed; and Cohasset (CST) near the northeastern ridge at 1600 feet. Springs that form the headwaters of Big Chico Creek are found at an approximate elevation of 5400 feet.

Reported monthly-accumulated precipitation totals were retrieved for the 10-year period of 2000-2010 from the California Data Exchange Center (CDEC). The 3-month averages before the March 2005 sampling were low compared to the 10-year averages, but high for March. However, more than 2 inches of rain fell on average across the watershed

during the first quarter than the second. Rainfall totals for the month of June were higher than the average at the three stations but less than 3 inches of rain fell during the month and no rainfall was recorded for July while the 3-month averages prior to the July 2005 sampling were high. August and September were also typical dry months in 2005.

Review of precipitation data for 10 years from three stations that sit on the boundary of the Big Chico Creek Watershed reveal that March precipitation is historically within 30% of the mean average rainfall for each station. July is the start of the dry season with historical average rainfall of 0.06 inches. September concludes the dry season with a historical average rainfall of 0.36 inches.

Geomorphic Units

Big Chico Creek watershed encompasses four distinct physiographic regions: mountains, canyons (and a gorge), uplands or foothills, and valley. The mountain region is assumed to be the primary recharge zone for the Butte Basin (Harwood et al., 1981; Doukas, 1983). Data collection for this project took place in the canyon uplands. Reported data evaluated for this project were collected in the alluvial plains and fans province of the Northern Sacramento Valley (Olmsted and Davis, 1961). Both units are similar in that the Chico Formation is the primary basal unit and thus has an effect on the reported chemical signature of the surface and ground waters.

Uplift created a westward dipping, asymmetrical structure referred to as the Chico Monocline in the northern two-thirds of the Tuscan Formation. Here, the Tuscan Formation dips sharply below Quaternary sediments of the Sacramento Valley. Southern exposure of the Tuscan Formation differs in that buttes can be seen extending west far from

the toe of the valley and foothills. Strata of the Tuscan Formation in the upper and central reaches of the watershed dip 2 to 3 degrees westward. The longitudinal gradient of Big Chico Creek is steeper than the dip of the Tuscan Formation exposing more permeable strata of the formation in the creek bed. This exposure may provide a path where ground water discharges to the stream, increasing flow and maintaining base flow. Bending at the monocline structure increases the dip of the Tuscan Formation to 15 degrees. In the lower reaches of the watershed, the Tuscan Formation dips steeper than the creek bed. Here, stream water may be lost to the more permeable strata as recharge to the Butte Basin aquifer system (Doukas, 1983). In addition, the deformation created fractures in the Tuscan Formation that tend to run normal to the longitudinal direction of the creek bed providing potential infiltration pathways. DeMucha (2006) found the Tuscan Formation less indurated in areas immediately surrounding fractures, increasing recharge potential where the creek flows across these fractures.

Canyon Uplands

The medial deposits of the Tuscan Formation dominate the geomorphology of this region. It is extensively eroded with southwest flowing streams forming deeply incised canyons and ridges of resistant lahar deposits (Figure 2). The underlying Lovejoy Basalt and Chico Formation can be found exposed only in the canyons. The Chico Formation is estimated to dip 10 degrees southwest in this region. Outcrops of the Lovejoy Basalt are visible throughout the study reach. The Lovejoy Basalt is prominent further downstream where Iron Canyon stands out as a prominent locality. The Tuscan Formation is a source of

sediments for both the alluvial plain and fan deposits in the valley (referenced in other works as the Victor Plain, e.g., Hull, 1984).

Valley Unit

The distal deposits of the Pliocene Tuscan Formation underlie the recent Pleistocene and Holocene alluvial sediments of the Quaternary period. The shallow Quaternary deposits are poorly sorted, limiting capacity of the alluvial aquifer (Hull, 1984). The sedimentary rocks of the Tuscan Formation fine westward (Doukas, 1983). The fines of the distal deposits of the Tuscan Formation add to the confined nature of the aquifer system (e.g. Butte Basin) in the valley. California Department of Water Resources (2003) estimates that this formation maintains a constant thickness throughout the study area of this project but begins to thin west of Chico. The Tuscan Formation unconformably overlays the late Cretaceous Chico Formation.

The flood basin landscape of the Northern Sacramento Valley is hydrologically linked to the streams flowing from the Cascade Range to the Sacramento River. The source areas for Butte Basin ground water are varied; however, a 2005 study by LLNL indicates that deep percolation rarely occurs within the confines of the valley floor with the exception of shallow recharge in near-stream localities. Much of the ground water throughout the Northern Sacramento Valley is more than 50 years old with reported paleowaters greater than 20,000 years of age (Dawson, 2005; Moran et al., 2005; and Hull, 1984).

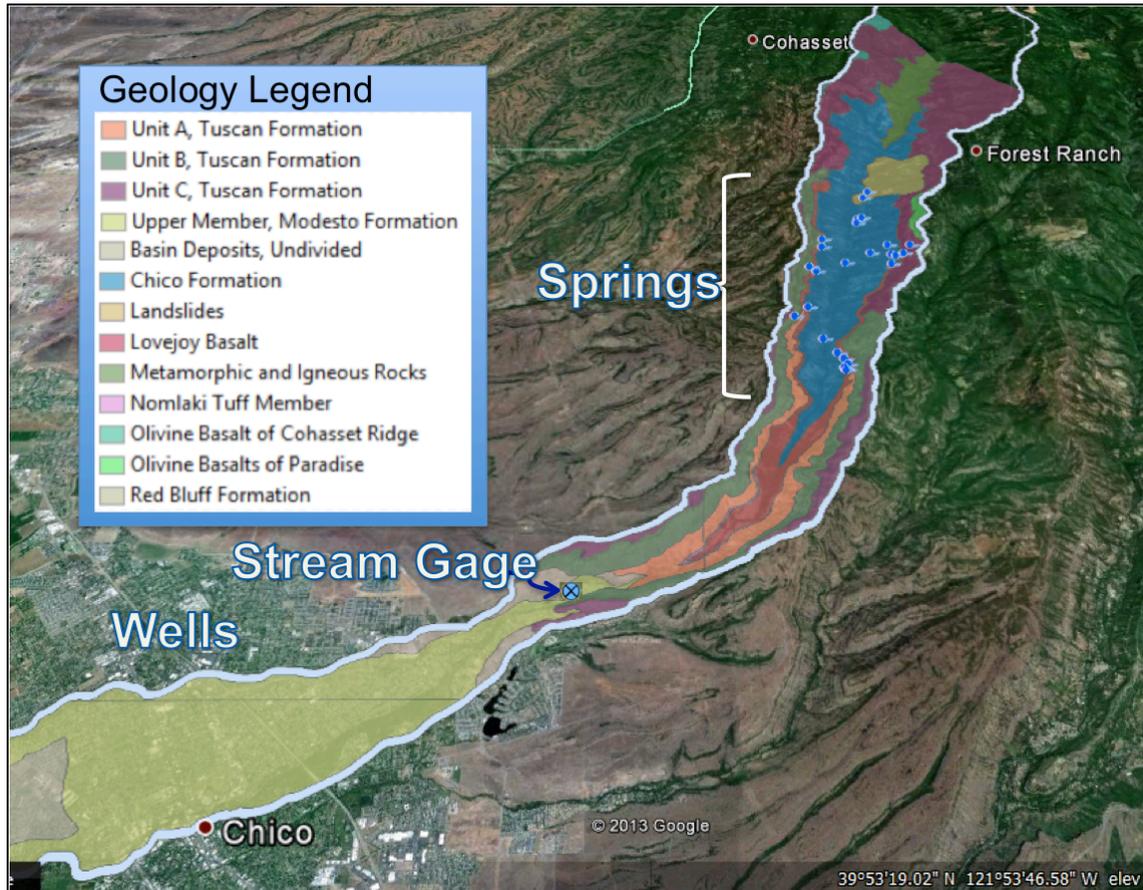


Figure 2. Springs, Wells, and Geology of Study Reach. Source: Data sources for map from Google Earth (March 2013); GeoSpatial Data Gateway, 2010, Watershed Boundary Dataset for HUC# 1802015705, CA: <http://datagateway.nrcs.usda.gov> (March 2013); Cal-Atlas, 2009, modified digital reproduction of the "Geologic Map of the Late Cenozoic Deposits of the Sacramento Valley and Northern Sierran Foothills, California," Edward J. Helley and David S. Harwood (USGS Publication MF-1790, 1985): <http://www.atlas.ca.gov> (March 2013).

Geology

Big Chico Creek exposes three geologic formations found in the Reserve:

Marine sandstones of the 80–85 Ma Chico Formation are overlain by the ca. 14 Ma

Lovejoy Basalt, which is overlain by 2–4 Ma Tuscan Formation, Figure 3. The Pliocene

Tuscan Formation and Miocene Lovejoy Basalt and subsequent Quaternary valley deposits

originate from the southern extent of the Cascade Range volcanic province (Harwood et al., 1981).

Tuscan Formation

The Tuscan Formation was created over 1.8 M years as layers of Pliocene age volcanic mudflows and fluvial sediments flowed toward and solidified in the Sacramento Valley. The surface extent of the Tuscan Formation begins near Lake Almanor and dips southwest plunging under fluvial Quaternary deposits at the Chico Monocline (Doukas, 1983). The Tuscan Formation is exposed along the eastern edge of the Northern Sacramento Valley for approximately 65 miles. The southern extent begins roughly 8 miles north of Oroville, CA and can be found in outcrop in the Dry Creek watershed southwest of the town of Paradise. The southern boundary loosely follows the West Branch of the Feather River to the northeast. The outcrop extends northward beyond Red Bluff, CA near the Inks Creek anticline (Harwood and Helley, 1987). The formation is found to extend in the subsurface south to the Sutter Buttes and west beyond the Sacramento River (Harwood et al., 1981; Doukas, 1983; Harwood and Helley, 1987).

Lithologically the Tuscan Formation formed as three very distinct units with varying numbers of lahar and sedimentary beds. The Nomlaki Tuff underlies the oldest, basal Unit A and the Ishi Tuff separates Unit B from the youngest deposits of Unit C. Sourceward or eastward, the formation is thicker and contains coarse-grained, volcanoclastic sediments with an estimated thickness of 1800 feet. The proximal sediments are poorly sorted, ungraded, matrix supported mudflows and coarse-grained sediments. Volcanic glass is abundant in both the mudflow and tuff deposits. Unit C, the upper most

and youngest member, was formed as a single lahar composed of 70% basalt and 30% andesite rock. This rock unit defines the western most ridgelines throughout the foothills in this region (DWR, 2003; Doukas, 1983).

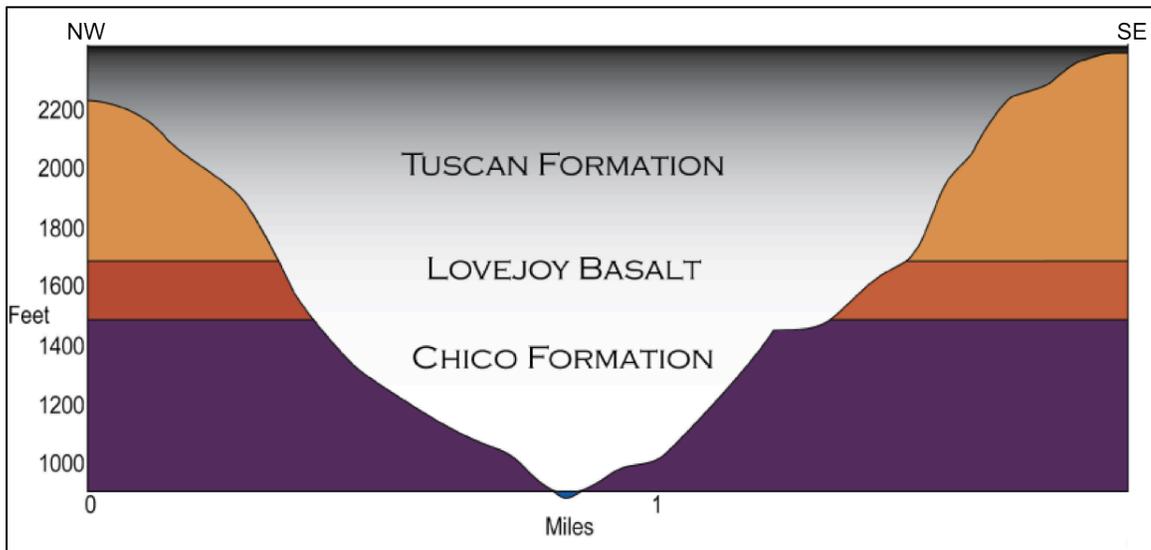


Figure 3. Conceptual Cross Section of Big Chico Creek. Source: Data source for profile created using Terrain Navigator Pro, ©MyTopo. A Trimble Company, (November, 2005).

The BCCER exists within the medial deposits of the volcanoclastic fan, where fluvial deposits of volcanic detritus are reported to begin. Doukas (1983) describes Unit B as eight andesitic lahars interbedded with sedimentary deposits comprising 48% of the rock composition. Fluvial strata include sands, gravels and conglomerates. Doukas identifies one massive basalt lahar and no sedimentary beds in his description of Unit C.

Unit A also formed as a single lahar with 78% of the unit composed of sedimentary deposits. Andesite is the predominant rock comprised of hypersthene, augite, and olivine minerals. Less than 10% of the Tuscan Formation consists of dacite as a rock

type. The lahars of the Tuscan Formation thin to the SW with a corresponding decrease in resistance to weathering of the matrix material that comprises 50 to 80 % of the rock, but this is highly variable. The grain size of the rock matrix ranges in size from clay to very coarse, sand size particles. Amorphous silica is the primary cementing agent, with traces of calcite present (Doukas, 1983).

A solid-phase composition analysis has not been completed for this formation. Harwood et al. (1981) identified the Tuscan Formation as strata deposits of volcanic breccia of hornblende, andesite, quartz, chert, greenstone, slate, and serpentine. Doukas (1983) performed a modal analysis on rock samples from a locality very near the Reserve. Primary mineral assemblages include plagioclase, olivine, clinopyroxene, orthopyroxene, hornblende, and magnetite. A more recent study describes the Tuscan Formation as consisting of plagioclase rich volcanic sandstones with mineral assemblages indicative of an intermediate or mafic igneous source rock similar to andesite (Brunkal, 2004).

Lovejoy Basalt

The Lovejoy Basal is an early Miocene highly fractured lava flow. Some exposures show distinct conchoidal weathering surfaces. The rock consists of mafic microcrystalline to extremely fine-grained, dense minerals (Harwood et al., 1981). The Lovejoy Basalt is believed to emanate from the same source of the Tuscan Formation. It is hypothesized that the basalt flow filled erosional depressions; while exposure of this formation is intermittent, its presence is extensive (Doukas, 1983). The intermittent nature of the Lovejoy Basalt creates well construction and pump performance problems and may be the source of black sands often reported in well logs reported to be the Tuscan

Formation. Maximum thickness of the Lovejoy Basalt is estimated to be 65 feet (DWR, 2000).

Chico Formation

The Chico Formation is a fossiliferous marine sandstone of granitic, plagioclase and alkali feldspar sediments. Doukas (1983) describes the Chico Formation as poorly to well indurated with calcite as a cementing agent forming an 'open matrix.' It contains lenticular beds of pebble to cobble sized conglomerates with minor siltstone. Conglomerate clasts are rounded to well-rounded consisting of chert, quartz, quartzite, granite and greenstone. Uplift that formed the Chico Monocline created a steeper westward dip within the Cretaceous Chico Formation than that of the younger, unconformable, overlying complex. Maximum estimated thickness of the Chico Formation is 2130 feet and thins eastward (DWR, 2000; Doukas, 1983; Harwood et al., 1981).

CHAPTER III

SPRING DESCRIPTIONS AND DATA SOURCES

Introduction to Spring Data

Prior to this project, reconnaissance efforts to map springs of the Big Chico Creek Ecological Reserve (BCCER) in 2001 through 2003 yielded clues to the varied hydrogeology of the reach. Spring water temperature, pH, oxidation-reduction potential (ORP), and electrical conductivity (EC) data were collected in the field. Spring elevation, location (latitude and longitude) and formation type were logged for 16 springs during these early efforts. Relationships and correlations between formation, elevation, water temperature, pH, ORP and EC were sought by graphing bivariate data (Cresswell, 2005).

For this project, reconnaissance of the BCCER in 2004 yielded more spring locations, bringing the total to over 37 (Figure 4). The locations and elevations were logged for these latest springs, but equipment failures prohibited field parameter data collection, and remote locations of many springs limited return trips. Many of the springs exist on the west side of the creek, opposite the entrance to the Reserve, which can be crossed safely only when discharge is low. Field parameters and elevation data indicate that 18 springs emanate from the Chico Formation, four from the Lovejoy Basalt, and only three springs appear to flow from the Tuscan Formation. The six springs studied in detail for this project are highlighted in Figure 4 below.

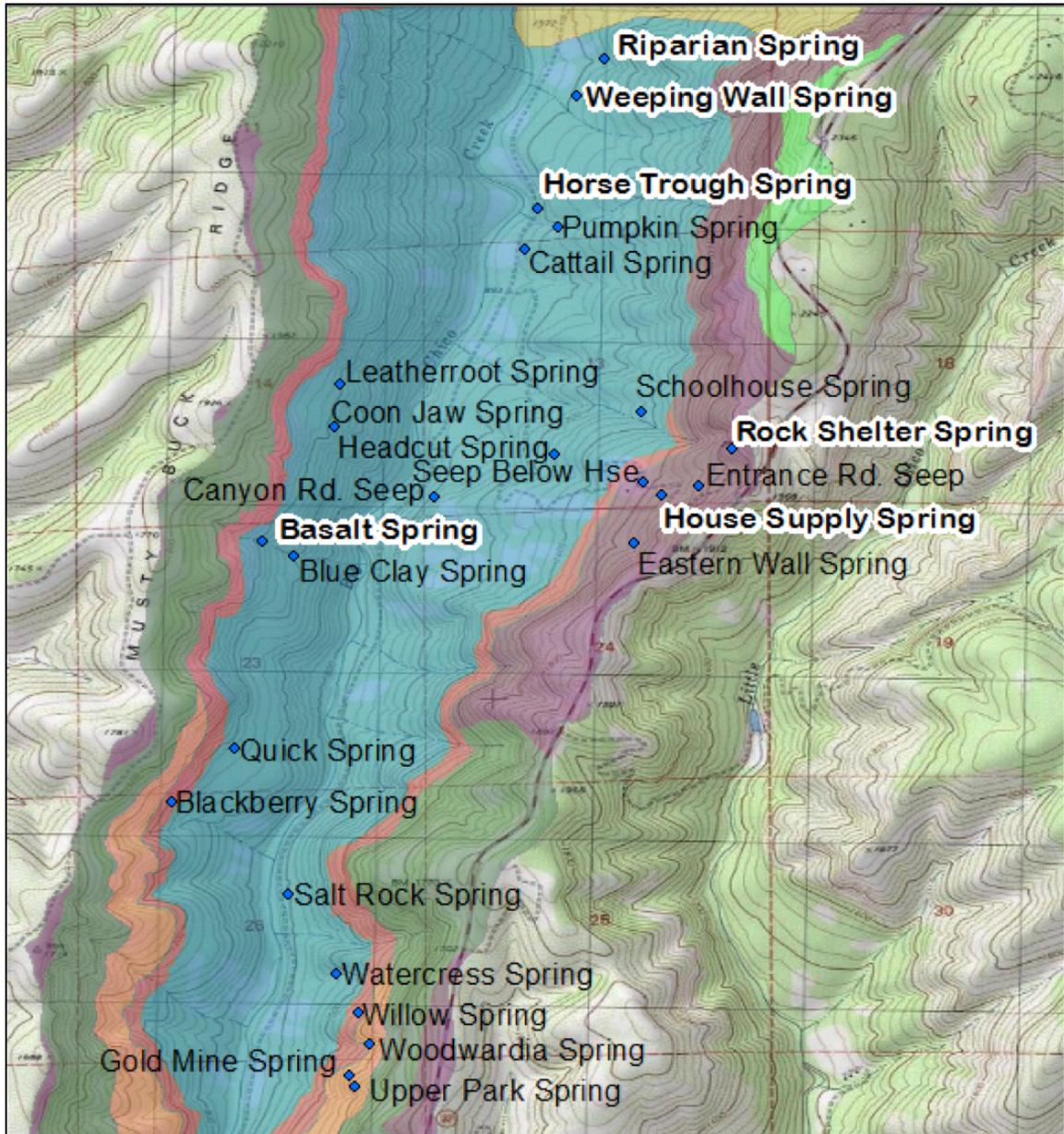


Figure 4. Spring Location Map. Source: Data sources for map from GeoSpatial Data Gateway, 2010, Watershed Boundary Dataset for HUC# 1802015705, CA: <http://datagateway.nrcs.usda.gov> (March 2013); Cal-Atlas, 2009, modified digital reproduction of the "Geologic Map of the Late Cenozoic Deposits of the Sacramento Valley and Northern Sierran Foothills, California," Edward J. Helley and David S. Harwood (USGS Publication MF-1790, 1985); <http://www.atlas.ca.gov> (March 2013).

This study characterizes the chemical changes as water moves through the Big Chico Creek watershed. Reported data were downloaded for precipitation in the form of snow. Existing datasets for Big Chico Creek and public supply wells in the terminal basin of the Big Chico Creek watershed were gathered to explore the lithologic and hydrologic connections between surface and ground water. Spring data were collected for this study at the end of March, and early July and September 2005.

Tuscan Formation Springs

Three of the springs located to date emanate from the Tuscan Formation based on elevation, measured field parameters, and exposed lithology. Elevations for these springs range between 1390 to 1670 feet. Only two of the springs, House Supply Spring and Rock Shelter Spring actually flow from the formation rock, while the others are seeps that pool in the soil. House Supply and Rock Shelter Springs were chosen as collection sites for this project and were sampled during March and July 2005.

House Supply Spring

The House Supply Spring occurs at a small, excavated opening in the Tuscan Formation outcrop. It appears to be a fracture that was exploited as a water supply (Figure 5). It remains as the sole supply of water to the residence at the Reserve. The spring is located in a steep section of the southeast wall of the Big Chico Creek canyon at 1575-foot elevation. The overlying rock is well vegetated and rises at a 35% slope to a resistive ridge at 1970 feet. The entrance is approximately 6.5 feet wide by 5 feet tall and appears to make a bend about 10 feet from the opening. Visible fractures exist in the walls of the excavation. The entire visible opening appears to be damp, with no specific source for the water pooled

at the base of the opening. Spring water for analysis was collected from this pool. The author did not explore beyond the entrance of the mined opening.



Figure 5. House Supply Spring.

Rock Shelter Spring

Rock Shelter Spring flows within a large opening in an outcrop of the Tuscan Formation as shown in Figure 6 and 7. The spring is located at the back of a cave carved into the Tuscan Formation. The cave is near the top of the canyon on the southeastern rim at 1624-foot elevation and lies below a thick layer of volcanoclastic sediments of the formation known as Unit C. With respect to the formation, the spring locality is very



Figure 6. Rock Shelter Spring.

different from the clast-dominant locality of House Supply Spring. The rock opening is over 20 feet deep and approximately 35 feet wide and height within the cave is approximately 8 feet. Some fracturing exists in the solid rock wall where algal mats have formed, and water seeps into the cave from numerous locations leaving evaporite deposits or precipitates as evidence of their long-term existence. The spring location is indicated by the darker rock coloring second from left at the back of the cave in Figure 6. Spring water was collected for analysis from a small pool at the base of a seep with the most abundant flow. Figure 7 provides greater detail of the spring and sampling site.



Figure 7. Sampling Rock Shelter Spring.

Areal imagery surrounding this spring location shows considerable exposed rock and little vegetation. Using the difference in elevations from Google Earth at the base of the cave and for the rock overlying the cave entrance indicates greater than 30 feet of overburden and a 50% gradient from cave opening to ridge where the elevation is 2050 feet. Imagery also shows that the overlying rock is a resistive material constituting a ridge very different than the downslope soils supporting vegetation or the grass-covered slopes surrounding this ridge. Rain aggregates on this ridge and falls across the cave opening as runoff during the wet season. It is possible that weathering exposed soils and rock surrounding this ridge conducive to infiltration and the percolating water feeds this permanent spring.

Chico Formation Springs

Seventeen of the springs located appear to emanate from the Chico Formation based on elevation, measured field parameters, and exposed lithology. Elevations for most springs range between 754 to 1288 feet. One seep exists at a much higher elevation, common with some of the Tuscan Formation springs at 1486 feet. The Chico Formation is thicker than the Tuscan Formation and considerable exposure exists in the study reach of Big Chico Creek canyon (Figure 2 and 4).

Three springs were chosen as collection sites for this project during March and July 2005. Each of the selected springs offers insight into the hydrologic and geologic controls at play. Horse Trough Spring exists at a roadcut in a steep section of the canyon. Its location rests 1300 vertical feet below a residential development on a ridge over a 0.75 miles east of the spring. Riparian Spring rests in the middle of a terrace close to Big Chico

Creek. Weeping Wall Spring exists on the bank of a small tributary near its confluence with Big Chico Creek.

There is some evidence supporting a hypothesis that Chico Formation aquifers store connate waters and as such are saline (Ryley, 1974; Maslin, n.d.). While Chico Formation springs have concentrations higher than other freshwater in Big Chico Creek watershed, water quality does not nearly approach concentration levels indicative of seawater. Most water collected and analyzed that leads to the connate water hypothesis, originates from deep wells in the middle of the Northern Sacramento Valley (Dudley, 2004). These are waters with potentially long flow paths and residence times.

Horse Trough Spring

The Horse Trough Spring exists at a roadcut in a steep section of the southeast wall of the Big Chico Creek canyon. The spring is located at 899-foot elevation at the base of the roadcut. Overlying rock is well vegetated, over 1300 feet thick and rises at a 36% gradient to a 2215-foot ridge more than 0.75 miles east. Water seeps from the Chico Formation into a trough approximately 25 feet long by 4 feet wide. Samples were taken at the break in the algal bloom (Figure 8) that covered most of the pooled water at the time of sampling in 2005. The extent of pooling fed by seepage from this spring is shown in Figure 9. Water samples were collected at this location under the consideration that fresh, abundant spring water was entering the trough here. Horse Trough Spring was chosen as a sampling site as a possible expression of the vertical connectivity between the Chico Formation and overlying Tuscan Formation.



Figure 8. Sampling Location of the Horse Trough Spring.

Riparian Spring

The Riparian Spring was found in a dry channel on a southeast terrace of the Big Chico Creek canyon, (Figure 10). The spring is located at 1037-foot elevation. The channel was investigated far upstream for other signs of flow, and no other water was found. No evidence of recent flow through the dry channel exists either. The Riparian Spring was chosen as a sampling site as a possible indicator of mixing between infiltrating, dilute rainfall and the more saline waters thought to exist in Chico Formation aquifers.



Figure 9. Sampling Horse Trough Spring.

Unclassified Springs

Water from two other springs was collected for major ion analysis. The Basalt Spring was chosen as a site thought to produce water emanating from the Lovejoy Basalt. Weeping Wall Spring appears to originate from a thick outcrop of the Chico Formation.

Weeping Wall Spring

The Weeping Wall Spring flows from a thick outcrop of the Chico Formation at the base of overlying soil and colluvium along a 10-foot section of cut bank at the confluence of a small perennial tributary with Big Chico Creek. This spring is located at



Figure 10. Riparian Spring.

971 feet above sea level. Water was collected from this spring in March and July 2005 for major ion analysis. This spring was found dry on a subsequent sampling trip in November 2005.

Basalt Spring

The Basalt Spring emanates from a basalt outcrop, but water pools in soil. This spring is located at 1391-foot elevation. Water was collected from this spring in September 2005 for major ion analysis.

Reported Chemical Data: Big Chico Creek

In 1974, W. E. Ryley published a thesis on the hydrology and geochemistry of Big Chico Creek. Ryley's work provides a compilation of over 20 water quality Bulletins for Big Chico Creek, California spanning the years 1952 through 1971. The United States Geological Survey (USGS) and the Department of Water Resources (DWR) produced these reports. Ryley's thesis contains 207 records organized by month and year, comprising discharge (Q) in cubic feet per second (cfs); concentration values for the major ions, nitrate, and boron; electrical conductivity, and pH. Sampling occurred throughout the year at varying discharge rates. Not all parameters were measured for each sampling period. Sulfate has the smallest measurement set and values exist primarily for samples collected in May and September.

Reported Chemical Data: Ground Water

Data were compiled from 1985–2000 Department of Water Resources (DWR) ground water quality records (DWR, 2005) for production wells within the City of Chico. Of the 77 records, 53 contained at least one measurement for a major ion. These 53 records represent 28 individual wells of which 10 comprise the bulk of the data. The other 18 wells were sampled only once during the recorded period. On average, water quality measurements were taken by DWR four times annually between 1985 and 1992, and biennially starting in 1994. However, measurements taken during the four years between 1989 and 1992 constitute 45 of the 77 records compiled for this study. Only two SiO₂ measurements were recorded between July and December for all years of record. No measurements were reported for the month of May.

Reported Chemical Data: Precipitation

Precipitation chemistry data were obtained from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) for Lassen Volcanic National Park (NADP, 2012). Appendix D describes the data analysis pertaining to this study. The major ion concentrations for Lassen precipitation do not include measurements for HCO_3^- and SiO_2 . Feth et al. (1964b) compiled and averaged chemistry data for more than 20 snow samples across various sites on the western slope of the Sierra Nevada. Feth's data provide a complete set of constituents as used in this study. Snow cores from individual sites were collected multiple times over a two-year period (1957-1958) regardless of event timing. Feth's concentrations are much greater than the NADP/NTN concentrations from Lassen. Feth did not normalize concentration measurements with precipitation volumes. Snow was sampled that had accumulated over time or had just fallen, but precipitation events and amounts were not recorded. The difference in magnitude (one or two orders) between Feth's data over the NADP data, which represent dissolved concentrations of wet deposition only, can be attributed to Feth's collection methods and indicates the importance of dry deposition to constituent contributions. Particulates resting on or in snow through wet and dry deposition react quickly with the frozen water resulting in concentrations that are much greater than dissolved solute concentrations present in the precipitation itself. The increase in dissolved concentrations of major ions from dry deposition varies depending on presence of vegetative cover, deposition conditions, and location. Williams and Melack (1997) estimate that dry deposition accounts for a wide range of dissolved nitrogen and sulfur inputs to forested catchments.

CHAPTER IV

METHODOLOGY

Introduction

This project looks at the hydrologic and geologic controls on major ion chemistry of spring, creek and ground water in the Big Chico Creek watershed. Current methods described in the literature use hydrogeochemical data as a tool for advancing watershed science. Geochemical data sets exist for creek water and ground water from municipal wells with proximity to Big Chico Creek in the valley. Little hydrogeochemical data exist for water emanating from the Tuscan and Chico Formations in regional literature that illustrate the connections between these important host aquifer formations and the creeks presumed to be the principle recharge sources. This project focuses on new data from springs thought to be markers of source water for both the stream and ground water. Springs emerging from Tuscan and Chico Formations in the middle reach of the Big Chico Creek watershed were identified that reflect the unique lithology of each formation. Spring waters were sampled for physical and chemical variables (major ions and standard field hydrologic parameters).

Spring Hydrochemical Data

Springs were classified from field assessments of the surficial geology and elevation, and crosschecked against the Chico Monocline geologic map (Harwood et al.,

1981). The Chico Formation is dominant along the creek banks in this reach. Where outcrops often indicated otherwise, it was determined that they were remnants of landslides or colluvium of overlying formations. For detailed study, two springs emerging from each of the Tuscan and Chico Formations were selected. The Weeping Wall Spring was also of interest as a spring interpreted to flow through colluvium and soil that overlies an impermeable layer of the Chico Formation. Springs were also chosen based on accessibility enabling sample collection from all springs in one day.

On March 31, and July 18, 2005, field data and water samples were collected for laboratory analyses from Rock Shelter Spring and House Supply Spring (Tuscan Formation springs) and Horse Trough Spring and Riparian Spring (Chico Formation springs) and Weeping Wall Spring. Paul Maslin later found a spring that appeared to emanate from the Lovejoy Basalt Formation and named it Basalt Spring. On September 8, 2005 water samples and field parameter data for Basalt Spring were collected. Three samples from each spring were collected and transported to an independent lab for analysis as delineated below. The rate of discharge for all springs is low and flow was not calculated or estimated. Flow contribution to Big Chico Creek cannot be quantified from the springs discovered during this study and previous reconnaissance efforts.

Field Parameter Equipment and Procedures

The equipment and techniques listed below were used for all spring field sampling from 2001 through 2005. Prior to sampling for laboratory analysis, spring water temperature, pH, ORP, EC and spring location and elevation were measured.

Equipment. The location and elevation of the springs were found with a Brunton MNS handheld GPS receiver. All location data were uncorrected and acquired in units of feet using North American Datum 1927 (NAD27) datum and Universal Transverse Mercator (UTM) projection. The GPS was set close to the spring as possible in a level location having little vegetative cover. The GPS receiver must communicate with at least three satellites to triangulate accurate position. Recordings of elevation and location were taken after sampling to allow the receiver time to stabilize.

Temperature, oxidation-reduction potential (ORP or redox) and pH field data were measured with a Thermo Orion Model 290A pH/ISE voltmeter and Thermo Orion probes: pH (Triode 9107BN) and ORP (Triode 9180BN) with Automatic Temperature Compensation. The relative accuracy of the pH probe is ± 0.02 pH unit. Spring water temperature was measured at the same time that ORP was measured. The meter does not require temperature calibration for pH measurements; the accuracy of the ORP probe for temperature is ± 1.0 °C (Thermo, 2003). Electrical conductivity was measured using a Thermo Orion QuiKcheK meter (Model 116 – a handheld, combination meter and probe). The QuiKcheK has a sampling resolution of 10 $\mu\text{S}/\text{cm}$ and automatic temperature compensation with an accuracy $\pm 2\%$ of full scale. This meter does not require calibration or maintenance.

The voltmeter and pH probe must be calibrated prior to use for field measurements against known pH values. The meter was calibrated against three commercial buffer solutions that bracket the expected sample range with pH values of 4.01, 7.00, and 10.01. Calibration verifies that the meter and probe are working correctly and sets

the slope coefficient for the 3-point, straight-line equation that converts a millivolt reading at the sample temperature into a pH value (Thermo, 2003).

Prior to field measurements the ORP probe was cleaned with deionized water and filled with potassium chloride standard solution (1.5 M KCl – Orion 900011). The voltmeter and probe were calibrated using an Orion ORP standard (Orion 967901 or 967961). The ORP probe contains a platinum redox sensor and a silver/silver chloride reference fill solution. The sensor material and fill solution define how measurements relate to the Standard or Normal Hydrogen Electrode (SHE/NHE). Field measurements of oxidation-reduction potential for aqueous solutions have many variables creating uncertainty in this data (Nordstrom, 2005); specifications regarding accuracy and precision for the probe and meter do not exist.

Field Parameter Collection Procedures. Spring water for field analyses was collected with a 500ml polyethylene beaker. All probes and equipment were equilibrated to the sampled spring by rinsing three times. Spent water was discarded away from the sampling site. The pH and ORP probes were placed in the sample and gently swirled until the temperatures of the probe and water sample equalized. ORP and pH are a function of temperature; therefore it is important that the probe and solution reach temperature equilibrium with the sample. The pH and ORP probes were removed and the EC probe was placed in the captured sample, readings were acquired quickly.

Sample Collection: Laboratory Analysis. Basic Laboratory, Inc. (Basic Labs) located in Redding, California was selected to provide major ion and silica analyses of the spring water samples. Spring waters were analyzed for three broad parameters requiring

unique sample handling and preservatives: silica (SiO_2) and cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+); anions (Cl^- , F^- , SO_4^{2-} , and NO_3^-); and carbon (alkalinity as CaCO_3 , HCO_3^- , CO_3^{2-}). Basic Labs provided bottles with measured preservative, if required, and the sampling procedures appropriate to the analytical parameters (Cady, 2005).

All samples were collected with a 1L polyethylene beaker. The size of the collection container was much greater than the laboratory bottles used for analysis. The extra volume ensured that exposure to air was minimized for filtered samples. A hand operated peristaltic pump with an inline 0.45-micron polycarbonate filter with membrane (Millipore) was used when required. The collection container and the filter were rinsed in the lab with deionized water prior to field excursions. Care was taken not to contaminate the inside walls and mouth of the container or the intake and outlet of the filter pump throughout the sample collection process. Approximately 300ml of conditioning spring water was pumped through the filter prior to capturing a filtered sample. During collection, every attempt was made to limit disturbance to ponded waters. Weeping Wall Spring and Rock Shelter Spring provided a source of flowing water that could be captured.

Spring water samples collected for dissolved carbon analyses were filtered into a 125 mL borosilicate glass bottle containing 0.5 mL of sulfuric acid (H_2SO_4) as a preservative, which lowers the pH to <2 limiting further reactions that would change the chemistry of the sample. Care was taken to fill bottles to the top and seal tightly without spillage of sample or preservative. Samples collected for dissolved metals (cations and silica) analyses were filtered into a 250 mL polyethylene bottle containing 0.5 mL nitric acid (HNO_3) as a preservative, lowering pH to <2 . Bottles were filled carefully without

spillage of sample or preservative and sealed tightly. Samples for anion analyses were collected in a one-liter polyethylene bottle without filtering or preservatives. All samples were labeled with spring identifier, date, and time of capture and placed in the shipping cooler. Upon returning from the field, all sample identifier data were transferred to the Chain of Custody record. Ice was placed in the cooler to drop sample temperatures to approximately 4°C; the cooler was sealed with shipping tape. Chain of Custody records were completed and signed by responsible parties. Basic Labs transported the samples to their lab within 24 hours of sampling and placed samples under refrigeration. Analyses were performed within a week of each sampling date.

Nitric acid prevents chemical reactions such as the precipitation of Fe and Al in water samples prior to analysis and is used to preserve samples for cation analyses. Sulfuric acid prevents biological reactions and is used to preserve samples tested for organic carbon. Both preservatives have adverse effects on anions; samples for anion analysis were left unpreserved. Standard practice recommends storage of all samples at temperatures between 2-4°C (Coffey, 1978). Cooling samples immediately stops decomposition, but is not critical for inorganic components, which are stable and have a long shelf life compared to volatile organic compounds (VOCs). VOCs were not analyzed for this study.

Laboratory Analytical Methods

A carrier from Basic Labs picked up the sealed cooler with samples within 24 hours of sample collection. All parameter analyses were performed within one week of sampling at the Redding laboratory with one exception. March 2005 samples were forwarded to a subcontracting laboratory, Del Mar Analytical of Irvine, California for the

dissolved organic carbon (DOC) analysis. Del Mar Analytical followed Environmental Protection Agency (EPA) method 415.1 for this analysis. DOC was not detected in any of the samples analyzed by Del Mar Analytical or Basic Labs. Basic Labs followed Standard Method (SM) 2320B for carbon analyses.

Dissolved metals (silica and cations) in spring water samples were measured using inductively coupled plasma-mass spectrometry under EPA method 200.7. Anions were measured using ion chromatography under EPA method 300.1 for Cl^- , SO_4^{2-} , and F^- ; EPA method 353.2 for nitrate (NO_3^-) as nitrogen; and total dissolved solids (TDS) were analyzed per SM 2540C. Laboratory results were compiled in Excel (Appendix C). All six springs were analyzed for NO_3^- during the July and September 2005 sampling periods in addition to the other analytical parameters listed above.

Uncertainty associated with laboratory measurements is controlled through in-house quality assurance standards. Standards include sample replication, reporting limits, instrumentation resolution and an equipment calibration system necessary to evaluate statistical fluctuations to produce the highest level of precision.

Numerical and Graphical Methods

Numerical and graphical methods were employed to further characterize source waters for Big Chico Creek and ground water with proximity to the creek. The models used in this study progress from graphical assessments of the data that enable qualitative analyses and refinement of hypotheses to more specific numeric analyses that may provide quantitative insight to processes and controls. Piper diagrams and scatterplots (bivariate

plots) illustrate relationships between variables that help identify processes leading to the presence of solutes in water. These plots may also illustrate classifications or water types and trends in the evolution of water. Speciation models are used to explore the distribution of the major components in solution as ions, molecules, solids, compounds or complexes. Saturation models indicate whether the solution is in a state of undersaturation or supersaturation with respect to appropriate minerals based on concentrations of major elements. Full characterization of the chemical evolution of waters in a watershed involves some knowledge of the mineralogy of the water-bearing rocks. Inverse mass-balance modeling based on the solutes in the water can help qualify mineral phases and weathering processes.

Methods Applied to Reported Data

Stream data from Ryley (1974) were entered into a Microsoft Excel spreadsheet for further interpretation using collected spring data and reported ground water data from wells near Big Chico Creek. The mean and standard deviation were calculated for each of the major ions for the stream data set. Representative samples of stream water were selected to explore seasonal controls: one sample each for May (runoff or high flow) and September (base flow). Records for May and September were identified, as these are the only months for which sulfate data is available. The representative records contain a complete set of major ion concentration data (mg/L). All solute measurements fell within one standard deviation of the mean for the two selected records.

Ground water data acquired from DWR were entered into a Microsoft Excel spreadsheet for numerical analysis and interpretation using collected spring data and

reported stream water from Big Chico Creek. The mean and standard deviation were calculated for each of the major ions for the ground water data set. Representative samples were selected to explore seasonal controls: one sample each for March and September. Records for March and September were identified, as these are the only months for which a complete set of major ion concentration data was available. All solute measurements fell within one standard deviation of the mean for the two selected records.

Piper Diagrams and Bivariate Scatter Plots

Piper diagrams are routinely used in aqueous geochemistry to classify water types and can potentially reveal the evolution of water chemistry or the chemical relations between water bodies (Ali et al., 2010; James and Roulet, 2006; Cronin et al., 2005). A Piper diagram comprises two standard ternary plots displaying 3-axes proportions for cation (Ca^{2+} , Mg^{2+} , and $\text{Na}^+ + \text{K}^+$) and anion ($\text{HCO}_3^- + \text{CO}_3^{2-}$, SO_4^{2-} , and Cl^-) normalities and a 4-axes quadrilateral that combines cation and anion data and expresses the total dissolved solids of each sample. Concentrations are converted to equivalents and cations and anions are normalized separately to sum to 100 percent. The normalized concentrations are plotted on the two ternary plots and extended to the quadrilateral.

An equivalent (eq) is a standardized expression of ions per liter of solution that reflects the ionic charge. Ion concentrations are converted from mass concentrations as mg/L to equivalents by dividing the ion weight by its molar mass (the formula weight of a substance expressed as grams per mol) and scaling the result by the ionic charge.

Equation (1) converts the concentration measurement of SO_4^{2-} as 162 mg/L to 3.37 meq/L.

The molecular weight of sulfur is 32.07 grams per mole and the molecular weight of four oxygens is 64 grams per mole. The charge for sulfate is 2^- .

$$\left[\left(\frac{162}{(32.07+64)} \right) \left(\frac{mg}{L} \right) \left(\frac{mole}{g} \right) \left(\frac{g}{1000 mg} \right) \right] \times 2 \left(\frac{eq}{mole} \right) \left(\frac{1000 meq}{eq} \right) = 3.37 \frac{meq}{L} \quad (1)$$

Scatter plots provide a graphical method of analyzing two independent variables such as Cl^- and SO_4^{2-} . If known relations exist, dependent variables (for example the measured chemical constituents) are plotted on the y-axis and independent variables (e.g. time or flow) on the x-axis. Scatter plots may show correlation between variables, can be used to classify water types and analyze mixing relations, or provide clues to sources leading to the presence of plotted variables (Gao et al., 2009; Elbaz-Poulichet et al., 2002; Hooper et al., 1990).

Mixing Models for Stream and Ground Water

Mixing of water is a process that occurs throughout a watershed between various sources such as rain, soilwater, or runoff. A source found to have a consistent chemical signature throughout space and time can be described as an end member. For example, the chemistry of snow and snowmelt or rain can be considered invariant in time and space within the geographic expanse of a watershed. The study of natural tracers such as those used in this study, provide information about the hydrologic and geologic controls affecting the chemical signature of an end member. For catchment-scale processes, three end members adequately describe the variability found in stream chemistry. As such, appropriately selected end members should define the boundary of observed hydrochemistry within that watershed.

Stream water chemistry reflects the sources contributing to flow and is a catchment-scale indicator of processes occurring upstream in the watershed (Hooper, 2001). Big Chico Creek is a perennial stream fed by snowmelt runoff and base flow contributions from the watershed formations through the entire dry season (Ryley, 1974; Maslin, n.d.). These three sources – runoff and spring discharge from the Tuscan and Chico Formations – are hypothesized as the end members responsible for the chemistry of the creek. Mixing may also occur within ground water providing insight about recharge sources and ground water flow paths. Creeks flowing into Butte Basin are thought to be a major source contributing to ground water recharge (Hoover, 2005); therefore the well-water chemistry studied in this project should reflect BCC as well as the host aquifer formation – the Tuscan Formation. This study characterizes the Chico and Tuscan Formation ground water chemistry as two end members providing base flow contributions to the chemistry of Big Chico Creek and well water. Both Big Chico Creek and ground water in the Sacramento Valley reflect a mixture of end members. Mixing was assessed graphically to determine if there are possibly other end members affecting the chemistry of the creek and ground water. Contributing fractions of each end member are quantified using the numerical method described by Faure (1998).

The weight fraction for component A of a two-part mixture is equal to the ratio of A to the sum of both components (A and B) as described in equation (2).

$$f_A = \frac{W_A}{W_A + W_B} \quad (2)$$

The weight fractions of both components sum to one. Therefore $0 \leq f_A \leq 1$ and $f_B = (1 - f_A)$, where f_A represents the fraction of A. In this case A and B may represent the Tuscan

Formation (TF), the Chico Formation (CF), or snow(melt), which constitutes the third *known* end member (S), and the water sampled from Big Chico Creek is the mixture (*M*). This project uses the nomenclature of a two dimensional X-Y coordinate system for the scatter plots, where all values of X and Y are positive. X_M and Y_M will represent two constituents measured at time t in the mixture *M*. The concentration of any conservative constituent X_M is a function of the concentrations (X_E) of two end members (where E represents one of the end members TF, CF, or S) and their weight fractions (f_E). This equation can be rearranged into an equation of a straight line for constituent X_M , which can be rewritten to solve for the weight fraction f_E using the measured concentrations of the mixture and the end members TF, CF or S as expressed in equation (3).

$$f_{TF} = \frac{(X_M - X_{CF})}{(X_{TF} - X_{CF})} \quad (3)$$

Selection of Representative End Members

Representative tracer values used in models that employ end member mixing analysis (EMMA), a term coined by Christophersen et al. (1990), are often the calculated central tendency of an entire data set. For this project, tracer measurements taken at the same point in space and time for precipitation, Big Chico Creek, Butte Basin ground water, and springs were selected as representative values for graphical analysis. End members were selected from the reported data set for precipitation using the mean and standard deviation of the entire data set as a selection baseline. Tracer measurements for the Horse Trough Spring (CF) and Rock Shelter Spring (TF) were selected as the formation end member values. The selected end members for the formations and precipitation constitute a

representative suite of conservative tracers. Big Chico Creek and Butte Basin ground water are mixtures and all data was plotted against selected end members.

EQ3 Speciation Analysis

Bulk chemical data for each spring water sample were entered into EQ3, a Fortran-based aqueous speciation program (Wolery, 1992). EQ3 solves simultaneous equations for mass conservation, charge balance, and the Law of Mass Action for each independent chemical reaction. EQ3 uses a database of analytically and theoretically derived thermodynamic data for water-gas-rock interactions to develop an equilibrium model that indicates potential ionic complexes, saturation states relative to mineral phases, and saturation states for dissolved gases. EQ3 tests electroneutrality of a solution based on sample composition. Electroneutrality is maintained by changes in speciation as gas-water-rock interactions occur. Charge-balance error (CBE) is a common test for analytical results of ion concentrations, and acceptable limits range from 3% to 10% for different researchers. For this study, a charge-balance error of 5% was established as a test criterion signifying a complete analysis of major ions was performed (Fritz, 1994). Imbalance may be the result of the presence of an ion(s) not measured or analytical error or a change in the speciation of samples during transport from field to laboratory. The EQ3 was constrained to adjust HCO_3^- concentrations to maintain charge balance in the EQ3 modeled water.

CHAPTER V

RESULTS AND INTERPRETATION

Introduction

This study provides new data that characterize the hydrochemistry of springs emanating from the Tuscan and Chico Formations in the Big Chico Creek watershed. Spring water chemistry reflects water-rock-gas interactions within the formation geology as well as seasonal hydrologic changes. Spring data were interpreted in the context of published hydrochemical data for Big Chico Creek and ground water from wells chosen with proximity to the creek. During winter and spring, the wet season between November and March, the chemistry of Big Chico Creek is dominated by meteoric water. During summer and fall, the dry season between April and October, creek water chemistry shows an influence of spring discharge. Hydrochemical data for ground water presumed to come from Tuscan Formation aquifers differ from the hydrochemistry of Tuscan Formation springs. These data show an influence of local recharge from Big Chico Creek, but indicate that formation geology and residence time and impacts from pumping ultimately impart a stronger control on the chemistry of ground water.

Methods discussed in Chapter IV are employed to further assess the controls on spring, creek, and ground water chemistry using the new data collected through this study and published results. Selection criteria are established for end member spring candidates for mixing analysis of creek and ground water. Springs that do not emanate from a primary

aquifer formation are also analyzed to better understand controls on their hydrochemical signatures.

New Data: Big Chico Creek Springs

Five springs were sampled and their geochemical composition analyzed during March and July 2005; one spring was sampled and analyzed only in September 2005. Field parameter results for all springs were collected and interpreted in the context of the hydrochemical data. Significant variations in the chemistry due to lithology are evident. Little seasonal variation is apparent with the exception of Rock Shelter Spring and Weeping Wall Spring. The lack of seasonal variation in some springs indicates little mixing with recently infiltrated precipitation. All spring waters are of mixed chemical type and differ when comparing dominant cations and anions. Dominance occurs when one ion exceeds 50% of the relative concentration for similarly charged ions. When examining the data on an equivalents basis, bicarbonate is the dominant anion with the exception of Riparian Spring waters in which sulfate shows dominance. Cation concentrations are mixed with percent differences surrounding the dominance criterion within analytical error. Calcium is close to 50% in all but the Horse Trough Spring, where Na + K concentrations exceed calcium by 10% and Rock Shelter Spring for which calcium exceeds 50% of the total cations. Silica is present in high concentrations in Tuscan Formation spring water, nearly twice the sum of cations, while comprising less than a fifth of the sum of cations found in Chico Formation spring water. The average concentrations of Tuscan Formation spring waters are similar to the average concentrations reported by Feth et al. (1964a,b) and Garrels and Mackenzie (1967) from Sierra Nevada springs emanating from volcanic rocks.

Relative Change and Difference

One objective of this project examines seasonal hydrochemical changes on spring, creek and ground water. Percent change between sampling periods was calculated using equation (4). Table 1 lists the results of these calculations for the physical parameters of the spring waters. The *Old Value* is the ion concentration for the March sampling and the *New Value* represents concentrations from the July sampling. A negative percent change indicates that the ionic concentration was lower in July than the March sampling.

$$\left[\frac{\text{New value} - \text{Old value}}{\text{Old value}} \right] \times 100 = \text{Percent change (\%)} \quad (4)$$

TABLE 1. SEASONAL VARIATIONS BETWEEN SAMPLING PERIODS

<i>Percent Change (n%)</i>	Ca²⁺	Mg²⁺	Na⁺	K⁺	HCO₃⁻	Cl⁻	SO₄²⁻	SiO₂	pH	T
Riparian Spring	-2	0	-2	0	0	0	0	2	-2	19
Horse Trough Spring	8	0	-3	--	5	7	-3	4	-2	84
House Supply Spring	4	0	0	0	6	5	-5	-1	-2	12
Rock Shelter Spring	62	60	25	0	72	18	47	19	29	27
Weeping Wall Spring	33	33	13	--	15	91	40	6	20	35

Note: Temperature (T) and pH measured in the field. (--) indicates solute was not detected in March, but was detected in July.

Surface effects on spring water are evidenced in the correlations between temperature, pH, and a change in constituent concentrations over the sampling periods (Table 1). It is interesting to note that the two springs (House Supply Spring and Riparian Spring) with the least amount of variation in water temperature between sampling periods have the least overall variation in ionic concentrations. Changes in pH can affect the carbonate system, equilibrium reactions and solubility. The pH for all springs fell within the near neutral range, corresponding to laboratory results of total carbonate reported as

HCO_3^- . Those springs with the greatest change in pH over time exhibit the greatest change in concentration as evidenced in the Rock Shelter and Weeping Wall springs, Table 1. Horse Trough Spring waters appear to be in equilibrium as little change in pH and concentrations occurred over time while temperature increased considerably.

Percent difference calculations are used to compare similar parameters between waters of different formations as well as creek and ground water. Equation (5) shows a typical calculation for comparison of concentrations, where C_1 and C_2 are concentration values of a specific ion for two different springs. Use of the average concentration in the denominator indicates that neither spring has a value more important than the other and eliminates problems with zero values.

$$\left[\frac{(\text{abs}(C_1 - C_2))}{(\text{avg}(C_1, C_2))} \right] \times 100 = \text{Percent Difference (\%)} \quad (5)$$

Spring Hydrochemical Data: Tuscan Formation

The chemistry of spring water from the Tuscan Formation springs and Basalt Spring shows low solute concentrations. The chemical data of these waters corresponds closely with the averages from volcanic springs sampled by Feth et al., (1964a) from the Sierra Nevada and Cascade Ranges. Feth et al. found a significant difference in spring hydrochemistry between granitic and volcanic terranes. More specifically, Feth et al. found that volcanic waters have 1.5 times as much total dissolved solids (TDS) as waters from granitic rocks and more than twice as much magnesium. Feth et al. attributes these differences to 'less completely' crystallized lavas and tuffs and mineralogy that is more magnesium-dominant. Waters emanating from the Tuscan Formation could be young with

short travel paths. Springs in the Tuscan Formation are perennial, meaning that water seeps from the rock regardless of the timing of precipitation events. The Tuscan Formation rock is intermediate in composition, consisting of plagioclase, olivine, ortho- and clinopyroxenes, hornblende, magnetite, and feldspar minerals (Harwood, et al., 1981; Doukas, 1983). These minerals are susceptible to chemical weathering and dissolution.

The dissolved major ion concentrations for the Tuscan Formation springs do not vary spatially implying consistency in the geologic controls on spring water chemistry (Figure 4). Speciation modeling with EQ3 shows that solutes found in Tuscan Formation spring waters are uncomplexed species. The Tuscan Formation spring water is of a Ca-HCO₃ type with equivalent concentrations of HCO₃⁻ almost twice that of the Ca²⁺ concentrations. Field measurements for water temperature range from 13.8 to 18.8 °C and pH ranges from 6.1 to 7.8. The temperature of all the springs was less in March than as measured in July. EC values for the Tuscan Formation springs and Basalt Spring range from 180 to 260 μS/cm, and field values of ORP range from 105.6 to 194 mV indicating Tuscan Formation waters are oxidizing.

The percent difference in ionic concentrations between Tuscan Formation springs for each sampling period, calculated using equation (5), are tabulated in Table 2. Ionic concentrations for House Supply Spring are higher than those of Rock Shelter Spring in March, but concentration data for Rock Shelter Spring from July tend toward values of House Supply Spring for the same sampling period. The hydrochemistry of Rock Shelter Spring appears to be temporal and transient evolving to the steady state concentrations depicted in House Supply Spring waters.

TABLE 2. DIFFERENCES BETWEEN TUSCAN FORMATION SPRINGS

<i>Percent Difference of measured solutes (in %)</i>	Ca²⁺	Mg²⁺	Na⁺	K⁺	HCO₃⁻	Cl⁻	SO₄²⁻	SiO₂
March 2005	56	75	40	67	56	21	58	24
July 2005	13	32	18	67	9	9	16	5

House Supply Spring

Dissolved concentrations of HCO₃⁻ and Ca²⁺ were the only constituents that varied between sampling periods when examining equivalent concentrations of ions measured in water from the House Supply Spring (Table 3). The consistency of the spring water chemistry over differing hydrologic regimes indicates that the source of water feeding this spring neither dilutes nor changes the chemistry of the water flowing through the rock to the spring outlet. The House Supply Spring waters are dilute; infiltrating recharge water probably reacts quickly with the surrounding soil and rock reaching the measured concentration at discharge. This consistency does not hold true for the hydrochemical data collected from the Rock Shelter Spring (Table 4). Its chemical signature approaches the values of the House Supply Spring, exhibiting an increase in all ionic concentrations over the sampling period. The overlying rock above each of the Tuscan Formation springs is approximately 380 feet thick. However, the area surrounding House Supply Spring has a much gentler slope, appears to have experienced much greater soil development, and consequently is well vegetated. Infiltrating water of the House Supply Spring must have a greater travel path that allows the chemistry of dilute water to become more concentrated while percolating to the spring outlet. Soil water is CO₂-enriched by respiration in the root zone over dissolved concentrations at equilibrium

with atmospheric $\text{CO}_{2(\text{g})}$. CO_2 -enriched soil water is slightly acidic and reacts quickly to weather soil and rock. Water from the House Supply Spring provides a representative sample of water that has reached steady-state with the primary Tuscan Formation minerals and the secondary soil minerals derived from them (Garrels and Mackenzie, 1967).

TABLE 3. SOLUTE CONCENTRATIONS FOR HOUSE SUPPLY SPRING

Measured solutes	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ^{-*}	Cl ⁻	SO ₄ ²⁻	SiO ₂	
March	(mg/L)	23.0	11.0	6.0	2.0	135.0	1.52	1.83	76.0
	(meq/L)	1.15	0.9	0.26	0.05	2.21	0.04	0.04	--
July	(mg/L)	24.0	11.0	6.0	2.0	143.0	1.59	1.74	75.1
	(meq/L)	1.2	0.9	0.26	0.05	2.34	0.04	0.04	--

Note: Major ion and silica concentrations for House Supply Spring, Tuscan Formation, sampled March 31 and July 18, 2005. Reported analytical data in (mg/L) and calculated concentrations in equivalent units.

* Total carbonate expressed as bicarbonate.

Calcium is the dominant cation for the House Supply Spring, representing nearly 50% of the total cation charge. HCO_3^- is the dominant anion for all Tuscan Formation springs representing more than 95% of the total anion charge. There was approximately a 6% increase in HCO_3^- over the sampling periods for this spring balancing the measured increase in the Ca^{2+} concentration. Total Dissolved Solids (TDS) decreased slightly from 186.0 to 176.0 (mg/L). Spring water temperature increased between sampling periods, as it did for all springs, from 13.8 to 15.4 °C. Decreases were measured in EC from 220 to 210 $\mu\text{S}/\text{cm}$, for pH 6.559 to 6.409, and ORP dropped, as a function of temperature change, from 172.4 to 118.0 mV March to July. The observations mentioned above support the model that major ion concentrations of the House Supply Spring provide

a good estimate for base flow contributions to Big Chico Creek from the Tuscan Formation.

Rock Shelter Spring

Dissolved concentrations of all constituents increased between the March and July sampling for water emanating from this spring (Table 4). It is apparent that water evolves as it flows through the rock to the spring outlet, approaching the steady-state values for waters of the House Supply Spring. Concentration of the water may be a result of evaporation occurring in fractures or water-rock interactions. Little data were collected that allow for conclusive or well-constrained analysis of residence time for spring waters of the Big Chico Creek watershed. This spring provides a good site for future exploration of age and residence time data for waters of the Tuscan Formation.

Increases in Ca^{2+} and SiO_2 concentrations are indicators of water-gas-rock interactions, such as the dissolution of calcite and silicates, as a result of the increase in pH and HCO_3^- concentration that nearly doubled in July relative to March. The increase in HCO_3^- is accompanied by a decrease, between sampling periods, in the partial pressure of $\text{CO}_{2(g)}$ as modeled by EQ3 (Figure 11). Garrels and Mackenzie (1967) assert that SiO_2 present in granitic spring waters is a function of the weathering reactions involving the conversion of CO_2 to HCO_3^- through dissolution and dissociation.

Water seeps from the host rock and is exposed to air similarly at both Tuscan Formation springs, ruling out evaporation as the cause for enrichment of one spring while the other appears to be in steady-state with the formation mineralogy. Calcium was the dominant cation in the Rock Shelter Spring and increased more than 60% between

sampling periods; however, the ratio between Ca and Mg stayed consistent. While aqueous complexing of the EQ3 modeled water is not extensive, it does show that the spring water is undersaturated in March and becomes saturated or supersaturated with respect to minerals (calcite, sepiolite, and talc) that could lead to the measured increases in concentration.

TABLE 4. SOLUTE CONCENTRATIONS FOR ROCK SHELTER SPRING

Measured solutes	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ^{-*}	Cl ⁻	SO ₄ ²⁻	SiO ₂	
March	(mg/L)	13.0	5.0	4.0	1.0	76.0	1.23	1.01	60.0
	(meq/L)	0.65	0.41	0.17	0.03	1.25	0.03	0.02	--
July	(mg/L)	21.0	8.0	5.0	1.0	131.0	1.45	1.48	71.3
	(meq/L)	1.05	0.66	0.22	0.03	2.15	0.04	0.03	--

Note: Major ion and silica concentrations for Rock Shelter Spring, Tuscan Formation, sampled March 31 and July 18, 2005. Reported analytical data in (mg/L) and calculated concentrations in equivalent units.

* Total carbonate expressed as bicarbonate.

Spring water temperature measurements of 14.8 and 18.8 °C were recorded for March and July respectively. EC was recorded only for March of 180 µS/cm, but a subsequent measurement of field parameters collected September 5, 2005 showed an increase to 250 µS/cm for this spring. A decrease in ORP from 194.0 to 105.6 mV was measured while pH increased from 6.084 to 7.835. While the increase in pH in July could be questioned given the lack of EC data, the pH was found to remain high (7.952) during field sampling in September. The increase in pH over from March to July and September appears to be a result of CO₂ degassing and further evidence that during the wet season mixing occurs providing the more dilute signature in March. The decrease in the partial pressure (fugacity) of carbon dioxide is shown in Figure 11 from EQ3 modeled water.

Spring 18: Rock Shelter Mar '05				Spring 18: Rock Shelter July '05			
Mineral		Log Q/K	Aff, kcal	State	Log Q/K	Aff, kcal	State
Anhydrite		-4.4466	-5.8589		-4.0914	-5.4658	
Aragonite		-2.5784	-3.3974		-0.4015	-0.5363	
Calcite		-2.4335	-3.2064		-0.2568	-0.343	satd
Chalcedony	SiO2	0.9431	1.2427	ssatd	0.9258	1.2368	ssatd
Coesite	SiO2	0.387	0.5099	ssatd	0.3766	0.5032	ssatd
Cristobalite(alpha)	SiO2	0.6501	0.8566	ssatd	0.6383	0.8527	ssatd
Cristobalite(beta)	SiO2	0.1778	0.2343	satd	0.1777	0.2374	satd
Dolomite		-3.9323	-5.1813		0.4409	0.5891	ssatd
Fluorite		-4.6511	-6.1283		---	---	
Gypsum		-4.1697	-5.494		-3.8545	-5.1493	
Magnesite		-3.1913	-4.2049		-0.9693	-1.2949	
Quartz	SiO2	1.224	1.6127	ssatd	1.2028	1.6068	ssatd
Sepiolite		---	---		-0.2145	-0.2865	satd
SiO2(am)		-0.1446	-0.1905	satd	-0.132	-0.1764	satd
Talc		---	---		2.8809	3.8486	ssatd
Tremolite		---	---		-1.1253	-1.5033	
Tridymite	SiO2	1.0409	1.3715	ssatd	1.0247	1.3689	ssatd
Gas		Fugacity	Log fugacity		Fugacity	Log fugacity	
CO2(g)		5.34E-02	-1.2726		1.5149E-03	-2.8196	

Figure 11. EQ3 Mineral Speciation of Modeled Water for Rock Shelter Spring.

Sulfate is enriched in Tuscan Formation spring water relative to reported precipitation data used for this project. Sulfate concentrations for the House Supply and Rock Shelter Springs indicate that the mineral content of this formation must provide a sulfate source. Measurements of sulfate ranged from a low of 1.01 mg/L for Rock Shelter Spring in March to 1.83 mg/L for House Supply Spring also measured in March. The reported concentration for sulfate used to represent the meteoric component for analysis in this study is 1.06 mg/L (Feth et al., 1964b) from 21 samples of snow collected on the western slopes of the Sierra Nevada Range. Sulfate in snow is below the steady state concentration found in House Supply Spring. The increase in SO_4^{2-} concentrations in waters of the Rock Shelter Spring reflects enrichment from water-rock interactions taking place along the flow path or fractures that feed the Tuscan Formation springs indicating a sulfur source.

Spring Hydrochemical Data: Chico Formation

Similar to the Tuscan Formation, the Chico Formation is a sedimentary rock. Unlike the rapidly placed deposits of the Tuscan Formation that formed during hot, turbulent and explosive events of mostly pyroclastic sediments and cement-like in flow (Greene, 2012), the Chico Formation formed over more than 3 m.y. from well-worked sediments settling in a near shore or deltaic environment (Haggart and Ward, 1984). This environment and subsequent burial and uplift from millions of years of tectonic activity have left a rock formation that is poorly to well indurated with interbedded layers of sediments that range from fine grained to conglomerate in texture (Doukas, 1983). The chemistry of the springs measured indicates that the Chico Formation has been flushed over the millions of years since oceanic waters receded leaving water in the rock that is far removed from the hydrochemistry of sea water.

The Chico Formation has been mapped and well studied since 1856, and Big Chico Creek exposures have provided the type locality and principal field sites since 1940. Haggart and Ward's (1984) study of eastern exposures of the Upper Cretaceous strata within the Great Valley formalized three member designations originally identified by Saul (1959, 1961). Saul named the principal members, listed oldest to most recent, as Ponderosa Way, Musty Buck, and Ten Mile (Haggart and Ward, 1984). Haggart and Ward concluded that an additional lithologic member exists in the Big Chico Creek exposure that rests stratigraphically but unconformably above the Ten Mile Member. They interpret this member as near-shore, shallow marine or deltaic sediments of a nonfossiliferous, sandstone similar in age with other mid- to upper Campanian age deposits found in the region due to

their stratigraphic proximity with older Campanian sediments (Haggart and Ward, 1984). Three of the four lithologic members identified in the Big Chico Creek watershed consist of an arkosic sandstone matrix. The clasts, if they exist, differ in composition, size, and texture in each of the units. Haggart and Ward identify clasts in the Musty Buck Member as having been derived from the underlying metamorphic basement rock. The varying depositional environments and length of time elapsed during deposition of these lithologic units provide for differing hydrochemical signatures of which two are detected in this study.

The chemistry of spring water from the Chico Formation shows high solute concentrations compared with the Tuscan Formation springs. There is significant spatial variability between Riparian Spring and Horse Trough Spring, but little temporal change between sampling periods for both springs (Table 5). These results indicate that lithology has greater control over the hydrochemistry of these springs than hydrology. Electrical conductivity values are 2-3 times greater and TDS concentrations are in excess of 75% over Tuscan Formation spring water. HCO_3^- concentrations of the Chico Formation springs are 30 to 116% greater than those of the Tuscan Formation springs, even though this solute is the most abundant of the ions measured in waters of the Tuscan Formation. Similar to most of the springs sampled throughout this watershed, these spring waters have near-neutral pH; however, pH values are a unit higher than those recorded for the Tuscan Formation springs. Spring water temperatures are within the range of Tuscan Formation springs; all show an increase in July relative to March. The near constant concentrations between samplings and that of the chemical parameters modeled by EQ3 appear to indicate

buffering by the carbonate system is a dominant process controlling the chemistry of the Chico Formation springs.

TABLE 5. DIFFERENCES BETWEEN CHICO FORMATION SPRINGS

<i>Percent Difference of measured solutes (%)</i>	Ca²⁺	Mg²⁺	Na⁺	K⁺	HCO₃⁻	Cl⁻	SO₄²⁻	SiO₂
March 2005	18	6	65	67	38	177	50	14
July 2005	9	6	63	0	43	178	53	11

The Chico Formation is considered to mark the base of freshwater throughout the valley (Dudley, 2004), and therefore it is expected that springs from this formation would exhibit high Cl⁻ concentrations. While springs that emanate from the Chico Formation have considerably higher solute concentrations including Cl⁻ and Na⁺, they do not fall along a mixing line consistent with seawater as an end member as shown on the Piper diagram.

Horse Trough Spring

Most dissolved constituents measured in this spring varied between sampling periods (Table 6), but not enough to indicate strong hydrologic controls on the chemistry of the water. Increases of Ca²⁺ and Cl⁻ concentrations may be a result of evaporation from March to July, while the slight decrease in SO₄²⁻ and Na⁺ concentrations could be indicative of mineral equilibrium as modeled by EQ3. Chloride concentrations for this spring are very high and consistent between sampling periods. Chloride concentrations in Riparian and Weeping Wall Springs are comparatively very low. Similarly, the Chico Formation springs differ widely in concentrations of Na⁺ and SO₄²⁻. These hydrochemical

differences identify the importance of lithologic controls on the chemistry of the Chico Formation springs. Horse Trough Spring is downstream and slightly lower in elevation at 899 feet than Riparian Spring, which rests on a terrace at 1037 feet.

Ionic balances for all major ions analyzed for this spring fall below a CBE of 5% for both sampling periods. Water temperature increased significantly between sampling events, from 11.1 to 20.4 °C, but appears to correspond to fluctuations in ambient air temperatures, as do all the springs with multiple sampling dates. Decreases were measured in EC from 770 to 760 $\mu\text{S}/\text{cm}$, for pH from 7.592 to 7.411, and ORP from 146.4 to 122.3 mV in the period March to July. EQ3 analyses indicate uncomplexed aqueous species and no remarkable change in mineral saturation states.

The TDS value (481 mg/L) for the Horse Trough Spring is considerably higher than all other spring water analyzed in the Big Chico Creek watershed and it did not vary between sampling dates. This water is a Na-HCO₃ type with HCO₃⁻ representing slightly more than 50% of all anions tested and Na⁺ representing slightly less than 50% of all cations on an equivalents basis. Sulfate concentrations are slightly higher than chloride in this spring but nearly half concentrations found in Riparian Spring. There is nearly 200% more chloride present in these waters than in any other spring water sampled. The sodium concentrations are also high, more than double concentrations in Riparian Spring waters, while the Ca²⁺ and Mg²⁺ concentrations are slightly less. A scatter plot of Na⁺ versus Cl⁻ indicates that spring waters are enriched in Na⁺ compared to Cl⁻ and that halite dissolution, represented by a 1:1 equi-line, does not provide the source of sodium present in these waters (Ettazarini, 2005). Halite is a result of seawater evaporation and as such could be

indicative of connate water. Release of sodium through weathering of feldspar rich sediments provides a likely source for high Na^+ concentrations found in Chico Formation springs. K^+ concentrations fall in the range typical of all the waters sampled in the watershed. The Horse Trough Spring provides the best example of water emanating from the Chico Formation.

A small housing community dependent on septic systems exists on the ridge above Horse Trough Spring. The ridge is 1300 vertical feet above the spring and more than 0.5 mile east. Nitrate can be an indicator of anthropogenic pollution from sewage and other organic waste streams. Hem (1985) states that time or lengthy flow paths are often necessary to oxidize nitrogen in the form of ammonium (NH_4^+) to nitrate (NO_3^-). Chloride is a conservative solute and as such can be used as a tracer to assess flow paths where

TABLE 6. SOLUTE CONCENTRATIONS FOR HORSE TROUGH SPRING

Measured solutes	Ca^{2+}	Mg^{2+}	Na^+	K^+	$\text{HCO}_3^-^*$	Cl^-	SO_4^{2-}	SiO_2	
March	(mg/L)	50.0	17.0	86.0	1.0	285.0	55.8	96.8	27.0
	(meq/L)	2.5	1.4	3.74	0.03	4.67	1.57	2.02	--
July	(mg/L)	54.0	17.0	83.0	2.0	300.0	59.5	93.8	28.2
	(meq/L)	2.69	1.4	3.61	0.05	4.92	1.68	1.95	--

Note: Major ion and silica concentrations for Horse Trough Spring, Chico Formation, sampled March 31 and July 18, 2005. Reported analytical data in (mg/L) and calculated concentrations in equivalent units.

* Total carbonate expressed as bicarbonate.

elevated concentrations exist and thought to be the result of anthropogenic sources such as sewage. Because Cl^- concentrations, in the March 2005 samples, were significantly greater than what was detected in Riparian Spring, anthropogenic sources were considered. Nitrate

(NO₃⁻ as N) was analyzed for this spring water in July and was not detected. Nitrate was detected at very low levels in the Tuscan Formation springs (House Supply 1.74 mg/L and Rock Shelter 0.33 mg/L), Basalt Spring (0.17 mg/L), and Weeping Wall Spring (1.54 mg/L).

Riparian Spring

All measured dissolved concentrations were remarkably consistent between sampling dates for the Riparian Spring (Table 7). This consistency in chemistry over differing hydrologic regimes indicates that dilute recharge waters percolating through the thin overburden surrounding the outlet does not immediately affect the hydrochemistry of this spring. Na⁺ concentrations are considerably less than the values measured in the Horse Trough Spring. Riparian Spring water is a mixed type with SO₄²⁻ representing ~50% and HCO₃⁻ ~48% of all anions tested. Ca²⁺ represents 46% of the cations, with Na + K at 30% and Mg²⁺ at 23%. Chloride concentrations for this spring are considerably depleted compared with concentrations found in the Horse Trough Spring.

Ionic balances for all major ions analyzed for this spring fall below a CBE of 5% for both sampling periods. Sulfate concentrations are high in this spring. The odor of hydrogen sulfide gas was detected around this spring July 2005 and others known to emanate from the Chico Formation. These findings are consistent with reducing conditions detected in March 2005. The ORP measurement in March indicated these waters were reducing at -78.0 mV and increased to 24.3 mV in July. Water temperature increased between sampling events, from 13.5 to 16.1 °C. Previously sampled data from October 2003 shows spring water temperature remains constant until fall rains begin. Decreases

were measured in EC from 660 to 610 $\mu\text{S}/\text{cm}$ and pH 7.633 to 7.504 March to July. EQ3 analyses indicate uncomplexed aqueous species and no remarkable change in mineral saturation states, with the exception of talc.

TABLE 7. SOLUTE CONCENTRATIONS FOR RIPARIAN SPRING

Measured solutes	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^{-*}	Cl^-	SO_4^{2-}	SiO_2	
March	(mg/L)	60.0	18.0	44.0	2.0	193.0	3.42	162.0	31.0
	(meq/L)	2.99	1.48	1.91	0.05	3.16	0.1	3.37	--
July	(mg/L)	59.0	18.0	43.0	2.0	193.0	3.42	162.0	31.5
	(meq/L)	2.94	1.48	1.87	0.05	3.16	0.1	3.37	--

Note: Major ion and silica concentrations for Riparian Spring, Chico Formation, sampled March 31 and July 18, 2005. Reported analytical data in (mg/L) and calculated concentrations in equivalent units.

* Total carbonate expressed as bicarbonate.

Unclassified Springs

Water from two other springs was collected for major ion analysis. The Basalt Spring was chosen as a site thought to produce water emanating from the Lovejoy Basalt Formation. Weeping Wall Spring appears to originate from a thick outcrop of the Chico Formation.

Basalt Spring

This spring and five others were discovered after the July sampling of the Tuscan and Chico Formation springs documented above. Basalt Spring was analyzed because it appeared that this spring emanates from the Lovejoy Basalt. Its chemical signature closely resembles the hydrochemistry of the two Tuscan Formation springs, House Supply Spring and Rock Shelter Spring with the exception of the lower sulfate

concentration (Table 8). All other measured constituents fall within the range of data collected for the Tuscan Formation springs. Spring water temperature was 17.6 °C, ORP was recorded as 164.9 mV, pH was 7.2, and EC was measured at 260 μ S/cm.

TABLE 8. SOLUTE CONCENTRATIONS FOR BASALT SPRING

Measured solutes	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ^{-*}	Cl ⁻	SO ₄ ²⁻	SiO ₂
(mg/L)	18.0	9.0	5.0	1.0	123.0	1.44	0.71	68.0
(meq/L)	0.9	0.74	0.22	0.03	2.02	0.04	0.01	--

Note: Major ion and silica concentrations for Basalt Spring, Lovejoy Basalt, sampled September 8, 2005. Reported analytical data in (mg/L) and calculated concentrations in equivalent units.

* Total carbonate expressed as bicarbonate.

Weeping Wall Spring

The Weeping Wall Spring was sampled in March and July 2005 at the same time two springs each from the Tuscan and Chico formations were sampled as discussed above (Table 9). A subsequent field excursion in November 2005 found the spring dry. This spring is an intermittent spring that appears to flow across the Chico Formation, but carries evidence that the waters have spent time in the Tuscan Formation. Interestingly, all ion concentrations are enriched from March to the July sampling. Calcium and magnesium appear to be limited by Tuscan Formation water, falling within the range of concentrations measured in the Tuscan Formation springs, and greatly depleted compared to water from the Chico Formation springs. K⁺ is depleted when compared against all waters. Sodium concentrations are nearly three times greater than measured for Tuscan Formation springs, but considerably depleted compared against values recorded for Chico Formation springs. SiO₂ concentrations are similar to Chico Formation waters and less than half the

measurements of Tuscan Formation waters. Sulfate concentrations for spring water from the Tuscan Formation averages 1.5 mg/L while Chico Formation waters average 129 mg/L.

TABLE 9. SOLUTE CONCENTRATIONS FOR WEEPING WALL SPRING

Measured solutes	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ^{-*}	Cl ⁻	SO ₄ ²⁻	SiO ₂	
March	(mg/L)	21.0	6.0	16.0	0.0	89.0	3.63	35.2	32.0
	(meq/L)	1.05	0.49	0.7	--	1.46	0.1	0.73	--
July	(mg/L)	28.0	8.0	18.0	0.3	102.0	6.95	49.2	34.0
	(meq/L)	1.4	0.66	0.78	0.01	1.67	0.2	1.02	--

Note: Major ion and silica concentrations for Weeping Wall Spring, sampled March 31 and July 18, 2005. Reported analytical data in (mg/L) and calculated concentrations in equivalent units.
* Total carbonate expressed as bicarbonate.

Chloride concentrations are also unique: the March measurement is similar to concentrations found in the Riparian Spring (3.42 mg/L for March and July), but is enriched by July. This enrichment could be correlated to a flow path with proximity to the same Chico Formation member from which the Horse Trough Spring emanates. Bicarbonate concentrations are low compared with measured values of springs from both the Tuscan and Chico formations. The aqueous CO_{2(aq)} species is identified through EQ3 modeling to constitute a significant portion of the HCO₃⁻ concentrations for March (43%), but drop below 5% for the July measurement. This is a reflection of the change in pH over the sampling period from 6.516 to 7.821. While this water is more concentrated than waters from the Tuscan Formation, the TDS values (153 to 197 mg/L) fall within the range of values from this formation, and are less than half of those recorded for the Chico Formation waters. Field measurements for water temperature (13.8 to 18.8 °C) and EC (280 to 350

$\mu\text{S/cm}$) increased between sampling periods, while the ORP measurement fell from 150.7 to 124.8 mV.

Fluoride Concentrations

Fluoride concentrations in the Tuscan Formation springs were very low during the sampling in March and not detected in July; fluoride was not detected in the Basalt Spring during the September sampling. Chico Formation spring water has significantly greater concentrations in March than the Tuscan Formation springs, but becomes depleted in July. Concentrations of fluoride found in the Weeping Wall Spring in March are similar to the depleted values of the Chico Formation springs and follow the same pattern experienced for all springs in July. Fluoride is more abundant in sedimentary rock, and weathering of continental rock the greatest source of this constituent found in natural water (Hem, 1985). The fluoride ion is negatively charged and approximately the same size as the hydroxyl ion easing exchange between the two (Hem, 1985). In the Big Chico Creek watershed, fluoride may be adsorbed during the formation of clays, providing an explanation for the depleted concentrations noted in July.

Analysis of Field Parameters

More than 25 springs have been located and field assessed for water temperature, pH, ORP, and EC in the Big Chico Creek watershed. Water temperature of the Tuscan Formation springs ranges from 12.3 to 18.8 °C, and shows a definitive downward trend as sampling dates move into the cooler and wetter months of the year. Tuscan Formation water temperatures tend to fall at the lower end of temperatures of waters from

the Chico Formation as sampling dates transition from the hot, dry months of July through December. Temperatures recorded for springs emanating from the Chico Formation range from 10.6 to 25.6 °C, and have a greater range (4.5 °C versus 2.3 °C) of averages for the dry versus wet months. Three temperature measurements during September have been recorded for Lovejoy Basalt formation springs. The geomorphological location of these springs has an aspect and slope gradient that provides greater sun exposure, which may cause slightly warmer water temperatures than Tuscan Formation water. Regardless of the effects from differing hydrologic regimes, the pH range of Tuscan Formation springs is much tighter than Chico Formation springs. The Tuscan spring waters average 6.4 pH with the exception of Rock Shelter Spring. Measurements taken July and September 2005 for Rock Shelter Spring, during the dry period of a water year, indicate pH values of 7.8 and 7.9, respectively. These measurements are much greater than two recorded in February 2002 and March 2005 of 6.5 and 6.1 pH. The increase in pH correlates with the increase in bicarbonate measured in July 2005 and the decrease in $\text{CO}_{2(\text{aq})}$ modeled in EQ3 for the corresponding field and analytical data set. Waters from the Chico Formation appear to reflect changes in the hydrologic regime through the water year. Measured pH depicts a greater range during precipitation months than during the dry months. The average pH for Chico Formation springs is 7.2.

Field measurements of ORP and temperature are used to calculate Eh. ORP values greater than 100 mV are indicative of an oxidizing environment, while values less than 100 mV indicate a reducing environment. Chico Formation springs range from 50.7 to 630.6 mV, with five field measurements from four springs showing reducing conditions.

Two of these springs exhibited conditions typical of a reducing environment: an odor of hydrogen sulfide gas and bacterial formations at the spring outlet. Because only three springs have been identified as Tuscan Formation waters, limited field data exists. These waters exhibit a much tighter Eh range of 350.7 to 534.6 mV. Springs of the Basalt Formation fall within the range of data collected for the Tuscan Formation with an average Eh of 423.6 mV. Electrical conductivity values for waters of the Tuscan Formation range from 180 to 250 $\mu\text{S}/\text{cm}$. Three EC measurements were taken for springs believed to flow from the Lovejoy Basalt, which range from 200 to 260 $\mu\text{S}/\text{cm}$. Measured EC values for waters of the Chico Formation show the greatest variability, ranging from 170 to 1840 $\mu\text{S}/\text{cm}$.

Introduction to Published Data

Existing data were obtained representing Big Chico Creek stream water and ground water. Wells were selected based on proximity to the creek with the expectation that recharge comes from this stream. Data were interpreted to develop an understanding of source waters, water-rock interactions, and interactions between waters within the Big Chico Creek watershed. This project uses spring, creek, and ground water geochemical data to investigate hydrologic and geologic controls on the composition of the waters within the Big Chico Creek watershed. Big Chico Creek is a perennial stream; therefore its hydrochemistry reflects water that discharges to the stream (i.e., spring water) during base flow and a mixture of spring water and meteoric water over the remainder of the water year. If the principal aquifer system in the Tuscan Formation near Chico, California is

locally recharged by Big Chico Creek, then Butte Basin ground water should reflect a mixture of creek water and host rock water.

Reported Data: Big Chico Creek

This study uses reported stream hydrochemical data and flow data for Big Chico Creek collected at the USGS gaging station 11-3840 (Figure 2) for the period 1952 to 1971. Records were compiled by Ryley (1974) and entered into an Excel database during this study. The data set contains 207 records of major ion chemistry, NO_3^- , boron, E.C., pH, and runoff collected during this period. Chemical analyses data were reported in parts per million (ppm). Runoff data were reported in cubic feet per second (cfs). The flow gage sits near the eastern extent of the groundwater basin in the Holocene alluvium sediments of the Red Bluff or Modesto Formations, downstream of stream bank exposures of the Tuscan, Lovejoy Basalt, and Chico Formations (Figure 2). Big Chico Creek waters are a mixture of discharge from these formations; runoff during the months of November through April when all significant annual precipitation occurs; and snow melt that maintains an average flow rate approaching 100 cfs through June. Formation waters, runoff, and snowmelt assume a distinct chemical signature that combine seasonally to produce creek water chemistry. Reported values for pH show a tight range of 7.5–8 with little variation due to seasonal hydrologic changes. The reported E.C. for the creek varies temporally, as depicted in this data set, and spatially as reported by Ryley (1974) from his longitudinal study of the creek. Ryley reports that salinity increases downstream can be attributed to discharge from the Chico Formation.

Flow characteristics

Reported flow measurements for Big Chico Creek average 17 (+/- 2) readings per month for the period of record and were recorded throughout the year. Flow rates range from 19 to 2530 cfs. Runoff in Big Chico Creek watershed is rainfall dominated November through February, and snowmelt dominated March through June. Of the reported flow readings, 49% had flow rates with a range of 19 to 48 cfs and an average of 30 cfs. Flow values collected in July averaged 31 cfs and flow values collected August through October averaged 26 cfs. These values represent the average base flow rate for the uplands reach of Big Chico Creek during the dry season, July through October. Discharge from ground water such as flow from springs studied in this project dominates runoff during these months when stream chemistry acquires a compositionally high signature in early fall during base flow. Some variations exist when low flow continued through January and started as early as June. One reading reflects a flow exceeding 50 cfs in August. It appears from stream flow readings that this particular year was wetter than usual and may have had a significant snow pack. Abnormal flow rates can be representative of dry years, a shift in the precipitation scheme, ground water pumping too close to the stream, or variations may mark events when runoff from a rapid snowmelt results in an unusually late runoff spike. Reported flow values for November through June indicate a much greater range for high flow of 50 to 500 cfs, and represent 46% of the total flow readings collected during the reported measurement period. The stream acquires a compositionally low signature in early spring when meteoric water as rainfall or snowmelt dominates runoff. Eleven flow measurements (only 5% of all reported flow values) exceeded 550 cfs. These values

indicate a flashy response to heavy rainfall in December through February or probable rapid snowmelt with warm rains in March through June. Six reported values averaged 1607 cfs for December through February; runoff averages 135 cfs for these three months. Five of the high flow rates occurred in March and April, generating an average runoff of 712 cfs. These flashy responses exceeded the average for these two months of 90 cfs by more than 7 times.

Chemical characteristics

Figure 12 is a conceptual mixing model of Big Chico Creek showing a typical change in chemistry due to seasonal hydrologic changes and geologic controls. During the wet winter months, stream chemistry assumes a dilute signature influenced by the dominant formation in the watershed, the Tuscan Formation. During the dry season, stream chemistry

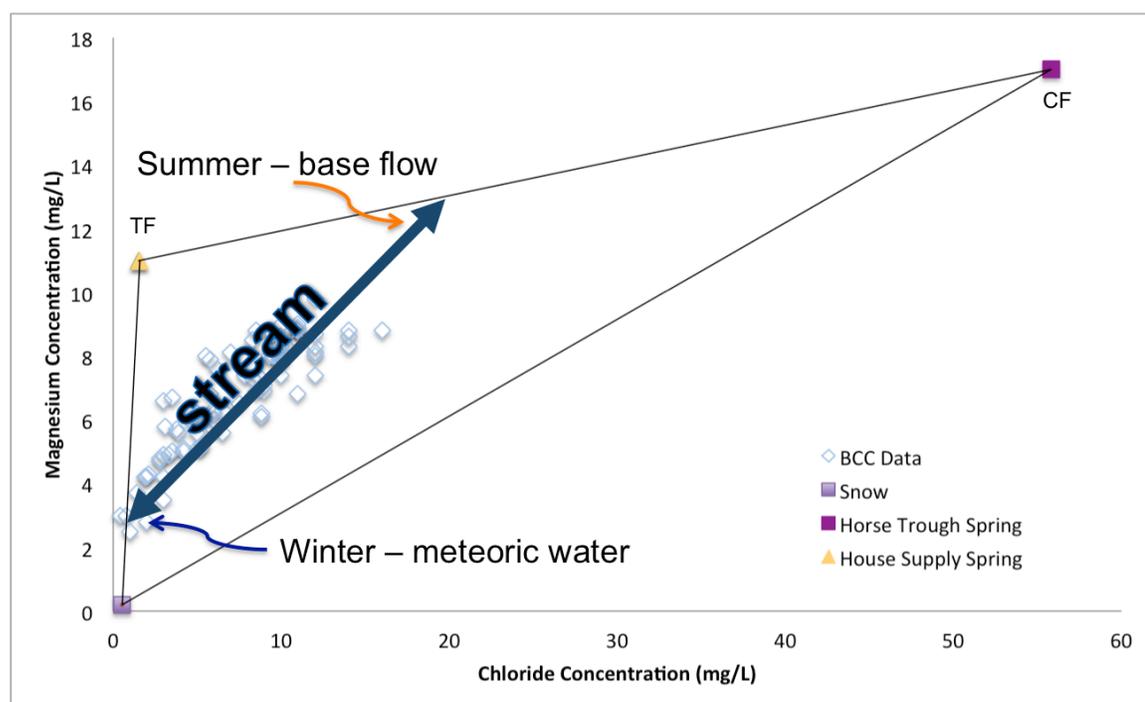


Figure 12. Conceptual Seasonal Changes in Big Chico Creek Chemistry.

moves toward the mixing line defined by the formation end member springs: House Supply Spring (Tuscan Formation) and the Horse Trough Spring (Chico Formation). This cyclical pattern in stream chemistry is shown again in Figure 13. This figure shows the average monthly concentrations for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and Cl^- in Big Chico Creek vary seasonally reflecting a mixture of spring discharge, meteoric inputs and runoff. Monthly averages for Ca^{2+} , Na^+ , and Cl^- plot in parallel throughout the year suggesting that these solutes behave conservatively. The HCO_3^- average monthly trend, Figure 14, shows the same seasonal variation as the major cations. It is worth mentioning here that averaging concentration data is risky. Averages mask variation due to processes and sources that

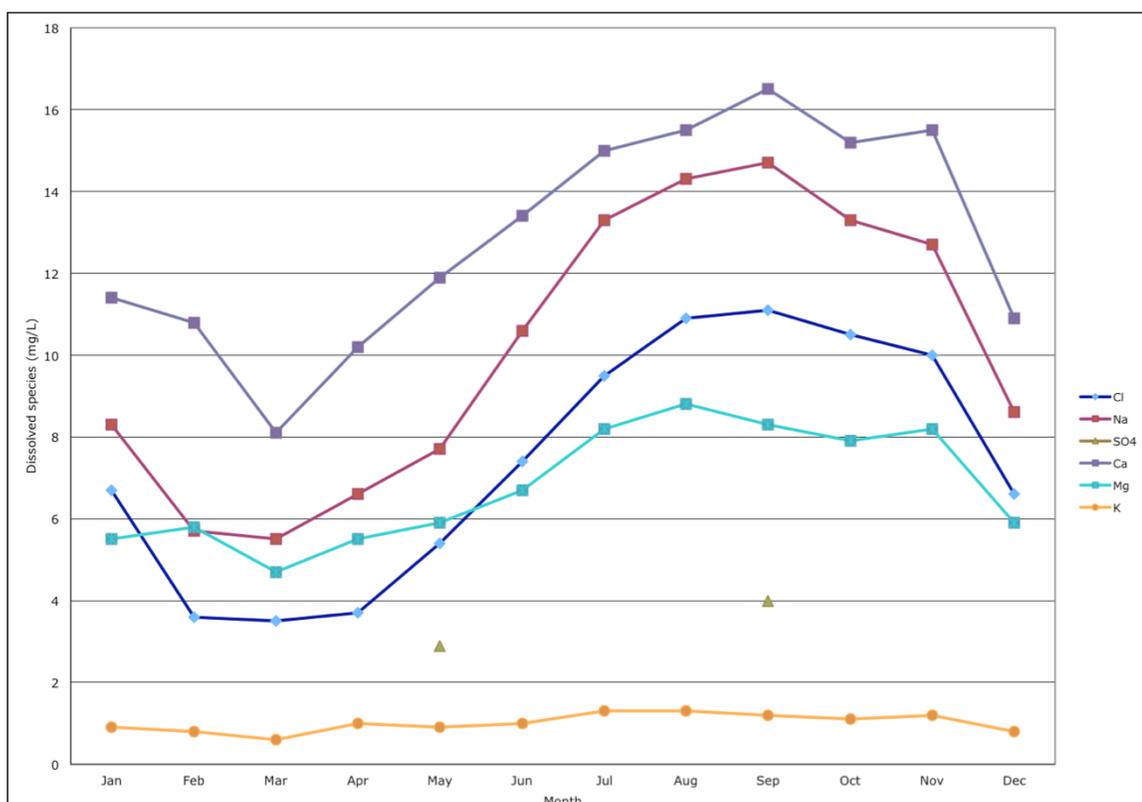


Figure 13. Seasonal Variations in Big Chico Creek.

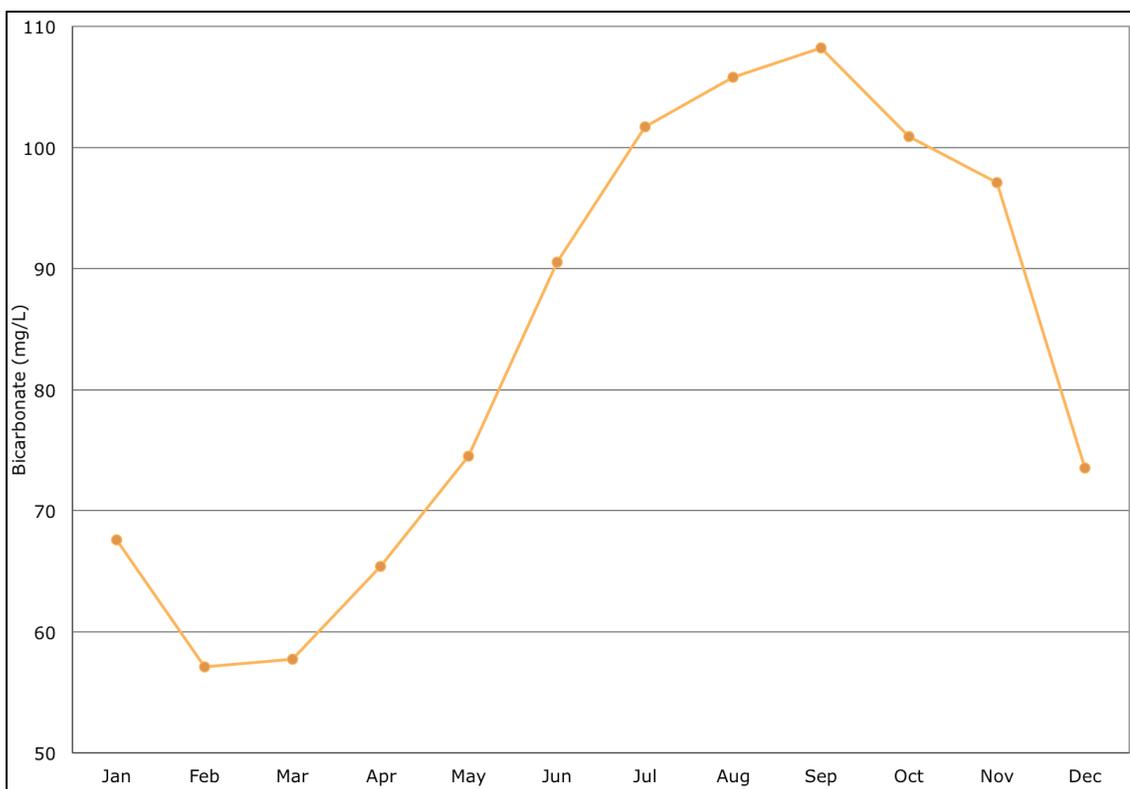


Figure 14. Average Monthly HCO_3^- Concentrations of Big Chico Creek.

affect dissolved solute concentrations inherent in a complex system. Averages are not robust; they are sensitive to extreme values. All six analytes show an interesting drop in average concentrations for October reported values. October flow data shows the least variability; however, there were three sampling dates with higher than average flows and very low average concentrations. Representative records containing a complete set of major ion concentration data (mg/L) for high and low flow in Big Chico Creek were selected from the Ryley (1974) data set (Table 10). The mean and standard deviation were calculated for each of the major ions for the data set. All solute measurements fell within one standard deviation of the mean for the two selected records. These data provide a basis for further investigation into the possible solute sources and processes affecting measured

concentrations in the stream and are referred to later in this study to represent creek water concentrations for analysis of ground water samples.

TABLE 10. REPRESENTATIVE RECORDS FOR BIG CHICO CREEK

End member solute concentrations		Ca²⁺	Mg²⁺	Na⁺	K⁺	HCO₃⁻	Cl⁻	SO₄²⁻
High flow spring runoff Q (cfs) 59 May 1964	(mg/L)	14.0	6.9	10	0.9	82.0	8.5	4.0
	(meq/L)	0.7	0.57	0.45	0.02	1.34	0.24	0.08
Low flow – base flow Q (cfs) 24 September 1957	(mg/L)	16.0	8.0	15.0	1.6	108.0	12.0	4.6
	(meq/L)	0.8	0.66	0.65	0.04	1.77	0.34	0.1

Note: Major ion concentrations for Big Chico Creek showing seasonal variation in stream chemistry during spring runoff at high flow and low (base) flow during the fall. Data derived from Ryley (1974).

Monthly averages for Mg²⁺ and K⁺ (Figure 13) illustrate damped signals indicating that additional controls such as adsorption or biological processes affect the presence of these solutes in the stream. K⁺ concentrations show a slight upward trend above 1.0 mg/L occurring in July and August, but only two reported values (2.2 and 2.3 mg/L) exceed the maximum concentration of 2.0 mg/L measured in the six springs. K⁺ may have several mechanisms limiting its presence. K⁺ is a valuable plant nutrient that is readily adsorbed by vegetation and can be removed from solution by adsorption to clay minerals.

Vegetative cover in the Big Chico Creek watershed is considerable. Drever (1997) points to the growth and decay of vegetation as providing considerable control on the mass-balance of Ca²⁺ and K⁺ ions within a watershed on short time scales.

Interpretation of reported data from a number of researchers in the Hubbard Brook

watershed, New Hampshire, indicates that biomass uptake of K^+ in the watershed can exceed its production or release through weathering by as much as 80% (Drever, 1997).

The relationship between chloride concentrations and stream flow for Big Chico Creek is shown in Figure 15. In general, Cl^- concentrations decrease with flow. The relationship depicted in this graph is typical for many watersheds (White and Blum, 1995) and applies to all major ions reported for Big Chico Creek with the exception of SO_4^{2-} . The consistency seen in Figure 15 at concentration values above 10 mg/L is an artifact of recording significant figures in the original data. Concentrations of Cl^- at base flow ($Q < 50$ cfs) are greater with a larger range than concentrations recorded during runoff ($Q > 50$). At base flow, the chemistry of the creek is more concentrated reflecting a mixture of discharge from the Tuscan and Chico Formations. As runoff increases with increasing precipitation, decreases in solute concentrations occur as a result of dilution of discharge chemistry with meteoric water. At flow rates above 250 cfs, not shown in Figure 15, the variability in Cl^- concentrations diminishes identifying a potential limit for chloride concentration that can be attributed to meteoric origins. At higher values of flow we expect less reaction time with the rocks and little to no influence on the concentration values once the soil has had sufficient time to become saturated with infiltrating precipitation. At this point in an event, infiltration is limited and excess precipitation simply runs off.

White and Blum compiled reported chemical, physical and climatological data collected from 68 granitic watersheds distributed worldwide. They examined major ion concentrations and SiO_2 in stream runoff and precipitation to explore climatic effects on weathering. White and Blum sought correlations between solute concentration and flux

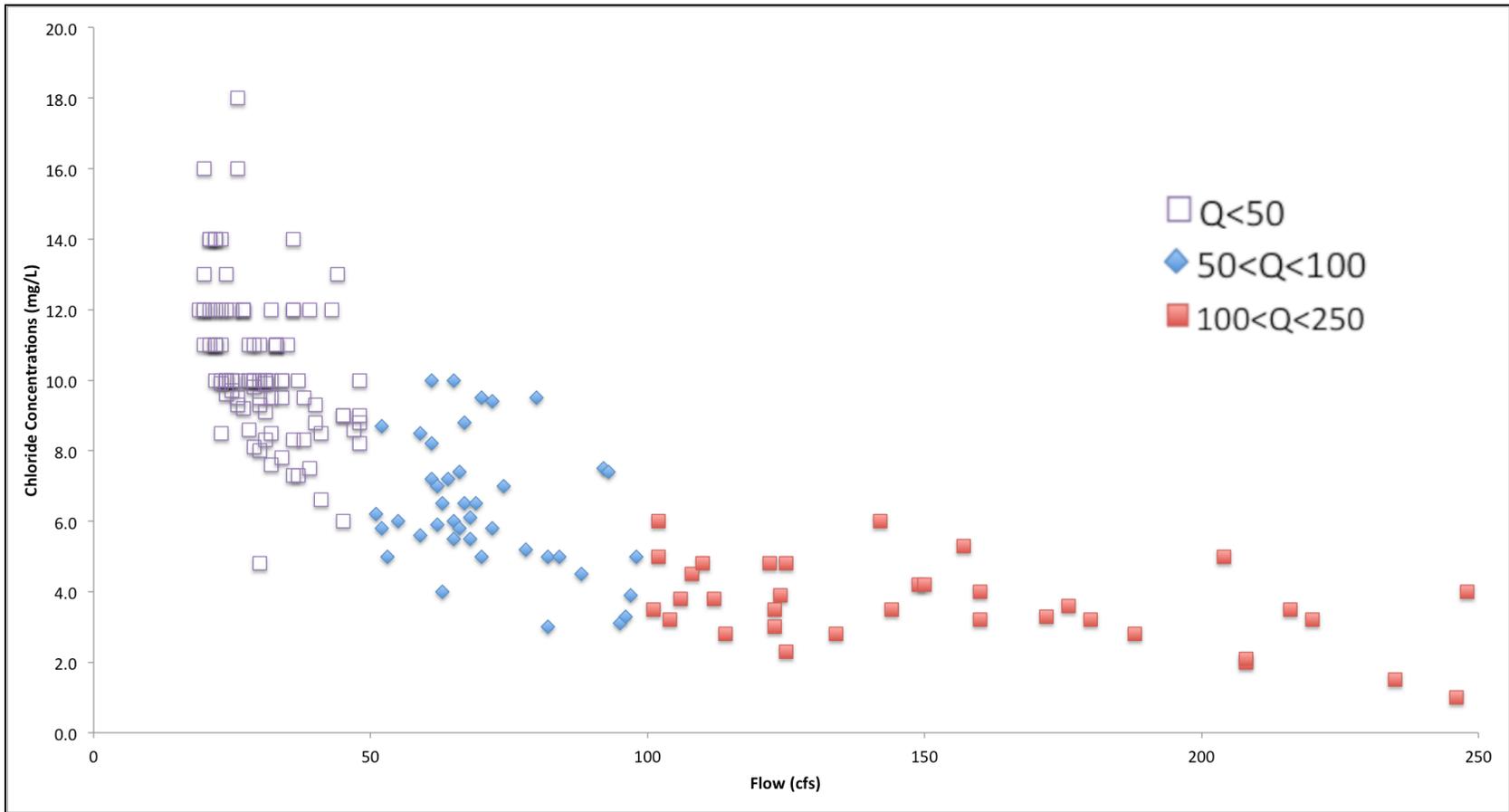


Figure 15. Relationship Between Flow and Cl^- Concentrations for Big Chico Creek.

variations with temperature, precipitation, runoff and evapotranspiration (ET). They found solute concentrations have a strong correlation with proportionally weighted ET losses.

White and Blum assert that evaporative concentration makes stream solute concentration measurements a poor analog of chemical weathering within a watershed.

Limited data exist for SO_4^{2-} concentrations in Big Chico Creek for the period of record. Reported sulfate measurements were collected primarily in May and September and show no correlation with lithologic or hydrologic controls established through this study. SO_4^{2-} concentrations in Big Chico Creek water are greatly depleted in relation to the Chico Formation spring end member, Horse Trough Spring (Table 11). Sulfate and Cl^- concentrations with respect to flow are displayed in Figure 16. Sulfate is considered a conservative solute (Christopherson and Hooper, 1992; Burns, et al., 2001; van Verseveld et al., 2008); however, concentrations will vary as a result of hydrologic conditions that induce mixing and the biological and geochemical processes taking place along the flow path. Williams and Melack (1991) found sulfate concentrations in meltwaters of the Sierra Nevada Range were depleted when compared to measurements from the snowpack. They identified adsorption within soils as the primary control on sulfate concentrations. SO_4^{2-} concentrations exhibit no correlation with seasonal changes in flow as seen in Cl^- concentrations. Effervescence of gas was visible at in the Riparian Spring pool in July 2005 with a scent of hydrogen sulfide present. These are indicators that sulfur undergoes chemical changes due to oxidation and reduction processes that are spatially variable within the heterogenetic Chico Formation.

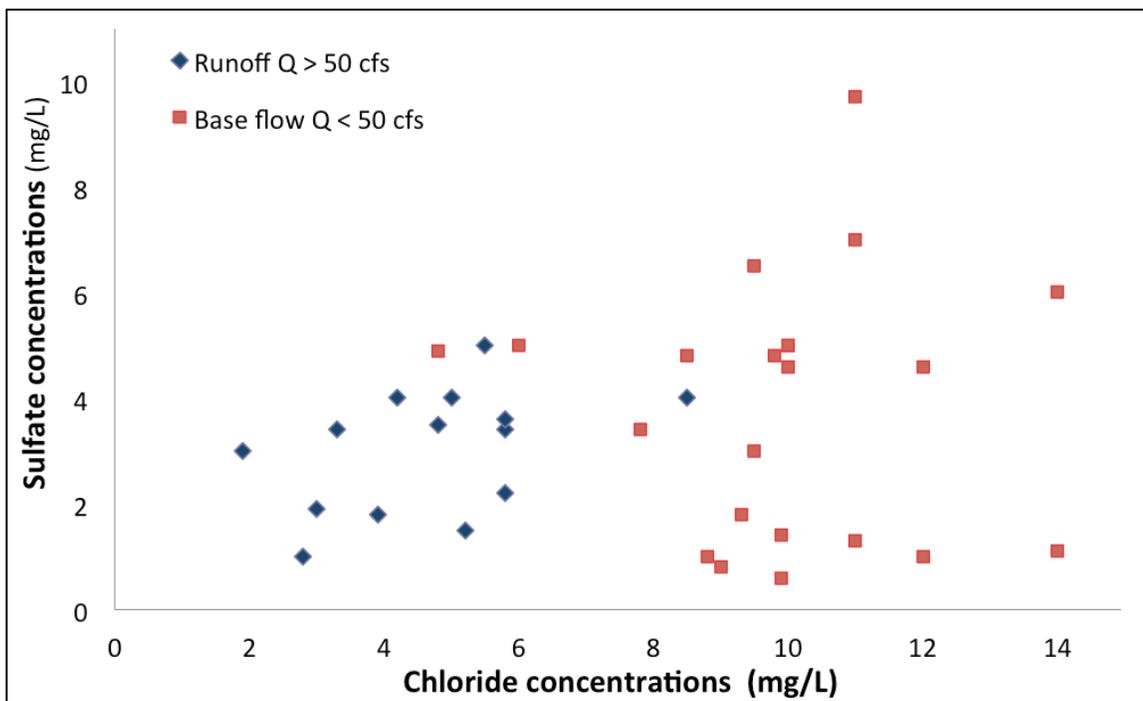


Figure 16. Composition Diagram of Cl^- and SO_4^{2-} for Big Chico Creek.

Stream Mixing Models

This project hypothesizes that two seasonally dependent, mixing processes control creek water chemistry throughout the year: (1) dry season base flow modeled as a mixture of Tuscan and Chico Formation discharge water; and (2) wet season runoff modeled as a mixture of meteoric and spring water discharge. These mixing models are assessed using two different forms of the bivariate scatter plot. Creek water chemistry during base flow should plot as a straight line indicating a mixture of the dilute Tuscan Formation waters and the more concentrated Chico Formation waters. Creek water chemistry during the runoff season should plot within the mixing space defined by the formation end member springs and meteoric water. The chemistry of runoff water in this

watershed will range between a very dilute signature similar to snow and a signature enriched by water-gas-rock interactions in the soil zone. While the winter-spring runoff in Big Chico Creek is really a ternary mixture, Faure (1998) indicates that this type of water can be modeled as a binary mixture followed by dilution. Natural processes in the Big Chico Creek watershed fit the model as described by Faure as shown in Figure 17. As a perennial stream, Big Chico Creek is fed year round by discharge from the Tuscan and Chico Formations. During the wet season meteoric water falls, mixes, and dilutes the more concentrated discharge from the formations. The Snow-TF dilution line happens to intersect an observation, while the Snow-TC dilution line was generated to intersect the data point, dp (10, 7.4), as shown.

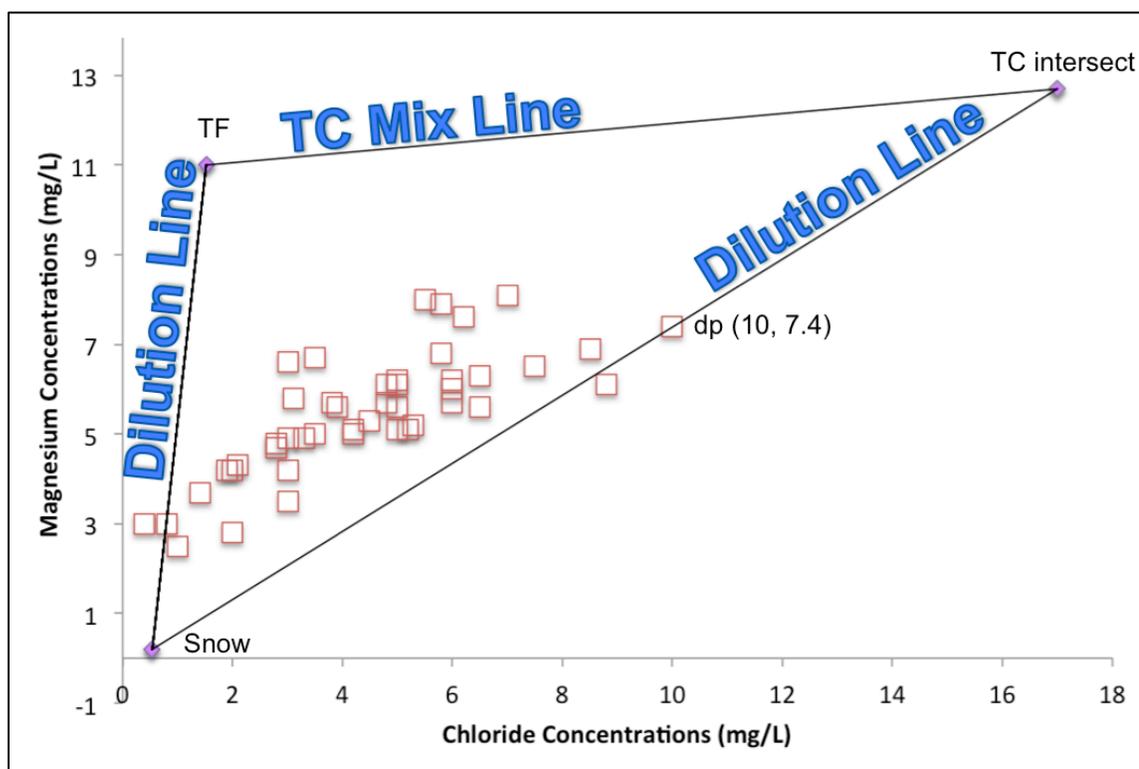


Figure 17. Ternary Mixing Model.

Major ion concentrations are listed in Table 11 for two samplings taken March and July 2005 for the formation spring end members: House Supply Spring (Tuscan Formation) and Horse Trough Spring (Chico Formation). These springs were selected as end members to explore the controls on creek water chemistry as shown in Figure 17 and below in Figure 19 and 20 of which all display compositional relationships between Cl^- , Ca^{2+} , and Mg^{2+} . Thyne et al., (1999) point out in their study of interbasin flow in the Sierras that the accuracy of a mixing model is sensitive to the seasonal variations in end member concentrations.

TABLE 11. MAJOR ION CONCENTRATIONS OF END MEMBER SPRINGS

End member solute concentrations		Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}
House Supply Spring (Tuscan Formation)	March (mg/L)	23.0	11.0	6.0	2.0	135.0	1.52	1.83
	(meq/L)	1.15	0.9	0.26	0.05	2.21	0.04	0.04
	July (mg/L)	24.0	11.0	6.0	2.0	143.0	1.6	1.7
	(meq/L)	1.2	0.9	0.26	0.05	2.34	0.04	0.04
Horse Trough Spring (Chico Formation)	March (mg/L)	50.0	17	86.0	1.0	82.0	55.8	96.8
	(meq/L)	2.5	1.4	3.74	0.03	1.34	1.57	2.02
	July (mg/L)	54.0	17	83.0	2.0	108.	59.5	93.8
	(meq/L)	2.7	1.4	3.61	0.05	1.77	1.68	1.95

Chloride ions are considered good tracers for the movement of natural waters because of their conservative behavior. There are few interactions for which Cl^- participates that change its concentration once it becomes a dissolved solute: evaporation and mixing are two. Evaporation of soil water or pooled water and evapotranspiration (ET) increase solute concentrations and may result in salts precipitating as evaporites in the soils.

Weeping Wall Spring could provide a basis for exploring evaporative concentration effects due to the geomorphologic structure surrounding this spring site. It is possible that a majority of the water that flows to this spring follows a path through shallow soils with considerable vegetative cover. While Cl^- concentrations increased 90% from the March to July samplings at this spring; concentrations in Big Chico Creek are significantly higher throughout the year. In addition, Cl^- concentrations ranged from 3.4 to ~60 mg/L for the Chico Formation springs. These phenomena obscure any signal that might result from evaporative enrichment.

Mixing occurs throughout the hydrologic continuum of the natural environment. Water mixtures display as straight lines (Mazor, 1997; Faure, 1998) or as a cloud of points falling within end member boundaries (Hooper et al., 1990) on bivariate plots as shown in Figure 18 and Figure 19. The first graph shows a strong relationship between Cl^- and total dissolved ions (TDI). Faure states that diluting waters have concentrations near zero forcing the mixing line to the origin of the plot. Mazor provides a different interpretation specific to the TDI plot. Mixing lines that cross the horizontal axis are indicative of diluting water with abscissa values greater than the correlating variable, for example Cl^- as shown in Figure 18. If the ordinate variable of the diluting water has a greater concentration in general than other ions in solution, mixing lines will cross the vertical axis. For example Ca^{2+} and Mg^{2+} are dominant constituents in Big Chico Creek waters. When these variables are plotted as the ordinate, resulting mixing lines trend toward the vertical axis. This set of data supports the hypothesis that Big Chico Creek at

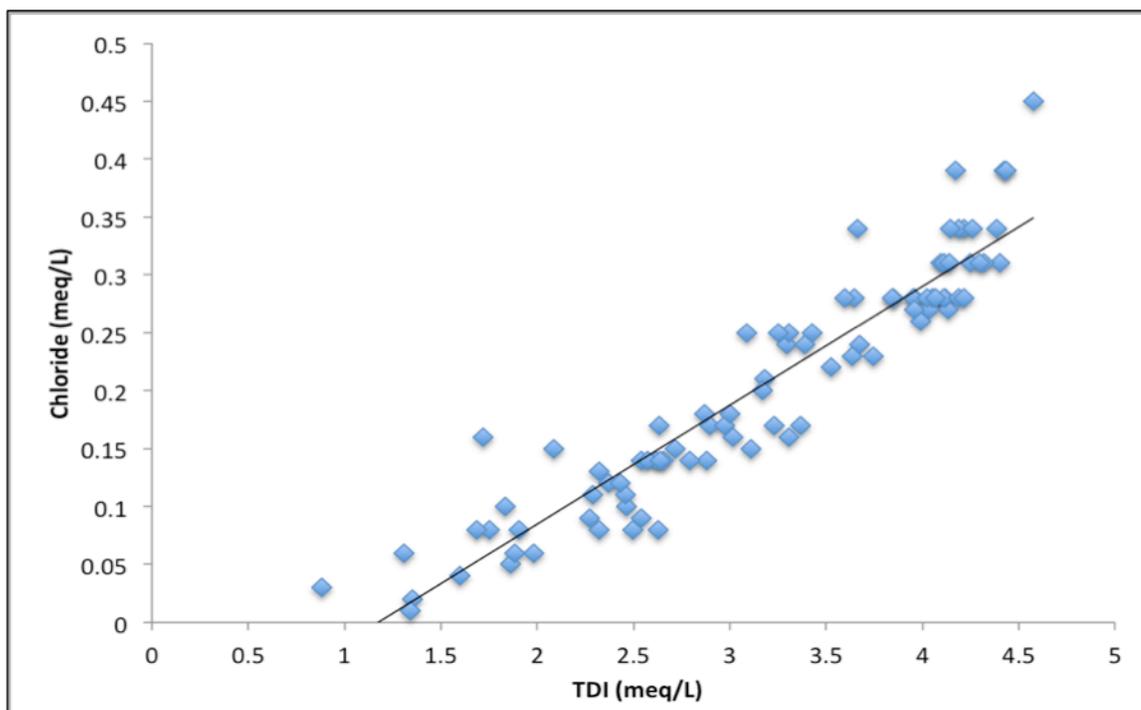


Figure 18. Bivariate Plot of Cl^- and Total Dissolved Ions (TDI) for Big Chico Creek.

base flow is a mixture of more concentrated, high chloride and high TDI Chico Formation waters and dilute, low TDI Tuscan Formation waters. The bivariate mixing space plot displaying Ca^{2+} and Cl^- concentrations of Big Chico Creek (Figure 19) corroborate the information of Figure 18. Creek waters fall within the mixing space defined by the mixing line boundaries of the formation end members and snow; and these data further show the seasonal variation in creek water concentrations between the spring discharge mixture and meteoric water.

The concentration units selected for the various graphs are dependent on the variables plotted. Figure 18 displays variables in their equivalent weights as opposed to weight units (mg/L) used in other graphs. Piper and Durov diagrams present another example where equivalent weight units must be calculated. Natural waters are electrically

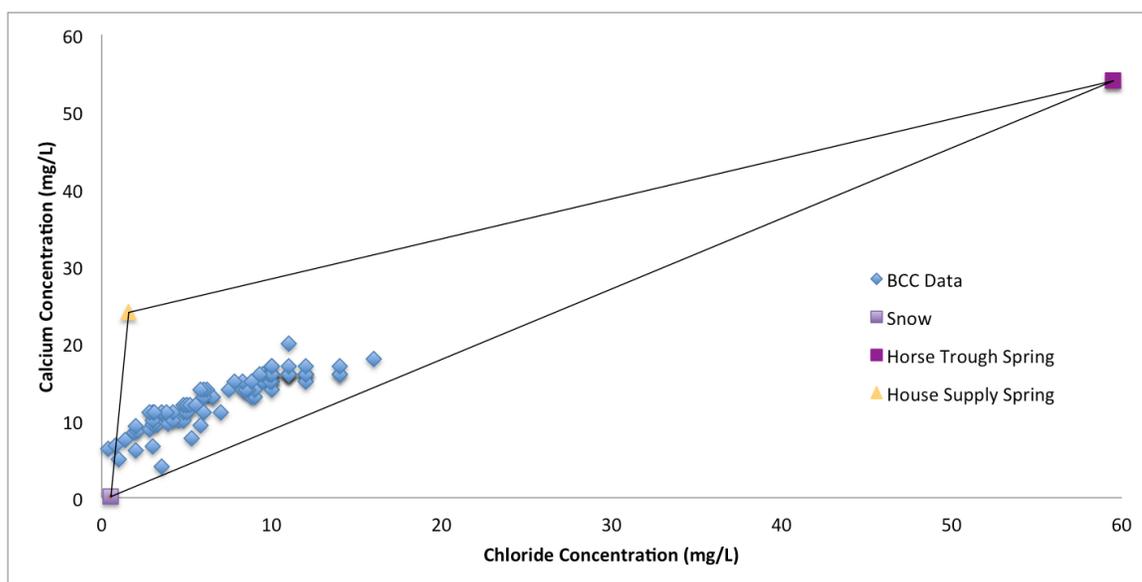


Figure 19. Cl^- and Ca^{2+} Mixing Space Diagram for Big Chico Creek.

balanced and as such this balance forms a constraint on water chemistry to remain charge balanced. When comparing concentrations involving all measured ions in solution, for example the total dissolved ions displayed in Figure 18, electrical charge is an important criteria.

Plots of Mg^{2+} , K^+ and HCO_3^- as a function of Cl^- are similar to Figure 19 showing creek water concentrations fall neatly within the defined mixing space. Plots of magnesium concentration data for Big Chico Creek are shown in Figure 20 and Figure 21. Based on the mixing model, the amount of creek water discharged from the Tuscan Formation during the dry season can be determined using information derived from these two plots. The mix line (TC) for Tuscan-Chico Formation waters is the upper boundary of the mixing space defined in Figure 20 and runs between the House Supply Spring and

Horse Trough Spring data. The equation for the TC mix line was found using Excel's trendline function for the spring end member data and is defined as (6).

$$y_{(TC)} = 0.11x + 10.83 \quad (6)$$

The variable x represents Cl^- concentrations and y represents Mg^{2+} concentrations shown in Figure 20. The trendline function in Excel was used to define the equation for the subset of creek water data representing winter-spring runoff (R).

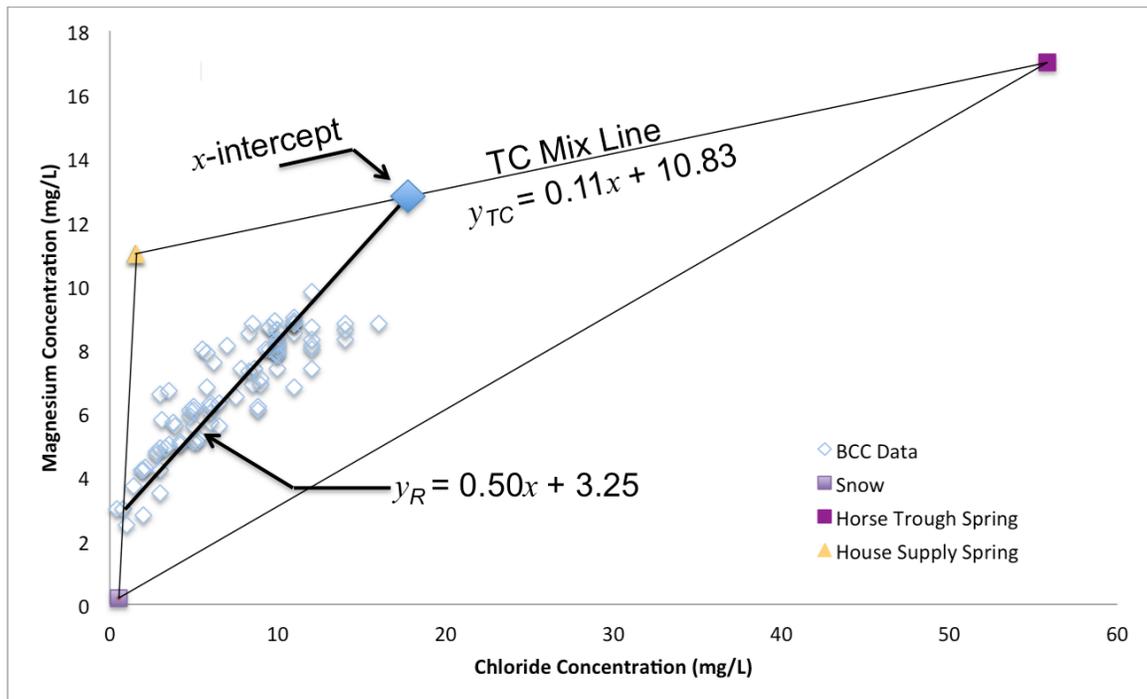


Figure 20. Mixing Space Diagram of Cl^- and Mg^{2+} for Big Chico Creek.

The trendline equation describing the runoff data is defined as (7) and is extrapolated to the TC mix line by setting $y_{(R)}$ equal to $y_{(TC)}$ and solving for x : the TC x -intercept.

$$y_{(R)} = 0.50x + 3.25 \quad (7)$$

The x -intercept is the predicted Cl^- concentration for the mixture, in this case creek water during runoff, at the TC boundary and is 19.4 mg/L (X_M). The fraction of Tuscan Formation water is defined by equation (8). Derivation of the mix fraction equation is discussed in Chapter IV.

$$f_{TF} = \frac{(X_M - X_{CF})}{(X_{TF} - X_{CF})} \quad (8)$$

X_{TF} and X_{CF} are the Cl^- concentrations for the Tuscan and Chico Formation end member springs, respectively. These values can be found in Table 11 for the March sampling and X_M is given above. Solving equation (8) using the Mg^{2+} concentration values generates a fraction (f_{TF}) for Tuscan Formation water of 68% during runoff for this model. These data support the model that Big Chico Creek water is a binary mixture of discharge from formation water and dilution by meteoric water during the wet season when flow in Big Chico Creek is dominated by runoff.

Applying the same methodology to the Ca^{2+} data generates a very different mix ratio indicating that only 38% of creek water is Tuscan Formation discharge. The mixing model should provide consistent results when applied across the suite of conservative tracers. The possible conservative tracers in this study were identified in Figure 13 as Ca^{2+} , Na^+ , and Cl^- . These solutes appear to have additional sources and processes affecting their conservative behavior that have not been identified in this study. Christophersen et al., (1990) and Faure (1998) identify three assumptions regarding mixing models: (1) constituents are conservative; (2) only the end members contribute to the chemical

composition of the mixture; (3) composition of end- members remains constant (in space and time). Data that scatter around the mixing line is evidence that these assumptions are not strictly satisfied in nature (Faure, 1998). It can be concluded from these model results that there are processes affecting the chemistry of waters in the Big Chico Creek watershed that have not been captured in this study; and other waters that drain to the stream during the runoff season have not been identified.

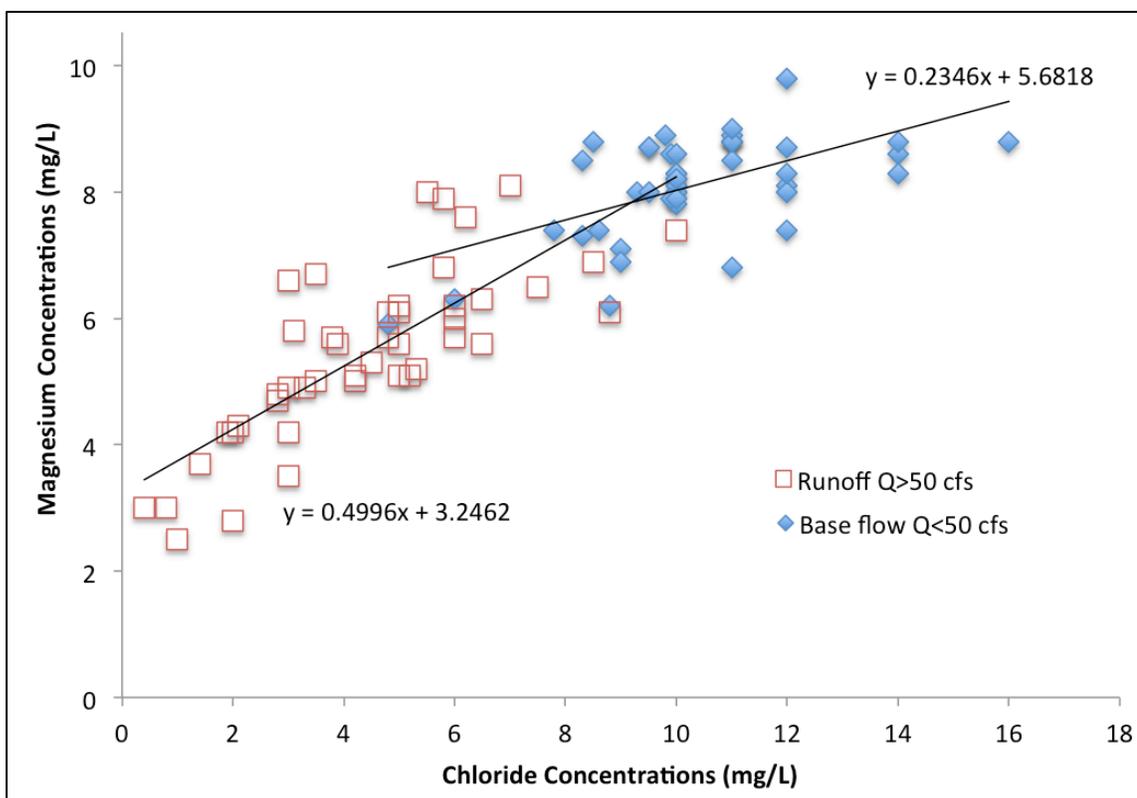


Figure 21. Seasonal Variations in Cl^- and Mg^{2+} Concentrations in Big Chico Creek.

The following assertions can be generated regarding the applicability of these mixing models to this study. (1) Conservative behavior of constituents must be more

closely explored. (2) Soil water and the water-gas-rock interactions that are known to occur in this 'reservoir' have not been adequately tested in this study. (3) Interpretation of Chico Formation spring water chemistry indicates two distinct water types. Ryley (1974) measured a stream flow rate increase of 15 to 30 cfs in Big Chico Creek between two measurement stations August 31, 1972. Ryley identifies the reach as one that cuts through the Chico Formation and he attributes the flow increase to discharge from this formation. The fact that the Chico Formation appears to discharge copious amounts of water and that the heterogeneity of the formation has not been captured in two water samples contribute to the ambiguity apparent from this modeling.

Reported Data: Butte Basin Ground Water

This study uses reported hydrochemical data for ground water collected annually from 1985 through 1991, and biennially from 1992 to 2000 from 28 wells in Chico with proximity to Big Chico Creek. The data were compiled in Excel as part of this project and consist of 45 records with the complete suite of the major ion chemistry used in this project (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , and SO_4^{2-}). Twenty-four records contain SiO_2 data. Sampling was sporadic; the 45 complete records contain data from nineteen wells that were sampled once; three wells were sampled twice, and only six wells were sampled 4 or more times. Data collected in March, June, and August constitute 75% of the records. The majority of SiO_2 data is reported for the March and June samplings. A single record exists each for the months of October and December, and ten samples collected during July and September make up the rest of the complete records.

Hydrogeologic Characteristics

The geology and lithology of the host rock that Butte Basin wells encounter varies spatially and with depth. The construction and depth of the wells, for this study, is unknown. Well construction, or the 'as built' design of the well, identifies the host rock for which water is pumped. Often the physical characteristics of rock vary with depth. Thus, the hydrochemical facies of such a well may be varied and pumped water will be a mixture. The wells for this study were selected by DWR to meet three requirements: (1) general proximity to Big Chico Creek; (2) availability of a full suite of major ion analyses; and (3) assumption that the Tuscan Formation was the host rock for each well.

Chemical Characteristics

March data were collected in 1992 from eleven wells. June data were collected in two separate years (1989 and 1992) from eleven wells different than those sampled in March. August data consists of 12 complete records that were collected from nine wells over a range of years of which four have no previous sampling history in this record set. SiO₂ data were not collected in August, while March and June samplings constitute 22 of the 24 SiO₂ measurements.

The data collected June 1992 looks similar to that collected in March and is considerably different from the data collected June 1989. The six water samples collected in June 1989 have SiO₂ concentrations (with an average of 24 mg/L) less than half that of the 18 other water samples tested for SiO₂ (with an average of 63 mg/L). However, the June 1989 records and those collected in August, across the temporal scale, exhibit averages and standard deviations for bulk chemistry similar to the entire 45-record set. The

June 1992 and March data sets have much lower averages and a smaller standard deviation. In addition, the Ca^{2+} and Mg^{2+} concentrations for the June 1989 samples appear to be bimodal. Two records average 60 mg/L Ca^{2+} with Mg^{2+} concentrations at 55 mg/L. Four records average 22 and 14 mg/L respectively. Using the June 1989 Ca^{2+} and Mg^{2+} concentrations to classify all 45 ground water records (Figure 22), observations can be divided into three significantly different sample concentration ranges: high, mid, and low. These divisions hold consistent for all other major ions and TDS. For example, the nine records that contain the highest Ca^{2+} and Mg^{2+} concentrations (ranging between 55-70 mg/L for both ions) also have the highest ion concentrations for Na^+ , K^+ , alkalinity, Cl^- , SO_4^{2-} and the highest TDS values. The high range ground waters are similar to spring waters emerging from the Chico Formation upstream in the Big Chico Creek watershed. The nine high value samples plotted in Figure 22 represent data from four wells sampled over a number of years. The trendlines are drawn to illustrate the differences in the hydrochemistry of the wells. These data indicate that additional processes are occurring within the aquifer system not explained by mixing or waters becoming more concentrated with time.

Fourteen of the ground water records contain mid-range concentrations of 27 to 49 mg/L and 17 to 45 mg/L for Ca^{2+} and Mg^{2+} respectively. The low-range values for these ions respectively are 14 to 25 mg/L and 8 to 19 mg/L. The low range ground waters are similar to the Tuscan Formation spring waters emerging in the watershed upstream. It is tempting to define these sample populations as hydrochemical facies; however, some wells that have been sampled multiple times exhibit hydrochemical differences (Well ID No. 4,

10, 12, 13). The hydrochemical facies at a given well should not change with time without an external forcing; facies are however variable on a spatial scale. Differences in hydrochemistry can be the result of natural hydrologic phenomena such as drought or changes in the timing and type of precipitation. Anthropogenic processes can also affect ground water chemistry such as pumping regimes, depth of wells, and screening intervals. Information concerning the design and use of wells was not provided for this project.

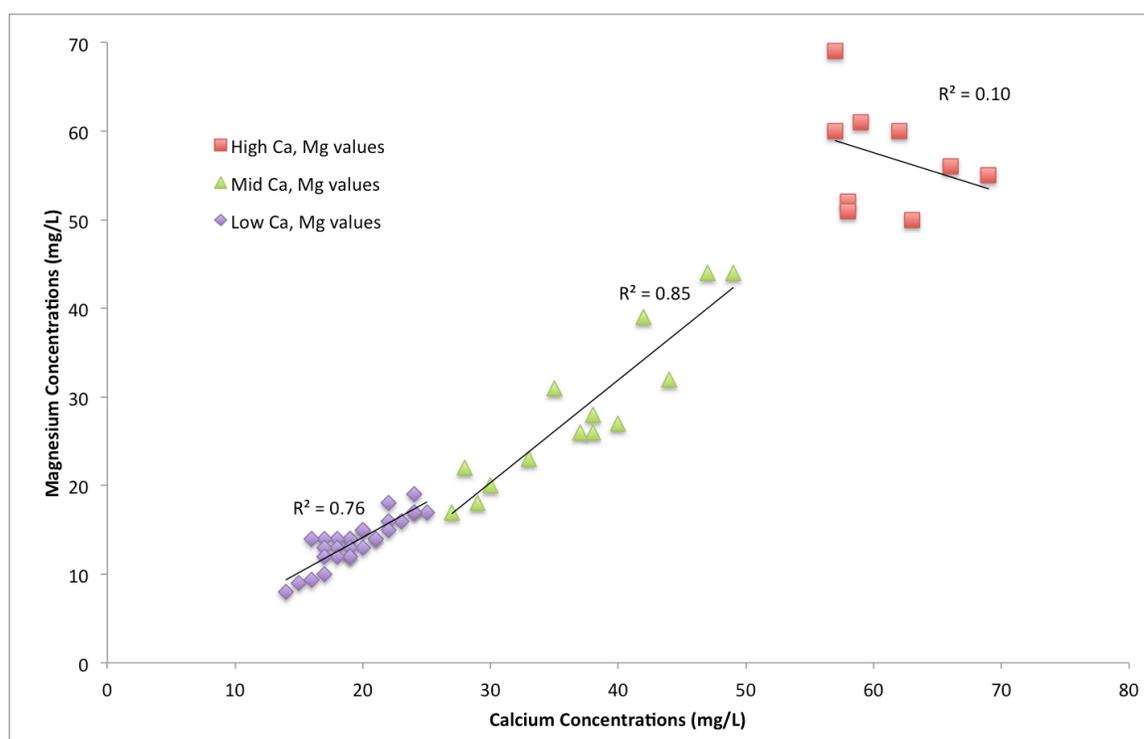


Figure 22. Ca^{2+} and Mg^{2+} Ions in Butte Basin Ground Water.

The Durov diagram provides cation and anion classifications similar to the Piper and further classifies water chemistry based on TDS and pH of the plotted samples. Butte Basin well water was classified into two groups, for the Durov plot of Figure 23,

based on the Ca^{2+} concentrations: high-range samples are in red. Ground water chemistry high in Ca^{2+} concentrations appear to be controlled by processes such as calcite dissolution. Calcium and HCO_3^- concentrations are increasing at the expense of Mg^{2+} and SO_4^{2-} , while $\text{Na} + \text{K}$ and Cl^- concentrations remain constant. These waters also exhibit higher TDS values over all, but have a tighter range than ground waters with Ca^{2+} concentrations in the low to mid range. In this example, use of the Durov plot over the Piper clearly distinguishes differences in the physicochemical characteristics of the water samples.

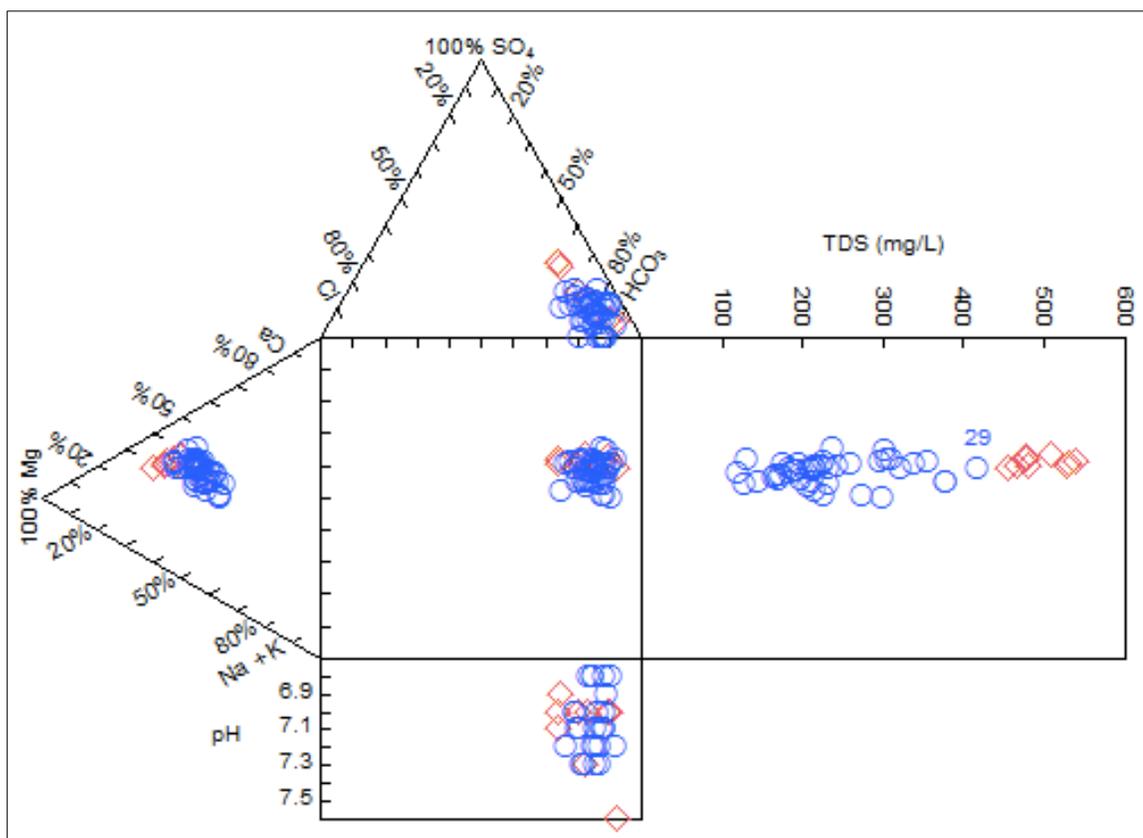


Figure 23. Durov Diagram of Butte Basin Ground Water.

Limited data exists across the seasonal regime, however, seasonal variations due to changes in the hydrologic regime are apparent in the plot of average concentrations for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , and Cl^- ions as displayed in Figure 24. Ground water, similar to Big Chico Creek, is most dilute in March for all ions but K^+ . Ground water reaches a maximum average concentration in August, with the exception of Na^+ , K^+ , and SO_4^{2-} ions. Creek waters reach maximum concentrations during base flow in September. Average peak concentrations in the creek are more dilute than the ground water, possibly resulting in the concentration decrease seen in September. Pumping of ground water may also cause seasonal fluctuations in the chemistry of these sampled waters. The average

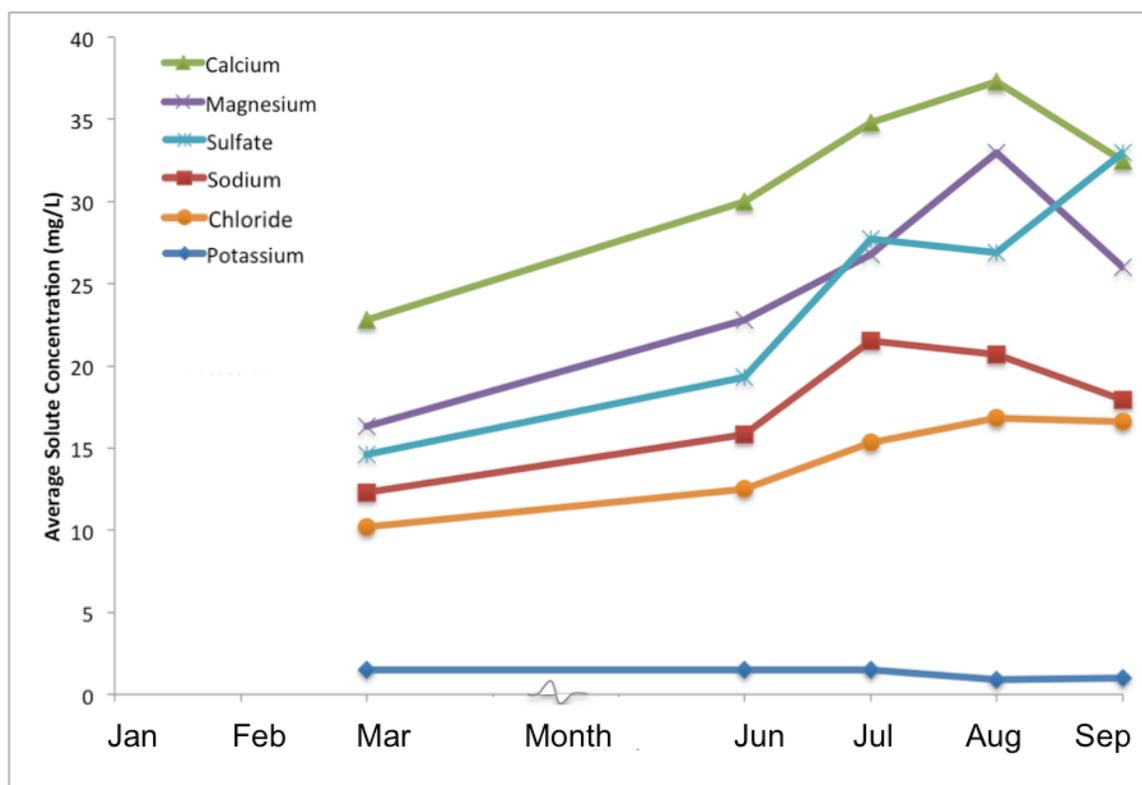


Figure 24. Seasonal Variations in Butte Basin Ground Water.

concentrations for K^+ are consistent with other waters assessed in the Big Chico Creek watershed showing steady state conditions for which controls cannot be readily identified. Six samples were tested in September for K^+ and SO_4^{2-} and the increases displayed for these ions reflect the sensitivity exhibited by averaging data. The ground water data set does not reflect the consistency expected in long-term monitoring because sampling was sporadic: only one well provides enough long-term data (Well ID No. 13) shown in Figure 25. Nine of the 28 wells were sampled with some replication across the reported sampling period, but only five have a complete record for more than two years. The same 9 wells were the only wells sampled in August and September for the period of record, but sampling consecutive months in the same year occurred only twice (Well ID No. 12 & 13).

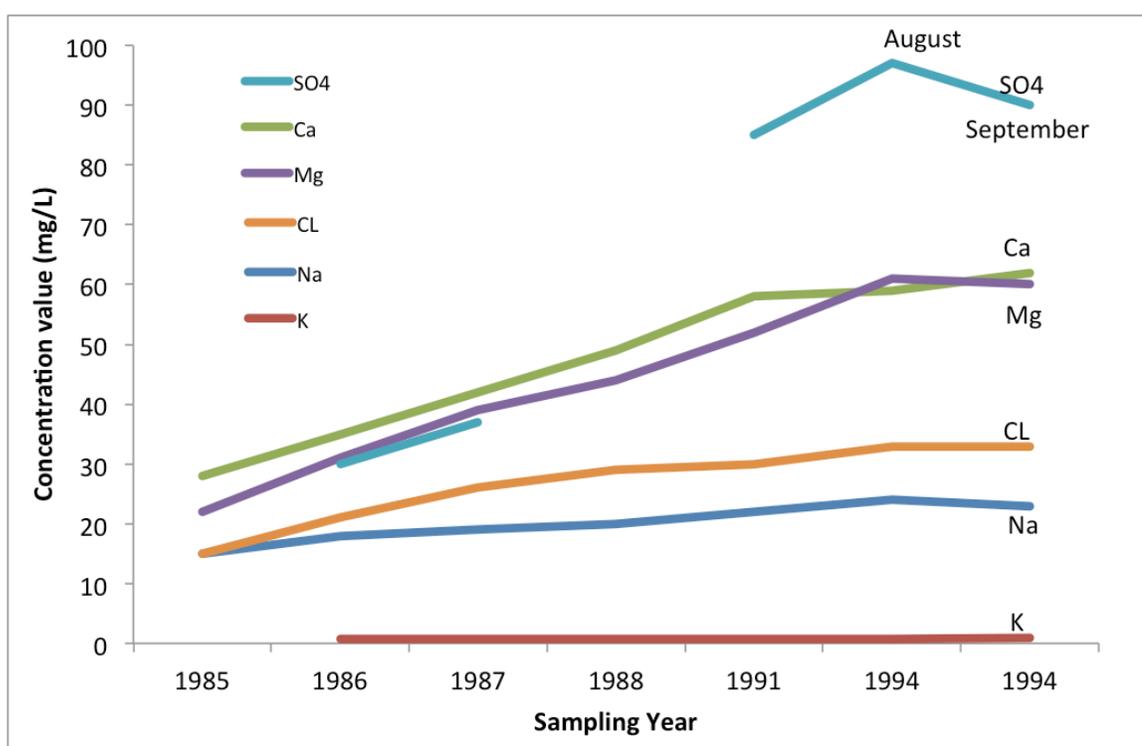


Figure 25. Temporal Changes in Dissolved Species (Well ID No. 13).

Bulk ion concentrations for Well No. 12 collected August 1994 are a standard deviation lower than concentrations for this well measured four times across the temporal scale (including a September 1994 sampling). Well ID No. 13 has the longest running record across multiple years and the waters in this well evolve over time from the low end of the mid-range water type to the most concentrated water sampled (Figure 25). Two other wells also show a significant difference in concentrations between samplings. Well No. 4 (four complete records across different sampling dates) and 10 (only two complete sampling records) also show considerable variation in bulk chemistry between samplings. In general, it is not apparent that concentration or dilution of Butte Basin ground water is occurring over the time scale represented by this record set.

Comparison of Data Sets

Durov and Piper diagrams were used for comparative interpretations of the waters of the Big Chico Creek watershed. Data for the representative samples from formation springs, Big Chico Creek, and Butte Basin ground water are shown in Table 12. Two possible conditions help qualify the relationships between these representative sample sets: (1) Do ground water data fall on a mixing line between Tuscan Formation and creek water end members? (2) Do sampled ground waters, assumed to come from Tuscan Formation host rock, show chemical influences from more concentrated Chico Formation waters?

There is agreement in the cation and anion plot spaces between the Piper and Durov plots shown in Figure 26 and 27. Cation and anion concentrations of creek water during both the dry and wet seasons, as shown in the Piper diagram (Figure 26), reflect a

mixture of Chico and Tuscan Formation waters. Calcium concentrations are approximately 10% lower than Tuscan Formation springs pulling representative samples from the mixing line. Creek waters reflecting winter-spring runoff are enriched in Mg^{2+} by Tuscan Formation discharge, but depleted in Na^+ compared to base flow waters that reflect a greater signal from Chico Formation discharge during the dry season. There is little seasonal variation in anion concentrations, which reflect enrichment by Chico Formation discharge in Cl^- and SO_4^{2-} concentrations that pulls these samples slightly off the mix line.

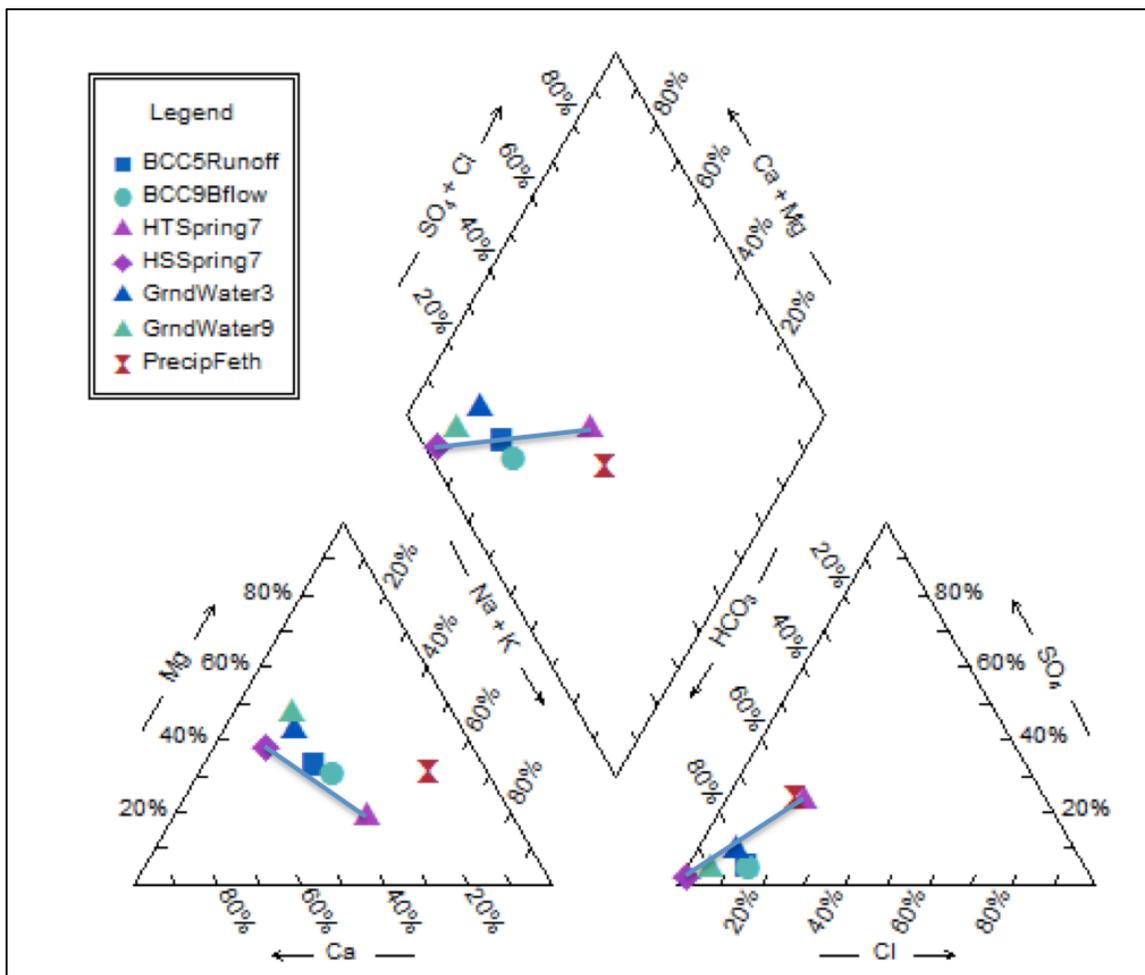


Figure 26. Piper Diagram of Representative Samples.

The increase in these ions is countered by a decrease in HCO_3^- . Runoff waters fall on the mix line in the combined ion plot space, showing a greater proportion of Tuscan Formation discharge. Creek waters during base flow are enriched over Tuscan Formation spring water in Na + K and $\text{SO}_4 + \text{Cl}$ by more concentrated discharge from the Chico Formation that pulls the representative sample off the mix line. A greater proportion of Tuscan Formation discharge dominates the overall signature of creek water. The Durov plot in Figure 27 indicates that creek waters are more dilute in terms of total dissolved solids than Tuscan Formation spring water with little seasonal change and little apparent influence by discharge from the more concentrated Chico Formation waters.

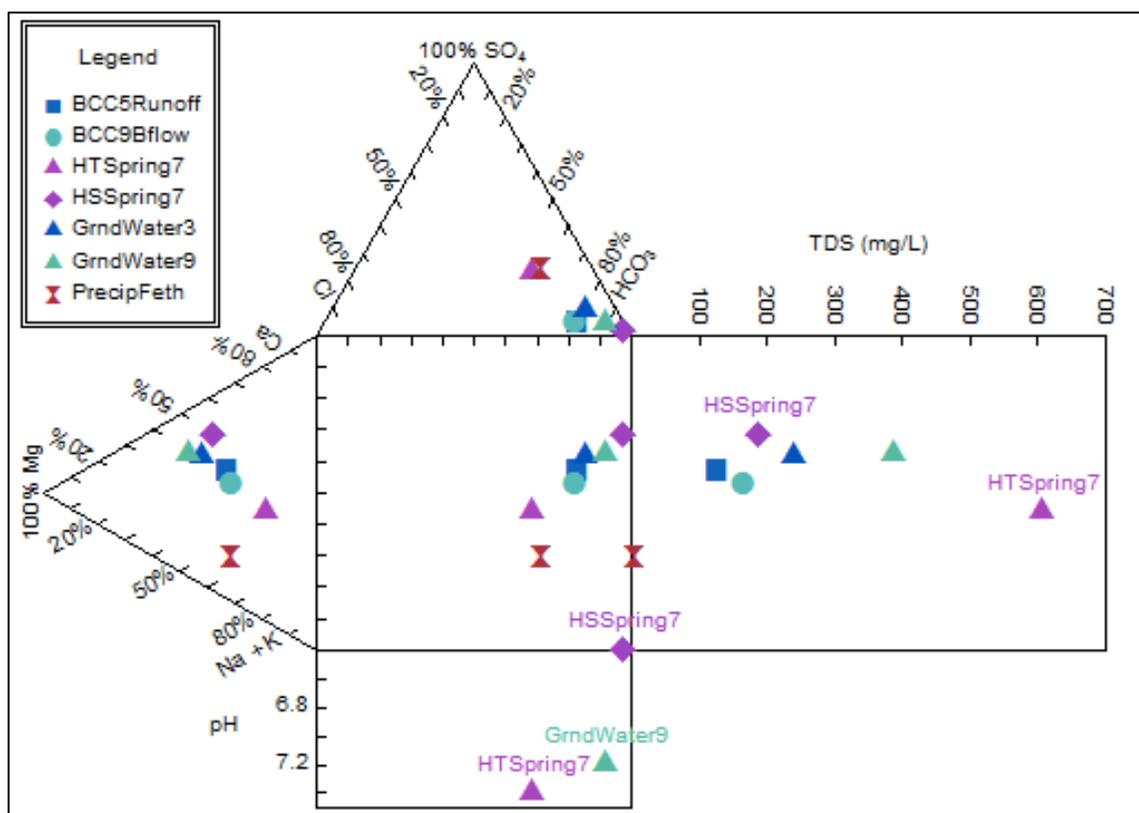


Figure 27. Durov Diagram of Representative Samples.

Figure 26 shows ground water samples are slightly enriched in Mg^{2+} and Na^+ and depleted in Ca^{2+} compared to Tuscan Formation springs. Calcium concentrations are similar compared to creek water end members, but greatly enriched in Mg^{2+} concentrations balanced by a depletion in $Na + K$. Ground water sampled during the dry season falls on a mixing line in the anion space between Tuscan Formation water and creek water. These waters show the dominance of HCO_3^- ions found in Tuscan Formation springs that moves dry season samples toward the HCO_3^- apex. Dry season ground water has similar SO_4^{2-} concentrations as creek water, but is depleted in Cl^- . Wet season ground water samples plot very close to creek water in the anion plot space; slightly enriched in SO_4^{2-} balanced by a slight decrease in Cl^- concentrations. The combined $SO_4 + Cl$ concentrations have a more profound affect on the relative chemistry of the representative ground water samples than Na^+ concentrations as illustrated in the combined ion plot space. Ground waters in Figure 27 show a broad range of TDS values (250 - 400 mg/L) with a dilute signature early in the spring, similar to Tuscan Formation water. The ground waters become more concentrated trending toward TDS values of the Chico Formation springs near the end of the dry season. Ground water is not an apparent mixture of Tuscan Formation water and stream water. However, ground water does reflect the host rock from which it is pumped and shows an influence by creek water; especially samples collected in March. Condition (1) cannot be proved with this set of data. While at least one ground water sample shows influence of Chico Formation water, it is not apparent that this data set shows condition (2) exists for all sampled wells. Additional factors such as depth of wells, production zones, and pumping regimes appear to exert some control on ground water chemistry.

TABLE 12. REPRESENTATIVE RECORDS FOR SPRINGS, STREAM, AND GROUND WATER

Solute concentrations		Ca²⁺	Mg²⁺	Na⁺	K⁺	HCO₃⁻	Cl⁻	SO₄²⁻
Representative records		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
		(meq/L)	(meq/L)	(meq/L)	(meq/L)	(meq/L)	(meq/L)	(meq/L)
House Supply Spring (Tuscan Fm.)	3/05	23.0	11.0	6.0	2.0	135.0	1.52	1.83
	7/05	24.0	11.0	6.0	2.0	143.0	1.6	1.7
Horse Trough Spring (Chico Fm.)	3/05	50.0	17.0	86.0	1.0	285.0	55.8	96.8
	7/05	54.0	17.0	83.0	2.0	300.0	59.5	93.8
Runoff 59 cfs Base flow 24 cfs	5/64	14.0	6.9	10.0	0.9	82.0	8.5	4.0
	9/57	16.0	8.0	15.0	1.6	108.0	12.0	4.6
Butte Basin ground water	3/92	17.0	13.0	27.0	1.2	159.0	11.0	14.0
	9/88	32.0	19.0	44.0	0.9	273.0	11.0	9.0

LABORATORY DATA FOR SPRINGS

Springs that emanate from Chico Formation (concentration units mg/L)

	HCO3	SO4	Cl	F	Ca	Mg	Na	K	SiO2	CaCO3	TDS	
Riparian Spring	3/05	193.0	162.0	3.42	0.20	60.0	18.0	44.0	2.0	31.0	158.0	416.0
Riparian Spring	7/05	193.0	162.0	3.42	0.11	59.0	18.0	43.0	2.0	31.5	158.0	288.0
Horse Trough Spring	3/05	285.0	96.8	55.80	0.44	50.0	17.0	86.0	1.0	27.0	234.0	481.0
Horse Trough Spring	7/05	300.0	93.8	59.50	0.33	54.0	17.0	83.0	2.0	28.2	246.0	481.0

Springs that emanate from the Tuscan Formation

	HCO3	SO4	Cl	F	Ca	Mg	Na	K	SiO2	CaCO3	TDS	
Supply House Spring	3/05	135.0	1.83	1.52	0.08	23.0	11.0	6.0	2.0	76.0	111.0	186.0
Supply House Spring	7/05	143.0	1.74	1.59	*nd	24.0	11.0	6.0	2.0	75.1	117.0	176.0
Rock Shelter Spring	3/05	76.0	1.01	1.23	0.05	13.0	5.0	4.0	1.0	60.0	62.0	112.0
Rock Shelter Spring	7/05	131.0	1.48	1.45	*nd	21.0	8.0	5.0	1.0	71.3	108.0	153.0

Springs with indeterminate origin

	HCO3	SO4	Cl	F	Ca	Mg	Na	K	SiO2	CaCO3	TDS	
Weeping Wall Spring	3/05	89.0	35.2	3.63	0.10	21.0	6.0	16.0	0.0	32.0	73.0	153.0
Weeping Wall Spring	7/05	102.0	49.2	6.95	0.05	28.0	8.0	18.0	0.3	34.0	84.0	197.0
Basalt Spring	9/05	123.0	0.71	1.44	*nd	18.0	9.0	5.0	1.0	68.0	101.0	150.0

CHAPTER VI

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Summary

This study focused on the hydrochemical characterization the of the primary aquifer formations of the Big Chico Creek watershed within the context of lithologic and seasonal hydrologic variations. Chapter VI provides a summary of the methods, results and conclusions developed herein. In addition, this chapter includes recommendations for future research and next steps.

Research Questions and Hypotheses

This study investigated the hydrochemistry of springs to identify and quantify differences in water chemistry under varying lithologic and hydrologic conditions. This study covers the first steps necessary to interpret ‘the where,’ ‘the how,’ and ‘the why’ behind the presence of water in the Big Chico Creek watershed, and more specifically the presence of inorganic chemical constituents in those waters. The study of spring water yields a small window into the exploration of ground water-rock interactions without expensive, exploitive processes. The springs in the BCCER offer a unique opportunity to examine ground water quality from various host rocks in a setting relevant to controls on creek and aquifer water quality and interactions of surface and ground waters along the two study reaches of Big Chico Creek. This investigation sought insight for the following ideas:

(1) Big Chico Creek should reflect a mixture of meteoric and formation water during the runoff season; (2) Big Chico Creek should reflect a mixture of end member formation waters during base flow; and (3) if streams east of the basin are the primary source for ground water recharge, the hydrochemical signature of the ground water should exhibit a mixture of creek water and water from the host rock, the Tuscan Formation.

Conclusions

Exposures of the primary aquifer formations (Chico and Tuscan Formations) in the BCCER enabled identification of a distinct hydrochemical signature for the regionally significant ground water supply: the Butte Basin aquifer system. Interpretation of spring water geochemical data show a difference in formation waters. Tuscan Formation waters are of a Ca-HCO₃ type and similar to volcanic terrane springs interpreted by Feth et al., (1964a) throughout the Sierra Nevada and southern Cascade Ranges. Chico Formation spring waters vary, possibly identifying differences in the formation members. The chemical variations in Chico Formation springs may also reflect differences in travel paths and residence time. Chico Formation springs are considerably more concentrated than Tuscan Formation springs, but water emerging from the sampled springs do not reflect connate water or seawater mixing with fresh, dilute water.

The differences in chemical signatures between the formation springs investigated during this project show no hydrologic connection. Based on the springs studied, flow through these rocks cannot be characterized by vertical connectivity between formations. Tuscan Formation springs manifest perched water or seepage from crevices and fractures as opposed to a water table intersecting the rock surface. The chemical

signature of the Chico Formation has a significant influence on the chemistry of the stream as well as an influence on some ground water data interpreted as part of this project.

All of the springs show temperature increases with season, indicating that surface effects are important. Rock Shelter shows evolution toward a steady state composition represented by House Supply Spring. Basalt Spring may reflect water that has quickly passed through basalt rock, but is greatly influenced by Tuscan Formation soil. The Chico Formation springs (Horse Trough and Riparian Springs) show a nearly constant chemical composition under varying hydrologic conditions. Weeping Wall Spring may provide a good surrogate for Chico Formation soil water.

The chemistry of Big Chico Creek during base flow is a function of discharge from the Tuscan and Chico Formations that corresponds with the binary mixing model established for this study. During runoff, the chemistry of the creek should reflect a mixture of meteoric water and Tuscan and Chico Formation discharge. This ternary mixing model was described as mixing of formation waters followed by dilution from meteoric water and illustrated using Mg^{2+} and Cl^{-} concentrations of the three end members. However, this mixing model does not hold consistently for the three conservative constituents identified for the stream water: Ca^{2+} , Na^{+} , and Cl^{-} . Two conclusions can be drawn from this interpretation: (1) additional processes occur within the watershed affecting the chemistry of waters discharging to the stream; and (2) additional water sources discharge to the stream during runoff, which have not been identified.

Ground water data was too disparate in time and space to make clear distinctions or draw elaborate conclusions. It does appear that during the runoff season,

reported ground water is a mixture of Tuscan Formation water and infiltrating waters more dilute than the waters modeled by the Tuscan Formation springs. The possible seasonality exhibited by this data set could also be an effect of pumping that results in the downward movement of fresh, shallow ground water and subsequent mixing. At least one well appears to show mixing with Chico Formation water.

Future Research Recommendations

Many opportunities exist for further research in the Big Chico Creek Watershed to help advance the understanding of the hydrologic processes affecting the Tuscan Formation aquifer system particular to recharge that sustains this regional water supply. Some of the following recommendations are made in consideration to enhance the interpretation of past and future hydrologic studies in this region:

- ❖ Correlate spring locations with the work of Doukas (1983) for the Tuscan Formation and Haggart and Ward (1984) for the Chico Formation. Doukas provides a petrographic modal analysis that can support an inverse mass-balance analysis, providing a more robust interpretation of the Tuscan Formation water chemistry. Haggart and Ward provide type localities that might enable association of Chico Formation springs with the different members of this formation.

- ❖ Use the type localities of Doukas (1983) and Haggart and Ward (1984) to explore for new springs and seeps. An expanded piezometer network in the BCCER will enhance an understanding of flow in the Chico Formation and lead to a better characterization of the formation extent.

- ❖ Expand the existing piezometer network around the creek in the BCCER and sample for chemical constituents for a better understanding of the discharge processes contributing to base flow in the upper reach of the creek. While not within the boundaries of the BCCER, the Red Bluff Formation that surrounds the stream gage may be of particular interest.
- ❖ Expand isotopic data collection from the springs used in this study and correlate results from this study to strengthen interpretation of recharge processes reliant on isotopic data.
- ❖ Use speciation models to further explore and identify mineralogy of the Tuscan Formation at spring sites as well as Butte Basin wells.
- ❖ Search existing data sets for more complete analyses of ground water that have continuous ‘consecutive’ records by month and by year.
- ❖ Gather data on well design and production information or estimations. Correlate this information with known stratigraphy.

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APPENDIX A

GEOGRAPHICAL DATA FOR SPRING SITES

Spring ID	Name	Longitude (DD)	Latitude (DD)	Elevation (feet)	Formation
0	Riparian Spring	-121.703	39.868	1037	Chico Fm.
1	Weeping Wall Spring	-121.705	39.866	971	Chico Fm.
2	Horse Trough Spring	-121.707	39.860	899	Chico Fm.
3	Cattail Spring	-121.708	39.858	892	Chico Fm.
4	Schoolhouse Spring	-121.701	39.849	1288	Chico Fm.
5	Pumpkin Spring	-121.706	39.859	910	Chico Fm.
6	Headcut Spring	-121.706	39.847	1201	Chico Fm.
7	Entrance Road Seep	-121.698	39.845	1669	Tuscan Fm.
8	House Supply Spring	-121.700	39.844	1608	Tuscan Fm.
9	Canyon Rd. Seep	-121.713	39.844	906	Chico Fm.
10	Salt Rock Spring	-121.721	39.823	754	Chico Fm.
11	Watercress Spring	-121.718	39.818	899	Chico Fm.
12	Willow Spring	-121.717	39.816	1060	Chico Fm.
13	Woodwardia Spring	-121.716	39.815	1072	Chico Fm.
14	Gold Mine Spring	-121.717	39.813	1049	Chico Fm.
15	Upper Park Spring	-121.717	39.812	1072	Chico Fm.
16	Seep Below House	-121.701	39.845	1486	Chico Fm.
17	Eastern Wall Spring	-121.702	39.842	1607	Lovejoy Basalt
18	Rock Shelter Spring			1624	Tuscan Fm.
19	Basalt Spring	-121.722	39.842	1391	Lovejoy Basalt
20	Blackberry Spring	-121.727	39.828	889	Chico Fm.
21	Quick Spring	-121.723	39.831	1198	Chico Fm.
22	Blue Clay Spring	-121.720	39.841	1283	Chico Fm.
23	Leatherroot Spring	-121.718	39.850	1480	Lovejoy Basalt
24	Coon Jaw Spring	-121.718	39.848	1463	Lovejoy Basalt
25	East Branch Spring	-121.739	39.814	1394	Unknown
26	Monkey Flowers Spring	-121.736	39.817	1542	Unknown
27	Sycamore Spring	-121.736	39.817	1565	Unknown
28	Serengeti Spring	-121.747	39.818	1506	Unknown
29	Mud Creek Spring	-121.738	39.835	1394	Unknown
30	Eden Spring	-121.740	39.835	1371	Unknown
31	Four Sisters Spring	-121.736	39.836	1457	Unknown
32	East Sister Spring	-121.736	39.836	1447	Unknown
33	Middle Sister Spring	-121.736	39.836	1447	Unknown
34	West Sister Spring	-121.736	39.836	1447	Unknown
35	Deergrass Spring	-121.730	39.826	1490	Unknown
36	Holly's Spring	-121.728	39.817	1050	Unknown
	Stream Gage	-121.779	39.768	285	Modesto Fm.

APPENDIX B

FIELD DATA FOR SPRINGS

ID	Name	Date Sampled	pH	Temp (C)	ORP (mV)	Eh (mV)	Conduct (uScm ⁻¹)
0	Riparian Spring	Oct-03	7.63	16.6	145.6	392.1	590
0	Riparian Spring	Mar-05	7.63	13.5	-78.0	170.5	660
0	Riparian Spring	Jul-05	7.50	16.1	24.3	271.2	610
1	Weeping Wall Spring	Feb-02	6.31	13.9	351.0	599.3	
1	Weeping Wall Spring	Mar-05	6.52	13.9	150.7	399.0	280
1	Weeping Wall Spring	Jul-05	7.82	18.8	124.8	369.9	350
1	Weeping Wall Spring	Nov-05			Spring was dry		
2	Horse Trough Spring	Oct-03	7.60	15.0	166.0	413.6	1060
2	Horse Trough Spring	Feb-02	7.46	10.6	227.3	477.7	
2	Horse Trough Spring	Sep-03	7.76	18.9	212.6	457.6	1220
2	Horse Trough Spring	Mar-05	7.59	11.1	146.4	396.5	770
2	Horse Trough Spring	Jul-05	7.41	20.4	122.3	366.4	760
2	Horse Trough Spring	Nov-05	7.63	15.4	125.0	372.3	790
3	Cattail Spring	Feb-02	7.92	17.2	-159.9	86.2	
3	Cattail Spring	Sep-03	8.03	25.6	-190.0	50.7	1840
3	Cattail Spring	Oct-03	7.73	19.4	179.6	424.3	0
4	Schoolhouse Spring	Feb-02	6.21	12.7	381.5	630.6	
4	Schoolhouse Spring	Oct-03	6.59	14.2	213.0	461.1	250
5	Pumpkin Spring	Nov-05	7.23	14.9	-30.3	217.3	580
6	Headcut Spring	Feb-02	6.75	14.6	123.6	371.4	
7	Entrance Rd. Spring	Mar-03	6.67	14.2	286.5	534.6	
7	Entrance Rd Spring	Oct-03	6.50	15.2	154.1	401.5	220
7	Entrance Rd Spring	Dec-03	6.55	12.3			220
8	House Supply Spring	Feb-02	6.63	13.4	208.3	456.9	
8	House Supply Spring	Nov-03	6.26	13.5			230
8	House Supply Spring	Mar-05	6.56	13.8	172.4	420.8	220
8	House Supply Spring	Jul-05	6.41	15.4	118.0	365.3	210
8	House Supply Spring	Sep-05	6.32	14.5	169.6	417.5	240
9	Canyon Road Seep	Feb-02	8.38	12.1	142.7	392.2	
9	Canyon Road Seep	Nov-03	8.15	12.4			300
10	Salt Rock Spring	Mar-03	7.60	16.5	-51.3	195.3	
11	Watercress Spring	Mar-03	6.51	17.1	252.1	498.3	
12	Willow Spring	Mar-03	6.42	14.8	161.4	409.1	
13	Woodwardia Spring	Mar-03	6.69	12.5	269.8	519.0	
14	Gold Mine Spring	Mar-03	7.12	15.3	274.3	521.7	
15	Upper Park Spring	Mar-03	7.67	14.8	263.8	511.5	
16	Seep Below House	Oct-03	6.55	16.8	178.2	424.6	255
16	Seep Below House	Dec-03	6.50	15.0			250
17	Eastern Wall Spring	Nov-03	6.38	14.2			180

FIELD DATA FOR SPRINGS (CONTINUED)

ID	Name	Date Sampled	pH	Temp (C)	ORP (mV)	Eh (mV)	Conduct (uScm ⁻¹)
18	Rock Shelter Spring	Feb-02	6.48	14.4	203.4	451.4	
18	Rock Shelter Spring	Mar-05	6.08	14.8	194.0	441.7	180
18	Rock Shelter Spring	Jul-05	7.84	18.8	105.6	350.7	--
18	Rock Shelter Spring	Sep-05	7.95	16.6	149.3	395.8	250
19	Basalt Spring	Sep-05	7.19	17.6	164.9	410.8	260
20	Blackberry Spring	Sep-05	7.14	18.5	183.8	429.1	170
21	Quick Spring	Sep-05	6.68	19.3	53.0	297.8	210
22	Blue Clay Spring	Sep-05	6.59	15.2	174.2	421.6	210
23	Leatherroot Spring	Sep-05	6.72	16.4	180.6	427.3	200
24	Coon Jaw Spring	Sep-05	6.71	16.3	186.0	432.7	250

APPENDIX C

LABORATORY DATA FOR SPRINGS

Springs that emanate from Chico Formation (concentration units mg/L)												
	HCO3	SO4	Cl	F	Ca	Mg	Na	K	SiO2	CaCO3	TDS	
Riparian Spring	3/05	193.0	162.0	3.42	0.20	60.0	18.0	44.0	2.0	31.0	158.0	416.0
Riparian Spring	7/05	193.0	162.0	3.42	0.11	59.0	18.0	43.0	2.0	31.5	158.0	288.0
Horse Trough Spring	3/05	285.0	96.8	55.80	0.44	50.0	17.0	86.0	1.0	27.0	234.0	481.0
Horse Trough Spring	7/05	300.0	93.8	59.50	0.33	54.0	17.0	83.0	2.0	28.2	246.0	481.0

Springs that emanate from the Tuscan Formation

	HCO3	SO4	Cl	F	Ca	Mg	Na	K	SiO2	CaCO3	TDS	
Supply House Spring	3/05	135.0	1.83	1.52	0.08	23.0	11.0	6.0	2.0	76.0	111.0	186.0
Supply House Spring	7/05	143.0	1.74	1.59	*nd	24.0	11.0	6.0	2.0	75.1	117.0	176.0
Rock Shelter Spring	3/05	76.0	1.01	1.23	0.05	13.0	5.0	4.0	1.0	60.0	62.0	112.0
Rock Shelter Spring	7/05	131.0	1.48	1.45	*nd	21.0	8.0	5.0	1.0	71.3	108.0	153.0

Springs with indeterminate origin

	HCO3	SO4	Cl	F	Ca	Mg	Na	K	SiO2	CaCO3	TDS	
Weeping Wall Spring	3/05	89.0	35.2	3.63	0.10	21.0	6.0	16.0	0.0	32.0	73.0	153.0
Weeping Wall Spring	7/05	102.0	49.2	6.95	0.05	28.0	8.0	18.0	0.3	34.0	84.0	197.0
Basalt Spring	9/05	123.0	0.71	1.44	*nd	18.0	9.0	5.0	1.0	68.0	101.0	150.0

APPENDIX D

SUMMARY OF REPORTED DATA

D1. Big Chico Creek

Reported data compiled from monthly water quality records from United States Geological Survey (USGS) Water-Supply Papers and Water Resources Data for California, Water Quality Records and Department of Water Resources (DWR) Bulletins for USGS gaging station 11-3840, at Big Chico Creek, California (Ryley, 1974) from 1952 to 1971. Chemical analyses data were reported in parts per million. The gauge on Big Chico Creek is approximately 6.42 miles SSW from the headquarters of the Reserve.

Sensor and Gauge Location on Big Chico Creek			
Station ID	BIC	Elevation	274 feet
Latitude	39.867° N	Longitude	121.777° W

Data available: Hourly values for discharge, stage, water temperature and turbidity. Records date back to July 1997.

The reported data set includes major ion chemistry, discharge (cfs), NO_3^- , Boron, E.C., and pH for 207 samples. Representative values for Big Chico Creek major ion concentration data (mg/L) are listed in the table below. The mean and standard deviation were calculated for each of the major ions for the data set. All solute measurements of the representative values for high flow (runoff) and low flow (base flow) fell within one standard deviation of the mean for the reported population set.

Sampling occurred throughout the year at varying discharge rates. The data set represents samples collected on average 16 times for each month of the year. Not all

parameters were measured during each sampling period. Sulfate has the smallest measurement set and values existed primarily for samples collected in May and September. Data records for two dates, May and September, were then checked against the statistical parameters of the smaller set of samples containing sulfate to ensure the best representative values were selected.

Period	Year	Q (cfs)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
May	1964	59	14.0	6.9	10.0	0.9	82.0	8.5	4.0
September	1957	24	16.0	8.0	15.0	1.6	108.0	12.0	4.6
	Mean data set	144	13.0	6.8	10.1	1.0	83.4	7.5	3.7
	Std Dev of set	299	3.3	1.7	4.2	0.4	23.6	3.7	2.0
	Mean sulfate data	68	13.8	7.1	10.9	1.0	89.1	8.0	3.7
	Std Dev	64	3.0	1.5	4.0	0.4	19.8	3.5	2.0

Note: May data represents the high flow period or runoff. September data represents the low flow or base flow.

D1.1 Precipitation Stations

Four precipitation stations near the Big Chico Creek watershed boundary were selected to analyze rainfall events before, during and after sampling took place in 2005. CDEC has historical accumulated precipitation records for DSB and PRD from 01/01/1905 and 10/01/1925 respectively, and provides an annual monthly average. Records for BTM (Feather River watershed) and CST historical accumulated precipitation data exist from 01/01/1984 to present, but no annual averaged data exists.

BUTTE MEADOWS (BTM)

Station ID	BTM	Elevation	4880 feet
Latitude	40.1000°N	Longitude	121.5000°W

20.8 miles NNE of the Reserve headquarters.

COHASSET (CST)

Station ID	CST	Elevation	1600 feet
Latitude	39.8753°N	Longitude	121.7706°W

3.7 miles WNW of the Reserve headquarters.

DE SABLE (DSB)

Station ID:	DSB	Elevation:	2710 feet
Latitude:	39.8670°N	Longitude:	121.6170°W

5.25 miles ENE of the Reserve headquarters. This is a PG&E maintained station.

PARADISE FIRE STATION (PRD)

Station ID:	PRD	Elevation:	1750 feet
Latitude:	39.7500° N	Longitude:	121.6170° W

8.4 miles SE of the Reserve headquarters.

D1.2 Butte Basin Ground Water

Reported data compiled from 1985–2000 Department of Water Resources (DWR) ground water quality records. The records involve production wells within the City of Chico, chosen by DWR upon request that have proximity to Big Chico Creek. Of the 77

records received only 53 contained at least one measurement for a major ion. These 53 records represent 28 individual wells. Of the 28 wells, 10 comprise the bulk of the data. The other 18 wells were measured only once during the recorded period.

On average, water quality measurements were taken four times annually between 1985 and 1992, and biennially starting in 1994. However, measurements taken during the four years between 1989 and 1992 constitute 45 of the 77 records compiled for this study.

Constituent	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	SiO ₂
N	52	46	52	52	53	37	45	24
Mean	17	1.3	31	25	15	209	24	53
Std Dev	7	0.5	16	17	8	105	22	19
March 1992	13	1.2	27	17	11	378	14	60
September 1988	19	0.9	44	32	11	252	9	—

Representative concentrations (mg/L) of major ions and silica for ground water with proximity to Big Chico Creek near the City of Chico. HCO₃⁻ concentration data were calculated from alkalinity reported as CaCO₃. The mean and standard deviation were calculated for each of the major ions for the data set. All solute measurements of the representative values for March and September fell within one standard deviation of the mean of the reported population set. Only two SiO₂ measurements were recorded between July and December for all years of record. No measurements were reported for the month of May.

D1.3 Mount Lassen Snow Data

Snow data reported for Mount Lassen comprised the third end member for the mixing diagrams. Downloaded data were compiled from the National Atmospheric Deposition Program, National Trends Network (NADP/NTN) for Lassen Volcanic National Park at Manzanita Lake (Site ID: CA96). The monitoring station is located at 5754.6 foot-elevation; 40.539° N latitude; and 121.577° W longitude. The station includes a precipitation chemistry collector and gage. The automated collector ensures that the sample is exposed only during precipitation (wet-only-sampling). Precipitation is analyzed weekly; data are compiled annually and represent precipitation-weighted means. Reported data includes major ion concentration data (mg/L) for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , and SO_4^{2-} . The mean and standard deviation were calculated for each of the major ions for annual data from 2000 to 2010. All solute measurements of the representative record for 2008 fell within one standard deviation of the mean (outlined in red).

Year	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	SO_4^{2-}
2000	0.031	0.006	0.011	0.042	0.065	0.253
2001	0.04	0.007	0.007	0.023	0.041	0.155
2002	0.018	0.004	0.003	0.028	0.054	0.107
2003	0.025	0.003	0.004	0.021	0.042	0.12
2004	0.026	0.004	0.005	0.026	0.052	0.141
2005	0.024	0.004	0.005	0.02	0.041	0.158
2006	0.026	0.004	0.005	0.027	0.048	0.117
2007	0.031	0.006	0.007	0.034	0.061	0.156
2008	0.027	0.004	0.008	0.033	0.057	0.129
2009	0.025	0.004	0.004	0.021	0.043	0.122
2010	0.022	0.005	0.005	0.037	0.066	0.135
Mean	0.027	0.005	0.006	0.028	0.052	0.145
Std Dev	0.005	0.001	0.002	0.007	0.009	0.038

Year	pH	Cond.	Fld pH	Fld Cond	NH4	NO3
2000	5.09	5.44	4.95	6.8	0.094	0.581
2001	5.34	3.38	5.22	3.8	0.051	0.291
2002	5.36	3.34	5.19	3.9	0.061	0.289
2003	5.36	3.06	5.14	3.6	0.061	0.231
2004	5.35	3.18	5.14	3.6	0.045	0.22
2005	5.32	3.26	—	—	0.038	0.2
2006	5.38	2.74	—	—	0.039	0.183
2007	5.33	3.21	—	—	0.052	0.225
2008	5.48	2.81	—	—	0.071	0.203
2009	5.33	2.94	—	—	0.034	0.2
2010	5.33	2.89	—	—	0.05	0.184

D1.4 Comparison of Chemical Constituents of Snow

The major ion concentrations from Lassen are interesting from a perspective of what might actually be present in meteoric water falling on the Big Chico Creek watershed, but the data set does not include HCO_3^- data and no measurements for SiO_2 . The data from Lassen are compared to a more complete set of data of Sierra Nevada snow compiled from various sites from Feth et al. (1964b) still used by workers today.

Measured solutes (mg/L)	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	SiO ₂
Sierra Nevada (1957-1959)	0.49	0.32	0.15	0.2	0.54	3.31	1.06	0.18
N	26	26	20	20	29	26	21	21
Lassen Volcanic NP (2008)	0.033	0.008	0.027	0.004	0.057	—	0.29	—

APPENDIX E

EQ3 INPUT AND OUTPUT FILE

EQ3/6, Version 7.2c (EQ3/6-V7-REL-V7.2c-PC)
 EQ3NR Speciation-Solubility Code (EQ3/6-V7-EQ3NR-EXE-R141-P6)
 Supported by the EQLIB library (EQ3/6-V7-EQLIB-LIB-R172-P6)

Copyright (c) 1987, 1990-1993, 1995, 1998 The Regents of the
 University of California, Lawrence Livermore National Laboratory.
 All rights reserved.

This work is subject to additional statements and disclaimers which
 may be found in the README.txt file included in the EQ3/6 software
 transmittal package.

Run 11:17:17 12Dec2005

--- Reading the input file ---

```

-----
EQ3NR input file name= 08_0305.3i
Description= Aqueous speciation of spring data from BCCER

Supply House Spring: small adit dug into Tuscan

Spring was sampled Mar 2005 by W.M. Murphy and C.L. Perkins

General Chemistry based on Basic Laboratory results
Field data for pH: 6.559, OR pot: 172.4, EC: 220microS/cm, and
temperature 13.8 C.
  
```

```

Redox potential was converted from field measured mV to Eh values
using the Excel spreadsheet OR_potenconv.xls.
  
```

```

-----
Temperature (C)          | 13.80          | Density(gm/cm3) | 1.00000
  
```

```

-----
Total Dissolved Salts   |                | mg/kg | mg/l | *not used
  
```

```

-----
Electrical Balancing on |HCO3-          | code selects |
  
```

```

-----
SPECIES      | BASIS SWITCH/CONSTRAINT | CONCENTRATION | UNITS OR TYPE
  
```

```

-----
Redox        |                        | 0.421         | Eh
Ca++         |                        | 23.           | mg/L
Mg++         |                        | 11.           | mg/L
Cl-          |                        | 1.52          | mg/L
F-           |                        | 0.08          | mg/L
HCO3-        |                        | 135.          | mg/L
SO4--        |                        | 1.83          | mg/L
SiO2(aq)     |                        | 76.           | mg/L
  
```

H+		6.559	pH
Na+		6.	mg/L
K+		2.	mg/L

Input Solid Solutions			

none			

SUPPRESSED SPECIES (suppress,replace,augmentk,augmentg) value			

none			

OPTIONS			

- SOLID SOLUTIONS -			
* ignore solid solutions			
process hypothetical solid solutions			
process input and hypothetical solid solutions			
- LOADING OF SPECIES INTO MEMORY -			
* does nothing			
lists species loaded into memory			
- ECHO DATABASE INFORMATION -			
* does nothing			
lists all reactions			
lists reactions and log K values			
lists reactions, log K values and polynomial coef.			
- LIST OF AQUEOUS SPECIES (ordering) -			
* in order of decreasing concentration			
in same order as input file			
- LIST OF AQUEOUS SPECIES (concentration limit) -			
all species			
only species > 10**-20 molal			
* only species > 10**-12 molal			
not printed			
- LIST OF AQUEOUS SPECIES (by element) -			
* print major species			
print all species			
don't print			
- MINERAL SATURATION STATES -			
* print if affinity > -10 kcals			
print all			
don't print			
- pH SCALE CONVENTION -			
* modified NBS			
internal			
rational			
- ACTIVITY COEFFICIENT OPTIONS -			
* use B-dot equation			
Davies' equation			
Pitzer's equations			
- AUTO BASIS SWITCHING -			
* off			

```

- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PICKUP FILE -
  * write pickup file
    don't write pickup file
- LIST MEAN IONIC PROPERTIES -
  * don't print
    print
- LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
  * print
    don't print
- CONVERGENCE CRITERIA -
  * test both residual functions and correction terms
    test only residual functions

```

```
-----
DEBUGGING SWITCHES (o-off, 1,2-on, default is off)
-----
```

```

0 generic debugging information
0 print details of pre-Newton-Raphson iteration
0 print details of Newton-Raphson iteration
0 print details of stoichiometric factors
0 print details of stoichiometric factors calculation
0 write reactions on RLIST
0 list stoichiometric concentrations of master species
0 request iteration variables to be killed

```

```
-----
DEVELOPMENT OPTIONS (used for code development)
-----
```

```
none
```

```
-----
TOLERANCES (desired values) (defaults)
-----
```

residual functions	1.e-10
correction terms	1.e-10
saturation state	0.5
number of N-R iterations	30

```

--- The input file has been successfully read ---
--- Reading the datal file ---
--- The datal file has been successfully read ---

```

```

eeee   qqq   33333   n   n   rrrr
e     q   q     3   nn  n   r   r
eeee   q   q     33   n  n  n   rrrr
e     q   q   q     3   n  nn  r   r
eeee   qqq   3333   n   n   r   r
      q

```

```

EQ3NR, version 7.2c (R141    )
  supported by EQLIB, version 7.2c (R172    )
|EQ3NR input file name= 08_0305.3i
|Description= Aqueous speciation of spring data from BCCER
|
|Supply House Spring: small adit dug into Tuscan
|
|Spring was sampled Mar 2005 by W.M. Murphy and C.L. Perkins
|
|General Chemistry based on Basic Laboratory results
|Field data for pH: 6.559, OR pot: 172.4, EC: 220microS/cm, and
|temperature 13.8 C.
|
|Redox potential was converted from field measured mV to Eh values
|using the Excel spreadsheet OR_potenconv.xls.
|

```

```

data0.cmp.V8.R6
CII: GEMBOCHS.V2-EQ8-data0.cmp.V8.R6 (cmp = com)
THERMODYNAMIC DATABASE
generated by GEMBOCHS.V2-Jewel.src.R5 03-dec-1996 14:19:25
Output package: eq3
Data set:      com

```

The activity coefficients of aqueous solute species and the activity of water are calculated according to the B-dot equation plus others

Temperature= 13.80 degrees Celsius
pressure= 1.0132 bars

The default redox state is constrained by Eh = 0.42100 volts

Solution density = 1.00000 g/mL

--- Input Constraints ---

Species	Csp	Jflag	Input Type/Co-species
Ca++	2.3000E+01	2	Total conc, mg/L
Mg++	1.1000E+01	2	Total conc, mg/L
Cl-	1.5200E+00	2	Total conc, mg/L
F-	8.0000E-02	2	Total conc, mg/L
HCO3-	1.3500E+02	2	Total conc, mg/L
SO4--	1.8300E+00	2	Total conc, mg/L
SiO2(aq)	7.6000E+01	2	Total conc, mg/L
H+	-6.5590E+00	16	Log activity
Na+	6.0000E+00	2	Total conc, mg/L
K+	2.0000E+00	2	Total conc, mg/L

Electrical balance will be achieved by adjusting the concentration of "HCO3- ". Any other specified constraint will be overridden.

--- Inactive Aqueous Species ---
 --- Modified Input Constraints ---

Species	Csp	Jflag	Input Type/Co-species
Ca++	5.7388E-04	0	Total conc, molal
Cl-	4.2874E-05	0	Total conc, molal
F-	4.2109E-06	0	Total conc, molal
H+	-6.5590E+00	16	Log activity
HCO3-	2.2125E-03	0	Total conc, molal
K+	5.1153E-05	0	Total conc, molal
Mg++	4.5258E-04	0	Total conc, molal
Na+	2.6099E-04	0	Total conc, molal
SO4--	1.9050E-05	0	Total conc, molal
SiO2(aq)	1.2649E-03	0	Total conc, molal
H2(aq)	0.0000E+00	27	Dependent species
O2(aq)	0.0000E+00	27	Dependent species

--- Optimization ended within requested limits ---

--- Summary of the Aqueous Solution ---

--- Elemental Composition of the Aqueous Solution ---

Element	mg/L	mg/kg	Moles/kg
O	0.88830E+06	0.88830E+06	0.5552101947E+02
Ca	23.000	23.000	0.5738809594E-03
Cl	1.5200	1.5200	0.4287402856E-04
F	0.80000E-01	0.80000E-01	0.4210881116E-05
H	0.11190E+06	0.11190E+06	0.1110191493E+03
C	46.236	46.236	0.3849451852E-02
K	2.0000	2.0000	0.5115312162E-04
Mg	11.000	11.000	0.4525817948E-03
Na	6.0000	6.0000	0.2609856595E-03
S	0.61085	0.61085	0.1904988036E-04
Si	35.525	35.525	0.1264889557E-02

--- Elemental Composition as Strict Basis Species ---

Species	mg/L	mg/kg	Moles/kg
H2O	0.10002E+07	0.10002E+07	0.5552101947E+02
Ca++	23.000	23.000	0.5738809594E-03
Cl-	1.5200	1.5200	0.4287402856E-04
F-	0.80000E-01	0.80000E-01	0.4210881116E-05
H+	0.11190E+06	0.11190E+06	0.1110191493E+03
HCO3-	234.88	234.88	0.3849451852E-02
K+	2.0000	2.0000	0.5115312162E-04
Mg++	11.000	11.000	0.4525817948E-03
Na+	6.0000	6.0000	0.2609856595E-03
SO4--	1.8300	1.8300	0.1904988036E-04
SiO2(aq)	76.000	76.000	0.1264889557E-02

--- Equivalent Composition of the Aqueous Solution ---

--- Original Basis ---

Species	Moles/kg H2O
H2O	0.5552101947E+02
Ca++	0.5738809594E-03
Cl-	0.4287402856E-04
F-	0.4210881116E-05
H+	0.1110191493E+03
HCO3-	0.3849451852E-02
K+	0.5115312162E-04
Mg++	0.4525817948E-03
Na+	0.2609856595E-03
SO4--	0.1904988036E-04
SiO2(aq)	0.1264889557E-02

--- Current Basis (cte) ---

Species	Moles/kg H2O
H2O	0.5552101947E+02
Ca++	0.5738809594E-03
Cl-	0.4287402856E-04
F-	0.4210881116E-05
H+	0.1110191493E+03
HCO3-	0.3849451852E-02
K+	0.5115312162E-04
Mg++	0.4525817948E-03
Na+	0.2609856595E-03
SO4--	0.1904988036E-04
SiO2(aq)	0.1264889557E-02

Single ion activities and activity coefficients are here defined with respect to the modified NBS pH scale

	pH	Eh	pe
modified NBS pH scale	6.5590	0.4210	7.3945E+00
rational pH scale	6.5336	0.4224	7.4199E+00

pHCl = 10.9538

Activity of water = 0.99989
Log activity of water = -0.00005

True osmotic coefficient= 0.97941
Stoichiometric osmotic coefficient= 0.78653

Sum of true molalities= 0.0064965584832
Sum of stoichiometric molalities= 0.0080896859534

True ionic strength= 0.0033629166314
Stoichiometric ionic strength= 0.0049806671501

--- Electrical Balance Totals ---

equiv/kg H2O

Sigma(mz) cations = 0.2340596184E-02
Sigma(mz) anions = -0.2340596184E-02
Total charge = 0.4681192368E-02
Mean charge = 0.2340596184E-02
Charge imbalance = 0.2010978190E-14

Total charge = sigma(mz) cations + abs (sigma(mz) anions)
Mean charge = 1/2 total charge

The electrical imbalance is

0.430E-10 per cent of the total charge
0.859E-10 per cent of the mean charge
0.859E-10 per cent of sigma(mz) cations
0.859E-10 per cent of abs (sigma(mz) anions)

--- Electrical Balancing on HCO3----

	mg/L	mg/kg	Moles/kg
input	135.00	135.00	0.2212493185E-02
final	234.88	234.88	0.3849451852E-02
adj	99.883	99.883	0.1636958667E-02

--- Activity Ratios of Ions -----

Log (act(Ca++) / act(H+)xx 2) =	9.7617*
Log (act(Cl-) x act(H+)xx 1) =	-10.9538
Log (act(F-) x act(H+)xx 1) =	-11.9656
Log (act(HCO3-) x act(H+)xx 1) =	-9.2317
Log (act(K+) / act(H+)xx 1) =	2.2398*
Log (act(Mg++) / act(H+)xx 2) =	9.6619*
Log (act(Na+) / act(H+)xx 1) =	2.9464*
Log (act(SO4--) x act(H+)xx 2) =	-17.9850
Log (act(SiO2(aq))) =	-2.8981*

--- Distribution of Aqueous Species ---

(Species with concentrations .lt. 1.e-12 are not listed)

Species	Molality	Log molality	Log gamma	Log activity
HCO3-	2.2577E-03	-2.6463	-0.0263	-2.6727
CO2(aq)	1.5703E-03	-2.8040	0.0004	-2.8037
SiO2(aq)	1.2645E-03	-2.8981	0.0000	-2.8981
Ca++	5.6170E-04	-3.2505	-0.1058	-3.3563
Mg++	4.4289E-04	-3.3537	-0.1024	-3.4561
Na+	2.6004E-04	-3.5850	-0.0276	-3.6126
K+	5.1148E-05	-4.2912	-0.0281	-4.3192
Cl-	4.2857E-05	-4.3680	-0.0268	-4.3948
SO4--	1.7378E-05	-4.7600	-0.1070	-4.8670
CaHCO3+	1.1238E-05	-4.9493	-0.0276	-4.9769
MgHCO3+	8.6472E-06	-5.0631	-0.0276	-5.0907
F-	4.1683E-06	-5.3800	-0.0266	-5.4066
NaHCO3(aq)	9.1733E-07	-6.0375	0.0000	-6.0375
MgSO4(aq)	9.1673E-07	-6.0378	0.0000	-6.0378
CaSO4(aq)	7.2630E-07	-6.1389	0.0000	-6.1389
HSiO3-	3.7012E-07	-6.4317	-0.0263	-6.4580
CO3--	3.5489E-07	-6.4499	-0.1060	-6.5560
H+	2.9268E-07	-6.5336	-0.0254	-6.5590
CaCO3(aq)	2.0745E-07	-6.6831	0.0000	-6.6831
MgCO3(aq)	8.2388E-08	-7.0841	0.0000	-7.0841
MgF+	3.2872E-08	-7.4832	-0.0276	-7.5108
NaSO4-	2.3270E-08	-7.6332	-0.0263	-7.6595
OH-	1.5750E-08	-7.8027	-0.0266	-7.8293
MgCl+	1.1537E-08	-7.9379	-0.0276	-7.9655
CaF+	8.3418E-09	-8.0787	-0.0276	-8.1063

KSO4-	5.1440E-09	-8.2887	-0.0263	-8.3150
NaHSiO3(aq)	4.8212E-09	-8.3168	0.0000	-8.3168
CaCl+	3.7908E-09	-8.4213	-0.0276	-8.4489
NaCl(aq)	1.5401E-09	-8.8125	0.0000	-8.8125
HF(aq)	1.3052E-09	-8.8843	0.0000	-8.8843
NaCO3-	3.2131E-10	-9.4931	-0.0263	-9.5194
HSO4-	2.8433E-10	-9.5462	-0.0263	-9.5725
CaOH+	2.4001E-10	-9.6198	-0.0276	-9.6474
NaF(aq)	8.7281E-11	-10.0591	0.0000	-10.0591
KCl(aq)	4.9752E-11	-10.3032	0.0000	-10.3032
HCl(aq)	2.4156E-12	-11.6170	0.0000	-11.6170

--- Major Aqueous Species Contributing to Mass Balances ---

Aqueous species accounting for 99% or more of Ca++

Species	Factor	Molality	Per Cent
Ca++	1.00	5.6170E-04	97.88
CaHCO3+	1.00	1.1238E-05	1.96

Total		5.7388E-04	99.84

Aqueous species accounting for 99% or more of Cl-

Species	Factor	Molality	Per Cent
Cl-	1.00	4.2857E-05	99.96

Total		4.2874E-05	99.96

Aqueous species accounting for 99% or more of F-

Species	Factor	Molality	Per Cent
F-	1.00	4.1683E-06	98.99
MgF+	1.00	3.2872E-08	7.806E-01

Total		4.2109E-06	99.77

Aqueous species accounting for 99% or more of HCO3-

Species	Factor	Molality	Per Cent
HCO3-	1.00	2.2577E-03	58.65
CO2(aq)	1.00	1.5703E-03	40.79

Total		3.8495E-03	99.44

Aqueous species accounting for 99% or more of K+

Species	Factor	Molality	Per Cent
K+	1.00	5.1148E-05	99.99

Total		5.1153E-05	99.99

Aqueous species accounting for 99% or more of Mg⁺⁺

Species	Factor	Molality	Per Cent
Mg ⁺⁺	1.00	4.4289E-04	97.86
MgHCO ₃ ⁺	1.00	8.6472E-06	1.91

Total		4.5258E-04	99.77

Aqueous species accounting for 99% or more of Na⁺

Species	Factor	Molality	Per Cent
Na ⁺	1.00	2.6004E-04	99.64

Total		2.6099E-04	99.64

Aqueous species accounting for 99% or more of SO₄⁻⁻

Species	Factor	Molality	Per Cent
SO ₄ ⁻⁻	1.00	1.7378E-05	91.22
MgSO ₄ (aq)	1.00	9.1673E-07	4.81
CaSO ₄ (aq)	1.00	7.2630E-07	3.81

Total		1.9050E-05	99.85

Aqueous species accounting for 99% or more of SiO₂(aq)

Species	Factor	Molality	Per Cent
SiO ₂ (aq)	1.00	1.2645E-03	99.97

Total		1.2649E-03	99.97

--- Summary of Aqueous Non-equilibrium Non-redox Reactions ---

Reaction	Log Q/K	Aff, kcal	State
None			

--- Summary of Pure Mineral Saturation States ---

(Minerals with affinities .lt. -10 kcal are not listed)

Mineral	Log Q/K	Aff, kcal	State
Anhydrite	-4.0231	-5.2825	
Aragonite	-1.6320	-2.1429	
Bassanite	-4.6712	-6.1334	
Brucite	-7.3997	-9.7161	
CaSO ₄ :0.5H ₂ O(beta)	-4.8537	-6.3730	
Calcite	-1.4871	-1.9526	
Chalcedony	1.0691	1.4038	ssatd
Coesite	0.5112	0.6712	ssatd
Cristobalite(alpha)	0.7747	1.0172	ssatd

Cristobalite(beta)	0.2994	0.3931	satd
Dolomite	-1.9487	-2.5587	
Dolomite-dis	-3.5770	-4.6967	
Dolomite-ord	-1.9487	-2.5587	
Enstatite	-5.1054	-6.7036	
Epsomite	-6.3611	-8.3524	
Fluorite	-4.0324	-5.2947	
Gypsum	-3.7361	-4.9057	
Hexahydrite	-6.5966	-8.6615	
Ice	-0.0959	-0.1259	satd
Kalycinite	-7.2756	-9.5531	
Lansfordite	-4.4109	-5.7917	
Magnesite	-2.1606	-2.8370	
Monohydrocalcite	-2.2929	-3.0107	
Nahcolite	-6.0523	-7.9469	
Nesquehonite	-5.0094	-6.5775	
Okenite	-6.5122	-8.5507	
Pentahydrite	-6.9361	-9.1074	
Quartz	1.3509	1.7738	ssatd
Sellaite	-4.9540	-6.5047	
SiO2(am)	-0.0263	-0.0345	satd
Tridymite	1.1665	1.5317	ssatd

3 approx. saturated pure minerals
0 approx. saturated input solid solutions
0 saturated hypothetical solid solutions

5 supersaturated pure minerals
0 supersatd. input solid solutions
0 supersatd. hypothetical solid solutions

--- Summary of Gases ---

Gas	Fugacity	Log fugacity
C(g)	7.9967-166	-165.0971
C2H4(g)	1.5240-154	-153.8170
CH4(g)	2.8993E-90	-89.5377
CO(g)	7.2383E-34	-33.1404
CO2(g)	3.2826E-02	-1.4838
Ca(g)	3.7683-146	-145.4239
Chlorine	9.7145E-43	-42.0126
Fluorine	8.6945-100	-99.0608
H2(g)	6.7187E-29	-28.1727
H2O(g)	1.2926E-02	-1.8885
H2S(g)	5.7129E-88	-87.2431
HCl(g)	1.7162E-18	-17.7654
HF(g)	3.1814E-14	-13.4974
K(g)	5.4410E-75	-74.2643
Mg(g)	1.1057-122	-121.9564
Na(g)	1.2983E-73	-72.8866
O2(g)	2.0974E-31	-30.6783
S2(g)	1.1122-145	-144.9538
SO2(g)	7.1660E-42	-41.1447
Si(g)	4.5436-199	-198.3426
SiF4(g)	1.8307E-36	-35.7374

--- Reading the input file ---

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End time = 11:17:19 12Dec2005

Run time = 1.42 seconds

Normal exit