CALIFORNIA STATE POLYTECHNIC UNIVERSITY, POMONA
THESIS ELECTRONIC SIGNATURE PAGE

Submitted: Term Summer Year 2021
Bronco ID: 010369307
Email Address: dakunath@cpp.edu

THESIS INFORMATION

THESIS TITLE: Sources of salinity and fluids in a spring/oil seep system in the Santa Susana M
AUTHOR: Debbie A. Kunath-Leatham
PROGRAM: Geology, M.S.

SIGNATURES

Committee Chair Name: Stephen Osborn
Position: Thesis Committee Chair
Department: Professor
Organization: Geological Sciences

DocuSigned by:
Stephen Osborn
B1E6BFB18441457...
Signature: 8/17/2021
Email: sgosborn@cpp.edu

Committee Member 2 Name: Jonathan Nourse
Position: Project Advisor
Department: Professor, Chair
Organization: Geological Sciences

DocuSigned by:
Jonathan Nourse
562E96F6E80E44B...
Signature: 8/17/2021
Email: janourse@cpp.edu

Committee Member 3 Name: Frank Jordan
Position: Project Advisor
Department: Professional Geologist, CEG, CHG
Organization: San Bernardino County

DocuSigned by:
Frank Jordan
0604C03760B940E...
Signature: 8/17/2021
Email: geo.jordan@gmail.com

Upload Thesis Attachment:

Revised August 2020,
Graduate Studies Office

SOURCES OF SALINITY AND FLUIDS IN A SPRING/OIL SEEP SYSTEM IN THE SANTA SUSANA MOUNTAINS, CALIFORNIA

A Thesis

Presented to the

Faculty of

California State Polytechnic University, Pomona

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

In

Geology

By

Debbie A. Kunath-Leatham

2021

SIGNATURE PAGE

THESIS:	SOURCES OF SALINITY AND FLUIDS IN A SPRING/OIL SEEP SYSTEM IN THE SANTA SUSANA MOUNTAINS, CALIFORNIA
AUTHOR:	Debbie A. Kunath-Leatham
DATE SUBMITTED:	Summer 2021
	Department of Geological Sciences

Dr. Stephen Osborn
Thesis Committee Chair
Geological Sciences ____

Dr. Jonathan Nourse
Chair of
Geological Sciences ____

Frank Jordan
Professional Geologist, CEG, CHG
San Bernardino County ____

ABSTRACT

Towsley and Wiley canyons located near Santa Clarita, California, provides an outdoor laboratory setting for studying hypersaline fluid migration from natural oil/tar seeps and springs. More than 30 active seeps and springs were identified within the project area with detailed mapping. The geologic mapping of the water source area indicated a dynamic hydrogeologic system than was interconnected through geologic materials and controlled by structural deformation features. Fractures and faults associated with an anticlinorial geologic setting, provide conduits for deep hypersaline/ paleo marine source waters to migrate toward the ground surface and mix with the meteoric waters. Geochemical analyses of the water samples collected from proximal seeps and springs were used to constrain the sources of water and identify seasonal effects caused by drought conditions. A spring to summer, seasonal shift in the hydroconductivity of the system was determined by using bromide (Br^-) and chloride (Cl^-) anions. The shift allowed hypersaline waters that are associated with the oils and natural gases to migrate to the surface.

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SECTION 1: INTRODUCTION

The Towsley Canyon area, located in Los Angeles County, California, hosts a complex hydrogeological system that is known for its naturally occurring oil/tar seeps, gaseous bubbling springs with elevated salinity, and stream-lined canyons. The area is locally recognized for its scenic hiking trails, with local gyms and marathon trainers utilizing its trails regularly (personal communication with visitors, 2014). However, each time visitors come to this location they trek through the saline waters, lumber over oil stained soils and rocks that cross the paths and are subjected to the odor of rotten eggs which is evidence of gasses emitting from the canyons' many springs and oil seeps. Yet little publicly available data exists assessing the environmental concerns of this canyon area.

In addition, watershed reports also indicate that the Santa Clara River Valley Groundwater Basin, East Subbasin, to which the canyons' streams are tributaries, has had an ongoing high chloride concentration problem of its groundwater for many years (Department of Water Resources, 1968; CH2MHill, 2005; Impact Science, Inc, 2010; Morgan, 2014). A 2010 Environmental Investigations Report (EIR), from Impact Sciences, Inc. states, that the parts of this basin have been "identified as an "impaired water body"" by the State Regional Water Quality Control Board due to chloride concentrations beyond those allowed by the Chloride Total Maximum Daily Load (TMDL) which was established for the basin in 2005 by the SRWQCB. Considering this, the project's preliminary objectives were to identify potential source(s) of fluids, gain insight into the hydrogeology of the fluid migration system and conduct basic assessment of water quality.

SECTION 1.1: GEOLOGY OVERVIEW

The research was conducted in Towsley and Wiley canyons that are within a conservation park of Los Angeles County, California. Located immediately west of Interstate

Highway 5 and south of the City of Valencia, the area is bounded by faults on the north and south sides (CDMG, 1977a, 1977b, 1977c, 1977d, 1978). The geology is composed of three soil formations which are marine in origin , the Pico, Towsley, and the Modelo formations (Winterer and Durham, 1958 and 1962; D.W.R., 1968; Morton, 1976; CH2MHill, 2005; Bedrossian and Roffers, 2012; Campbell et al., 2014; D.O.G.G.R., 2014). This geologic setting has resulted in thought-provoking sedimentary landforms, ephemeral streams, steep terrain, and narrow canyons that draw visitors to the park. However, this setting is also prone to natural seismic shaking events, earthquakes, due to the proximity of several active faults (CDMG, 1977a, 1977b, 1977c, 1977d, and 1978; Impact Sciences, Inc., 2010). Earthquakes can produce fracturing in the subsurface. Fractures, may or may not, allow fluids to migrate from depth (Weeks, 1958; Gurevich et al., 1993; Kharaka and Hanor, 2005). The geology of the Towsley Canyon area potentially provides a natural setting in which the fluid migration of oil, water, and gases could be scientifically explored.

SECTION 1.2: HYDROGEOLOGY OVERVIEW

Since the soil formations in this area are marine in origin, it is reasonable to hypothesize that the canyons' streams represent the shallower freshwater system and the presence of spring water, oil, and gases may indicate that deep marine water source(s) also interact with the shallower system. The deeper hypersaline source(s) is/are inferred by the relationship between brines and the presence of oil seeps. Brines (hypersaline waters) can develop during oil genesis, as organic materials in deep marine sediments are subject to compaction during sedimentary deposition (burial) over time (Buckley et al., 1958; Emery, 1958; Carpenter, 1978; Kharaka and Hanor, 2005). Hypersaline waters can also form from other natural processes such as the evaporation of marine water and the dissolution of evaporites in the shallow water system. The differences in the formation processes may be identified by using salinity, particularly, concentrations of chloride to bromide, to trace the origin of water (Carpenter, 1978; Eastoe et al., 2001; Kharaka and Hanor, 2005). Carpenter (1978) indicates that deep marine sources have high chloride and bromide concentrations with levels of toxicity that can be measured as salinity, which differs from the low concentrations of chloride and bromide found in most meteoric waters. In addition to salinity concentrations, changes in deuterium and stable oxygen isotopes may be useful in identifying different sources of water in the canyons' hydrologic system (Craig, 1961; Kendal and Coplen, 2001; Wang and Jiao, 2012).

SECTION 1.3: RESEARCH QUESTIONS

Sparse background sources of information were preliminarily found for the region. In lieu of the area's geology and its possible hydrogeologic implications, the project served tri-fold purposes, A) to gain some understanding on the hydrogeology of a spring and oil seep natural setting, B) to identify the sources of fluids in this system, and C) to collect information about the basic water quality that may provide some answers or perception for entities connected to the water and oil industries. With these in mind, the project was developed in the attempt to answer the following research questions.

1. What control does the geology have on fluid flow?
2. What is/are the source(s) of the fluids?
3. What is the basic water quality in the canyons?

SECTION 1.4: BACKGROUND

The research area is in a mountainous region that is bordered by the highly populated cities of Valencia and Santa Clarita on the north and, Northridge, and the San Fernando Valley on the south. The project is within the Oat Mountain Quadrangle, Township and Range T3N R16W Sections 8, 9, 16, and 17 (California Division of Mines and Geology, 1976). A California State and regional site map indicating the location of the research area is shown in Figure 1. The terrain consists of steep mountain faces and incised streams at the bottom of deep canyons and has a topographic relief of about 1200 feet. The area is owned by the Santa Monica Mountains Conservancy and the City of Santa Clarita (Walker, 2008) but is managed by the Mountain Recreation and Conservancy (Santa Monica Mountains Conservancy, 2014).

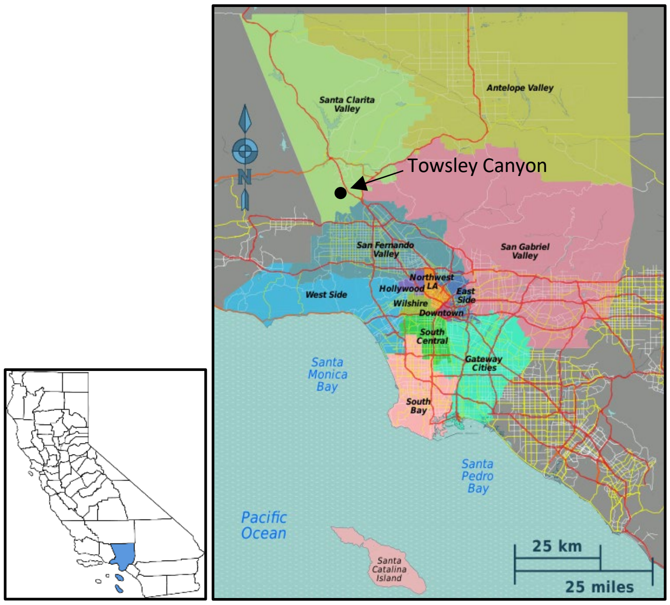


FIGURE 1. CALIFORNIA STATE AND REGIONAL, SITE LOCATION MAP.
The state map shows the location of Los Angeles County in blue. The regional, site location map indicates the approximate location of the project site (CALSPro, 2021 and after Wikimedia Commons, 2020).

History of the oil industry within the canyons

Early oil industry maps indicate that oil seeps were a natural part of the setting in these canyons prior to the first reported oil well in 1865 (Winterer and Durham, 1958; DOGGR, 2014). The project site was also a former oil production area and is part of the Newhall Oil Field (DOGGR, 2014). The Department of Oil, Gas, & Geothermal Resources' (DOGGR) records show that the last oil derrick was plugged in 1995 (DOGGR, 2014). Therefore, it should be anticipated that the natural hazards, geologic, and hydrologic conditions associated with the formation of oil/tar can be expected in the conservancy park area of Towsley and Wiley canyons. These conditions may also influence hydrologically connected systems of the region north of this area, the Santa Clarita Valley.

One natural hazard is ever-present in the canyons. It is the rotten egg smell which comes from the gases emitted from the springs and oil/tar seeps. The odor is a characteristic of hydrogen sulfide which is a colorless gas that can accumulate in low lying areas, is corrosive, and flammable. This gas can also be explosive and very poisonous in certain concentrations (OSHA, 1995). Hydrogen sulfide can result from anaerobic processes and is often associated with oil and gas (Tissot and Welte, 1978).

SECTION 1.5: LITERATURE REVIEW

Geologic Setting and Stratigraphy

The literature review for this project revealed that regional information was mostly limited to older maps, watershed reports, and oil field reports, with most of the geologic investigations done prior to the 1960's. Winterer and Durham (1958 and 1962) have provided the most complete work to date on the area's geology. Their work was focused on geologic information for the oil industry and was completed before tectonic theory impacted geologic science. This thesis project will connect current geologic practices and theory to an area that hasn't been investigated thoroughly in more than 50 years.

The Department of Oil Gas and Geothermal Resources have a library on the oil wells of the area which date back into the 1930's (DOGGR, 2014) but the reports also indicate that drilling in Wiley Canyon had begun before 1865 (DOGGR, 2014). Some of these reports include well logs and other subsurface geophysical data but are not always complete nor are the locations of wells traceable. The Department of Water Resources (1968 and 1997) has regional water quality data and local watershed reports (CH2MHill, 2005; Watersheds coalition of Ventura County, 2006; Impact Sciences, Inc., 2010) which also include geologic insight to the groundwater basin and its tributary systems. Geologic maps of the area are also available (Winterer and Durham, 1958; Morton, 1976; Yerkes, 2005; and Campbell et al., 2014) but most are small scaled and indicate few geologic structural controls for the fluid flow other than the Pico Anticline, which is a major topographic feature located in the Santa Susana Mountains.

The project area is mainly underlain by three geologic formations, the Pico, Towsley, and Modelo. A regional geologic map is found in Figure 2 on the following pages. Winterer and Durham (1962) report that the three formations were formed by marine depositional processes and the presence of oil/tar seeps also supports that they were deeply buried in the geologic past for oil/tar to form. The Pico formation can be found in the northern part of the project area along the north limb of the Pico anticline. It is reported to be Pliocene in age and is composed of marine fine-grained silty sandstone which contains small reddish-brown concretions (Winterer and Durham, 1958), light olive gray and medium bluish gray siltstone and is interbedded with light colored sandstone and conglomerate that contains sandstone clasts.

The Towsley formation is reported by Winterer and Durham (1962) to be late Miocene to early Pliocene age and is composed of a sequence of light-colored sandstones and

Regional Geologic Map

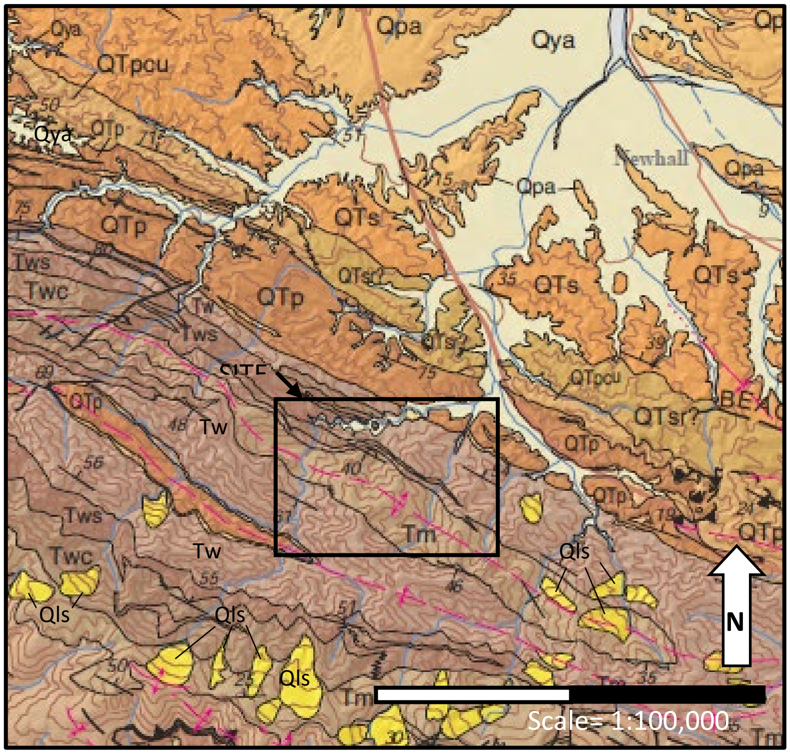


FIGURE 2. REGIONAL GEOLOGIC MAP.

(After Campbell, R.H., Willis, C.J., Irvine, P.J., and Swanson, B.J., 2014).

Explanation of Symbols

Qls	Landslide deposits (Holocene)
Qya	Young alluvium (Holocene to Pleistocene)
Qpa	Pacoima Formation, undivided (Pleistocene)
QTs	Saugus Formation, undivided (Pleistocene to Pliocene)
QTp	Pico Formation, undivided (Pliocene)
QTpcu	Pico Formation, coarse-grained (Pliocene)
QTpc	Pico Formation, sandstone (Pliocene)
Tw	Towsley Formation, undivided (late Miocene to early Pliocene)
Tws	Towsley Formation, siltstone (late Miocene to early Pliocene)
Twc	Towsley Formation, conglomerate (late Miocene to early Pliocene)
Tm	Modelo Formation, undivided (Miocene)

35	Inclined bedding
75	Overturned bedding
15	Inclined crumpled bedding
——— —— ——	Contact between map units – Solid where accurately or approximately located; short dash where inferred.

——— — — - - ?.	Fault – Solid where accurately located; long dash where approximately located; short dash where inferred; dotted where concealed; queried where identity or existence is uncertain.
▲—— ▲ ▲?	Thrust fault – Barbs on upper plate; solid where accurately located; short dash where inferred; queried where identity or existence is uncertain.
↓↑ — — - ·	Syncline – Solid where accurately located, long dash where approximately located; dotted where concealed.
↕ — — - ·	Anticline – Solid where accurately located, long dash where approximately located dotted where concealed.
∼	Streams or rivers
—	Highways

conglomerates, siltstones, and mudstones. The Towsley formation is also located along the north limb of the Pico anticline with its best exposure in the Narrows of Towsley Canyon. It is also marine in origin and contains many rip-up clasts and is inverted in deposition order (fine- to coarse-grained graded beds) which indicates that it was formed by turbidity currents. This formation is variable in lithology and the lithology is reportedly stratigraphically inconsistent from canyon to canyon (Winterer and Durham, 1958). The Towsley formation is reported to be about 4000 feet thick and thins toward the northeast (the vicinity of the project area). Winterer and Durham (1958) also state that some of the thinning may be the result of successive overlap.

The Modelo formation is reported by Winterer and Durham (1962) to be Miocene age, based on foraminifera. In the project area, this formation is mainly composed of gray to brown siltstone and mudstone that varies in hardness and is largely thin bedded. The siltstone has light-colored silty to coarse-grained sandstones that are interbedded in some areas and are up to several feet thick. The basal unit of this formation is reported by Winterer and Durham (1958) to be about 300 feet thick and composed of medium- to coarse-grained sandstone with pebble to cobble conglomerate lenses. The entire thickness of the Modelo formation is unknown. Winterer and Durham (1958) reported that it has been drilled through to at least 5000 feet thickness without reaching its base. Foraminiferal faunas indicate that the Modelo formation is also a deep marine deposit, however, there is no reference that eludes to the presence of diatomites observed in the Modelo of Towsley Canyon. This formation is mainly associated with the seeps in the canyon areas.

The area is also part of the Transverse Ranges Geomorphic Province which is characterized by east-west mountain ranges that are bounded on the south by reverse and thrust fault systems (CDMG, 1977d). The Santa Susana fault is the major thrust fault in this region and is part of the Sierra Madre fault system (CDMG, 1977c). This thrust fault system is responsible for the compressional geomorphic expressions of northwest trending anticlines/synclines in this area (CDMG, 1977d). The Pico anticline axis trends northwest through the project area and so does the north limb of the Oat Mountain syncline, which shares the south limb of the Pico anticline (Winterer & Durham, 1958). These structures may provide the structural traps necessary for oil and brine formation (Winterer and Durham 1962).

A series of northwest striking strike-slip transform faults are located north and northwest of the area (San Gabriel, Holser, Del Valle, and Oak Ridge faults). These faults are associated with groundwater barriers and subsurface offsets of groundwater levels in the northern basin but are not known to extend to this part of the mountain range (CH2MHill, 2005). The Newhall Oil Field map shows faults in the Towsley and Wiley Canyon area, but these are not shown on any other geologic maps reviewed to date. No other faults are mapped in the vicinity of the project area (Campbell et al., 2014; CDMG, 1977a; CDMG, 1977b; CDMG, 1977c; CDMG, 1977d; CDMG, 1978; Morton, 1976; Treiman, 2000; Winterer and Durham, 1958, 1962; Yerkes, 2005). A local fault map has been provided in Figure 3.

Geologic structure and sediment type influences where fluids can and will flow. Structure includes bedding, contacts between rock and soil units, joints, fractures, and faults. Fluids can flow along cleavage planes between bedding, along contacts, joints, and fractures, whereas, faults and fine-grained sediments can act as barriers, or semi-barriers, for fluids (Weeks, 1958; Gurevich et al., 1993). Coarser materials generally have greater porosity and permeability which also allows fluids to flow (Buckley et al., 1958). Understanding the

Local Fault Map

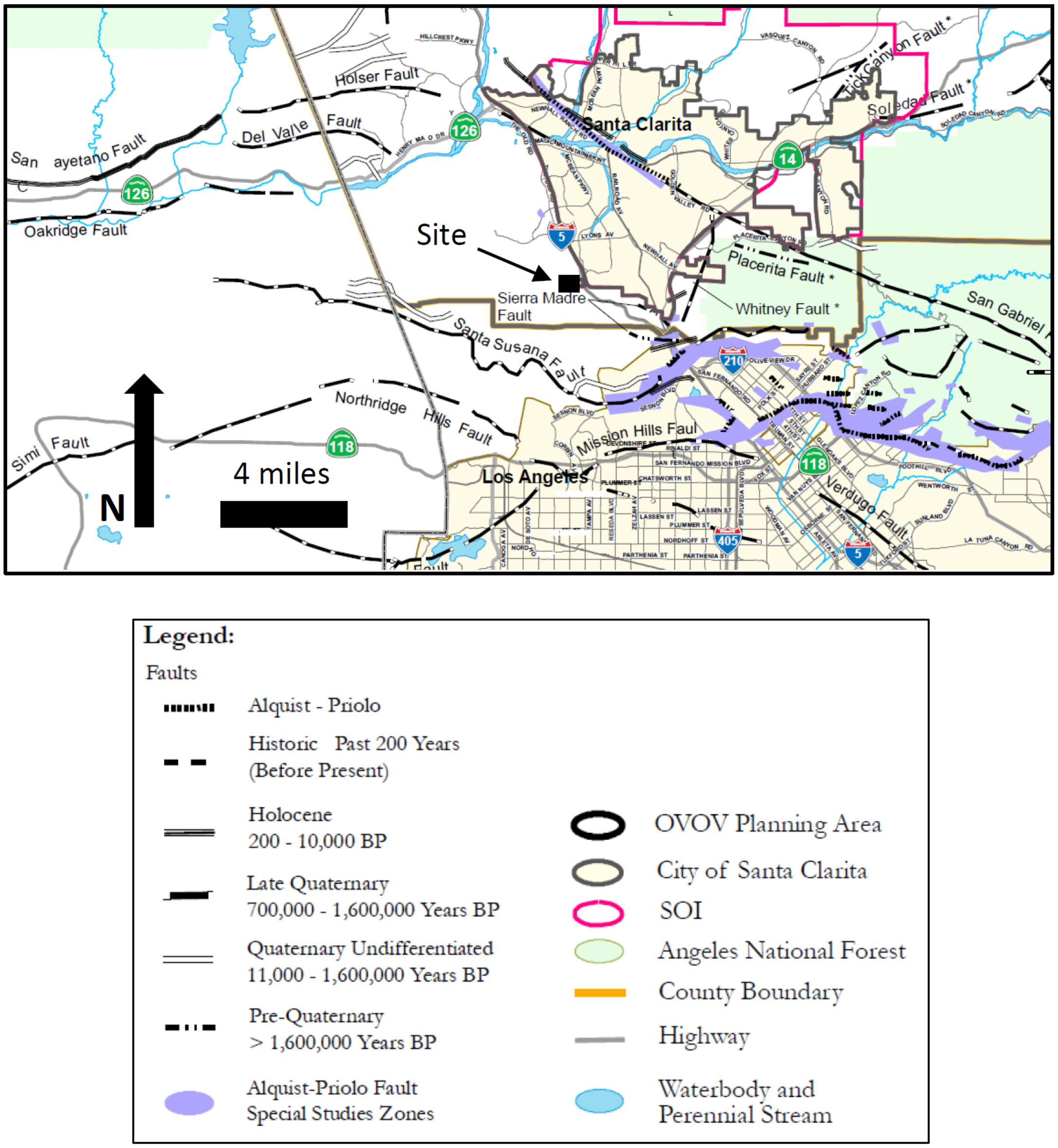


FIGURE 3. LOCAL FAULT MAP.
(After Impact Sciences, 2010). Map shows the proximity of know local faults to the Towsley Canyon area.

hydrogeologic properties in these canyons is key to understanding the fluid dynamics of this tributary system.

Hydrogeology

The study of oil systems involves the study of fluid-flow and contains water as an important element in this system. Waters can be divided into four types of subsurface waters, juvenile, meteoric, connate, and mixed (Selley, 1998). Juvenile waters are primarily of magmatic origin and are not considered to be part of this study. Meteoric fresh waters are subsurface waters that originated primarily as rainwater that migrates through sediments (Kharaka and Hanor, 2005). Meteoric fresh water becomes more reduced as it oxidizes organic matter as it flows through soils at shallow depths. These waters are low in salinity even though waters pick up salt content as they move through soils (Selley 1998; Kharaka and Hanor, 2005). The third type, connate waters, are more difficult to define and Selley (1998) states that there are several definitions for connate waters due to this. The definition used for this study is waters that have been separated from the hydrologic cycle for a long period of time and form in a closed system contemporaneous to their surroundings (Kharaka and Hanor, 2005). Connate waters are characterized by high salinity but differ from seawater in salinity and chemistry (Kharaka and Hanor, 2005). The fourth type of water is mixed, and it can be a combination of the other types of waters (Selley, 1998; Kharaka and Hanor, 2005). These water types can be differentiated by their different chemical properties which include salinity, elemental anions and cations, pH, dissolved oxygen content, and isotopes (Kharaka and Hanor, 2005).

According to Kharaka and Hanor (2005), salinity is defined as a measurement of the amount of dissolved particles and ions in water. This character can change as water evolves over time and as it migrates through soils. These diagenetic chemical characteristics are similar for similar processes and thus, may be used to identify water types and as indicators for the water's evolution (Carpenter, 1978; Kharaka and Hanor, 2005). Table 1 showing water classification based on salinity is shown below.

Table 1. Water Classification Based on Salinity

Water classification	Salinity (mg/L)
Fresh	<1,000
Brackish	1,000-10,000
Saline	10,000-100,000
Brine	>100,000

Note: Modified from G. Faure (1998)

Salinity can be measured as total dissolved solids (TDS) or as electrical conductance (EC) (Kharaka and Hanor, 2005) and is a required water standard for drinking water; the State of California has set the limit of TDS in drinking water at 1,000 mg/L (State Water Resources Control Board, 2010). Seawater has an average salinity of 35,000 mg/L of dissolved particles, whereas subsurface salinity is known to have a range from about 0 up to 642,798 mg/L (Selley, 1998; Kharaka and Hanor, 2005). Meteoric waters have negligible salinity, but the salinity of connate waters increases with depth, rarely exceeding 350,000 mg/L TDS (Weeks, 1958; Kharaka and Hanor, 2005). This salinity value is indicative of an oil field brine (Selley, 1998; Kharaka and Hanor, 2005). However, not all sedimentary basins contain brines (Kharaka and Hanor, 2005) just as not all sedimentary basins contain oil fields.

Another important factor about salinity is its correlations between margins and basin center. The salinity of basins tends to increase from margins toward the center (Selley, 1998). This is because the margins are usually topographically higher and more subject to rainwater and meteoric water influences in the subsurface than the center. Weeks (1958) and Selley (1998) maintain regions having pronounced salinity at margins may also have oil reserves, however, relative salinity will vary from basin to basin.

Salinity can include hundreds of different ions, but the most common ones are chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), sulfate (SO_4^-), calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+), iron (Fe), boron (B), and bicarbonate (HCO_3^-) (Selley, 1998; Kharaka and Hanor, 2005). This project will concentrate on chloride and bromide anions. Water types also have different elemental concentrations of ions (Carpenter, 1978; Selley, 1998; Kharaka and Hanor, 2005). Meteoric waters tend to have higher concentrations of bicarbonate and sulfate and lower concentrations of calcium and magnesium than connate waters (Selley, 1998). Seawater and connate waters differ in chemical composition too; connate waters contain lower concentrations of sulfates, magnesium, and often calcium but higher concentrations of sodium, potassium, and chlorides (Selley, 1998; Kharaka and Hanor, 2005). .

Chloride and Bromide

Carpenter (1978) and Kharaka and Hanor (2005) agree that chloride and bromide can also be used as markers for the evolution of water in sedimentary basins because they provide constraints for interpreting the sources of chloride in the waters. The constraints are primarily due to the conservative nature of these monovalent anions with similar radii, $Cl^- = 1.81$ Å and $Br^- = 1.96$ Å (Carpenter 1978; Kharaka and Hanor, 2005). Both sets of researchers (Carpenter, 1978; Kharaka and Hanor, 2005) recognized that the main sources for chloride in hypersaline waters include dissolved chloride within sediments at the time of deposition, chloride that was derived from the evaporative processes, and chloride that was derived from subsurface mineral dissolution processes (Buckley et al., 1958; Kharaka and Hanor, 2005). Both anions are also found in marine water in relatively high concentrations but have upper limits when this water is subject to evaporation, chloride = $\sim 2.5 \times 10^5$ mg/L and bromide = $\sim 0.6 \times 10^4$ mg/L (Kharaka and Hanor 2005). The ratio of Br/Cl increases steadily in the initial marine water evaporation process, when the Cl saturation is reached, Cl is preferentially coupled with Na to form halite and very little Br is interstitially captured in the halite mineral lattice. This results in a higher Br/Cl ratio. (Kharaka and Hanor, 2005). During subsurface dissolution of halite, the chloride concentration increases and results in a relatively low Br/Cl ratio value.

Stable Oxygen and Hydrogen Isotopes

In addition to chloride and bromide concentrations, stable isotopes of oxygen and deuterium can be used to trace the origins of waters (Craig, 1961; Kharaka and Hanor, 2005). This is due to the nuclides being sensitive to changes in temperature; changes in temperature will result in fractionation of the nuclides. The rate of fractionation is based on the individual nuclide's mass and can result in condensation or evaporation (Motzer, no date; Clark and Fritz, 1997). Lighter isotopes tend to evaporate before heavier isotopes which result in a more δ positive (+) value indicating that the sample has been enriched with the heavier isotope, and in condensation processes the resulting δ value would be more negative (Motzer, no date; Craig, 1961; Clark and Fritz, 1997; Kharaka and Hanor, 2005). Changes are small and reported as a δ value in units of per-million (0/00) (Clark and Fritz, 1997).

To effectively interpret the δ value changes of the ratios Oxygen-18 / Oxygen-16 ($\delta^{18}O/\delta^{16}O$) and Hydrogen-2 / Hydrogen-1 ($\delta^{2}H/\delta H$), it is necessary to compare them to a known standard such as the Vienna Standard Mean Ocean Water (VSMOW) which has been adopted for marine waters (Motzer, no date; Clark and Fritz, 1997, Kharaka and Hanor, 2005). Similarly, changes in δ value of $\delta^{18}O/\delta^{16}O$ and $\delta^{2}H/\delta H$ for watersheds should be compared to a Local Mean Water Line (LMWL) which has been developed from local precipitation events and therefore has the local climate's water "fingerprint" (Motzer, no date,). Correlation with the LMWL would allow local entities to determine that their water source has probably come from local precipitation.

<u>Regional water quality</u>

The Upper Santa Clara Valley River Groundwater Basin, East Subbasin, is located north of the project area. The ephemeral streams within Towsley and Wiley canyons (Santa Monica Mountains Conservancy, 2014) are reported to be tributaries to the South Fork branch of the Santa Clara River and joins the main stem of the river, west of the valley's wastewater treatment plant (CH2MHill, 2005). A map showing the relationship of the project to the groundwater basin is shown in Figure 4.

Regional Groundwater Basin Map

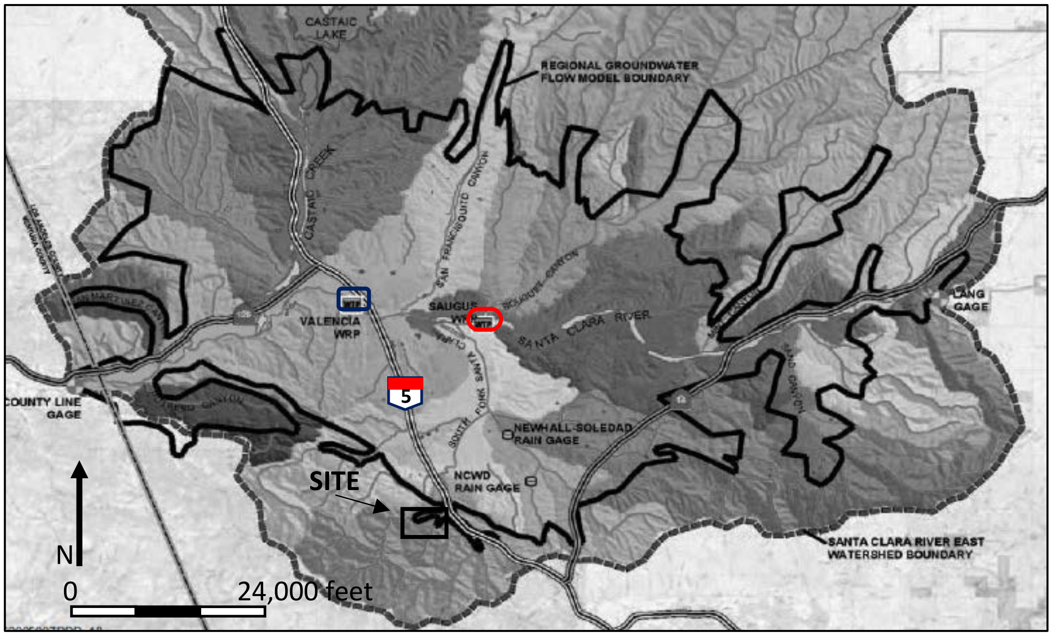


Figure 4. Regional Groundwater Basin Map.

Map of the upper Santa Clara River Groundwater Basin East Subbasin, the watershed for the Santa Clarita Valley, also showing the project area (after CH2MHill, 2005). Symbols: dashed line represents the extent of the Santa Clara River East Watershed boundary, thick black line represents the boundary used for regional groundwater flow modeling, which is not discussed in this report, red box shows the location of the Saugus Water Treatment Plant, and blue box shows the location of the City of Valencia's Water Treatment Plant.

The direction of hydrologic flow from the project area is northward but the Santa Clara River's main trunk flows from east to west. The streams are now ephemeral but reports by the Santa Monica Mountains Conservancy (2014) and park visitors indicate that these streams flowed year around before the present drought. Groundwaters from the project area still contribute to the basin's groundwater (CH2MHill, 2005). Water quality reports from wells in the vicinity of the South Fork branch have indicated higher levels of chloride that decrease toward the direction of basin center (DWR, 1968). The Watersheds Coalition of Ventura County (2006) reported high chloride waters were being discharged into their basin along the Santa Clara River from the east basin. They also attained that the chloride values are resulting from the wastewater treatment plant of the central Santa Clarita valley (Watersheds Coalition of Ventura County, 2006). Tony Morgan, Deputy General Manager of Groundwater & Water Resources for the United Water Conservation District, verified that the water quality of the waters entering the Ventura basin from the east basin remained virtually unchanged from 2006 to 2014 (personal communication October 1, 2014).

SECTION 2: METHODS

A two-way approach in data collection was adopted to address research questions and to provide insight about water quality and fluid flow dynamics. The area's hydrogeology was expected to be complex due to the region's geologic and tectonic history as well as known active faults in the vicinity. Detailed geologic maps of the area had not been found in the initial project research, other than those that were compiled in and before the 1960's which were pre-tectonic theory. This triggered the need to record the current geologic conditions of the area by mapping Towsley and Wiley canyons' geologic features. Geologic mapping was also needed to identify the relationships between fluid flow, soil/rock type, and geologic structural controls, such as folds, fractures, and faults, which can be barriers or conduits for fluid flow. Seeps and springs were also identified, described in detail, and their locations recorded on the field map. The geology surrounding those areas were also recorded and described in detail.

The geochemistry of the fluids also needed to be assessed to identify the sources of the fluids and salinity, as well as provide an environmental assessment for the canyons' water system. This task would be best accomplished by fluid collection and analyses of fluid properties in the field and in the laboratory. The geologic mapping of the project area was started in December 2013, fluid collection from mapped springs and oil/tar seeps (seeps) commenced soon afterwards. The field processes continued until February 2014.

SECTION 2.1: GEOLOGIC MAPPING

Geologic mapping was accomplished using Garmin GPS, model GPSmap 62S, to record the locations and approximate elevations where geologic measurements, features, and fluid data were collected. Precise waypoint locations were acquired in the National American Datum, 1927 (NAD 1927) coordinate system for the Continental United States (NAD 1927 CONUS) and were plotted by hand on the base map using the Universal Mercator System developed for the

United Postal Service (UTM UPS). Correlation between the NAD 1927 and UTM UPS systems was determined prior to mapping by overlaying the maps with the two systems on a light table and then transferring the correct UTM grid onto a digital copy of the base map using AutoCAD 2010 software. The Oat Mountain Quadrangle, California – Los Angeles County: 7.5 Minute Topographic Series, Special Studies Zones map, which was compiled by the California Division of Mines and Geology (1976), was used as the base map during the mapping process.

A Brunton compass was also used in the field to gather attitudes, bearings, and plunge angles from the rock formations, geologic structures, and stream beds. The canyons' sedimentary rock formations, stratigraphic contacts, material deformation, fractures, joint systems, faults, springs, oil/tar seeps, and general topographic notes were described in detail and pictures were taken at various locations for future reference. The mapping process was accomplished by first transecting the higher-elevated ridges along the east and west boundaries of the project area, then mapping the middle ridge between Wiley and Towsley canyons, which in turn was followed by transecting each deeply incised canyon and its streams. Mountain trails that were maintained for visitors were utilized when available but animal trails, moving through thick brush, rock-hopping along streams, and some rock climbing and repelling was also necessary at times to collect pertinent data.

The geologic map was drafted in the following manner. The UTM grid was placed on a light table and the base map was affixed on top of it. Each waypoint was then plotted by hand using geologic symbols and cartographic standards from Compton (1985) and the Federal Geographic Data Committee [U.S Geological Survey] (2006). The map's lithologic units were colored by hand then touched up digitally using Adobe Illustrator. While drafting the geologic map, standard naming conventions of the units had to be abandoned to easily distinguish between the formations and their members. Standard convention uses the geologic ages of the formation as the principal symbol and lower case or subscripts to identify the individual units. However, the units focused on for this project were of the same geologic age, the Miocene epoch, so the principal symbol was the same. This led to some confusion which resulted in the change of the naming convention. For this project, the first letter of the formation was used as the principal symbol followed by lower-case identifiers for the type of units. For example, the Towsley Formation symbols are Tss for Towsley sandstone, Tcg for Towsley conglomerate, and Tsh for Towsley shales while the Modelo Formation symbols are Mss for the Modelo sandstone and Msh for the Modelo shales. The P symbol was used for Pico Formation as it was undifferentiated.

SECTION 2.2: HYDROGEOLOGY AND HYDROGEOCHEMISTRY

Hydrogeologic Mapping

When springs and oil/tar seeps were identified for the first time, the geographic location was recorded on the base map and notes describing the location were recorded in the field notes for that day. Collection of fluids and field testing of gas concentration, pH, electrical conductance, and temperature of the fluid at the spring origin began soon after the sources were identified. Some springs were difficult to identify in the wet season but as the dry season progressed and turned into drought conditions, small areas of green vegetation, saturated soils, and the emission of gas bubbles on the ground's surface made the process much easier. The source areas of oil/tar seeps were easier to identify. Seeps either had pooling oil in the ground surface or flowing oil along the ground's surface, down gradient from the seeps. Pictures identifying these conditions are found in Figures 5 and 6. The origins at which seeps emerged to the surface were also located by the emission of gas bubbles in the oil or on the ground's surface of the flowing oil. This aided collecting samples from where the seeps flow originated at the ground surface.

Figure 5 . Oil Seep in Towsley Canyon, Pooling Oil.

Figure 6. Oil Seep in Towsley Canyon, Flowing Oil.

A total combined total of 31 spring and seep locations were identified in the duration of this project. Tables identifying the springs and seeps and their locations is found in Tables 2 and 3. However, only fourteen of these were sampled and processed for data due in part to budget constraints for materials, equipment, and outsourced laboratory testing for some of the fluid samples. Other reasons for not testing these locations included maintaining the Conservation Park's aesthetics along the trails as well as avoidance of areas that were already marked with

Table 2. Oil/Tar Seep and Spring Locations (Sampled)

Canyon	Seep/Spring	Location ID Number	Easting	Northing	Elevation (feet)
Towsley	Spring	SPR-1T	354920	3802553	1536
Towsley	Spring	SPR-2T	354931	3802213	1654
Wiley	Seep	SE-3W	354624	3801577	1694
Wiley	Spring	SPR-4W	356230	3801387	1745
Wiley	Seep	SE-5W	356178	3801255	1820
Wiley	Spring	SPR-6W	356141	3801211	1856
Wiley	Spring	SPR-7W	356132	3801320	1792
Wiley	Seep	SE-8W	356193	3801348	1761
Towsley	Seep	SE-10T	354817	3802066	1650
Towsley	Seep	SE-13T	354791	3802122	1623
Towsley	Seep	SE-14T	354788	3801978	1635
Towsley	Spring	SPR-15T	354767	3802014	1622
Towsley	Spring	SPR-19T	354917	3802515	1582

Table 3. Oil/Tar Seep and Spring Locations (Not Sampled)

Canyon	Seep/Spring	ID Number	Easting	Northing	Elevation (feet)
Towsley	Seep	SE-9T	354840	3802110	1575
Towsley	Seep	SE-11T	354812	3802019	1659
Towsley	Seep	SE-12T	354793	3802099	1641
Towsley	Seep	SE-16T	354777	3801999	1636
Towsley	Seep	SE-17T	354774	3802003	1635
Towsley	Seep	SE-18T	354790	3801983	1637
Towsley	Spring	SPR-20T	354950	3802469	1600
Towsley	Spring	SPR- 21T	354970	3802451	1607
Towsley	Spring	SPR-22T	354848	3802155	1648
Wiley	Seep	SE-23W	356191	3801312	1775
Wiley	Seep	SE-24W	356192	3801297	1787
Wiley	Spring	SPR-25W	356172	3801319	1781
Towsley	Spring	SPR-26T	354904	3802420	1645?
Towsley	Spring	SPR-27T	354934	3802437	1763
Towsley	Seep	SE-28T	354868	3802082	1696
Towsley	Seep	SE-29T	354925	3802051	1776
Towsley	Seep	SE-30T	354940	3802054	1793
Towsley	Spring	SPR-31T	354839	3802100	1657

evidence of slope instability and rockfall problems; collecting in these locations may have led to an increase in erosion or compromised slope stability. Other locations, mainly newly identified oil/tar seeps, could not be sampled with the equipment available and other oil/tar seep locations were not identified until the close of the current project.

Water Geochemistry

The geochemistry of the fluids was employed as a two-phase process which included both field work and laboratory analyses. The field work consisted of water collection, filtration of the samples, and *in situ* water quality testing. Fluid extraction from both springs and seeps started out as the same process but had to be modified later due to the substantial costs of collection materials that were incurred during the collection process at some of the springs and seeps. These modifications will be described in detail later in this section.

Field methods

Where possible, the fluids were collected using California State water collection practices (ADEQ, 2005). Fluids were collected as close to the origin of the spring and seep as physically possible. The spring water was directly collected from the apparent flowing source with a sterile syringe. A 0.45 micron filter was attached to the syringe and used to filter the water as it was transferred from the syringe into pre-cleaned collection bottles. Four sample bottles were collected at each location. The samples were clearly marked with the sample number, date, and color coded for pH, isotope, anion, and cation testing. The cation sample bottle contained two drops of pure optima-grade nitric acid to keep the cations in solution until processing. The water samples were then kept on ice in a cooler until delivered to the laboratory, for cold-storage in a refrigerator, before processing.

The first modified method for collecting fluids was first deployed at a spring in Wiley Canyon. The spring was flowing from saturated soils and when collected with a syringe the filtration process was not only time consuming but monetarily costly with the consumption of many filters to produce one sample bottle. Instead of filtering in the field and separating the sample into four bottles, a large sample bottle was used to collect the non-filtered water bulk sample of water. The large bottle was labeled with location and date and placed on ice until it was delivered to the laboratory. At the laboratory the sample was allowed to settle overnight in refrigerated conditions and was then filtered using a vacuum system. The phrase "*bulk sampling*" was coined for this process and is discussed in the Laboratory Methods section.

After the samples were collected, *in situ* field analyses of the source waters was performed using an Eco Sense meter, YSI pH100 model. Water temperature, pH, electrical conductance. Total volatile organic gasses (VOC) were also recorded; the method for this is discussed below. Notes for air temperature, precipitation, fog, and any disturbances to the source sites were also recorded. Collections and analyses for each location were done monthly over the research period.

Field measurements of VOCs were also conducted using a Tiger handheld photo ionization detector (PID). Measurements were taken as a precaution due to observations of bubbling gas emissions from seeps and springs in both Wiley and Towsley canyons. These emissions were also accompanied by a strong rotten egg odor, indicating the presence of hydrogen sulfide gas. This gas is colorless and can accumulate in low lying areas. It is also corrosive, flammable, and can be explosive and poisonous in certain concentrations after certain lengths of exposure (OSHA, 1995). Hydrogen sulfide gas was also a concern due to its numbing effect on the olfactory senses after prolonged exposure to concentrations of only 20 to 30 ppm. This effect disables individuals from detecting the gas by its odor. A list of physiological responses to hydrogen sulfide gas exposure and concentration levels can be found in Table 4 on the next page. Concentrations of total volatile organic compounds (VOCs) were detected, using a PID, while collecting fluid samples from all spring and oil seep locations. VOC measurements were taken in the down-wind direction up to 10 feet from the spring and seep location.

Laboratory methods

After the field work was completed for the day, the fluid samples were delivered to the Hydrogeology Laboratory located on the California State Polytechnic University campus in Pomona. Laboratory analyses for bulk-water samples, total alkalinity, and anions concentrations were completed at this location. Select samples were analyzed for Oxygen and Hydrogen isotope values and cations which was completed at an outside facility, the University of Arizona.

TABLE 4. PHYSIOLOGICAL RESPONSES TO HYDROGEN SULFIDE GAS EXPOSURE

Concentration (ppm)	Physiological response
0.02	No odor
0.13	Minimal perceptible odor
0.77	Faint but readily perceptible odor
4.6	Easily detectable, moderate odor
20-30	May dull sense of smell due to prolonged exposure
27.0	Strong, unpleasant odor, but not intolerable
10	Beginning eye irritation
50-100	Slight conjunctivitis and respiratory tract irritation after 1 hour exposure
100	Cough, eye irritation, loss of sense of smell after 2-15 minutes. Altered respiration, pain in the eyes, and drowsiness after 15-30 minutes followed by throat irritation after 1 hour. Several hours exposure results in gradual increase in severity of these symptoms and death may occur within the next 48 hours.
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour of exposure.
500-700	Loss of consciousness and possibly death in 30 minutes to 1 hour.
700-1,000	Rapid unconsciousness, cessation of respiration, and death.
1,000-2,000	Unconsciousness at once, with early cessation of respiration and death in a few minutes. Death may occur even if individual is removed to fresh air at once.

Note: Odor should not be used to indicate nonhazardous concentrations. Exposure to 10 ppm of hydrogen sulfide is acceptable to avoid discomfort, but concentrations can fluctuate up to 20 ppm within an eight-hour, five-day week to protect health. If there are no other exposures in a day, a single ten-minute exposure to 50 ppm should not be hazardous. There is no time-weighted average exposure for this gas. (OSHA, 1995)

THE BULK SAMPLING FILTRATION PROCESS

The *bulk sampling* filtering process was completed in the Hydrogeology Laboratory. This was accomplished by connecting the bulk sample to a compressor in which the flow of air had been mechanically reversed to act as a vacuum system. When the compressor was turned on, the vacuum extracted the air from the end collection bottle and the sample fluid was pulled through the filter and collected in the end bottle. A picture of the setup can be found in Figure 7. The fluid was filtered using a graduated process, first filtered using a 1.0 micron filter, then a 0.8 micron filter, a 0.6 micron filter, and lastly a 0.45 micron filter. The filtered fluids were then dispensed into the four smaller, color coded, sample bottles described earlier. This same process was also used to process the fluid samples collected from many of the oil seeps in both Wiley and Towsley canyons and one spring in Towsley Canyon.

FIGURE 7. BULK-SAMPLING FILTRATION SYSTEM.

TOTAL ALKALINITY ANALYSES

The pH values were used in the laboratory to determine the total alkalinity of the samples. The pH and total alkalinity of groundwater systems can act as a buffer or catalyst to some weathering processes, depending on the relationship of these two factors. Therefore, determining these values can be useful in identifying some of those environmental conditions. Temperature and pH were measured *in situ* in the field as part of the collection process. Those values provide insight into the conditions of the surficial geologic conditions. Total alkalinity will provide insight into the subsurface conditions when looked at in conjunction with the pH of the groundwater and the soil/rock units in which the water resides.

Testing the water samples' total alkalinity was accomplished with a benchtop meter using a titration method. First, 15 to 20 ml of water from the samples was measured by weight on an American Scientific Products Electronic Balance (CAT No. B1240). A magnetic stir rod along with a Fisher Scientific lab disc was used to stir the sample water in a beaker during the titration process. The fluid's pH was constantly measured using a Thermo Scientific stylus and pH meter (Orion STAR A211 model). The stylus was also connected to an Eco Sense EC300 display meter to measure the electroconductivity of the fluid and constantly monitor the pH during titration with hydrochloric acid (0.1 normality). A bottle top titrator [Titrette® brand with 0.25 ml class A precision] was used to dispense the hydrochloric acid solution. Titration continued until the pH values neared a pH of 4.5 without going under that value. Final values for pH, electrical-conductivity, temperature of the water, and the volume of the dispensed hydrochloric acid was then recorded. The total alkalinity of the water sample was then calculated using the formula,

$$\text{Total Alkalinity (mg/L)} = \frac{[\text{volume of acid added (ml)}] * [\text{normality of acid}]}{[\text{volume of sample(ml)}]} \text{ x } 50{,}000.$$

The total alkalinity was recorded, and the process was repeated for each sample collected.

ANION ANALYSES

Anion analyses of the water samples was accomplished using a Dionex Ion Chromatography System (IC), model ICS-1100, with a Dionex AS22 column, and Dionex automated sampler, model AS40, and running Chromeleon Chromatography software. An instruction check-list was prepared for this procedure and can be found in Appendix 10. Ion chromatography is used to detect the concentrations of anion species in water samples by comparing sample concentrations to known concentrations of anion species in a prepared standard. An eluent is used to increase the ion attraction for anion species within the water samples. Those anion species that are not slowed by the attraction pass through the plates of the chromatograph more quickly and their electroconductivity is measured. Different anion species peak at different time intervals and these responses are recorded on a graph with the y-axis indicating the electric current levels and the x-axis indicating time. The resulting three-point curve is compared to the three-point curve of the standards that were prepared beforehand and ran through the system before a set of prepared samples. The program then calculates the area under the sinuous curve and records that value in parts per million (ppm) for the anion species. If selected anion species are not within detectable concentration limits, the electric charge of the water samples produces a flat line.

The eluent was prepared was also prepared in the laboratory each time the anion testing was done. This eluent solution was prepared by measuring 10 milliliters of Dionex AS22 Eluent Concentrate (Sodium Carbonate) solution, pouring it into a 1000 milliliter clean glass flask, then filling the flask with distilled water to the 1000 milliliter line. The solution was then inverted in the flask several time to mix. The resulting eluent solution was then transferred into an empty Ion Chromatograph's receptacle bottle. Every 5 to 6 samples tested using the Ion Chromatograph required 1000 milliliters of prepared eluent.

In addition to the preparation of the eluent, anion species standards had to be prepared beforehand by the following method. Laboratory approved anion concentrations (shown in parentheses) for fluoride (1.003 g/mL), chloride (1.005 g/mL), bromide (1.001 g/mL), nitrate (1.002 g/mL), and sulfate (1.001 g/mL) were used to prepare the standards. Preliminary anion concentrations for the prepared standards were determined by assuming the expected values of anions in similar environmental systems and working the math backwards. For example, if the assumed expected value of chloride was 400 ppm, then a chloride standard of 400 mg/L needs to be prepared accordingly. The laboratory concentration of chloride comes in 1000 milligrams per liter (mg/L). Using the following formulas,

$$(400\ \text{mg/L})*(\text{L}/1000\ \text{mL})*(100\ \text{mL}) = 40\ \text{mg},$$

$$\text{then, } (40\ \text{mg})*(\text{L}/1000\ \text{mg}) = (0.04\ \text{L})*(1000\ \text{mL/L}) = 40\ \text{mL},$$

it was determined that 40 mL of chloride at 1000 mg/L concentration is needed to prepare the 400 ppm chloride standard for the Ion Chromatograph. This same process was repeated for each anion species.

The IC anion species standards were prepared using the following method. Three concentration standards, a high-, middle-, and a low- concentration standard, were needed for the IC to analyze for anion concentrations with precision. The highest concentration standard was prepared first, by weighing a sterile 150 mL bottle, recording its weight. The balance was then tarred with the empty bottle on the balance. A pipette was then used to extract and measure the previously determined amount of anion species that was needed, and this fluid was ejected into the bottle on the balance. The actual weight was recorded, and the balance was tarred again. This was repeated for each anion species for which the collected water samples were going to be assessed. After all the needed anion species were added, the actual weights were summed then subtracted from 100. The difference was the amount of distilled water that was needed to complete the standard solution. The calculated amount of distilled water was then measured using a pipette and combined with the anion species solution and the final weight was recorded. The final High Standard Concentration solution was then inverted several times to mix thoroughly. Both the middle and low standard concentrations were prepared by measuring an amount of the high standard concentration and combining it with distilled water at ratios of 1:5 (for the Middle Concentration Standard) and 1:150 (for the Low

Concentration Standard) respectively. A representative example of the calculation process is shown in Table 5 below.

Table 5. Calculations for the Preparation of Ion Chromatograph Concentration Standards

Anion Species	Ideal (ppm)	Ideal Weight (g)	Actual Weight (g)	High Concentration (03)	Middle Concentration (02)	Low Concentration (01)
Fluoride	10	1	1.0072	10.1003	2.0210	1.06732
Chloride	400	40	39.9906	401.8296	80.4033	2.6782
Bromide	100	10	10.0186	100.2672	20.0628	0.6683
NO3	80	8	8.0019	80.1639	16.0402	0.5343
SO4	400	40	40.0054	400.3784	80.1129	2.6685
DI Water	-	-	0.9952	-	-	-
Sum			100.0189			

First, calculations for the preparation of Ion Chromatograph, concentration standards were recorded in the previously depicted table format for easing transfer into the IC's software before each sample run. Since the standards were prepared by weight, the bottle weight for each concentration had to be known prior to preparation. These were recorded in a table as shown below (Table 6).

Table 6. Bottle Weights for Concentrations Standards

High Concentration bottle Weight (g):	13.8707
Middle Concentration bottle weight (g):	13.8574
Low Concentration bottle weight (g):	13.88991

Calculations for species concentration in the High Concentration Standard (03) was determined using the following formula,

$$\text{Anion Species} = \frac{\text{(Actual Weight of anion species)(LAAC)}}{\text{Sum of Actual Weight for solution}} \times 1000 = \text{High Concentration Standard.}$$

Below are the calculations for each species using the above formula for the High Concentration Standard (03),

$$\text{Fluoride} = \frac{(1.0072\text{ g})(1.003\text{ mg/L})}{100.0189\text{ g}} \times \frac{1\text{ L}}{1000\text{ mg}} \times \frac{1000\text{ mg}}{1000\text{ mL}} = 10.1003\text{ mg/mL}$$

$$\text{Chloride} = \frac{(1.005\text{ g})(39.9906\text{ mg/L})}{100.0189\text{ g}} \times \frac{1\text{ L}}{1000\text{ mg}} \times \frac{1000\text{ mg}}{1000\text{ mL}} = 401.8296\text{ mg/mL}$$

$$\text{Bromide} = \frac{10.0186\text{ g})(1.001\text{ mg/L})}{100.0189\text{ g}} \times \frac{1\text{ L}}{1000\text{ mg}} \times \frac{1000\text{ mg}}{1000\text{ mL}} = 100.2672\text{ mg/mL}$$

$$NO_3 = \frac{(8.0019\text{ g})(1.002\text{ mg/L})}{100.0189\text{ g}} \times \frac{1\text{ L}}{1000\text{ mg}} \times \frac{1000\text{ mg}}{1000\text{ mL}} = 80.1639\text{ mg/mL}$$

$$SO_4 = \frac{(40.0054\text{ g})(1.00\text{ mg/L})}{100.0189\text{ g}} \times \frac{1\text{ L}}{1000\text{ mg}} \times \frac{1000\text{ mg}}{1000\text{ mL}} = 400.3784\text{ mg/mL.}$$

Next, the ideal concentrations for the Middle Concentration Standard and Low Concentration Standard were determined using the following formulas.

Middle Concentration (1:5) = 100 mL/5 = 20 mL

Low Concentration (1:150) = 100 mL/150 = 0.6666 mL

For the Middle Concentration Standard, 20 mL of the prepared High Concentration were extracted using a pipette and deposited in the pre-weighed bottle prepared for that standard. The weight of the deposited solution was recorded. Then, distilled water was added to the same bottle by pipette. The weight was monitored while adding the distilled water in attempt to get as close to 100 mg as possible. The final weight for the Middle Concentration Standard was recorded and the bottle was inverted several times to mix the solution thoroughly. The amount of distilled water that was added was then calculated by subtracting the actual weight of the initial extracted concentration from the actual weight of the prepared Middle Concentration Standard. The same process was followed for to prepare the Low Concentration Standard except 0.6666 mL of the prepared High Concentration was extracted to start the process. A table showing the format for recording the values for the preparation of these standard is shown in Table 7.

Table 7. Middle and Low Concentration Standards, Calculations

Concentration	Ratio to High Concentration	Actual Weight Extracted (mg)	Determined Weight of added Distilled Water	Actual Weight of Prepared Standard Concentration
Middle Concentration	1:05	20.0108	79.9967	100.0075
Low Concentration	1:150	0.6666	99.3524	100.019

Lastly, the true concentrations for the prepared middle and low standards had to be determined so they could be entered into the IC program. This was done using the following formula for both the middle and low concentrations.

$$\text{Concentration Standard} = \frac{\text{Actual Weight Extracted}}{\text{Actual Weight of Prepared Standard}}\ .$$

These values were then multiplied with the anion species determined and recorded for the High Concentration Standard and were recorded in the initial table for the species under the respective column for that concentration [Middle Concentration (02) and Low Concentration (01)]. Example of these calculation are shown below for each concentration.

(a) $\text{Middle Concentration Standard (02)} = \frac{20.0108\ \text{mg}}{100.0075\ \text{mg}} = 0.200093$

Fluoride (mid. Concentration) = 0.200093 x 10.1003 = 2.0210

(b) $\text{Low Concentration Standard} = \frac{0.6666\ \text{mg}}{100.019\ \text{mg}} = 0.006665$

Fluoride (low concentration) = 006665 x 10.1003 = 0.06732

The determined anion species concentrations for the high-, middle-, and low- concentration standards were used to check the precision of the Ion Chromatograph analyses as it progressed.

Next, 5 mL vials of the prepared concentrated standards were prepared along with the water samples to be analyzed. Trays for the Dionex AS40 automated sampler were filled in the following order to be analyzed; first row - High Concentration Standard, Middle Concentration Standard, Low Concentration Standard, DI water, water samples 1 through 6, Middle Concentration Standard, DI water, samples 1 through 6, Middle Concentration Standard, and DI water. The middle standard being placed between each set of 6 samples allowed monitoring of the analyses as the run progressed. The values of the IC run results for the prepared concentration standards had to be within acceptable limits or the run results were abandoned, a new set of standards and water samples were prepared, and the IC analyses started over for that set. The DI water between the sets of sampled water allowed the system to flush and was also used as a system check because the distilled water shouldn't have contained any of the anion species in the analysis and was expected to appear as flat-line on the screen, which indicated that it had no detectable anion concentrations. Each 5 mL sample vial took fifteen minutes to be processed.

Discovering that the water samples had chloride concentrations that exceeded the range of values of the prepared standards complicated the processing of anions. When this occurred, those specific samples were diluted and reprocessed in the IC. First, the amount of dilution had to be determined by the previous IC results. If the resulting chloride values were above the standard deviation but less than 2 standard deviations, the water sample was diluted by a factor of 2 with DI water and processed again. To accomplish this, ~5 g of the water sample was extracted with a pipette and deposited in a vial that had been pre-weighed. The actual weight of the water sample was recorded and then DI water was added to the sample water with a pipette. The weight was monitored during the addition and only enough DI water was added to double the amount of the sample. The final weight was recorded. An example of how this was formatted is shown in the Table 8.

Table 8. Dilution Calculations for Water Samples

Sample ID	Weight of Beaker and Vial (g)	Actual Sample Weight (g)	Total Weight [Sample + DI Water] (g)	Weight of DI Water [Total Weight - Sample Weight] (g)	Dilution [Sample Weight / Total Weight]
Spr-Towsley-2T	36.4396	5.0486	10.0602	5.0116	0.5018
Se-Towsley-3W	36.3853	5.0528	10.1243	5.0715	0.4991

The dilution factor was used to determine expected concentration values using the original IC values. These expected values were then compared to the dilution run values. The resulting values were acceptable if they were within 1 to 2 standard deviations. The expected concentrations were calculated using the following equation.

$$C_O = \frac{1}{\text{Dilution}} \times (\text{IC}_O \text{ result})$$

Example for Spr-Towsley-2T:

$$C_O = \frac{1}{0.5018} \times 1387.3852 = 2764.817$$

This value was then used as the standard of comparison for the resulting dilution run (DR). If the resulting value was between 1 to 2 standard deviations, it was considered acceptable.

ISOTOPIC ANALYSIS

Hydrogen and oxygen isotope analysis was performed at the University of Arizona. Isotope ratios are used for fingerprinting water sources such as precipitation, marine, hot springs, etc. Isotopic evaluation is based on the following equation,

$$\delta \text{ (isotope) in mils (0/00)} = [[R_{(sample)} - R_{(standard)}] / R_{(standard)}] – 1 \times 1{,}000.$$

Where: $R_{(sample)}$ = the ratio of the first and second isotope such as oxygen-18/oxygen-16 ($^{18}O/^{16}O$), and $R_{(standard)}$ = the ratio of the isotopes used in international or other standards. (Motzer, No Date)

In preparation for this analysis, four water samples were collected in the Santa Susana Mountains during rain events in 2012 (Gonzalez, 2012). Two additional samples from rain events were collected in 2014, while also collecting water samples from seeps and springs.

The following method was used to collect the 2014 samples. Three wide-mouthed glass jars were prepared to collect the rain samples by washing each thoroughly and then rinsing them three times with distilled water. These were left to air-dry in the upside-down position then capped with a plastic tight fitting lid that had been prepared the same way.

The day of the rain event, December 12, 2014, the prepared containers were taken along in addition to the other water sampling equipment to Towsley and Wiley canyons. The rain collection containers were placed in locations that were obscure, to prevent people and critters for tampering with them, but had enough open space to prevent dripping from surfaces into the containers, as dripping could have contaminated the rain event samples. Two locations had been chosen in advance. One of the three containers was uncapped and placed on the roof of the field vehicle (last resort). The second container was uncapped and left in a small open space near the trail head to Wiley Canyon. The third location was near the Towsley Canyon Narrows. The collection containers were left unattended for the day as water samples were collected from the seeps and springs of both canyons.

The rain event collection containers were retrieved on the rebound, first from Towsley Canyon then Wiley Canyon. The sample from Wiley Canyon had been tampered with and the container on the vehicle had been stolen. The surviving sample from the Towsley Canyon

Narrows was extracted from the collection container using a sterile syringe. The rainwater sample was then filtered with using a 0.45 micron filter attached to the syringe, and the fluid was plunged into the isotope collection bottle. The rain event sample was labeled with date and location and placed in refrigerated conditions until it could be delivered to the Hydrogeology Laboratory the following day.

The January 10, 2015, sample was collected in the city of Santa Clarita at my cousin's home in Haskell Canyon. The collection containers had been prepared in advanced and left with Dr. James, "just in case it rains." Dr. James had been instructed to leave them out on her patio in three different location which we had agreed upon earlier. She reportedly did as instructed. Two rainwater samples were collected, capped, and placed in her refrigerator overnight. The third collection container was upset by the winds and didn't survive. The next day, they were retrieved. A decision was made to combine the samples into one sample bottle since they were from the same location, and even combined there was only enough rainwater collected to fill one isotope sample bottle. The rainwater was extracted, filtered, and placed into an isotope sample bottle using the same methods previously listed. It was then labeled with date and location and delivered to the Hydrogeology Laboratory in Pomona the following day for cold-storage until processing. Both samples were processed at the University of Arizona. When the results arrived, they were used in addition to the Gonzalez 2012 results to prepare a local meteoric water line (LMWL). The LMWL was established as the fresh meteoric water standard for the project area.

GAS EMISSIONS

Volatile organic carbon (VOC) testing was conducted in the project area with a Tiger Photo Ion Detector (PID). Testing for gases was performed at all springs and oil/tar seeps but only those with recent fluid flow had gas emissions of with detectable concentration of VOC.

Concentration of VOC near the springs and seeps at the time of testing were always below levels that OSHA has correlated with detrimental health effects.

SECTION 3: RESULTS

SECTION 3.1: GEOLOGY

Nearly 1.5 square miles of the Towsley and Wiley canyons area, with a relief of 1200 feet was traversed by foot while mapping. Attention was focused on geologic structural features that can contribute or impede fluid flow, rock types and soil conditions, locations of spring and seeps. A geologic map showing the results of this feat is found in Figure 8 on the following page and on Plate 1. Cross sections were also prepared for each canyon from the map and can be found in Figure 9 on the next page and on Plate 2. A total of 31 spring and oil/tar seeps were mapped in this area of which 13 had water samples collected on near monthly intervals. A complete list of the seeps and springs, sampled and not sampled, can be found on Tables 2 and 3.

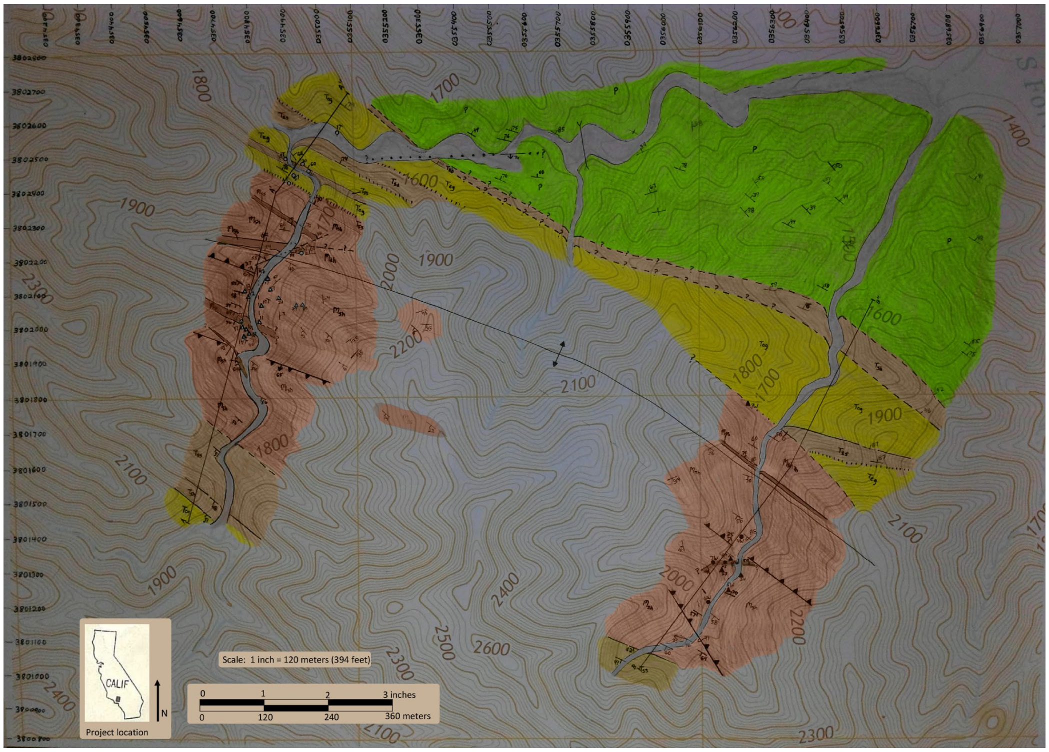


FIGURE 8. GEOLOGIC MAP, TOWSLEY AND WILEY CANYONS (PREVIEW).
Base map: U.S. Geological Survey, 2012, Oat Mountain Quadrangle, Los Angeles County, California, 7.5 Minute Series (Topographic). Legend and explanation of symbols is found in Appendix.

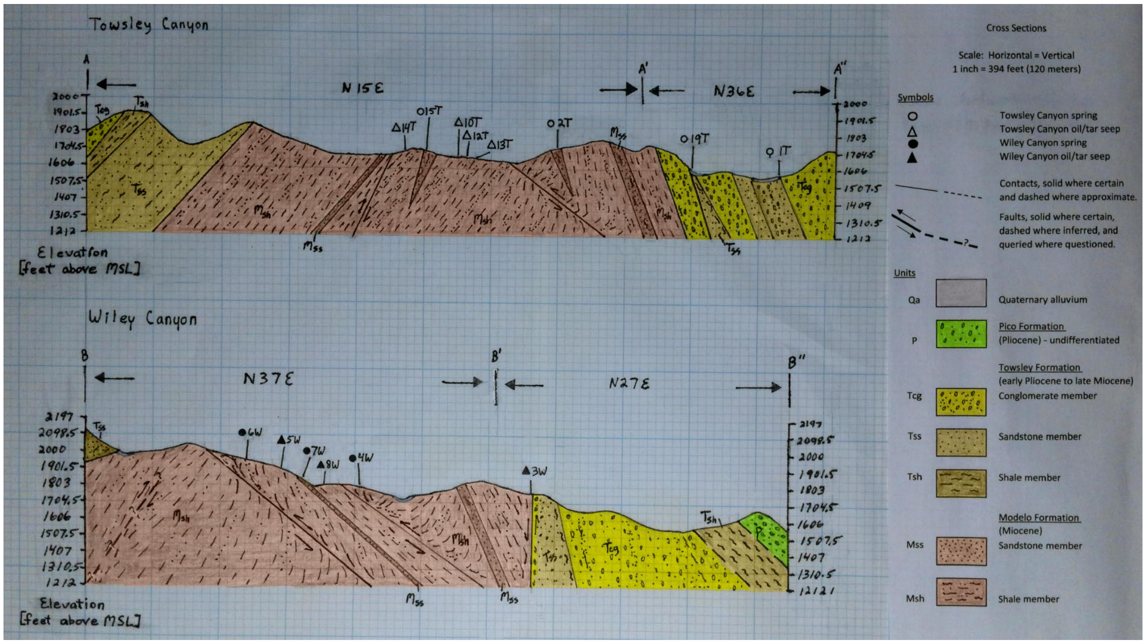


FIGURE 9. CROSS SECTIONS, TOWSLEY AND WILEY CANYONS (PREVIEW).

Mapping confirmed that there are three geologic formations exposed in the area, the younger Pico Formation, which is reported as Pliocene in age, the early Pliocene to late Miocene Towsley Formation, and the Modelo Formation which is Miocene (Winterer and Durham, 1962). A stratigraphic section showing the relationship of these units is found in Figure 10.

In the project area, the Pico Formation was found to consist of a fine-grained pebble conglomerate with beds of siltstone and mudstone interfingered. Fine-grained sandstone beds which graded into the pebble conglomerate were also mapped. Due to the fine-grained characteristics of the pebble conglomerate matrix and the sandstone, it was difficult to distinguish between the two units at times without a petrographic study which was beyond this scope of this project. However, the interfingered siltstone and mudstone beds were easy to identify. These shaley members of the Pico Formation were located in the northeastern part of the project area. The differences in the attitudes found within the Pico Formation appear to be the result of landslides and/or deformation due to faults in the vicinity. The faults will be discussed later in this report. No springs or seep were identified in the vicinity of the Pico Formation, so this lithologic unit is shown to be undifferentiated on the map (P).

The Towsley Formation was best exposed in the narrows of Towsley Canyon located in the northeastern part of the project area. It was found to consist of three identifiable members, a cobble conglomerate (Tcg), a medium-to coarse-grained sandstone (Tss), and shaley siltstones and mudstones (Tsh). The cobble conglomerate member was matrix supported in a medium- to coarse-grained sandstone, had some boulders. The sandstone member graded into the cobble conglomerate in several locations. In some areas this member also had a basal unit of a dark gray siltstone and along the contact rip up clasts and flame structures were identified and

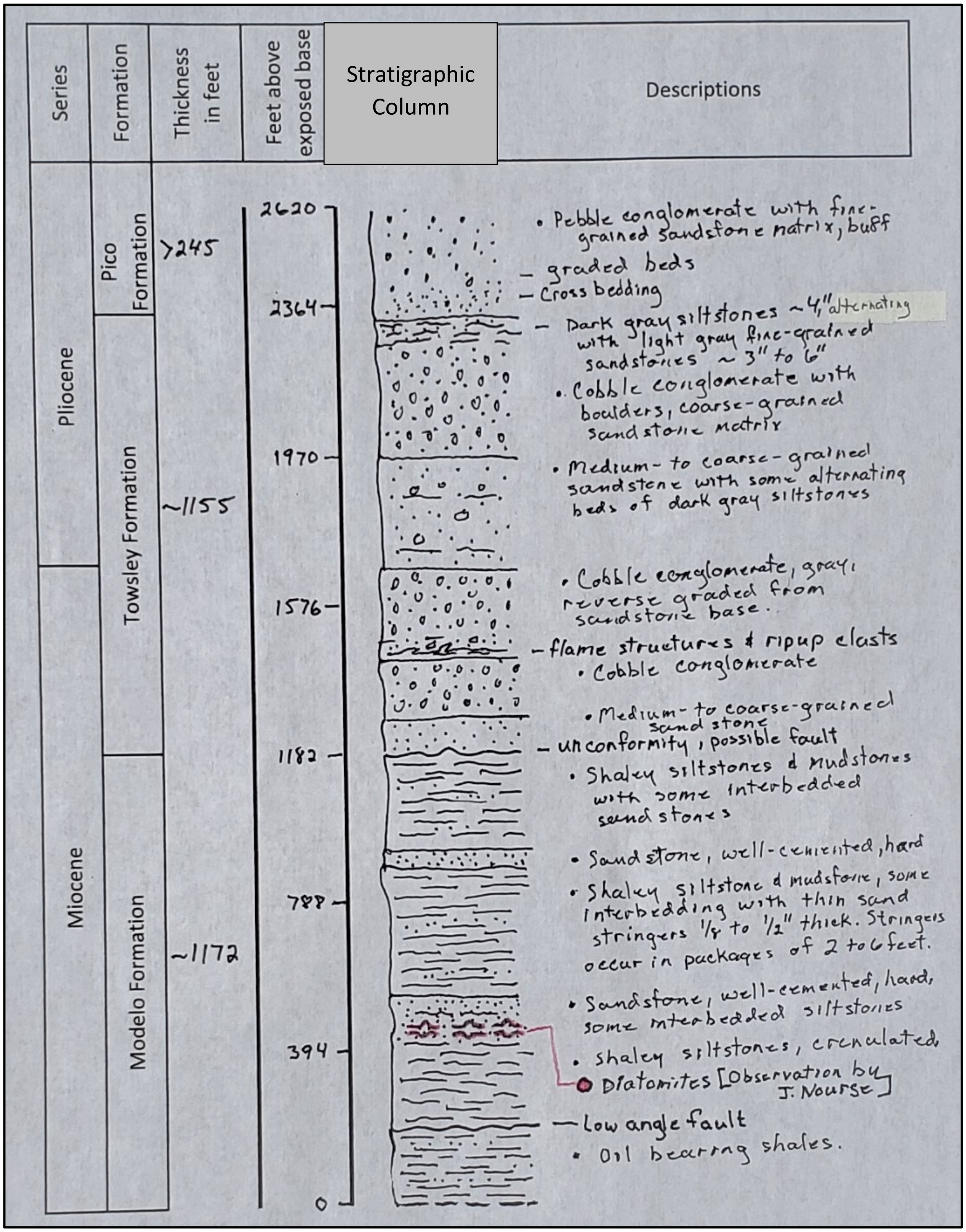


FIGURE 10. STRATIGRAPHIC COLUMN FOR TOWSLEY CANYON.

reverse graded sediments stratigraphically above the contact, or these siltstones were alternately bedded with the sandstone member. Since these gray siltstones were not on a scale that was mappable but are important lithologic unit markers, they are included in the sandstone member of this formation. This was also done because they were always found in conjunction with the Towsley' sandstone member. Stratigraphically lower in the section, the shaley siltstone and mudstone member was found to interbed with the sandstone member of the Towsley Formation. The shaley siltstone and mudstones are brown and mostly soft, able to be broken between the fingers. Just south of the narrows, an outcrop of the Towsley formation exposes a siltstone flame structure roughly 18 inches in height. The shales at this point change in hardness and this point also marks the transition to the Modelo Formation.

In the project area, the Modelo Formation was found to be composed of two members, a thin shaley siltstone and mudstone (Msh) as well as a sandstone member (Mss). The thin shaley siltstones and mudstones were the main member in the project area. These shales were either soft, able to be broken with fingers, or hard, shattering with a hammer blow. They varied in color from orange-brown, dark brown, to varying shades of gray. The shales were often found coated with a soft yellow mineral which Winterer and Durham (1962) reported to possibly be jarosite. In many places the shales also had black staining, reportedly manganese stains (Winterer and Durham, 1962). The shales were often interfingered with sandstone stringers, 'so called' because they were very thin ranging from 1/8 inch to 2 inches in thickness and stained the same color of the shales in which they were interfingered. The stringers were found in packages that ranged in thickness from 2 feet to roughly 6 feet. The packaging of the stringers was markedly different from the sandstone member of the Modelo Formation. The sandstone member was gray in color, well-cemented, and very hard, not broken easily with repeated blows of a hammer. Thin siltstone beds, 1/8 to 3 inches, were interbedded in some of the sandstone beds. Winterer and Durham (1962) indicate that the siltstone beds are deep marine in origin based on foraminiferal fauna distributions found within the rock unit.

Seeps of asphaltic tar and oil along with groundwater were observed flowing along the ground surface in many areas of Towsley and Wiley canyons. The seeps were found in the Modelo formation of both canyons and were always found flowing from the shales. Springs were identified in both canyons as flowing from the Towsley and Modelo formations and were observed to be located within sandstone and conglomerate rock units and where extensive packages of sandstone stringers were present. Many of the spring were located near or along the contacts between lithologic units or along fault planes. The geographic distribution of spring and seep locations varied between the canyons and is depicted on the geologic map and cross sections (Figures 7 and 8, or Plates 1 and 2, respectively).

In Towsley Canyon, more springs were identified in the north end of the canyon than in the southern portion. The northern springs were observed to occur mainly along contacts and/or gradational contacts between the sandstone and conglomerate members of the Towsley formation. Gas emissions were undetectable near these springs, but the rotten egg odor indicated that hydrogen-sulfide gas emissions were present. Two more springs were identified within the Modelo formation, each was located along a contact between the sandstone member and the shale member of the Modelo. These springs are also positioned within steeply dipping strata on opposing limbs of the Pico Anticline. Each spring was identified by the bubbling gas emissions on the rock surface. The oil seeps in Towsley Canyon were located along the axis of the anticline and on the footwall of two thrust faults with opposing dips. The northern thrust fault is located on the north anticlinal limb and dips toward the north. The south thrust fault, is contrary, located on the south anticlinal limb and dipping southward. Both faults strike in the northwest direction and will be discussed later in this section.

In Wiley Canyon, the locations of springs and seeps alternate forming a seep, spring, seep, spring pattern. From north to south along the canyon, seep 3W was first to be identified along the trail by following the flow of oil/tar. The seep was located along the trace of a near vertical fault at the contact between the conglomerate member of the Towsley formation and the shale member of the Modelo. Gas emissions were prominent, profusely bubbling at the surface of the pool of oil, each time the seep was visited and/or fluids were collected. Spring 4W was located next flowing from a package of sandstone stringers within the shale member of the Modelo. This spring is also located on the hanging wall of a thrust fault, in proximity to the fault plane which will be discussed in detail later in this section. The next seep (8W) and spring (7W) were identified by the asphaltic nature of the oil in the vicinity. Both had intermittent fluid flow in which waters were not always available. The following seep (5W) consistently emitted gases like a boiling pot. The last spring identified in Wiley Canyon (6W) was located along the incised stream channel. Water was slowly flowing from an extensive package of sandstone stringers in the Modelo. This spring is also located along the axis of the Pico Anticline just north of the southern-most thrust fault, along which the rock units are overturned.

Several faults were identified within the project area, none of which have been shown on local or regional published maps in the initial research of this project. Two reverse faults were exposed in the incised valley walls of Towsley Canyon within the Modelo Formation, and others were mapped by Nourse during our GSC 491L investigation. The two reverse faults trend nearly N70W but have opposing dip directions as mentioned earlier in this section. The north fault is a thrust fault dipping 37NE and will be called ‘thrust A’ is the discussion part of this report. The southern reverse fault dips 65SW. The footwall between the two faults is where the oil bearing shales were mapped. The north thrust fault also appears to project through Wiley Canyon, where it strikes N55W and dips 35NE. The southern reverse fault was not exposed in Wiley Canyon, so it does not show on the geologic map. However, its presence at depth is inferred by the changes in the rock attitudes on the surface, so it was placed on the Wiley Canyon cross section as a blind reverse fault with its apparent dip and location interpreted from the attitudes measured from the surrounding rock exposures.

It is important to note here that the oil bearing shales in Wiley Canyon are not located just between these two reverse faults, like they are in Towsley Canyon. The oil bearing shales of the Modelo Formation are found at the contact of the Modelo and Towsley formations near the mapped location of seep 3W. The beds of the Towsley formation and the Modelo shales are nearly vertical along this contact, so it was mapped as an inferred fault. The cross sections of the inferred fault indicate that the Modelo shales may also have been overturned in this area, by normal fault motion, with the southern block on the downthrown side in relation to the Towsley formation along the inferred fault plane.

Another thrust fault, thrust B, was found in Wiley Canyon located south of thrust A. The strike of this thrust fault is N33W and has a dip of 41NE. The beds of Modelo shale are overturned in the hanging wall and dip northeast but the beds of shale in the footwall dip 64SW. The footwall's shales are contorted in the vicinity and slickensides were found that indicated motion between the shale beds in the direction of N75W making this a right-lateral, reverse fault with oblique motion.

Another vertical fault was found exposed in the Pico Formation northern section of Towsley Canyon that trends east to west, coinciding with the valley and ephemeral stream's trend, and dipping 76S. Slickensides in gouge found in a two-inch fracture of an outcrop towering ten-feet above the stream provided the evidence for this fault. However, relative motion can only be inferred by the geology surrounding this area as there were no marker beds to provide a sense of offset. The inferred motion is left-lateral strike-slip but oblique motion cannot be ruled out.

SECTION 3.2: HYDROGEOLOGY

Anion concentrations for Towsley Canyon Springs

Anion analyses for Towsley Canyon spring 1T revealed the following results for each anion species. Fluoride concentrations ranged from 0.55 mg/L to 1.97 mg/L with an average of 1.1256 mg/L and a standard deviation of +/- 0.399. Chloride concentrations ranged from 15.30 mg/L to 1427.51 mg/L with an average of 310.7 mg/L and a standard deviation of +/- 434.84. The highest chloride concentration was detected in November 2014. Nitrate concentrations ranged from non-detectable to 4.27 mg/L with an average of 1.065 mg/L and a standard deviation of +/- 1.55. Bromide concentrations ranged from 0.11 mg/L to 12.46 mg/L with an average of 4.20 mg/L and a standard deviation of +/- 4.1. Sulfate concentrations ranged from non-detectable to 2404.78 mg/L with an average of 886.35 mg/L and a standard deviation of +/- 944.23.

Anion analyses for Towsley Canyon spring 2T revealed the following results for each anion species. Fluoride concentrations ranged from 0.04 mg/L to 0.20 mg/L with an average of 0.13 mg/L and a standard deviation of +/- 0.04. Chloride concentration ranged from 351.43 mg/L to 3382.63 mg/L with an average of 1893.92 mg/L and a standard deviation of +/- 1218. The highest chloride concentration was detected in June 2014. Nitrate concentrations ranged from 1.55 mg/L to 26.51 mg/L. Bromide concentrations ranged from non-detectable to 23.11 mg/L with an average of 3.67 mg/L and a standard deviation of +/- 8.21. The highest bromide concentration was detected in June 2014. Sulfate concentrations ranged from non-detectable to 0.35 mg/L with an average of 0.15 mg/L and a standard deviation of +/- 0.15.

Anion analyses for Towsley Canyon spring 15T revealed the following results for each anion species. Fluoride concentrations ranged from 0.74 mg/L to 0.99 mg/L with and average of 0.88 mg/L and a standard deviation of +/-0.08. Chloride concentration ranged from 714.48 mg/L to 991.05 mg/L with an average of 858.82 mg/L and a standard deviation of +/- 98.39. The highest chloride concentration was detected in August 2014. Nitrate concentrations ranged from 0.61 mg/L to 8.42 mg/L with an average of 3.40 mg/L and a standard deviation of +/- 2.8. The highest nitrate concentration was detected in January 2015. Bromide concentration ranged from 7.21 mg/L to 10.25 mg/L with an average of 8.71 mg/L and a standard deviation of 1.1. The highest bromide concentration was detected in August 2014. Sulfate concentration ranging from 186.08 mg/L to 426.13 mg/L with an average of 254.44 mg/L and a standard deviation of +/- 87.78.

Anion analyses for Towsley Canyon spring 19T revealed the following results for each anion species. Fluoride concentrations ranged from 0.48 mg/L to 1.98 mg/L with an average of 1.24 mg/L and a standard deviation of +/- 0.44. Chloride concentrations ranged from 8.41 mg/L to 967.64 mg/L with an average of 262.66 mg/L and a standard deviation of +/- 344. The highest chloride concentration was detected in November 2014. Nitrate concentration ranged from non-detectable to 4.35 mg/L with an average of 0.804 mg/L and a standard deviation of +/- 1.59. The highest nitrate concentration was detected in December 2014. Bromide concentrations ranged from non-detectable to 9.89 mg/L with an average of 2.58 mg/L and a standard deviation of +/- 3.53. The highest bromide concentration was detected in November 2014. Sulfate concentrations ranged from 296.58 mg/L to 3343.92 mg/L with an average of 1537.23 mg/L and a standard deviation of +/- 1134.4. The highest sulfate concentration was detected in November 2014. A full list of anion results for Towsley Canyon springs can be found in Appendices 1 and 9.

Anion Concentrations for Towsley Canyon Seeps

Anion analyses for Towsley Canyon seep 10T revealed the following results for each anion species. Fluoride concentrations ranged from 0.21 mg/L to 0.35 mg/L with and average concentration of 0.27 mg/L and a standard deviation of +/- 0.05. Chloride concentration ranged from 8008.21 mg/L to 10094.02 mg/L with an average concentration of 8502 mg/L and a standard deviation of +/- 653. The highest chloride concentration was detected in June 2014. Nitrate concentrations ranged from non-detectable to 81.34 mg/L with and average concentration of 55.98 mg/L and a standard deviation of +/- 24.6. The highest nitrate concentration was detected in January 2015. Bromide concentrations ranged from 2.48 mg/L to 4.56 mg/L with an average concentration of 3.51 mg/L and a standard deviation of +/- 0.71. Sulfate concentrations ranged from non-detectable to 1.64 mg/L with an average concentration of 0.582 mg/L and a standard deviation of +/- 0.44.

Anion analyses for Towsley Canyon seep 13T revealed the following results for each anion species. Fluoride concentrations ranged from 0.06 mg/L to 0.72 mg/L with and average concentration of 0.42 mg/L and a standard deviation of +/- 0.2. Chloride concentration ranged from 37.95 mg/L to 2059.05 mg/L with an average concentration of 1119.9 mg/L and a standard deviation of +/- 756.9. The highest chloride concentration was detected in September 2014 and the lowest was detected in March 2014. Nitrate concentrations ranged from non-detectable to 15.18 mg/L with and average concentration of 5.545 mg/L and a standard deviation of +/- 5.21. The highest nitrate concentration was detected in June 2014. Bromide concentrations ranged from non-detectable to 17.19 mg/L with an average concentration of 5.41 mg/L and a standard deviation of +/- 5.99. Sulfate concentrations ranged from 0.14 mg/L to 3.22 mg/L with an average concentration of 1.75 mg/L and a standard deviation of 1.12.

Only two samples were extracted from Towsley Canyon seep 14T. These were sampled in March 2014 and April 2014. Anion analyses of these samples revealed the following results for each anion species. Fluoride concentration ranged from 0.59 mg/L to 0.91 mg/L with an average of 0.75 mg/L and a standard deviation of =/- 0.16. Chloride concentration ranged from 168.92 mg/L to 1417.73 mg/L with an average concentration of 793.33 mg/L and a standard deviation of +/- 624.4. Nitrate concentrations ranged from non-detectable to 1.28 mg/L with an average concentration of 0.64 mg/L and a standard deviation of +/- 0.69. Bromide concentrations ranged from 0.26 mg/L and 19.85 mg/L with and average concentration of 10.06 mg/L and a standard deviation of +/- 9.8. Sulfate concentrations ranged from 0.27 mg/L to 2.42 mg/L with and average concentration of 1.35 mg/L and a standard deviation of +/- 1.1. A full list of the anion results can be found in Appendices 2 and 9.

Anion concentrations for Wiley Canyon Springs

Anion analyses for Wiley Canyon spring 4W revealed the following results for each anion species. Fluoride concentration ranged from 0.09 mg/L to 0.41 mg/L with and average concentration of 0.25 mg/L and a standard deviation of +/- 0.1. Chloride concentration ranged from 712.66 mg/L to 5272.17 mg/L with an average concentration of 4480.4 mg/L and a standard deviation of +/- 1270.8. The highest chloride concentration was detected in June 2014. Nitrate concentration ranged from 3.61 mg/L to 32.06 mg/L with an average concentration of 20.9 mg/L and a standard deviation of +/- 9.1. Bromide concentrations ranged from non-detectable to 35.39 mg/L with and average concentration of 10.93 mg/L and a standard deviation of +/- 15.2. The highest bromide concentration was detected in August 2014. Sulfate concentrations ranged from 9.23 mg/L to 46.78 mg/L with an average sulfate concentration of 34.41 mg/L and a standard deviation of +/- 11.2. The highest sulfate concentrations were detected in June 2014 and December 2014.

Anion analyses for Wiley Canyon spring 6W revealed the following results for each anion species. Fluoride concentrations ranged from 0.76 mg/L to 2.70 mg/L with an average concentration of 1.53 mg/L and a standard deviation of +/- 0.56. Chloride concentrations ranged from 7.05 mg/L to 147.39 mg/L with an average concentration of 82.11 mg/L and a standard deviation of +/- 49.7. The highest chloride concentration was detected in September 2014. Nitrate concentration ranged from non-detectable to 3.19 mg/L with and average concentration of 1.24 mg/L and a standard deviation of +/- 1.083. Bromide concentrations ranged from non-detectable to 2.87 mg/L with an average concentration of 1.61 mg/L and a standard deviation of +/- 0.79. Sulfate concentration ranged from non-detectable to 2562.3 mg/L with an average concentration of 704.6 mg/L and a standard deviation of +/- 1031.

Anion analyses for Wiley Canyon spring 7W revealed the following results for each anion species. Fluoride concentration ranged from 1.04 mg/L to 3.82 mg/L. with an average concentration of 2.56 mg/L and a standard deviation of +/- 0.99. Chloride concentrations ranged from 8.75 mg/L to 309.76 mg/L with and average concentration of 133.18 mg/L and a standard deviation of +/- 97.8. Nitrate concentrations ranged from non-detectable to 12.94 mg/L with and average concentration of 4.12 mg/L and a standard deviation of +/- 4.57. Bromide concentration ranged from non-detectable to 7.09 mg/L with an average concentration of 1.74 mg/L and a standard deviation of +/- 2.13. Finally, sulfate concentration ranged from 0.65 mg/L to 942.60 mg/L with an average concentration of 200.1 mg/L and a standard deviation of +/- 299. A full list of anion result for Wiley Canyon springs can be found in Appendices 3 and 9.

<u>Anion concentrations for Wiley Canyon Seeps</u>

Anion analyses for Wiley Canyon seep 3W revealed the following results for each anion species. Fluoride concentration ranged from 0.14 mg/L to 0.32 mg/L with an average concentration of 0.25 mg/L and a standard deviation of +/- 0.05. Chloride concentration ranged from 248.35 mg/L to 2561.5 mg/L with an average concentration of 1789.6 mg/L and a standard deviation of +/- 745.94. The highest chloride concentration was detected in June 2014. Nitrate concentrations ranged from 2.32 mg/L to 42.21 mg/L with and average concentration of 17.62 mg/L and a standard deviation of +/- 16. The highest nitrate concentration was detected in June 2014. Bromide concentrations ranged from non-detectable to 35 mg/L with an average concentration of 12.3 mg/L and a standard deviation of +/- 16. Sulfate concentrations ranged from 0.03 mg/mL to 15.71 mg/L with an average concentration of 3.14 mg/L and a standard deviation of +/- 4.2.

Anion analyses for Wiley Canyon seep 5W revealed the following results for each anion species. Fluoride concentration ranged from 0.35 mg/L to 0.97 mg/L with and average concentration of 0.71 mg/L and a standard deviation of +/- 0.21. Chloride concentration ranged from 15.23 mg/L to 139.19 mg/L with and average concentration of 98.57 mg/L and a standard deviation of +/- 48.38. Nitrate concentration ranged from 0.21 mg/L to 5.72 mg/L with and average concentration of 2.54 mg/L and a standard deviation of +/- 1.8. The highest nitrate concentration was detected in June 2014. Bromide concentration ranged from 1.04 mg/L to 1.33 mg/L with and average concentration of 1.18 mg/L and a standard deviation of +/- 0.11. Sulfate concentrations ranged from 0.95 mg/L to 30.14 mg/L with an average concentration of 17.66 mg/L and a standard deviation of +/- 10.6.

Anion analyses for Wiley Canyon seep 8W revealed the following results for each anion species. Fluoride concentration ranged from 1.07 mg/L to 3.75 mg/L with and average concentration of 2.23 mg/L and a standard deviation of +/- 0.9. Chloride concentrations ranged from 12.37 mg/L to 543.11 mg/L with an average concentration of 180.98 mg/L and a standard deviation of +/-194.5. The highest chloride concentration detected was in September 2014.

Nitrate concentrations ranged from 0.57 mg/L to 14.31 mg/L with and average concentration of 471 mg/L and a standard deviation of +/- 4.9. The highest nitrate concentration was detected in September 2014. Bromide concentrations ranged from non-detectable to 2.22 mg/L with and average concentration of 1.53 mg/L and a standard deviation of +/- 0.83. Sampling for this seep was unattainable from June 2014 to August 2014. A full list of anion results for Wiley Canyon seeps can be found in Appendices 4 and 9.

Total Alkalinity and pH for Towsley Canyon Springs

Total alkalinity values for Towsley Canyon spring 1T ranged from 241.64 to a high of 1512.66 with an average total alkalinity of 950.69 +/- 459.5 and pH was consistent in the field, ranging from 8.13 to 8.26 with an average pH 8.2 +/- 0.04. For Towsley Canyon spring 2T, total alkalinity values were consistent, ranging from 2603.15 to 2771.06 with an average total alkalinity of 2705.1 +/- 40.2. PH values for spring 2T ranged from 7.3 to 7.9 *in situ* with and average pH of 7.5 +/- 0.2. For Towsley Canyon spring 15T, the total alkalinity values ranged from 1651.6 to 2262.9 with an average total alkalinity of 1961.6 +/- 202.3. Spring 2T's pH values ranged from 7.3 to 7.9 with an average pH of 7.5 +/- 0.2. Spring 19T in Towsley Canyon had a total alkalinity ranging from 445.12 to 1352.19 with an average total alkalinity of 704.5 +/- 315. Spring 19T had a pH ranging from 7.7 to 8.49 *in situ* with and average pH of 8.1 +/- 0.2. A complete list of these results along with temperature, electroconductivity, and measured dissolved oxygen levels can be found in Appendices 5 and 9.

Total Alkalinity and pH for Towsley Canyon Seeps

Total alkalinity values for Towsley Canyon seep 10T were consistent, ranging from 4166.23 to 4335.1 with an average total alkalinity of 4274.2 +/- 48.9 and *in situ* pH ranged from 7.5 to 8.1 with an average of 7.8 +/- 0.2. Towsley Canyon seep 13T had total alkalinity values ranging from 546.83 to 2909.13 with the highest ranges occurring from August until October.

The average total alkalinity for seep 10T was 1963.9 +/- 725.5, and pH this seep ranged from 7.4 to 8.3 with an average pH of 7.9 +/-0.3. Only two water samples were extracted for Towsley Canyon seep 14T, one in March and then in April. The total alkalinity ranged from 2447.96 and 2434.79 with an average total alkalinity of 2441.4 +/- 6.59. The pH was 7.92 and 7.94, respectively for those months with an average pH of 7.93 +/- 0.01. A complete list of these results along with temperature, electroconductivity, and measured dissolved oxygen levels can be found in Appendix 6 and 9.

Total Alkalinity and pH for Wiley Canyon Springs

Total alkalinity values for Wiley Canyon spring 4W ranged from 4014.58 to 4337.08 with an average total alkalinity of 4166.66 +/- 91.6. The pH for spring 4W ranged from 7.2 to 8.6 with an average pH of 7.8 +/- 0.5. Wiley Canyon spring 6W ranged from 333.50 to 2628.96 with an average total alkalinity of 1460.8 +/- 761.5 and had a pH ranging from 7.7 to 8.4 with an average pH of 8.1 +/- 0.3. Spring 7W in Wiley Canyon had total alkalinity values ranging from 914.74 to 3557.51 with an average total alkalinity of 2094.8 +/- 881.6 and this spring had pH ranging from 7.5 to 8.5 with an average pH of 8.0 +/- 0.4. A complete list of these results along with temperature, electroconductivity, and measured dissolved oxygen levels can be found in Appendixes 7 and 9.

Total Alkalinity and pH for Wiley Canyon Seeps

Total alkalinity values for Wiley Canyon seep 3W ranged from 4097.46 to 4797.98 with an average total alkalinity of 4570.2 +/- 206.8. The pH for seep 3W ranged from 7.7 to 8.2 with an average pH of 8.0 +/- 0.2. For Wiley Canyon seep 5W total alkalinity values ranged from 1840.33 to 1973.59 with an average total alkalinity of 18888.6 +/- 44.0 and pH ranged from 7.5 to 8.3 with an average pH of 7.9 +/-0.3. Seep 8W in Wiley Canyon had total alkalinity ranging from 792.38 to 3265.37 with an average total alkalinity of 1844.38 +/- 815.7. The pH ranged from 8.0 to 8.7 with an average pH of 8.2 +/- 0.2. A complete list of these results along with temperature, electroconductivity, and measured dissolved oxygen levels can be found in Appendixes 8 and 9.

Isotopic Analysis

The result of the hydrogen and oxygen isotope analysis were plotted in comparison to the local meteoric water line. For the springs $\delta^{18}O$ values ranged from -5.4 to -6.9 (0/00) with an average of -6.5 (0/00) and a standard deviation of +/- 3.9. The $\delta^{2}H$ values ranged from -27 to -41 (0/00) with an average of -24 (0/00) and a standard deviation of +/- 6.6.

For the seeps $\delta^{18}O$ values ranged from -3.2 to -6.0 (0/00) with an average of -5 (0/00) and a standard deviation of +/- 1.1. The $\delta^{2}H$ values ranged from -13 to -32 (0/00) with an average of (-24 (0/00) and a standard deviation of +/- 7.7.

SECTION 4: DISCUSSION

SECTION 4.1: GEOLOGY

Subsurface path for fluids

The canyons are nestled between a series of major active faults, mainly the Santa Susana thrust to the south and the San Andreas fault to the north. This tectonic setting has created compressional stresses that resulted in the formation of the Santa Susana Mountains and in turn the formation of a major anticline and several smaller scale folds along which the project area is located. This anticlinorial setting can act as a trap for oil and hypersaline water/brines that are associated with the formation of oil at depth. The Modelo formation is exposed along the axis of this anticline which accounts for the steeply dipping strata, differences in dip direction from north to south on opposite sides of the axis, and it is likely that there would be joints or fractures sub-parallel to the axial planes of the folds. The fractured and friable conditions of the Modelo shales, faulted sandstones, and the presence of faults in the canyons can also be attributed to these tectonic stresses. It is these geologic conditions that provide paths for deep fluids to migrate toward the surface (Gurevich et al., 1993).

Gas emissions observed with the fluid flow, in the Modelo formation, provides evidence for an important driving force for the oil and the deeper hypersaline waters. Gurevich et al. (1993) reported that gases formed from the organic processes associated with oil formation can provide enough pressure to overcome the capillary pressure at the upper water-gas interface to initiate vertical migration of fluids from great depths (Gurevich et al., 1993). The constant gas emissions from seeps and the spring within the Modelo formation are indicators that this condition exist in this location.

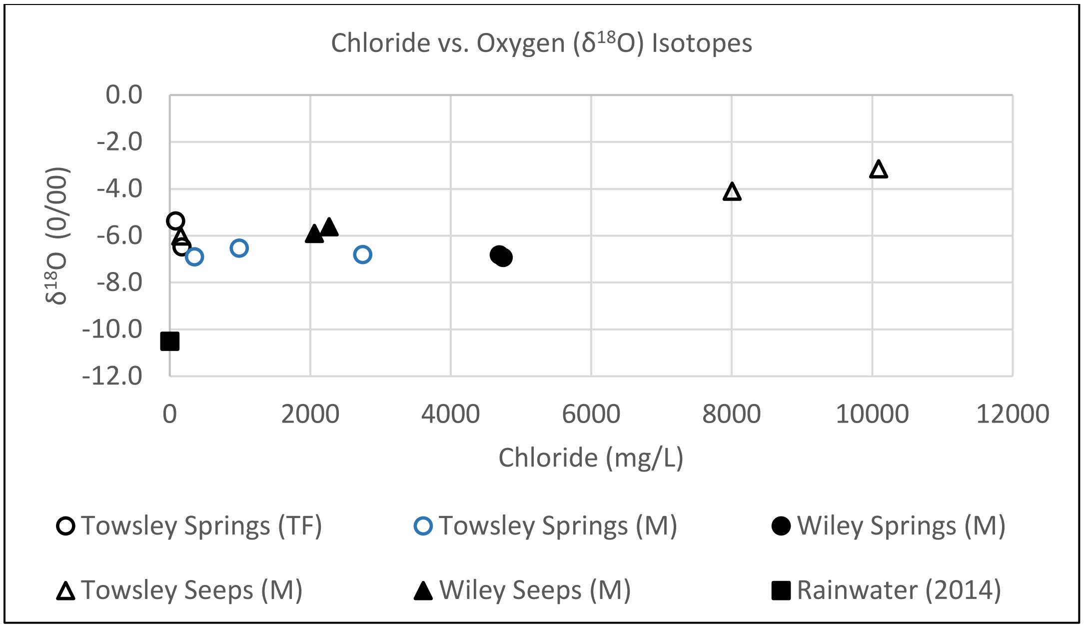
The differences in geologic materials where the springs and seeps flow appear to be controlled by a difference in the tortuosity in the materials. All the springs were associated with sandy conditions whereas the seeps occur within shales that have cleavage planes associated with faults and/or fractures. It is probable that the sands have greater intergranular tortuosity than the fractured shales which may prevent the longer, more complex, oil molecules from flowing through the sandy materials. The shales, however, would provide a less sinuous path for the fluids, with fractures and cleavage planes acting as conduits for oil and water alike.

SECTION 4.2: HYDROGEOLOGY

Sources of water

The oil seeps are only found within the Modelo formation which formed in a deep marine offshore environment (Winterer and Durham, 1962). Winterer and Durham (1962) also concluded that the packages of coarser materials interbedded in the Modelo were due to submarine landslides and turbidity currents. These marine depositional materials may have also trapped paleo marine waters which is still being detected as salinity in the water samples. The paleo marine water would have migrated from depth with the oil and gas as saline brine of marine origin, possibly mixing with a shallow water system that is relatively fresh water. The high chloride concentrations (up to 10,094 mg/L +/- 653.17) coupled with high bromide concentrations (up to 35.39 mg/L +/- 15.21) are good indicators that brines may be flowing into the shallow hydrologic system and mixing with freshwater to produce the brackish waters that are found in the canyons (Carpenter 1978; Kharaka and Hanor, 2005; Wang and Jiao, 2012).

To verify this, the relationship between stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) and chloride (Cl^{-}) concentrations from selected springs and seeps were plotted along with a rainwater sample that was collected from the project area (Figure 11). The rainwater sample represents the end member of the meteoric freshwater system with extremely low detectable chloride



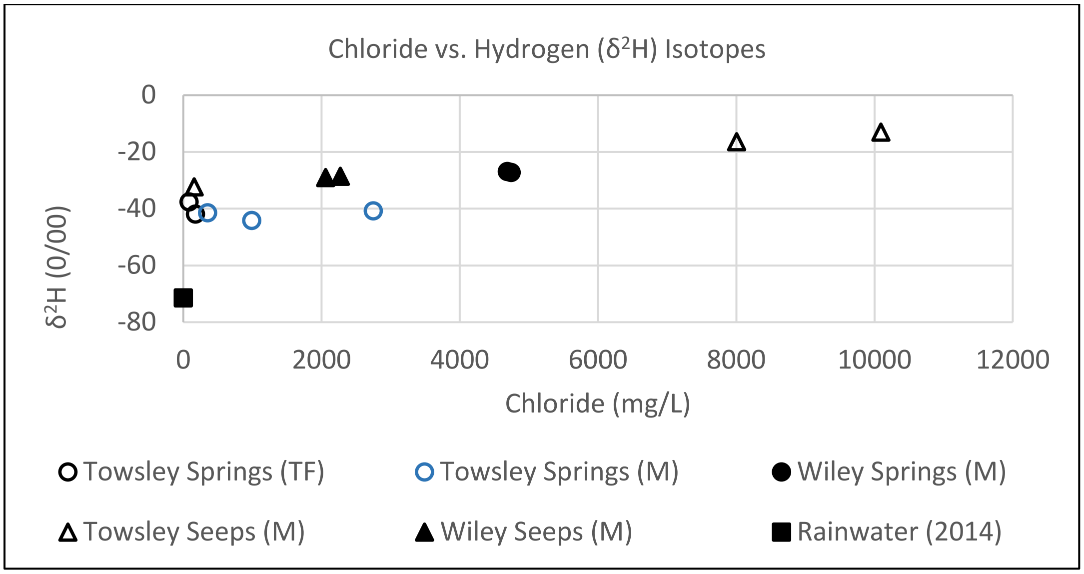


FIGURE 11: CHLORIDE VS. OXYGEN AND HYDROGEN ISOTOPES.
Rainwater is plotted as the meteoric end member. The enrichment of δ^{18}O and δ^{2}H and the elevated chloride concentrations may indicate a paleo marine water source. TF = Towsley Formation and M = Modelo Formation.

concentration and more negative δ^{18}O and δ^{2}H than those samples that had high chloride concentrations . Wang and Jiao (2012) report that a marine water source would be indicated by enrichment (less negative) of both δ^{18}O and δ^{2}H and high chloride concentrations. Both graphs in Figure 11 indicate two trends and possibly a third. Those samples that had low chloride values may represent the meteoric freshwater. Those waters that had high chloride concentrations and less negative oxygen-18 and hydrogen-2 could be interpreted as coming from deeper source water. The samples also have trends that appear to project outward from the rainwater sample. This suggests that these waters are influenced to some degree by mixing with meteoric freshwater sources. The trend that plots between the two end members in both graphs could possibly be a mixture of the two extremes.

Deuterium and oxygen isotopic analysis of selected water samples from Towsley and Wiley canyons can be found in Figure 12. Water samples that were collected from precipitation events in the Towsley Canyon area were plotted on the graph to produce a Local Meteoric Water Line (LMWL) There good correlation between the rainwater samples collected by Gonzalez in 2012 and those collected in 2014 for this project. The LMWL represents the average δ^{18}O and δ^{2}H isotopic signature (Motzer, no date; Kendal and Coplen, 2001) for the Towsley Canyon area. Two of the water samples collected from springs plot on the LMWL which indicates that those are likely to be from the meteoric fresh water source. Those samples that plot above the LMWL could be interpreted in two ways. First, that there is an organic influence in the water system which is confirmed by the presence of oil in the canyons and by the samples being extracted from an oil seep. Second, that these are possibly older waters which fell at a time when the area had a different LMWL trend. Using the deuterium and oxygen isotopic analysis alone without correlation from other sources could be misleading. However, by using this type of analysis along with other methods of geochemical assessments, like plotting chloride values with the isotopes (Figure 11), a better picture of the diagenesis of the water sources can be established. In addition to the isotope analyses, other geochemical assessments also support two different source waters in this hydrologic system.

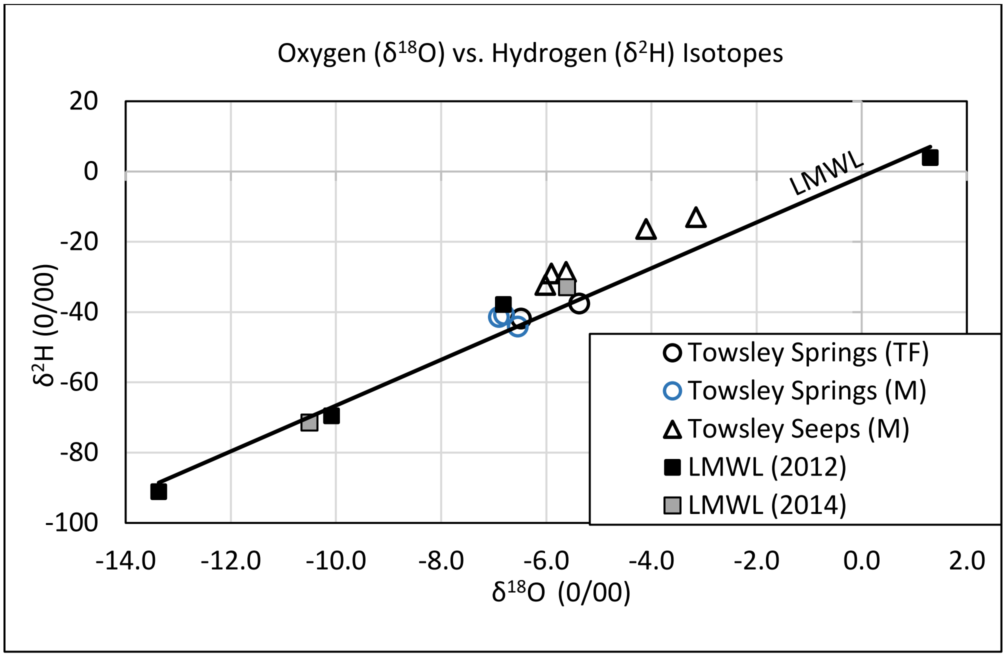
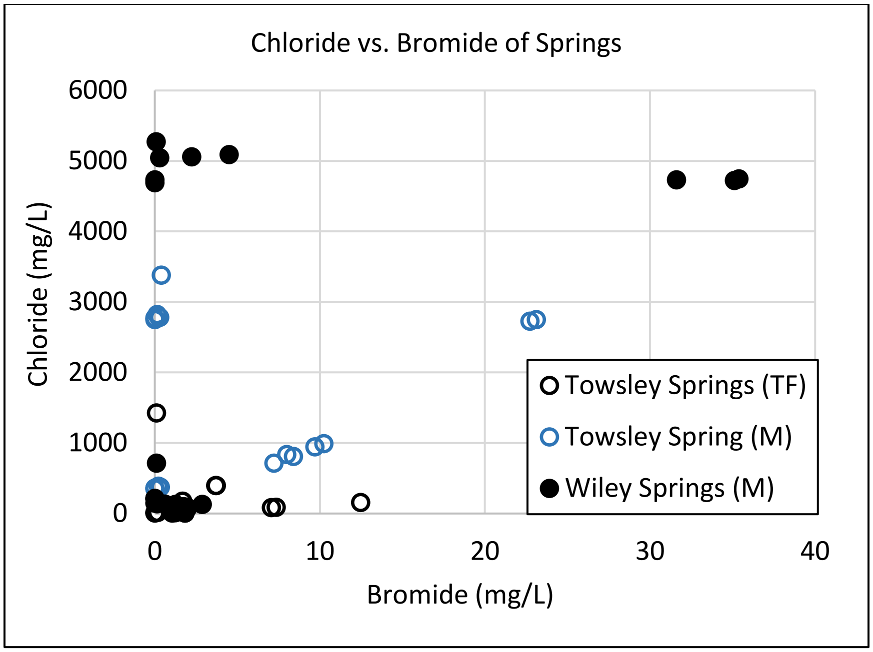


FIGURE 12. OXYGEN VS. HYDROGEN ISOTOPES.
Oxygen and hydrogen isotopes of water samples collected from precipitation events in the Santa Susana Mountains correlate well with some water samples collected from Towsley Canyon spring and oil/tar seeps in 2012 (Gonzalez) and in 2014 (Kunath-Leatham). The water samples plotting above the LMWL may indicate an organic influence within the hydrologic system (after Gonzalez, 2012). TF = Towsley Formation and M = Modelo Formation.

Anions of chloride and bromide can also be used as indicators of water type based on their conservative nature. Both chloride and bromide are halogens with similar radii, therefore they react chemically in very similar ways as electron receptors (Motzer, no date; Carpenter, 1978). Using only chloride in an analysis for waters having high concentrations of chloride, the only thing that can be said about the water source is that it wasn't meteoric freshwater. But using chloride along with bromide, the diagenesis of the waters may be interpreted (Kharaka and Hanor, 2005). This is because bromide is found in large quantities in seawater, typically ~65 mg/L, but it is found in negligible amounts in freshwater, typically less than 0.5 mg/L (Carpenter, 1978). This makes the pairing useful in analyses for marine and freshwater (Carpenter, 1978; Kharaka and Hanor, 2005). Kharaka and Hanor (2005) explain that the origins of saline waters in sedimentary basins can be determined by understanding the origins of the dissolved chloride in formation waters.

When marine water is subjected to evaporative conditions, both chloride and bromide increase in concentration, with respect to water, but the Br/Cl ratio remains constant (Kharaka and Hanor, 2005). As the water reaches halite saturation levels, Cl is coupled with Na and only a small fraction of Br is captured in the halite lattice [Na (Cl, Br)] as the mineral precipitates from the solution (Kharaka and Hanor, 2005) resulting in an increasing Br/Cl ratio with progressive evaporation. As saturation for halite decreases, K and Mg salts can form by capturing Br and the Br/Cl curve flattens. These processes along with low Br/Cl ratios found in meteoric water, allow their usage for ascertaining formation waters (Carpenter, 1978; Kharaka and Hanor, 2005).

Figure 13, on the next page, shows chloride versus bromide concentrations of springs and seeps in Towsley and Wiley canyons. The spring results were plotted separately from the seeps but both plots appear to indicate trimodal distribution patterns similar to the isotopic analyses. The water samples that show low bromide and high chloride values possibly indicate dissolution of halite from meteoric water (Kharaka and Hanor, 2005). The mineral gypsum was observed in several locations within the canyons while geologic mapping and forms as part of an evaporation sequence that includes halite, so it is plausible for halite to be found within the marine sedimentary rocks in the canyons or at depth. The samples that plot with high bromide to chloride values suggest that the water formed from the subaerial evaporation of deeper hypersaline water or brine, the high bromine is also indicative of marine sources (Carpenter, 1978). Those water samples that plot near the graph’s origin with low bromide and low chloride are most likely meteoric freshwater from the shallow hydrologic system (Kharaka and Hanor, 2005). There are also a few markers on the graphs that appear to plot slightly horizontal from the clusters. These may indicate mixing water sources.



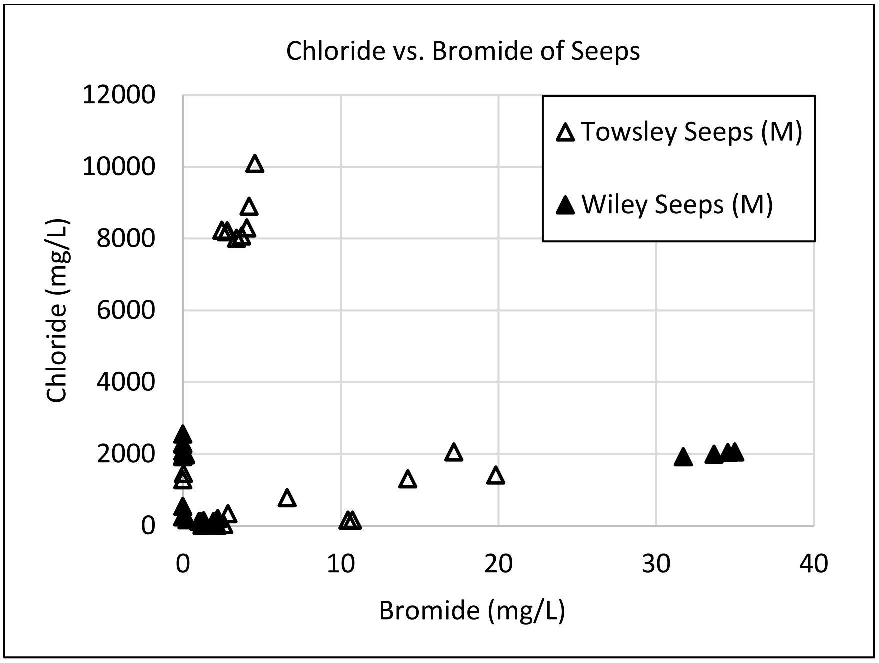


Figure 13. Chloride vs. Bromide of Springs and Seeps

The trimodal distribution pattern of the concentration values may indicate two water types (meteoric fresh water and hypersaline waters) are contributing to the hydrologic system and migrating to the surface. The meteoric fresh waters are indicated by the low bromide and low chloride. Trends with high bromide and high chloride are typically interpreted as marine water source. The third trend can be interpreted as the mixing of water sources. TF = Towsley Formation and M = Modelo Formation.

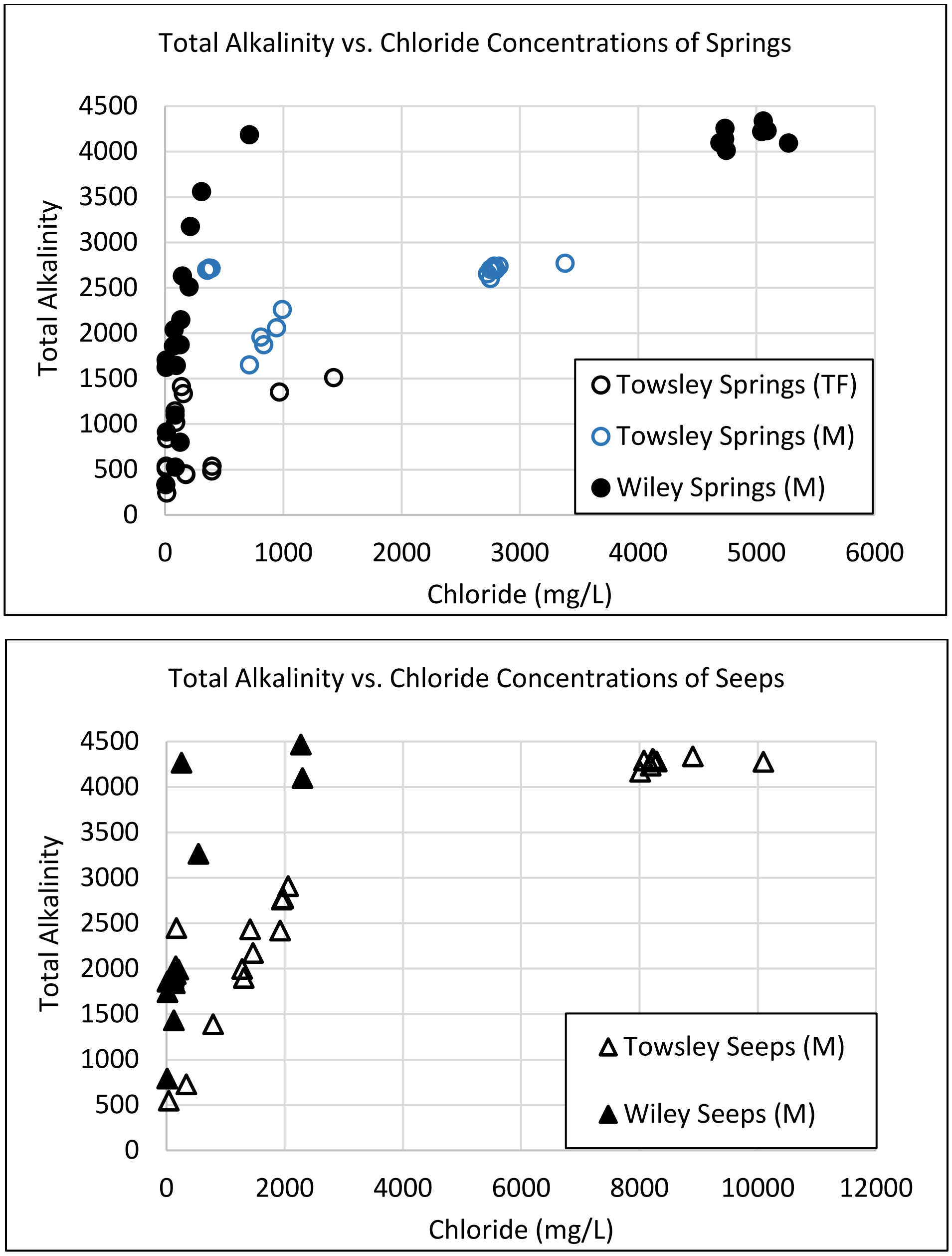
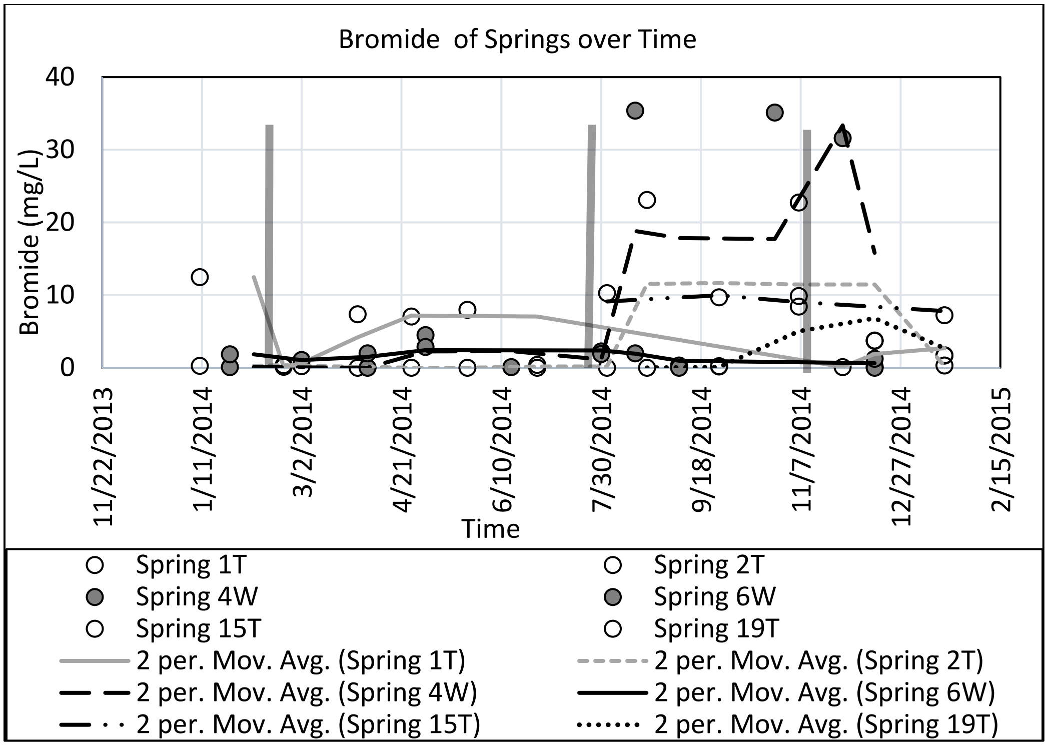


FIGURE 14. TOTAL ALKALINITY VS. CHLORIDE CONCENTRATIONS OF SPRINGS AND SEEPS.

The above graphs indicate three different water types in the hydrological system, with the trend that is central to the others as possibly representing mixing of water types at depth. High chloride concentrations indicate a source of hypersaline water in the hydrologic system while low chloride concentrations indicate meteoric freshwater contributions. TF = Towsley Formation and M = Modelo Formation.

This same trimodal distribution pattern is also found when plotting total alkalinity versus chloride concentrations, Figure 14. In these graphs, springs were again plotted separately from the seeps but a similar trimodal distribution pattern is indicated on both of these graphs. The trends with high chloride values indicate brackish to hypersaline waters (Carpenter, 1978). The high alkalinity accompanying the high chloride concentrations indicates that the water may also be older than the low chloride water with high alkalinity. This is due to water becoming more alkaline and saline with age as the waters have more residency time with the sedimentary rocks for mineral reactions to occur. Time is a component that allows the residuals from the weathering process to increase in concentrations within a sedimentary basin (Carpenter, 1978). The alkalinity vs. chloride graphs appear to indicate mixing within the different types of waters too. This is depicted by the clumping of the samples into groups with a few outlyers.in between trends

Figure 15 on the next page shows a plot of bromide of the springs and seeps over the period of one year with precipitation events indicated by vertical-gray lines. These graphs show that bromide concentrations drop during the precipitation events and that there is a lag in the concentrations recovering in both spring and seep water after these events. This lag is due to travel time of the fluids through the soil which is based on the porosity and permeability of the soils. The graphs also indicate a seasonal change in drought conditions in which bromide concentrations steadily increase and then peak before the winter season begins. This trend can be explained by changes in contributions from the shallow meteoric water system. If bromide is an indicator of deeper water sources migrating to the surface, then higher concentrations of bromide may indicate that more of the bromide source water is migrating to the surface or less meteoric fresh water is mixing with the older waters in this system. During rain events, meteoric fresh water floods the pore space of sedimentary rocks and it may also



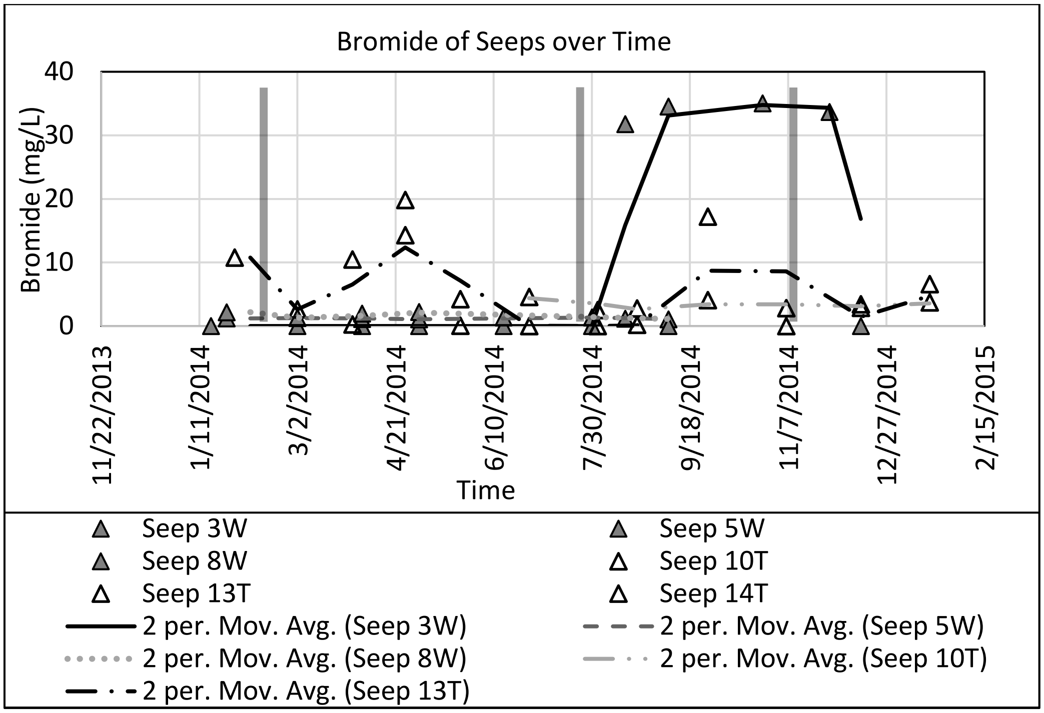


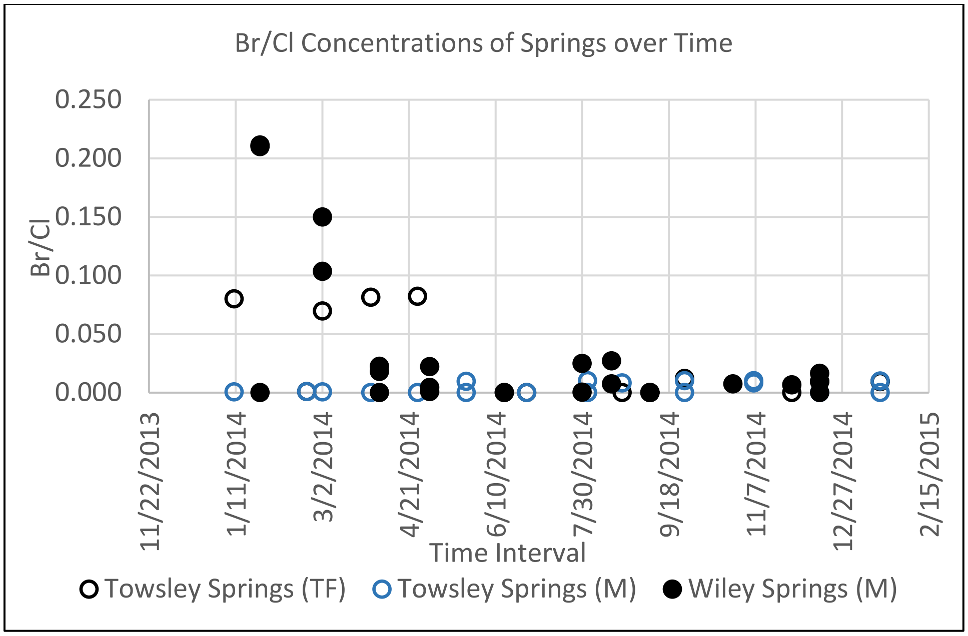
FIGURE 15. BROMIDE CONCENTRATIONS OVER TIME.

The vertical bars represent local precipitation events. The graphs indicate how meteoric fresh water influences this hydrologic system. The increase in bromide concentrations, after July 2014, indicates a seasonal change caused by drought conditions which resulted in the shutdown of the shallow hydrologic system and consequently changed the hydroconductivity. This type of change may have enabled deeper more saline water sources, with higher bromide concentrations, to migrate to the surface.

inhibit the flow of deeper source water from migrating to the surface. However, the lack of precipitation and increasing air and surface temperatures result in evaporation of meteoric water from shallow surface areas. This could plausibly result in a change in the hydroconductivity of the hydrologic system and allow the deeper-source water to flow to the surface in greater quantity, possibly resulting in the higher bromide concentrations found in the water samples (Kunath, Osborn, and Nourse, 2016).

In attempts to verify this, the ratio Br/Cl of chloride to bromide was plotted over time for the springs and seeps. The graph in Figure 16, found on the following page, shows a decreasing trend for the ratio. This trend could be the result of an increase in chloride by dissolution by meteoric water or if the subaerial soils were being enriched from below by a deeper water source. Given that southern California was in the midst of a drought during the time frame of this project, the source for meteoric dissolution was limited to less than a handful of rain events. This would indicate that a deep water source that was enriched with chloride was migrating to the surface.

The geochemistry supports that there are two sources of water in Towsley and Wiley canyons. The chemical signatures of the waters indicate a meteoric fresh water source and deeper source water that has the chemical signature of paleo marine waters. These deeper brackish waters migrate to the surface through the permeable rock conditions of the sedimentary strata. The permeability is the result of regional tectonic stresses that have fractured and faulted the sedimentary formations.



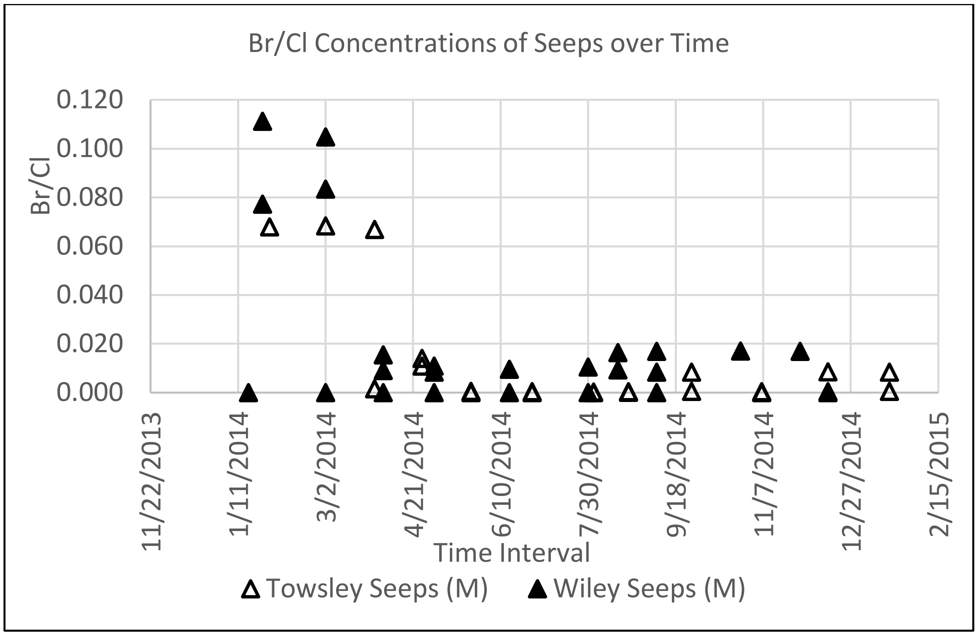


FIGURE 16. BROMIDE/CHLORIDE CONCENTRATIONS OF SPRING AND SEEPS OVER TIME.
Both graphs show a decreasing trend in the concentration ratio of bromide to chloride. Previous graphs show that bromide concentrations were increasing along this time interval. Therefore, this confirms the enrichment of chloride from deeper hypersaline source waters during the same time interval. TF = Towsley Formation and M = Modelo Formation.

Basic Water Quality

In lieu of the geochemical analyses that were performed for this project, the basic water quality assessment indicates that the surface waters in the Towsley Canyon area should be approached with caution. The chloride values of seven of the thirteen locations, that were regularly assessed, had average chloride concentrations that exceeded the MCL for the California Drinking Water Standard. The average chloride concentrations of three of those locations was three times greater than the standard and one other location's had concentration ~17 times greater than the California Drinking Water Standard. In addition, five out of the thirteen locations had sulfate maximum concentrations that exceeded the drinking water standards, and three out of the five maintained average sulfate concentrations in excess of the standards. Five out the thirteen locations tested had fluoride concentrations in excess of the standard for reporting to the State with only two maintaining average fluoride concentrations above the Maximum Contamination Level (MCL). Nitrate concentration were mostly within the drinking water standard with only one location exceeding the MCL. However, nearly all thirteen locations had nitrate levels above the reporting concentration. Water was also tested from the drinking fountain within the Conservancy Park and the water from this public source was well within the State's Drinking Water Standards. A table listing the State of California's drinking water standards for those chemical variants assessed in this report are found in Table 9 below.

TABLE 9. CALIFORNIA DRINKING WATER STANDARDS

	Maximum Contamination Level (MCL)	Detection Limit for Purposes of Reporting
Fluoride (natural)	2.0 mg/L	1.0 mg/L
Nitrate (NO3)	45 mg/L	2 mg/L
Chloride* (mg/L)	500 mg/L	-
Sulfate* (mg/L)	500 mg/L	0.5 mg/L

* Secondary Drinking Water Standard

Implications for the Santa Clara River Groundwater Basin

The Santa Clara River Groundwater Basin relies on the shallower aquifer for water production. The Saugus Formation, that is stratigraphically above the Pico Formation, is the aquifer for the water production. The basin is also subjected to the same anticlinorial tectonic stresses as the project area. If the basin has similar fractured and faulted subsurface conditions, it is possible for chloride-rich fluid flow from the deeper water source to infiltrate the shallow aquifer. This could account for the ongoing chloride concentration problem that the basin endures. Future assessment of this groundwater basin may benefit from using the chloride as a tool to identify source waters and possibly detect the diagenesis of those waters.

SECTION 5: CONCLUSIONS

- Fractures, faults, and permeable sedimentary strata which are the result of tectonic stresses, provide conduits for fluid migration in Towsley and Wiley canyons.
- Observed oil and gas emissions at springs and seep locations in the Modelo formation provide evidence for migration of fluids from depth.
- Geochemical analyses using the relationship between high chloride concentrations and stable oxygen and hydrogen isotopes has indicated that three types of water are flowing from the canyons' oil seep and springs, meteoric fresh water with low chloride and bromide concentrations, high chloride and low bromide water formed from the dissolution of halite, and most likely deep paleo marine waters.
- Deuterium and oxygen isotopes indicate shallow meteoric waters and waters that were subject to an organic influence, contribute to the surface waters in the Towsley and Wiley canyons' hydrologic system.
- Bromide and chloride concentration ratios indicate that there are three source waters.
- Based on the analysis of alkalinity and chloride concentrations, it is consistent with the salinity analyses of three source waters.
- Seasonal changes result in a change in hydroconductivity with shuts down the shallow meteoric water and allows deeper hypersaline waters to migrate to the surface.
- Basic water quality analyses indicate that the water flowing from springs and seeps in Towsley Canyon should not be considered as sources for drinking water. The surface waters should be approached with caution due to the high chloride content of many of the springs and oil seeps. .

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LIST OF APPENDICES

Appendix 1. Anion Data from Towsley Canyon Springs

ID Number	Sample Date	Fluoride (ppm)	Chloride (ppm)	Nitrate (ppm)	Bromide (ppm)	Sulfate (ppm)
SPR-1T	1/10/2014	0.95	155.81	0.28	12.46	164.30
SPR-1T	2/6/2014	-	-	-	-	-
SPR-1T	2/21/2014	1.02	139.87	n.a	0.14	153.47
SPR-1T	3/2/2014	0.55	15.30	0.63	1.07	n.a
SPR-1T	3/30/2014	0.96	90.13	n.a	7.35	229.14
SPR-1T	4/26/2014	0.88	85.91	n.a	7.06	281.26
SPR-1T	6/28/2014	n.a	n.a	n.a	n.a	n.a
SPR-1T	11/28/2014	1.97	1427.51	3.08	0.11	1855.55
SPR-1T	12/14/2014	1.39	396.29	4.27	3.69	2002.31
SPR-1T	1/18/2015	1.29	174.77	0.25	1.70	2404.78
SPR-2T	1/10/2014	0.09	360.50	2.21	0.26	0.01
SPR-2T	2/6/2014	-	-	-	-	-
SPR-2T	2/21/2014	0.09	374.04	2.24	0.34	0.01
SPR-2T	3/2/2014	0.09	388.94	2.37	0.23	0.01
SPR-2T	3/30/2014	0.09	351.43	2.02	n.a	n.a
SPR-2T	4/26/2014	0.04	358.46	1.99	n.a	n.a
SPR-2T	5/24/2014	0.15	2750.43	21.91	n.a	n.a
SPR-2T	6/28/2014	0.20	3382.63	23.36	0.38	0.26
SPR-2T	8/2/2014	0.16	2774.77	2.28	n.a	0.10
SPR-2T	8/22/2014	0.17	2749.87	1.55	23.11	0.23
SPR-2T	9/27/2014	0.16	2798.20	3.37	0.20	0.33
SPR-2T	11/6/2014	0.16	2725.55	3.31	22.72	0.35
SPR-2T	12/14/2014	0.18	2822.80	26.51	0.15	0.23
SPR-2T	1/18/2015	0.16	2783.37	25.12	0.29	0.40

Appendix 1. Anion Data from Towsley Canyon Springs

ID Number	Sample Date	Fluoride (ppm)	Chloride (ppm)	Nitrate (ppm)	Bromide (ppm)	Sulfate (ppm)
SPR-15T	5/24/2014	0.89	835.48	1.07	7.99	236.62
SPR-15T	8/2/2014	0.89	991.05	0.61	10.25	226.94
SPR-15T	9/27/2014	0.99	943.28	3.91	9.69	186.08
SPR-15T	11/6/2014	0.89	809.81	3.00	8.39	196.96
SPR-15T	1/18/2015	0.74	714.48	8.42	7.21	426.13
SPR-19T	6/28/2014	0.48	10.35	0.18	n.a	341.82
SPR-19T	8/22/2014	1.05	8.41	n.a	n.a	296.58
SPR-19T	9/27/2014	1.25	14.99	0.01	0.18	822.69
SPR-19T	11/6/2014	1.98	967.64	n.a	9.89	3343.92
SPR-19T	12/14/2014	1.40	398.66	4.35	3.73	2015.35
SPR-19T	1/18/2015	1.30	175.93	0.28	1.67	2403.03

Appendix 2. Anion Data from Towsey Canyon Seeps

ID Number	Sample Date	Fluoride (ppm)	Chloride (ppm)	Nitrate (ppm)	Bromide (ppm)	Sulfate (ppm)
SE-10T	5/24/2014	0.21	8901.75	64.68	4.21	n.a.
SE-10T	6/28/2014	0.26	10094.02	69.57	4.56	1.64
SE-10T	8/2/2014	0.27	8236.07	41.88	2.48	0.72
SE-10T	8/22/2014	0.34	8188.00	46.15	2.79	0.48
SE-10T	9/27/2014	0.27	8293.75	73.99	4.05	0.52
SE-10T	11/6/2014	0.35	8219.39	n.a.	2.82	0.54
SE-10T	12/14/2014	0.22	8008.21	70.23	3.41	0.33
SE-10T	1/18/2015	0.25	8075.06	81.34	3.73	0.43
SE-13T	1/29/2014	0.22	158.37	0.01	10.76	0.23
SE-13T	2/6/2014	-	-	-	-	-
SE-13T	3/2/2014	0.06	37.95	n.a.	2.59	0.14
SE-13T	3/30/2014	0.20	156.25	n.a.	10.46	0.18
SE-13T	4/26/2014	0.48	1309.41	n.a.	14.27	2.28
SE-13T	5/24/2014	0.53	1465.74	9.83	0.04	3.22
SE-13T	6/28/2014	0.71	1921.53	15.18	0.01	3.12
SE-13T	8/2/2014	0.72	1950.35	10.07	n.a.	0.76
SE-13T	8/22/2014	0.68	1975.81	10.92	0.19	2.23
SE-13T	9/27/2014	0.65	2059.05	3.50	17.19	2.42
SE-13T	11/6/2014	0.47	1280.13	10.45	n.a.	3.07
SE-13T	12/14/2014	0.15	337.12	1.99	2.86	1.85
SE-13T	1/18/2015	0.23	786.71	4.58	6.61	1.56
SE-14T	3/30/2014	0.59	168.92	1.28	0.26	0.27
SE-14T	4/26/2014	0.91	1417.73	n.a.	19.85	2.42

Appendix 3. Anion Data from Wiley Canyon Springs						
ID Number	Sample Date	Fluoride (ppm)	Chloride (ppm)	Nitrate (ppm)	Bromide (ppm)	Sulfate (ppm)
SPR-4W	1/25/2014	0.09	712.66	3.61	0.10	9.23
SPR-4W	2/6/2014	-	-	-	-	-
SPR-4W	2/21/2014	-	-	-	-	-
SPR-4W	4/4/2014	0.20	4690.38	32.06	n.a.	38.22
SPR-4W	5/3/2014	0.24	5091.48	25.72	4.51	35.99
SPR-4W	6/15/2014	0.19	5272.17	26.76	0.08	46.34
SPR-4W	7/30/2014	0.22	5057.74	16.64	2.24	45.64
SPR-4W	8/16/2014	0.28	4745.22	20.41	35.39	34.16
SPR-4W	9/7/2014	0.41	5045.09	25.14	0.29	36.69
SPR-4W	10/25/2014	0.36	4723.24	23.77	35.12	29.05
SPR-4W	11/28/2014	0.37	4734.07	5.69	31.60	21.96
SPR-4W	12/14/2014	0.14	4731.91	29.23	n.a.	46.78
SPR-6W	1/25/2014	1.05	8.68	0.35	1.83	133.79
SPR-6W	2/6/2014	-	-	-	-	-
SPR-6W	2/21/2014	-	-	-	-	-
SPR-6W	3/2/2014	1.20	7.05	2.01	1.06	n.a.
SPR-6W	4/4/2014	1.80	87.61	0.20	1.96	2562.30
SPR-6W	5/3/2014	1.81	128.45	n.a.	2.87	2407.06
SPR-6W	7/30/2014	1.57	76.60	3.19	1.91	73.36
SPR-6W	8/16/2014	1.37	72.62	1.01	1.98	186.99
SPR-6W	9/7/2014	2.70	147.39	0.76	n.a.	252.21
SPR-6W	12/14/2014	0.76	128.50	2.37	1.25	21.06

Appendix 3. Anion Data from Wiley Canyon Springs

ID Number	Sample Date	Fluoride (ppm)	Chloride (ppm)	Nitrate (ppm)	Bromide (ppm)	Sulfate (ppm)
SPR-7W	1/25/2014	1.04	8.75	0.33	1.84	134.68
SPR-7W	2/6/2014	-	-	-	-	-
SPR-7W	2/21/2014	-	-	-	-	-
SPR-7W	3/2/2014	1.09	12.06	0.72	1.25	122.25
SPR-7W	4/4/2014	2.51	97.11	3.80	1.75	337.08
SPR-7W	5/3/2014	2.66	133.46	n.a.	0.61	60.49
SPR-7W	6/15/2014	3.04	204.12	9.22	n.a.	1.91
SPR-7W	8/16/2014	3.81	309.76	n.a.	7.09	0.74
SPR-7W	9/7/2014	3.82	214.71	12.94	n.a.	0.65
SPR-7W	12/14/2014	2.48	85.45	5.94	1.40	942.60

Appendix 4. Anion Data from Wiley Canyon Seeps

ID Number	Sample Date	Fluoride (ppm)	Chloride (ppm)	Nitrate (ppm)	Bromide (ppm)	Sulfate (ppm)
SE-3W	1/17/2014	0.17	248.35	3.23	n.a.	0.03
SE-3W	2/6/2014	-	-	-	-	-
SE-3W	3/2/2014	0.14	256.29	2.94	n.a.	0.71
SE-3W	4/4/2014	0.23	2302.01	36.56	n.a.	15.71
SE-3W	5/3/2014	0.22	2271.89	35.62	n.a.	5.03
SE-3W	6/15/2014	0.30	2561.50	42.21	0.01	3.21
SE-3W	7/30/2014	0.26	2072.92	18.82	n.a.	1.11
SE-3W	8/16/2014	0.29	1928.83	2.32	31.74	1.09
SE-3W	9/7/2014	0.32	2041.83	5.00	34.55	2.64
SE-3W	10/25/2014	0.27	2058.98	5.13	35.00	2.87
SE-3W	11/28/2014	0.28	1996.96	4.89	33.67	1.48
SE-3W	12/14/2014	0.25	1945.51	37.08	n.a.	0.70
SE-5W	1/25/2014	0.39	15.75	0.23	1.22	0.95
SE-5W	2/6/2014	-	-	-	-	-
SE-5W	2/21/2014	-	-	-	-	-
SE-5W	3/2/2014	0.35	15.23	0.21	1.27	0.97
SE-5W	4/4/2014	0.69	119.89	2.90	1.08	20.56
SE-5W	5/3/2014	0.70	125.16	4.54	1.05	15.05
SE-5W	6/15/2014	0.84	139.19	5.72	1.33	25.30
SE-5W	7/30/2014	0.86	127.21	1.48	1.33	19.86
SE-5W	8/16/2014	0.88	120.93	2.69	1.13	28.42
SE-5W	9/7/2014	0.97	125.22	2.54	1.04	30.14

Appendix 4. Anion Data from Wiley Canyon Seeps						
ID Number	Sample Date	Fluoride (ppm)	Chloride (ppm)	Nitrate (ppm)	Bromide (ppm)	Sulfate (ppm)
SE-8W	1/25/2014	1.51	19.59	0.57	2.18	17.54
SE-8W	2/6/2014	-	-	-	-	-
SE-8W	2/21/2014	-	-	-	-	-
SE-8W	3/2/2014	1.07	12.37	1.88	1.30	152.23
SE-8W	4/4/2014	2.31	126.52	2.99	1.96	817.53
SE-8W	5/3/2014	2.50	203.30	3.79	2.22	314.23
SE-8W	9/7/2014	3.75	543.11	14.31	n.a.	3.25

Appendix 5. Towsley Canyon Spring Data

ID Number	Sample Date	Total Alkalinity	pH	Temperature (C°)	Electro Conductivity (mS)	Dissolved Oxygen (%)	Dissolved Oxygen (ppm)	Salinity (ppt)	Total Dissolved Solids (g/L)	Volatile Organic Carbon (ppm)
SPR-1T	1/10/2014	1335.50	8.26	-	-	-	-	-	-	-
SPR-1T	2/6/2014	-	-	13.6	2.84	-	-	-	-	-
SPR-1T	2/21/2014	1413.38	8.18	14.6	3.21	-	-	-	-	-
SPR-1T	3/2/2014	241.64	8.16	-	-	-	-	-	-	-
SPR-1T	3/30/2014	1020.12	8.20	-	-	-	-	-	-	-
SPR-1T	4/26/2014	1145.50	8.17	18.3	5.55	-	-	-	-	-
SPR-1T	6/28/2014			19.0	-	33.9	3.07	-	-	-
SPR-1T	11/28/2014	1512.66	8.13	-	-	-	-	-	-	-
SPR-1T	12/14/2014	485.27	8.15	8.9	3.25	-	-	-	-	-
SPR-1T	1/18/2015	451.47	8.24	10.5	3.19	n.a.	n.a.	2.4	2.86	n.a.
SPR-2T	1/10/2014	2695.88	7.90	-	-	-	-	-	-	-
SPR-2T	2/6/2014	-	-	14.9	4.45	-	-	-	-	-
SPR-2T	2/21/2014	2720.21	7.32	19.1	4.62	-	-	-	-	-
SPR-2T	3/2/2014	2714.77	7.39	-	-	-	-	-	-	-
SPR-2T	3/30/2014	2701.21	7.31	-	-	-	-	-	-	-
SPR-2T	4/26/2014	2692.92	7.26	19.1	6.24	-	-	-	-	n.a.
SPR-2T	5/24/2014	2705.29	7.43	-	-	-	-	-	-	n.a.
SPR-2T	6/28/2014	2771.06	7.72	19.4	-	4.4	0.40	-	-	-
SPR-2T	8/2/2014	2726.01	7.85	19.6	-	3.3	0.29	-	-	-
SPR-2T	8/22/2014	2603.15	7.68	20.1	-	3.6	0.32	-	-	-
SPR-2T	9/27/2014	2699.71	7.37	19.6	-	2.8	0.26	-	-	-

Appendix 5. Towsley Canyon Spring Data

ID Number	Sample Date	Total Alkalinity	pH	Temperature (C°)	Electro Conductivity (mS)	Dissolved Oxygen (%)	Dissolved Oxygen (ppm)	Salinity (ppt)	Total Dissolved Solids (g/L)	Volatile Organic Carbon (ppm)
SPR-2T	11/6/2014	2653.48	7.32	19.2	10.23	-	-	6.6	7.47	0.1
SPR-2T	12/14/2014	2741.20	7.28	18.7	4.00	-	-	-	-	0.1
SPR-2T	1/18/2015	2741.19	7.59	18.6	9.73	4.9	0.49	6.3	7.24	-
SPR-15T	5/24/2014	1874.21	8.88	-	-	-	-	-	-	-
SPR-15T	8/2/2014	2262.87	8.90	-	-	-	-	-	-	-
SPR-15T	9/27/2014	2061.79	8.80	-	-	-	-	-	-	-
SPR-15T	11/6/2014	1957.46	8.79	14.3	4.36	-	-	3.1	3.56	-
SPR-15T	1/18/2015	1651.60	8.73	11.3	1.92	84.1	9.15	1.4	1.73	-
SPR-19T	6/28/2014	513.24	8.39	-	-	-	-	-	-	-
SPR-19T	8/22/2014	537.75	7.96	19.5	-	25.5	2.42	-	-	-
SPR-19T	9/27/2014	841.38	7.82	16.5	-	6.9	0.69	-	-	-
SPR-19T	11/6/2014	1352.29	7.72	13.6	7.18	-	-	5.2	5.95	-
SPR-19T	12/14/2014	537.19	8.17	9.7	-	-	-	-	-	-
SPR-19T	1/18/2015	445.12	8.26	-	-	-	-	-	-	-

Appendix 6. Towsley Canyon Seep Data										
ID Number	Sample Date	Total Alkalinity	pH	Temperature (C°)	Electro Conductivity (mS)	Dissolved Oxygen (%)	Dissolved Oxygen (ppm)	Salinity (ppt)	Total Dissolved Solids (g/L)	Volatile Organic Carbon (ppm)
SE-10T	5/24/2014	4335.10	7.96	-	-	-	-	-	-	2.8
SE-10T	6/28/2014	4277.87	8.13	-	-	-	-	-	-	3.8
SE-10T	8/2/2014	4301.39	7.45	-	-	-	-	-	-	-
SE-10T	8/22/2014	4235.17	7.72	-	-	-	-	-	-	-
SE-10T	9/27/2014	4279.67	7.71	-	-	-	-	-	-	-
SE-10T	11/6/2014	4308.75	8.11	-	-	-	-	-	-	14.8
SE-10T	12/14/2014	4166.23	7.78	-	-	-	-	-	-	0.7
SE-10T	1/18/2015	4289.62	7.89	-	-	-	-	-	-	-
SE-13T	1/29/2014	2024.80	8.12	-	-	-	-	-	-	-
SE-13T	2/6/2014	-	-	20.2	2.77	-	-	-	-	-
SE-13T	3/2/2014	546.83	7.35	-	-	-	-	-	-	-
SE-13T	3/30/2014	1941.57	7.70	-	-	-	-	-	-	-
SE-13T	4/26/2014	1900.33	7.75	7.3	-	-	-	-	-	16.4
SE-13T	5/24/2014	2174.03	8.03	-	-	-	-	-	-	0.2
SE-13T	6/28/2014	2418.64	8.29	40.8	-	1.1	0.07	-	-	7.2
SE-13T	8/2/2014	2761.02	8.05	33.0	-	-	-	-	-	-
SE-13T	8/22/2014	2776.21	7.91	-	-	-	-	-	-	-
SE-13T	9/27/2014	2909.13	7.90	-	-	-	-	-	-	4.5
SE-13T	11/6/2014	1998.81	8.31	28.1	7.16	-	-	3.7	4.43	4.1
SE-13T	12/14/2014	727.58	7.63	16.7	-	-	-	-	-	1.7
SE-13T	1/18/2015	1388.35	7.71	18.7	3.99	3.6	0.33	2.4	2.94	-
SE-14T	3/30/2014	2447.96	7.92	-	-	-	-	-	-	-
SE-14T	4/26/2014	2434.79	7.94	-	-	-	-	-	-	-

Appendix 7. Wiley Canyon Spring Data

ID Number	Sample Date	Total Alkalinity	pH	Temperature (C°)	Electro Conductivity (mS)	Dissolved Oxygen (%)	Dissolved Oxygen (ppm)	Salinity (ppt)	Total Dissolved Solids (g/L)	Volatile Organic Carbon (ppm)
SPR-4W	1/25/2014	4185.29	8.61	-	-	-	-	-	-	-
SPR-4W	2/6/2014	-	-	16.1	7.98	-	-	-	-	-
SPR-4W	2/21/2014	-	-	13.2	8.44	-	-	-	-	-
SPR-4W	4/4/2014	4097.46	7.16	17.5	14.14	-	-	-	-	-
SPR-4W	5/3/2014	4230.56	8.56	15.6	15.96	-	-	-	-	-
SPR-4W	6/15/2014	4093.62	8.09	21.4	16.95	-	-	-	-	-
SPR-4W	7/30/2014	4337.08	7.98	31.0	-	21.3	1.45	-	-	-
SPR-4W	8/16/2014	4014.58	7.48	22.0	-	0.3	0.03	-	-	-
SPR-4W	9/7/2014	4220.96	7.63	25.4	-	4.6	0.38	-	-	-
SPR-4W	10/25/2014	4091.51	7.46	-	-	-	-	-	-	-
SPR-4W	11/28/2014	4257.37	7.18	-	-	-	-	-	-	-
SPR-4W	12/14/2014	4138.22	7.70	13.0	5mV	-	-	-	-	-
SPR-6W	1/25/2014	1625.19	8.32	-	-	-	-	-	-	-
SPR-6W	2/6/2014	-	-	17.1	1.80	-	-	-	-	-
SPR-6W	2/21/2014	-	-	13.5	1.56	-	-	-	-	-
SPR-6W	3/2/2014	333.50	7.90	-	-	-	-	-	-	-
SPR-6W	4/4/2014	525.29	7.70	13.0	3.27	-	-	-	-	-
SPR-6W	5/3/2014	799.88	7.65	16.1	3.94	-	-	-	-	-
SPR-6W	7/30/2014	2037.92	8.17	21.1	-	4.1	0.36	-	-	-
SPR-6W	8/16/2014	1860.14	8.38	-	-	-	-	-	-	-
SPR-6W	9/7/2014	2628.96	8.40	21.9	-	5.1	0.44	-	-	-
SPR-6W	12/14/2014	1875.17	7.97	18.0	23mV	-	-	-	-	10.8

Appendix 7. Wiley Canyon Spring Data

ID Number	Sample Date	Total Alkalinity	pH	Temperature (C°)	Electro Conductivity (mS)	Dissolved Oxygen (%)	Dissolved Oxygen (ppm)	Salinity (ppt)	Total Dissolved Solids (g/L)	Volatile Organic Carbon (ppm)
SPR-7W	1/25/2014	1706.92	8.49	-	-	-	-	-	-	-
SPR-7W	2/6/2014	-	-	17.8	1.33	-	-	-	-	-
SPR-7W	2/21/2014	-	-	11.4	2.05	-	-	-	-	-
SPR-7W	3/2/2014	914.74	8.34	-	-	-	-	-	-	-
SPR-7W	4/4/2014	1645.43	7.95	12.9	1.35	-	-	-	-	-
SPR-7W	5/3/2014	2149.16	7.65	17.5	3.33	-	-	-	-	-
SPR-7W	6/15/2014	2509.82	7.79	21.3	4.32	-	-	-	-	-
SPR-7W	8/16/2014	3557.51	7.50	23.4	-	1.2	0.10	-	-	-
SPR-7W	9/7/2014	3175.41	7.54	22.6	-	0.9	0.08	-	-	-
SPR-7W	12/14/2014	1099.34	8.34	10.6	26mV	-	-	-	-	10.6

Appendix 8. Wiley Canyon Seep Data

ID Number	Sample Date	Total Alkalinity	pH	Temperature (C°)	Electro Conductivity (mS)	Dissolved Oxygen (%)	Dissolved Oxygen (ppm)	Salinity (ppt)	Total Dissolved Solids (g/L)	Volatile Organic Carbon (ppm)
SE-3W	1/17/2014	4797.98	8.22	-	-	-	-	-	-	-
SE-3W	2/6/2014	-	-	18.5	4.84	-	-	-	-	-
SE-3W	3/2/2014	4266.00	8.13	-	-	-	-	-	-	-
SE-3W	4/4/2014	4097.46	7.91	20.4	8.59	-	-	-	-	-
SE-3W	5/3/2014	4467.73	7.97	-	-	-	-	-	-	-
SE-3W	6/15/2014	4690.18	8.14	22.4	4.74	-	-	-	-	5.0
SE-3W	7/30/2014	4537.76	7.70	25.8	-	5.0	33.0	-	-	-
SE-3W	8/16/2014	4631.19	7.79	-	-	-	-	-	-	-
SE-3W	9/7/2014	4621.19	7.82	-	-	-	-	-	-	-
SE-3W	10/25/2014	4759.32	8.14	-	-	-	-	-	-	-
SE-3W	11/28/2014	4693.89	8.15	-	-	-	-	-	-	8.0
SE-3W	12/14/2014	4709.46	8.07	-	-	-	-	-	-	1.7
SE-5W	1/25/2014	1858.54	8.25	-	-	-	-	-	-	-
SE-5W	2/6/2014	-	-	18.7	1.43	-	-	-	-	-
SE-5W	2/21/2014	-	-	13.5	1.56	-	-	-	-	-
SE-5W	3/2/2014	1856.70	7.80	-	-	-	-	-	-	-
SE-5W	4/4/2014	1973.59	7.70	17.5	1.17	-	-	-	-	-
SE-5W	5/3/2014	1848.92	7.68	18.3	2.80	-	-	-	-	-
SE-5W	6/15/2014	1840.33	8.22	25.8	3.33	-	-	-	-	18.0
SE-5W	7/30/2014	1915.37	7.75	25.4	-	2.0	0.16	-	-	-
SE-5W	8/16/2014	1885.25	7.48	24.0	-	1.1	0.09	-	-	-
SE-5W	9/7/2014	1929.75	8.08	27.7	-	0.8	0.06	-	-	-

Appendix 8. Wiley Canyon Seep Data

ID Number	Sample Date	Total Alkalinity	pH	Temperature (C°)	Electro Conductivity (mS)	Dissolved Oxygen (%)	Dissolved Oxygen (ppm)	Salinity (ppt)	Total Dissolved Solids (g/L)	Volatile Organic Carbon (ppm)
SE-8W	1/25/2014	1742.15	8.65	-	-	-	-	-	-	-
SE-8W	2/6/2014	-	-	18.9	1.56	-	-	-	-	-
SE-8W	2/21/2014	-	-	12.5	2.45	-	-	-	-	-
SE-8W	3/2/2014	792.38	8.24	-	-	-	-	-	-	-
SE-8W	4/4/2014	1432.51	8.14	13.8	2.42	-	-	-	-	-
SE-8W	5/3/2014	1989.48	8.07	16.4	26.50	-	-	-	-	-
SE-8W	9/7/2014	3265.37	7.97	22.1	-	2.6	0.22	-	-	-

Appendix 9.1

ID	Chloride			
	Min (mg/L)	Max (mg/L)	Mean (mg/L)	Std. Dev (=/-)
Spr-Towsley-1T	15.30	1427.51	310.70	434.84
Spr-Towsley-2T	351.43	3382.63	1893.92	1217.97
Spr-Towsley-15T	714.48	991.05	858.82	98.39
Spr-Towsley-19T	8.41	967.64	262.66	344.64
Spr-Towsley-4W	712.66	5272.17	4480.40	1270.79
Spr-Towsley-6W	7.05	147.39	82.11	49.67
Spr-Towsley-7W	8.75	309.76	133.18	97.85
Se-Towsley-10T	8008.21	10094.02	8502.03	653.17
Se-Towsley-13T	37.95	2059.05	1119.87	756.95
Se-Towsley-14T	168.92	1417.73	793.33	624.40
Se-Towsley-3W	248.35	2561.50	1789.55	745.94
Se-Towsley-5W	15.23	139.19	98.57	48.28
Se-Towsley-8W	12.37	543.11	180.98	194.46

Appendix 9.2

ID	Bromide			
	Min (mg/L)	Max (mg/L)	Mean (mg/L)	Std. Dev. (=/-)
Spr-Towsley-1T	0.11	12.46	4.20	4.12
Spr-Towsley-2T	n.d.	23.11	3.67	8.21
Spr-Towsley-15T	7.21	10.25	8.71	1.11
Spr-Towsley-19T	n.d.	9.89	2.58	3.53
Spr-Towsley-4W	n.d.	35.39	10.93	15.21
Spr-Towsley-6W	n.d.	2.87	1.61	0.79
Spr-Towsley-7W	n.d.	7.09	1.74	2.13
Se-Towsley-10T	2.48	4.56	3.51	0.71
Se-Towsley-13T	n.d.	17.19	5.41	5.99
Se-Towsley-14T	0.26	19.85	10.06	9.80
Se-Towsley-3W	n.d.	35.00	12.27	16.25
Se-Towsley-5W	1.04	1.33	1.18	0.11
Se-Towsley-8W	n.d.	2.22	1.53	0.83

Appendix 9.3				
ID	Fluoride			
	Min (mg/L)	Max (mg/L)	Mean (mg/L)	Std. Dev. (=/-)
Spr-Towsley-1T	0.55	1.97	1.13	0.40
Spr-Towsley-2T	0.04	0.20	0.13	0.04
Spr-Towsley-15T	0.74	0.99	0.88	0.08
Spr-Towsley-19T	0.48	1.98	1.24	0.44
Spr-Towsley-4W	0.09	0.41	0.25	0.10
Spr-Towsley-6W	0.76	2.70	1.53	0.56
Spr-Towsley-7W	1.04	3.82	2.56	0.99
Se-Towsley-10T	0.21	0.35	0.27	0.05
Se-Towsley-13T	0.06	0.72	0.42	0.23
Se-Towsley-14T	0.59	0.91	0.75	0.16
Se-Towsley-3W	0.14	0.32	0.25	0.05
Se-Towsley-5W	0.35	0.97	0.71	0.21
Se-Towsley-8W	1.07	3.75	2.23	0.92

Appendix 9.4				
ID	Nitrate			
	Min (mg/L)	Max (mg/L)	Mean (mg/L)	Std. Dev. (=/-)
Spr-Towsley-1T	n.d.	4.27	1.07	1.55
Spr-Towsley-2T	1.55	26.51	9.09	10.14
Spr-Towsley-15T	0.61	8.42	3.40	2.79
Spr-Towsley-19T	n.d.	4.35	0.80	1.59
Spr-Towsley-4W	3.61	32.06	20.90	9.09
Spr-Towsley-6W	n.d.	3.19	1.24	1.08
Spr-Towsley-7W	n.d.	12.94	4.12	4.57
Se-Towsley-10T	n.d.	81.34	55.98	24.65
Se-Towsley-13T	n.d.	15.18	5.55	5.21
Se-Towsley-14T	n.d.	1.28	0.64	0.64
Se-Towsley-3W	2.32	42.21	17.62	15.96
Se-Towsley-5W	0.21	5.72	2.54	1.81
Se-Towsley-8W	0.57	14.31	4.71	4.92

Appendix 9.5

ID	Sulfate			
	Min (mg/L)	Max (mg/L)	Mean (mg/L)	Std. Dev. (=/-)
Spr-Towsley-1T	n.d.	2404.78	886.35	944.23
Spr-Towsley-2T	n.d.	0.35	0.15	0.15
Spr-Towsley-15T	186.08	426.13	254.55	87.78
Spr-Towsley-19T	296.58	3343.92	1537.23	1134.40
Spr-Towsley-4W	9.23	46.78	34.41	11.23
Spr-Towsley-6W	n.d.	2562.30	704.60	1031.38
Spr-Towsley-7W	0.65	942.60	200.05	299.73
Se-Towsley-10T	n.d.	1.64	0.58	0.44
Se-Towsley-13T	0.14	3.22	1.75	1.12
Se-Towsley-14T	0.27	2.42	1.35	1.08
Se-Towsley-3W	0.03	15.71	3.14	4.21
Se-Towsley-5W	0.95	30.14	17.66	10.65
Se-Towsley-8W	3.25	817.53	260.96	300.03

Appendix 9.5

ID	Sulfate			
	Min (mg/L)	Max (mg/L)	Mean (mg/L)	Std. Dev. (=/-)
Spr-Towsley-1T	n.d.	2404.78	886.35	944.23
Spr-Towsley-2T	n.d.	0.35	0.15	0.15
Spr-Towsley-15T	186.08	426.13	254.55	87.78
Spr-Towsley-19T	296.58	3343.92	1537.23	1134.40
Spr-Towsley-4W	9.23	46.78	34.41	11.23
Spr-Towsley-6W	n.d.	2562.30	704.60	1031.38
Spr-Towsley-7W	0.65	942.60	200.05	299.73
Se-Towsley-10T	n.d.	1.64	0.58	0.44
Se-Towsley-13T	0.14	3.22	1.75	1.12
Se-Towsley-14T	0.27	2.42	1.35	1.08
Se-Towsley-3W	0.03	15.71	3.14	4.21
Se-Towsley-5W	0.95	30.14	17.66	10.65
Se-Towsley-8W	3.25	817.53	260.96	300.03

Appendix 9.7				
ID	pH			
	Min	Max	Mean	Std. Dev. (=/-)
Spr-Towsley-1T	8.13	8.26	8.19	0.04
Spr-Towsley-2T	2603.15	2771.06	2705.08	40.24
Spr-Towsley-15T	1651.60	2262.87	1961.59	202.27
Spr-Towsley-19T	7.72	8.39	8.05	0.24
Spr-Towsley-4W	7.16	8.61	7.79	0.49
Spr-Towsley-6W	7.65	8.40	8.06	0.28
Spr-Towsley-7W	7.50	8.49	7.95	0.37
Se-Towsley-10T	7.50	8.10	7.80	0.21
Se-Towsley-13T	7.40	8.30	7.90	0.27
Se-Towsley-14T	7.90	7.90	7.90	0.01
Se-Towsley-3W	7.70	8.20	8.00	0.17
Se-Towsley-5W	7.50	8.30	7.90	0.26
Se-Towsley-8W	7.97	8.65	8.21	0.24

Appendix 10

Ion Chromatograph Analysis Instructions

Prepared by Debbie Kunath-Leatham, 2014

TO START – TURN THE COMPUTER ON

- On Desktop, double click on GREEN "Chromeleon" icon.
- When the "warning" that pops up and click OK.

The Instrument Panel should appear first. Notice the GREEN button next to the "Disconnected". *This is good. – We will connect later.*

If new Eluent is needed, start with the instructions below "PREPARE ELUENT", otherwise, see section titled "STARTING THE ION CHROMATOGRAPH MACHINE".

PREPARE ELUENT

You will need 1 liter (1000 ml) to run 5 to 6 samples and 2 liters (2000 ml) to run more than this number of samples. If running consecutively over a day or so, prepare 2 liters.

Need the following:

1000 ml flask

10 ml of Eluent – Dionex AS22 Eluent Concentrate

5 ml automated pipette (purple)

MQ (distilled) water

Procedure:

- Have a 1000 ml flask out in work area
- The IC Machine's Eluent bottle sits on the top of the IC machine.
    - With the IC machine OFF, unscrew the light brown connector making sure "connector" DOESN'T TOUCH ANYTHING.
    - Then, unscrew the cap off the Eluent bottle, again, making sure that the inside cap guts and tubing DOESN'T TOUCH ANYTHING. You can use the "vise" on the center table to hold the cap in the air.
    - Discard the older Eluent by pouring it into the sink next to the lab's hood.
    - Keep the empty Eluent bottle close by.
- Prepare automated pipette
    - Near the top end of the pipette is a knob – turn the knob until the numbers just beneath it read 5.000 ml.
    - Then, place the pipette tip on the pipette – DO NOT TOUCH THE TIPS
    - Use the bag that contains the tips to position the tip so the automated pipette can make contact and not touch anything but the large end of the tip.

    - Insert end of automated pipette into the larger end of the tip – done.
    - If laying down – DO NOT ALLOW the tip to touch anything
- Take cap off the Dionex AS22 Eluent Concentrate and place it face up on the table
    - ***Using the automated pipette***,
        - Press the top button to the first position (not all the way down)
        - Place the tip into the bottle of Eluent Concentrate and remove finger slowly from top button as fluid draws into the pipette
        - Place end of pipette above the flask opening and press the top button on the automated pipette down to second position (all the way down) – liquid will be released into the flask
        - **Repeat from "*Using the automated pipette*" one more time.**
        - Place pipette down so tip DOESN'T TOUCH ANYTHING (You WILL need it again if you are preparing 2 liters of the Eluent).
        - Put cap back on the bottle of Dionex AS22 Eluent Concentrate.
- Take the flask, holding it around the neck with your thumb marking the position of the line on the neck (this is the 1000 ml or 1 liter line), and fill it BELOW this line with MQ water. Using a squeeze bottle, finish filling it so the fluid meniscus is level with the line on the neck of the flask.
- Empty flask contents into the Eluent bottle – holding the bottle at an angle to prevent splashing and not allowing the flask to touch the neck of the Eluent bottle.

Repeat above procedure if preparing 2000 ml, 2 liters of Eluent. If not, continue with the instructions below.

- Screw the cap back on the filled Eluent bottle making sure that the cap guts and tubing DOESN'T TOUCH ANYTHING except the inside of the Eluent bottle.
- Set the Eluent bottle in the space provided on the top of the IC Machine.
- Reconnect the brown connector – screwing it on until finger tight ONLY and making sure the tubing DOESN'T TOUCH ANYTHING.

STARTING THE ION CHROMATOGRAPH MACHINE

With Eluent bottle connected to the top of the IC Machine, make sure the switch on the back of the IC Machine is on.

Notice the GREEN button next to the "Disconnected", single click the GREEN button, so it says "Connect."

The IC Machine should make sounds.

On the computer – Instrument Panel (this should have been opened earlier)

- On the right-hand side of the screen, see "Eluent Fill Level". This shows how much Eluent is in the bottle attached to the screen.

  - This value needs to be changed if new Eluent was made and the bottle reattached.
  - Type in the value “1.00” or “2.00” [liter(s)] according to how much fluid you placed in the bottle.
  - If none was added, don’t change the value.
- Also, on the right-hand side of the screen, see “Pump – ICS – 1100” and click on PUMP.
- Open the front of the IC Machine, there is a diagram on the cover of the knobs and connectors. **Find the “Pump Head – Out” knob in the lower left-hand side** and turn it counter-clockwise until looser. DO NOT turn it very much or it will come off and fluid leak out. If fluid starts to leak, screw it in clockwise a little bit, but not so it is snug. This will Prime the machine.
- Allow machine to Prime for about 10 – 15 minutes.

When Done Priming – *****Warning ***NEVER turn on the SUPPRESSOR before the PUMPS.**

- On the Instrument Panel, right-hand side, see “Pump” and click OFF.
- Go to the front of the IC Machine, turn the “Pump Head – Out” knob clockwise until it is snug.
- Back in the computer’s Instrument Panel-
- Find the PUMP and click ON – watch the SIGNAL in the upper right hand corner.
- Find the SUPPRESSOR and click ON – run until the SIGNAL is steady, roughly 10 to 15 minutes.

Prepare the samples while waiting on the IC Machine.

On computer – Go to Data Page

PREPARING SAMPLES

Note: Need to allow for 15 minutes of run time for each sample. Load sample in hypothesized order of least to greatest salinity.

Samples should be close to room temperature.

Procedure –

A. Loading Samples in Trays –

- Trays must be loaded from **right to left from the dot** on the right-hand corner.
- **LOADING ORDER of all samples**:
  1. Low Concentration
  2. Mid Concentration
  3. High Concentration
  4. Sample number 1
  5. Sample number 2
  6. Sample number 3
  7. Sample number 4

8. Sample number 5
9. Sample number 6
10. Mid Check (Mid Concentration)
11. Di Water (MQ water)
12. Sample number 7
13. Sample number 8
14. Sample number 9
15. Sample number 10
16. Sample number 11
17. Sample number 12
18. Mid Check (Mid Concentration)
19. Di Water (MQ water)
20. Sample number, etc.…

After every six samples have a "Mid Check" (Mid Concentration) and a "Di Water" (MQ water) to make sure all is going well, even if you end with a "Mid Check" and a "Di Water"

B. Sample Recording and Preparing

- First, prepare the Standards in tubes in the order given above (low to high concentrations), then prepare your samples.
- Place a dot on the sample tube at the line, this is the fill line.
  DO NOT OVERFILL or ALLOW SAMPLE BOTTLE TO TOUCH THE TUBE'S SURFACE.
- Pour fluid into sample tube up to the fill line. If you overfill, pour some out in the sink or waste container.
- Put cap on the tube, stem side up, and be careful not to touch the larger end of the caps.
- Using the tool provided, push the cap into the tube (stem-opened side first).
- Then, turn the tool around and push the cap until it is flush with the top of the tube.
- Place sample tube in Loading Tray.
- **After the Standards are prepared,** On Data Page, single click on the name of **your sample** in the **fourth position down** (first three are the standards). Then, type in your first sample ID; do this before you prepare each sample. **Your next sample**, you will single click on the name in the fifth position down, etc… so the loading order listed above is the same as the one listed on the Data Page.
- **NOTE** – Keep your samples in the order they are loaded in the trays so you can record their order in the logbook after the run starts.

IC Machine should be ready – Check to see if Signal is steady on the Instrument Panel. If steady (~1800 µS), you can start the run.

- Automatic Sampler

  - First, load the trays in the Automatic Sampler. Placing the trays in front of spring loader in the order of front to back (front goes first) - keeping the order as you have recorded it in the computer.
  - Close lid
  - Press [Hold/Run] on front panel of Automatic Sampler.
- Computer
  - Click [START] – IC Machine will light up and start loading.
- Click "Data Processing" in the bottom left-hand corner
  - Right Click "ECD-1"
  - Click –
  - Click – Processing Method Tools
- You can view a graph of the run as it progresses from here by clicking on a sample name at the right.
- Click Report Generated to view the number results.
- Watch the Standard's results and how they plot to make sure that the run is off to a good start.

<u>Save Finished Run</u>

- From the Report Designer page, Click the CHARMELEON ICON located in the upper left-hand corner of the computer.
- Click "EXPORT" (Excel)
- Save in – IC Results/Grad Student/Your Name
- Save as – Run name

<u>Shut Down</u> – **After a run is complete **Note: NEVER shut down while a run is in progress.**

- Click on the Instrument Panel.
- "Suppressor", click OFF
- "Pump", click OFF
- GREEN button next to "Connect" (top of screen), click GREEN button (will then say "Disconnected")
- Flip the switch located on the back up right-hand side of the IC Machine (machine will shut off).

Plate 1A

Geologic Map -- Towsley & Wiley Canyons

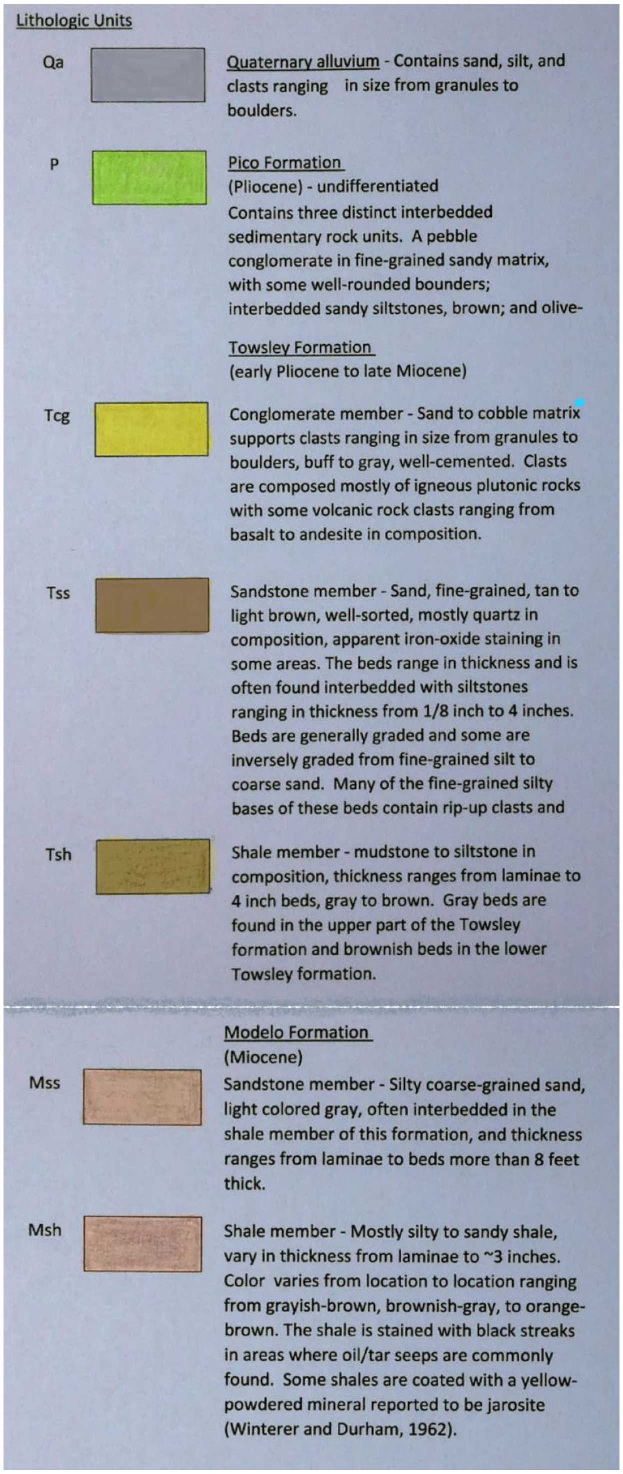
Topo Base: USGS (2012) Digital 7.5 min Oat Mountain Quadrangle, CA
--Drafted Geologic Data by D. Kunath-Leatham
--Digital Geological Overlay from observations of J. Nourse

Plate 1B

Geologic Map, Towsley and Wiley Canyons Legend

Geologic Map
Towsley and Wiley Canyons

Base map: U.S. Geological Survey, 2012, Oat Mountain Quadrangle, Los Angeles County, California, 7.5 Minute Series (Topographic)



Lithologic Units

Qa	▨	**Quaternary alluvium** - Contains sand, silt, and clasts ranging in size from granules to boulders.
P	🟩	**Pico Formation** (Pliocene) - undifferentiated Contains three distinct interbedded sedimentary rock units. A pebble conglomerate in fine-grained sandy matrix, with some well-rounded bounders; interbedded sandy siltstones, brown; and olive-
		Towsley Formation (early Pliocene to late Miocene)
Tcg	🟨	Conglomerate member - Sand to cobble matrix supports clasts ranging in size from granules to boulders, buff to gray, well-cemented. Clasts are composed mostly of igneous plutonic rocks with some volcanic rock clasts ranging from basalt to andesite in composition.
Tss	🟫	Sandstone member - Sand, fine-grained, tan to light brown, well-sorted, mostly quartz in composition, apparent iron-oxide staining in some areas. The beds range in thickness and is often found interbedded with siltstones ranging in thickness from 1/8 inch to 4 inches. Beds are generally graded and some are inversely graded from fine-grained silt to coarse sand. Many of the fine-grained silty bases of these beds contain rip-up clasts and
Tsh	▨	Shale member - mudstone to siltstone in composition, thickness ranges from laminae to 4 inch beds, gray to brown. Gray beds are found in the upper part of the Towsley formation and brownish beds in the lower Towsley formation.
		Modelo Formation (Miocene)
Mss	▨	Sandstone member - Silty coarse-grained sand, light colored gray, often interbedded in the shale member of this formation, and thickness ranges from laminae to beds more than 8 feet thick.
Msh	▨	Shale member - Mostly silty to sandy shale, vary in thickness from laminae to ~3 inches. Color varies from location to location ranging from grayish-brown, brownish-gray, to orange-brown. The shale is stained with black streaks in areas where oil/tar seeps are commonly found. Some shales are coated with a yellow-powdered mineral reported to be jarosite (Winterer and Durham, 1962).

Explanation of Symbols

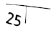
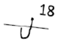
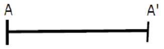
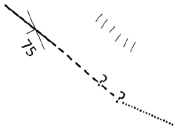
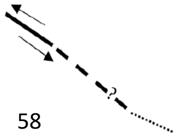
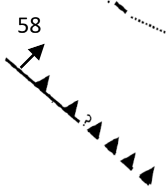
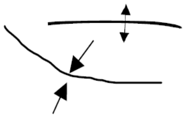
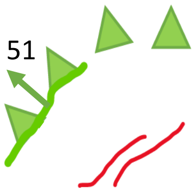
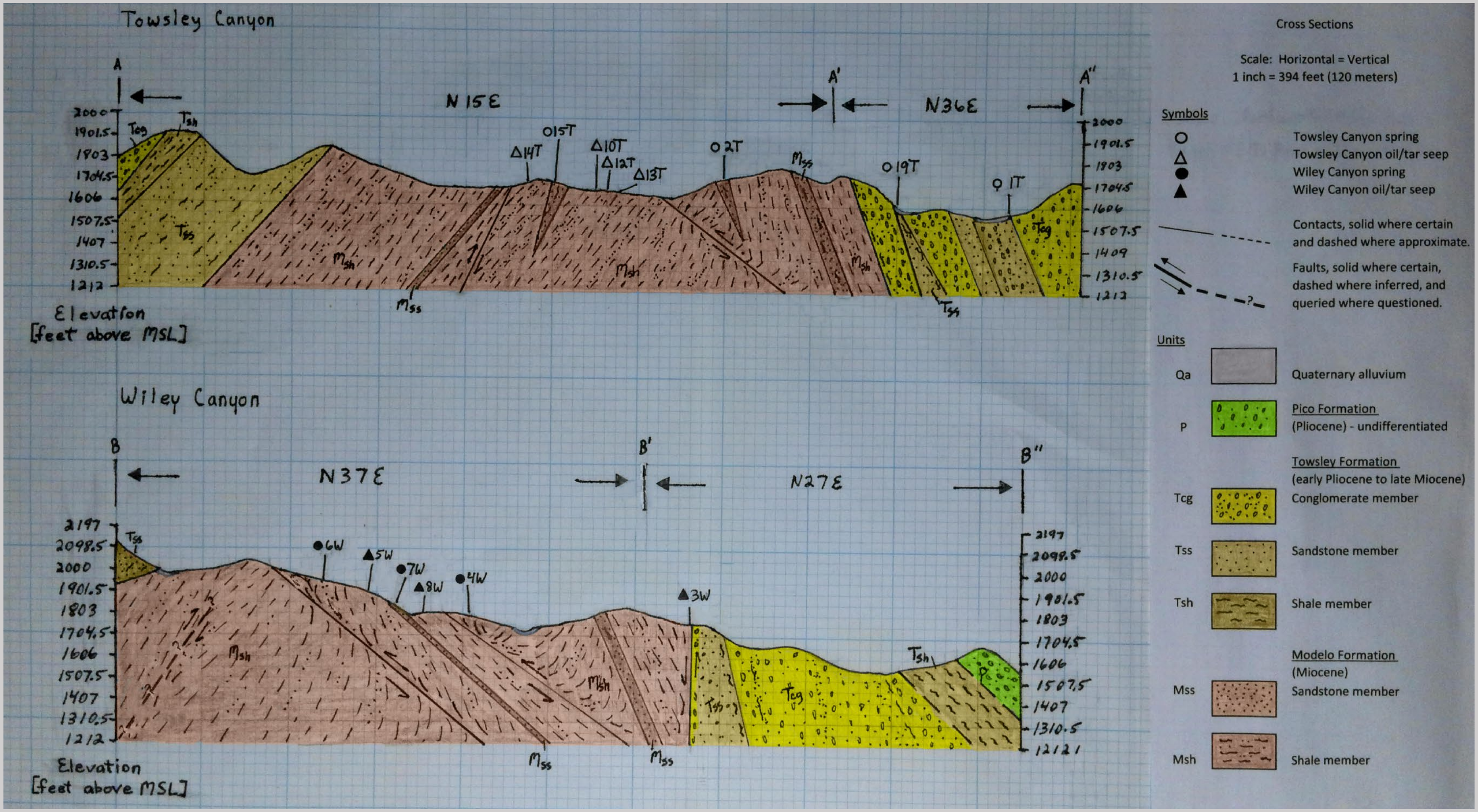
○	Towsley Canyon spring
△	Towsley Canyon oil/tar seep
●	Wiley Canyon spring
▲	Wiley Canyon oil/tar seep
	Strike and dip of sedimentary rock
	Strike of vertical sedimentary rock
	Arrow indicating trend and plunge of slickensides
	Strike and dip of overturned beds
	Cross section line
	Contacts, solid ranges from where accurately to approximately located, dashed where inferred, dotted where concealed, queried where questioned, and hatched where gradational.
	Faults, solid where accurately located, dashed where approximately located or inferred, queried where questioned. Arrows indicate direction of relative motion.
	Reverse faults, solid where accurately located, dashed where approximately located or inferred, queried where questioned. Teeth on upper plate. Arrows indicate direction of dip.
	Anticline, indicating trace of hinge Syncline, indicating trace of hinge
	Contributions by J. Nourse.
	Blue, strike and dip of sedimentary rock
	Purple, strike and dip of sedimentary rock along fault
	Orange, contact line, solid where certain, dashed where inferred
	Green, reverse faults, solid where accurately located, dashes where approximately located or inferred. Teeth on upper plate. Arrows indicate direction of dip.
	Red, diatomites

Plate 2

Cross Sections – Towsley and Wiley Canyons



Produced by D.A. Kunath-Leatham, 2021