THE USE OF GROUNDWATER GEOCHEMISTRY TO PROSPECT FOR BLIND GEOTHERMAL RESOURCES IN THE STATE OF HAWAII

A THESIS SUBMITTED TO
THE GLOBAL ENVIRONMENTAL SCIENCE
UNDERGRADUATE DIVISION IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

GLOBAL ENVIRONMENTAL SCIENCE

By

Tineill K. Dudoit

Thesis Advisor

Nicole Lautze

THE UNIVERSITY OF HAWAIʻI AT MĀNOA

DECEMBER 2018

I certify that I have read this thesis and that, in my opinion, it is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science.

THESIS ADVISOR

Nicole Lautze
Hawai‘i Institute of Geophysics and Planetology

DEDICATION

"For I am convinced that neither death nor life, neither angels nor demons, neither the present nor the future, nor any powers, neither height nor depth, nor anything else in all creation, will be able to separate us from the love of God that is in Christ Jesus our Lord."

–Romans 8:38-39

This is dedicated to Jesus, my Lord, Savior, and friend. Thank you for all that do, every opportunity that you have given, and your constant presence in both the hills and valleys of my life. Words cannot express my gratitude for all that you have done and continue to do. To God be the glory!

ACKNOWLEDGEMENTS

I would like to acknowledge Dr. Nicole Lautze, HIGP, Advisor, Members of the Hawaii Fairway Project: Dr. Donald Thomas (HIGP), Dr. Neil Frazier (GG), Dr. Garrett Ito (GG), Dr. Nicholas Hinz (UNR), Dr. Robert Whittier (GG), Colin Ferguson (GG) David Waller (GG), Hannah Schuchman (GES), Diamond Tachera (HIGP), Danny Powell (GG), and Justin Higa (GG), Leona Anthony SOEST Director of Student Services, Dr. Marek Kirs, WRRC, Assistant Researcher, GES Department Chair Dr. Michael Guidry and the Oceanography staff. Your advice, encouragement, and support were vital in the completion of this thesis.

ABSTRACT

The principle goal of this study was centralized on the use of groundwater geochemistry to prospect for blind geothermal resources throughout the State of Hawaii by the collection of water samples, analysis of water geochemistry data, and highlighting of wells that contained chemical signatures indicative of elevated subsurface heat. Water samples were collected in ten locations across the State of Hawaii that were identified as areas of potential geothermal resource in a recent geothermal prospect assessment, and analyzed for temperature, major and minor chemical species, and trace metals. A total of 61 samples were collected: 60 from existing wells and 1 spring was sampled in an area where no wells exist. The aqueous geothermal indicators: silica concentration, chloride/magnesium, sulphate/chloride, and temperature, were chosen because of the relative success as geochemical indicators in Hawaii. Additionally, thresholds were determined, based on compiled historical data and research, as chemical signatures that could signify subsurface heat under Hawaii conditions. As a result, various anomalies were detected on four islands within the State of Hawaii based on the criteria set within the project as potential indications of subsurface heat, and a potential geothermal source was identified on the Island of Lanai. However, positive indications of a subsurface heat anomaly based on this assessment could have an alternative non-thermal explanation. Given that these aqueous geochemical indicators can be affected by both natural and anthropogenic processes, further investigation is necessary. Furthermore, data collected could assist the Hawai‘i State Legislature to address the state’s growing energy demands through the identification, exploration, and use of available geothermal sources. The subsequent report provides the latest comprehensive water geochemistry data that may be used as a geothermal exploration tool for the State of Hawai‘i.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

1.1 Hawaii's Energy Issue

Located in the Pacific Ocean, Hawai‘i is an archipelago with a modern, energy-intensive, population which creates the groundwork for the state's energy problems (www.eesi.org). The State of Hawai‘i does not produce, nor has any proven reserves of petroleum, natural gas or coal (Yen & Iacofono, 1981). This fact, and the state's geographic isolation, create a dependence on imported crude oil and petroleum products to supply the state's electricity, transportation and other energy needs. As such, Hawai‘i is particularly vulnerable to fluctuations in the global energy market, as evidenced by the close correlation between the electricity price changes to oil price changes during the last two decades. Not only has Hawai‘i's energy crisis been well documented in both the scientific and public press, but historically Hawai‘i has had the highest electricity prices in the nation with the current price at 2.5 times the U.S. national average (Hawaii State Energy Office, 2017; Fig.1). In an effort to decrease dependence on imported fuels and conserve liquid fuels in the transportation sector, the Hawai‘i State Legislature set out policy objectives in order to address the state's energy predicament through the use of domestic renewable sources. The candidate from among these natural energy sources which showed the highest promise for early power generation was geothermal energy (Fig.2).

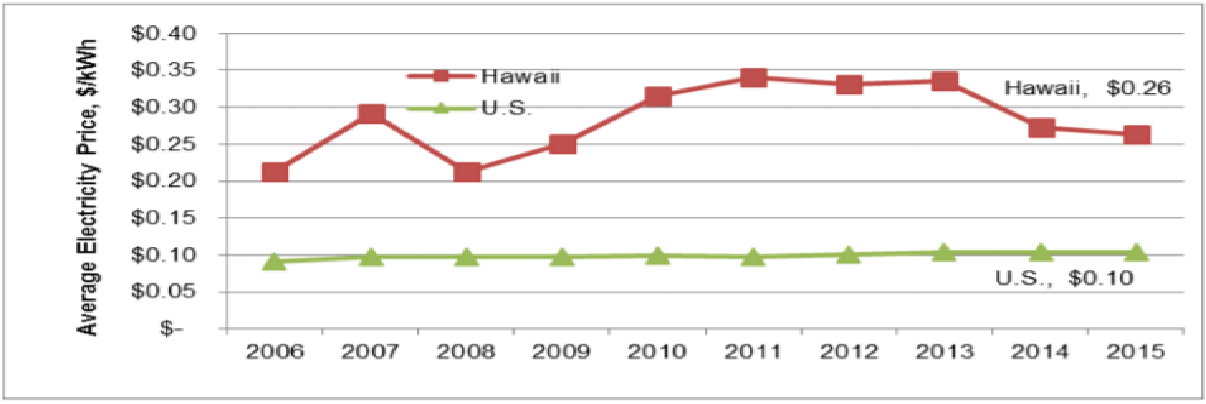


Figure 1. Average Electricity Price ($/kWh), in Hawaii compared to the rest of the United

States from 2006-2015. Source: Energy Information Administration (www.energy.hawaii.gov)

Capacity Factor Assumptions for Renewable Resources	Capacity Factors (assumed)*	MWh produced per MW Capacity
Biomass-Direct Firing	80%	7,000
Wind (Oahu, Hawaii, Kauai)**	35%	3,100
Wind (Lanai, Molokai)	40%	3,500
Wind (Maui)	45%	3,900
Geothermal	96%	8,400
Hydro	44%	3,900
Solar (rooftop)	23%	2,000
Solar (utility)	24%	2,100
Ocean	35%	3,100
Capacity factors in this table are assumptions used by Booz Allen, under contract to the National Renewable Energy Laboratory, in the Hawaii Clean Energy Initiative Scenario Analysis, Appendix C, Slide 26. March 2012. *Actual capacity factors may vary from the assumptions presented here. **The Pakini Nui wind farm (on Hawaii Island) generally has an annual capacity factor of over 60%		

Table 1. Capacity Factor Assumptions for Renewable Resources in Hawaii. Source: DBEDT Hawaii State Energy Office, Hawaii Energy Facts & Figures, May 2016 (www.energy.hawaii.gov)

1.2 Previous Geothermal Work in Hawaii

The recognition and use of geothermal energy in Hawaii likely dates to antiquity, however, while the Hawaiian Islands are an active volcanic hotspot, very few surface thermal manifestations exist when compared to other hotspots such as Yellowstone. Geothermal exploration began in 1961, when four privately financed exploratory wells were drilled into the Kīlauea east rift zone, on Hawaiʻi Island, by the Hawaiʻi Thermal Power Company (Fowler et al., 1980). Geothermal research continued from 1972 – 1977, however, largely as a result of a lack of thermal features, a majority of the geothermal surveys were concentrated on the Island of Hawaii. To date there is only one proven geothermal resource area located in Puna on the lower end of the east rift of the Kilauea Volcano (Cox & Thomas, 1979b). Before a temporary shutdown in March 2018, approximately 3% of the State of Hawaii and 25% of Hawaii Island's energy needs are provided for by the Puna Geothermal Venture (PGV) powerplant, operated by Ormat Technologies, Inc., which can produce up to 38 megawatts of electricity (Lautze et al., 2017a). Unfortunately, a limited number of exploratory geothermal surveys were conducted in other parts of the state and subsequently, the late 1970's was the last time a coordinated statewide effort was made to characterize thermal resources. The successive results were published in the 1985 State of Hawai'i's Geothermal Assessment, which identified potential geothermal resource areas on all the main Hawaiian Islands and suggested further investigation, however, minimal significant research has been done since (Thomas, 1986). Data compiled from the studies above detected anomalies relating to subsurface heat, nevertheless, difficulties in the interpretation and application of geothermal indicators led to the uncertainty of results.

1.3 Lack of Geothermal Data in Hawai'i

Valid aqueous geothermal indicators are difficult to ascertain because of the unique geologic and hydrologic subsurface environments and lack of pertinent water chemistry data across the State of Hawaii. Success obtained through the use of elements and ratios of elements to determine subsurface heat in a traditional continental setting, could not be evaluated in the same way because of the complexities of Hawaii's island environment (Cox & Thomas, 1979b). Initial investigations and compilations of geothermal data concentrated on a site-specific approach, consequently these analyses encountered difficulties due to variations in aquifer conditions, topography, well depth, geographic oceanic location, and permeability of source rock, which can lead to uncertainty in the interpretation of indicator data (Cox & Thomas, 1979b). Throughout the investigative process, researchers were able to identify common characteristics that would show the nature of the geothermal systems in Hawaii, modify conventional exploration techniques, and implement relatively new techniques, however, limitations of existing geothermal datasets remained. Moreover, while a large number of groundwater wells exist in

Hawaii, they lack relevant geochemical information relating to geothermal exploration (Lautze et al., 2017b). The next logical step in any current regional assessment of Hawai‘i’s geothermal potential is to address these shortcomings.

1.4 Goals of the Project

The principle goal of this thesis is centralized on the use of groundwater geochemistry to prospect for blind geothermal resources throughout the State of Hawaii by sampling and analyzing groundwater chemistry data identified in a recent geothermal prospect assessment and highlighting wells containing chemical signatures indicative of elevated subsurface heat. In 2014, the first phase of a Play Fairway Analysis (PFA) funded by the U.S. Department of Energy began in order to identify attributes necessary for a geothermal resource to exist in Hawaii (Lautze, et al., 2016a). Based on existing geological, geophysical, and geochemical datasets relevant to elevated subsurface heat, reservoir permeability and reservoir fluid (Ito, et al., 2017) and a source probability map was generated. This map identified areas of potential geothermal resource and the continued exploration for viable geothermal resources across the State of Hawai‘i was merited for the second phase of the project. Results also validated previous indications of probable subsurface geothermal resource and identified areas where additional geochemical data was needed to make an assessment. The methodology and application used in this PFA is centered on the successful techniques and research initiated by Don Thomas and Malcom Cox. Elements, ratios, compositions, and the basic knowledge relating to aqueous geochemistry establish the framework of this study, however, the use of geothermometry as a quantitative indicator goes beyond the scope of this work. The subsequent report provides the latest comprehensive water chemistry data that may be used as a geothermal exploration tool for the State of Hawai‘i.

2. BACKGROUND

2.1 Geologic Setting

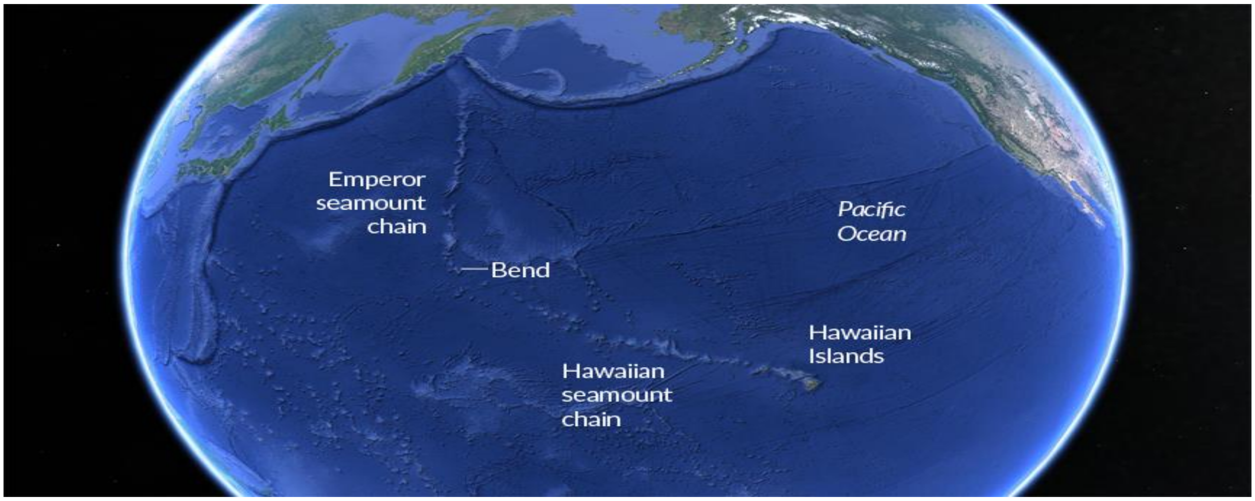


Figure 2. Hawaiian Archipelago also known as the Hawaiian-Emperor Chain in the Pacific Ocean (Sumner, 2015)**.**

Located approximately 4000 km from the nearest continent, the Hawaiian Islands comprise the most isolated archipelago on Earth. This sequence includes the eight major islands, several atolls, numerous smaller islets, and undersea seamounts, extending from the island of Hawaiʻi in the southeast, to the Emperor Seamount Chain in the northwest (Fig.3). The eight major islands at the northern end of the chain are, from west to east, Niʻihau, Kauaʻi, Oʻahu, Molokaʻi, Lānaʻi, Kahoʻolawe, Maui, and Hawaiʻi. Volcanic in origin, the highly permeable rock of the islands is characterized by a rugged landscape which is produced by a combination of factors including: rainfall, runoff, wind circulation, erosion, deposition and wave action, which has a pronounced effect on the more exposed windward section of all islands (Clague et al., 2014). The topography of the islands creates extreme variations in precipitation and tropical vegetation from one location to another. As a result, the taller and larger islands, extract most of the water from the circulating air currents, before it reaches the smaller islands of Niʻihau, Lānaʻi and Kahoʻolawe, leaving them dry and barren (MacDonald & Hubbard, 2006). Built up from the sea floor by numerous accumulated lava flows (Macdonald & Abbott, 1983), this volcanic mountain range includes individual volcanoes which rise as much as 9,000 meters above the sea floor and reach a diameter of 120 kilometers at their base (Dalrymple, Silver, & Jackson, 1973).

2.1.1 Ocean Island Hot Spot

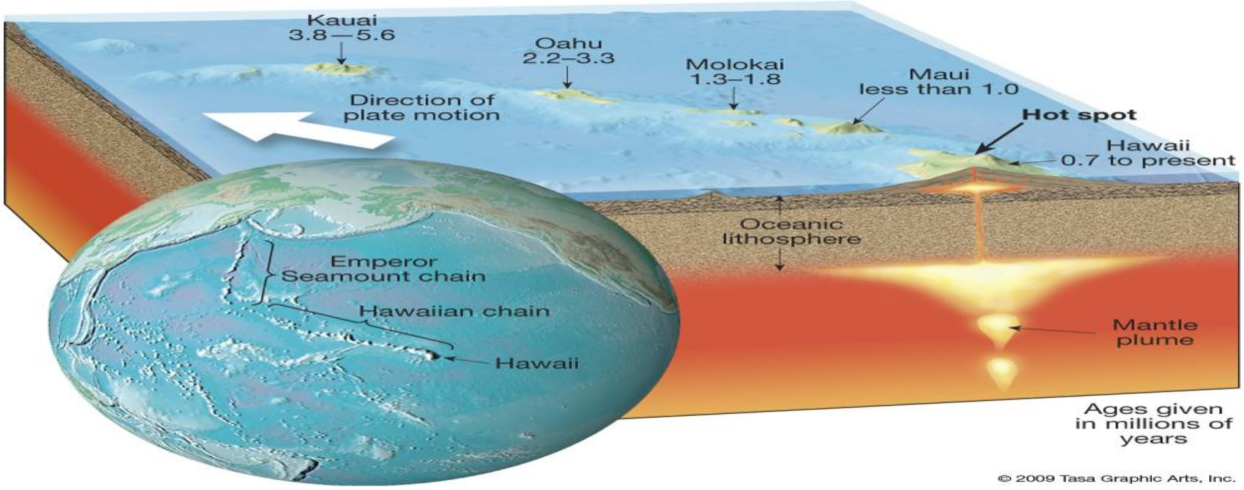


Figure 3. The mantle hotspot origin of magma, which provides the heat for Hawai‘i's geothermal resource. The names of the state's five biggest islands and the average age of the shield building stage of volcanism as shown. Note this age increases to the northwest (Map Source: Tasa Graphics, Inc-2009).

Geothermal heat in Hawai‘i is directly linked to Hawai‘i's ocean island hotspot volcanic setting, whereby magmatic intrusions supply the heat source (Lautze et al., 2017a). Intraplate or hotspot volcanism occurring in the middle of the Pacific is thought to be underlain by a plume of hotter, lighter, material deep within the mantle that rises by convection (Fig.4). Experimental data suggests that less dense isolated masses of molten rock, plastically deform, continue to aggregate, and rise buoyantly through unstable regions with in the mantle (http://www.geology.sdsu.edu). Ultimately this hot bulbous plume of mantle material erupts as lava onto the surface, cools within a duration of minutes to days upon discharge, and any residual heat is derived by intrusive magma (Lautze et al., 2017a). Resultant surface manifestations include, but are not limited to: calderas, rift zones, vents, and dikes. As the volcanic island continues to move away from the heat source, eruptive activity is reduced and ultimately terminated. Although the hot spot itself is relatively fixed or slow moving, the plate is moving and generates a chain of islands through magmatic eruptions. The melting products of mantle plumes and magmatic eruptions likely reflect variation in the geochemical composition, rate and amount of heat supplied to the Hawaiian hotspot overtime (Clague et al., 2014).

2.1.2 Age of the Islands

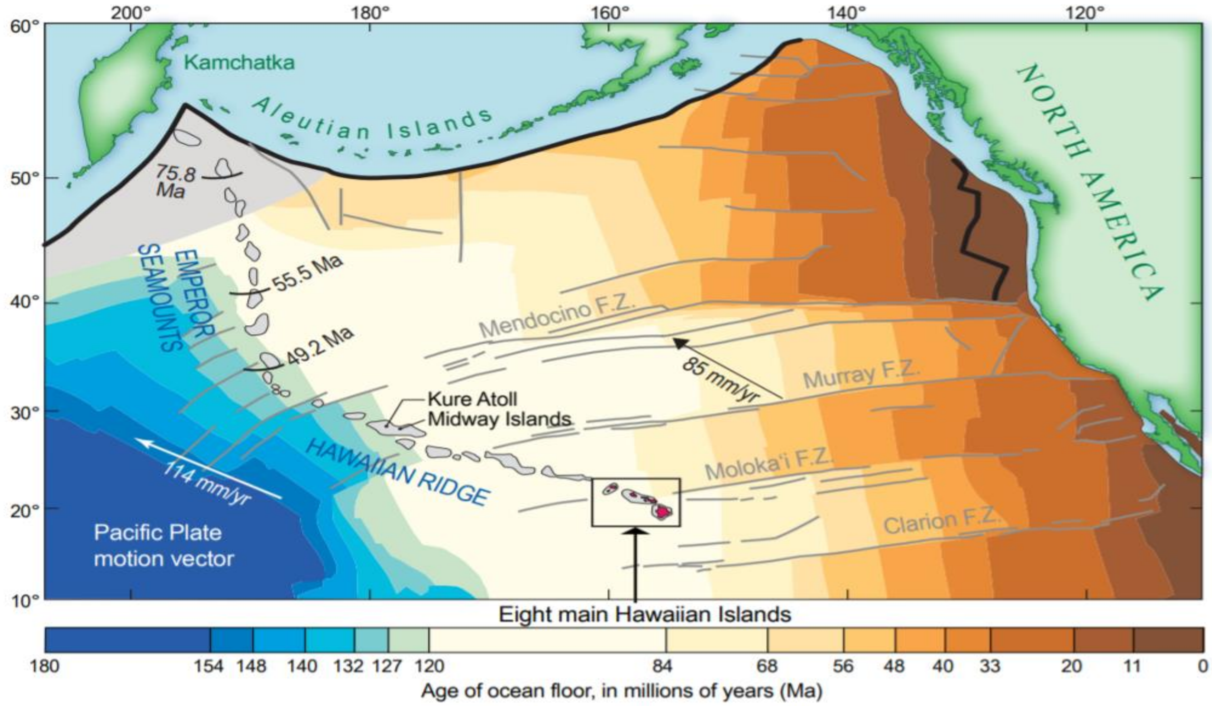


Figure 4. The Hawaiian Islands (red) and Hawaiian-Emperor volcanic chain, most of which consists of submarine seamounts, all depicted by their outlines at 2-km water depth (generalized from Clague and Dalrymple, 1987). Vector indicate Pacific Plate motion relative to presumed fixed mantle hotspot in millimeters per year (mm/yr; from Simkin and others, 2006). Fracture zones (F.Z.) from Atwater and Severinghaus (1989). Isochrons along Emperor Seamounts chain show age of volcanism in millions of years (Ma; Duncan and Keller, 2004). Ocean floor age (Muller and others, 1997) from imagery available on EarthByte Web site: (https:earthbyte.org/Resources/Agegrid/1997/digit_isochrons.html#anchorFTPao). Mercator projection (Clague et al., 2014)

In 1840, the first geologic study of the Hawaiian Islands was conducted, and renowned American geologist James D. Dana recognized and correctly deduced, largely by observing the increasing degree of erosion of volcanic peaks from Hawaiʻi to Kauaʻi, that the main Hawaiian Islands increased in age from southeast to the northwest (Ziegler, 2002; Fig.4). In general, all volcanoes along the Emperor Seamount-Hawaiian chain, increase in age and decrease in activity from southeast to northwest, with the northernmost and oldest, approximately 81 million years (Clague et al., 2014) in age, being subducted under Kamchatka of northeastern Asia (Fig.5). At present, volcanic eruptions are occurring on the Island of Hawaiʻi, however, previous volcanic activity from the Miocene epoch can be traced back to the northwest end of the Archipelago in the vicinity of what is today Midway Island (Grose et al., 1975). During the first one to two million years, primary volcanic growth occurs from successive eruptions from a central vent of fluid basaltic lava, building a mountainous accumulation that rises from the sea floor or submarine margins of a neighboring volcano. Once formed, Hawaiian volcanoes become subject to a spectrum of processes of degradation including: weathering, erosion, and volcanic extinction, that progressively increase as a volcano moves away from the hotspot. As magmatic eruptions cease, subaerial erosion continues, the density of the edifice overwhelms the oceanic crust, and the inundated volcanic structure becomes covered with reef (Ziegler, 2002). Eventually, over a period of approximately 15 million years, any volcanic vestige will be fully submerged and will continue its northwestward trek (Clague et al., 2014).

2.1.3 Stages of Volcanism

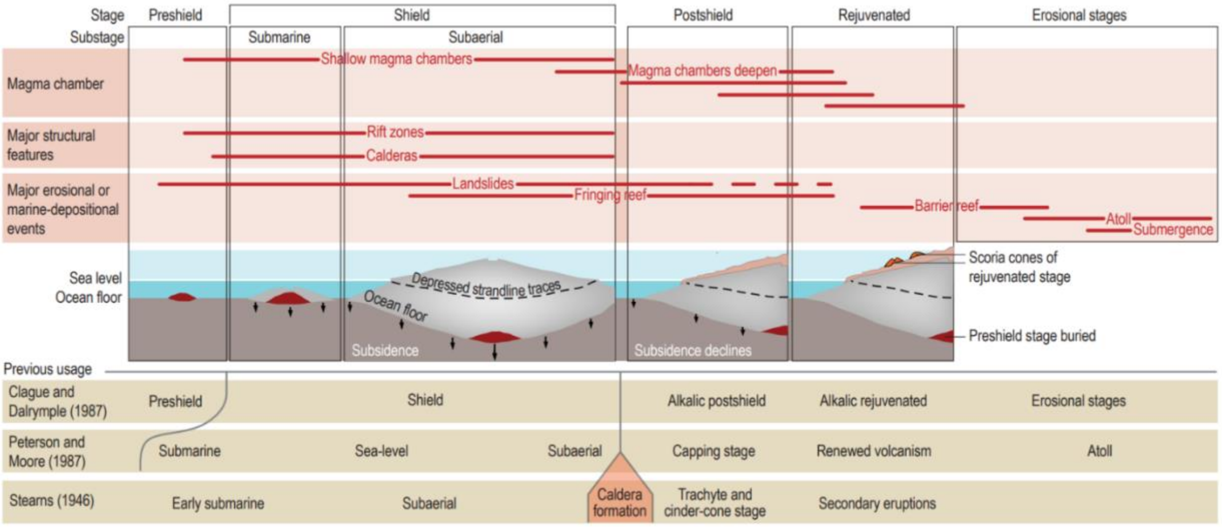


Figure 5. Evolution of Hawaiian Volcanoes as a sequence of Generalized Growth Stages (Clague et al., 2014)

Typically, the life sequence of each Hawaiian volcano exhibits four stages: pre-shield, shield building, post-shield, and rejuvenation stages, although, this is an idealized arrangement because not every volcano experiences each stage (Lautze et al. 2017a; Clague et al., 2014; Ziegler, 2002; Fig.6). Very little is known about the pre-shield stage of Hawaiian volcanism, but this stage includes the rapid upward growth rate of a submarine volcano from infrequent submarine lava masses that tend to pile up near the point of extrusion. The second, and most voluminous, is the shield building stage, evident by countless eruptions of fluid lava flows not only from vents near the summit but also from linear rift zones that pass through the summit and extend oriented parallel to the flanks of neighboring volcanoes, that cause emerging volcanoes to broaden and grow (Dalrymple, Silver, & Jackson, 1973). During the post-shield stage, the volcanic activity of a Hawaiian volcano begins to decline after approximately a half a million years of active subaerial growth (Ziegler, 2002). As the volcano continues to steadily drift away from the hotspot, any caldera present fills in and gradually disappears. The fourth and final stage of

Hawaiian volcanism is the rejuvenation stage. In this stage, renewed, sporadic episodes of isolated volcanic activity interspersed with periods of erosion, occur on the heavily eroded lower slopes of old volcanoes (Langenheim & Clague, 1987). The growth history and compositional variation are comprised in these stages, though imperfectly named, match our understanding of the Hawaiian volcanic process (Clague et al., 2014).

2.1.4 Compositional Variation of Hawaiian Volcanoes

In assessing the chemical variation of volcanoes in Hawaii, it is necessary to consider the chemical composition and mineral content of lava materials, and the life sequence of each volcano. In the growth and evolution of a Hawaiian volcano, a distinct chemical and mineral profile is produced sequentially within the lava and rocks formed (Table 1). Igneous rocks can be arranged into three general series: tholeiitic (poor in alkalis), alkalic (rich in alkalis), and nephelinitic (richer in alkalis) (Macdonald & Abbott, 1983). In comparison, lavas vary greatly in chemical composition, however, due to physical difficulties in sampling, analysis can only be done on solid material that has been cooled. The earliest observed lavas of young, rapidly growing Hawaiian volcanoes often consist of alkalic basalt and basanite lavas (Langenheim & Clague, 1987). A transition from alkalic to tholeiitic basalt happens during the main constructional stage of the volcano, and is substantiated by the analysis of materials from various accumulated eruptions (Dalrymple, Silver, & Jackson, 1973). The shift from shield to post-shield and eventually rejuvenated stage eruptions is also transitional, changing from tholeiitic to alkalic basaltic lavas. Alkalic post-shield and associated differentiated lavas (ankaramite, hawaiite, mugearite, trachyte, and nepheline basanite) develop late in the sequence and begin by forming a relatively thin cap that covers the main shield (Langenheim & Clague, 1987). Finally, approximately several million years after the construction of the main volcanic edifice, a period of inactivity and continued degradation occurs, and small amounts of nephelinitic and associated basalts may sporadically erupt (Dalrymple, Silver, & Jackson, 1973). In addition to chemical and mineral composition of lava materials, weathering and erosion rates, water chemistry can have a significant effect on the chemical variation of the Hawaiian aquifer environment.

Table 2. Average Chemical Composition of Rock Types in Hawaiʻi (Wt. %)

Elemental Composition	Alkalic Basalt	Hawaiite	Trachyte	Oceanite	Tholeiitic Basalt	Melilite and Nephelinite
SiO_2	46.5	48.6	61.7	46.4	49.4	36.7
TiO_2	3.0	3.2	0.5	2.0	2.5	2.8
Al_2O_3	14.6	16.5	18.0	8.5	13.9	10.8
Fe_2O_3	3.3	4.2	3.3	2.5	3.0	5.6
FeO	9.1	7.4	1.5	9.8	8.5	8.8
MnO	0.1	0.2	0.2	0.2	0.2	0.1
MgO	8.2	4.7	0.4	20.8	8.4	12.7
CaO	10.3	7.8	1.2	7.4	10.3	13.7
Na_2O	2.9	4.4	7.4	1.6	2.1	3.9
K_2O	0.8	1.6	4.2	0.3	0.4	0.9
P_2O_5	0.4	0.7	0.2	0.2	0.3	1.1

* The tholeiitic series comprises the following rocks, arranged in order from the most basic (magnesium- and iron-rich) to the most acidic (silica-rich): oceanite, tholeiitic olivine quartz basalt, rhyodacite. The alkalic series similarly consists of: ankaramite, alkalic olivine basalt, alkalic basalt, hawaiite, mugearite, trachyte. The nephelinites and basanites are even more strongly alkalic than the rocks of the main alkalic series, and form a by themselves. Source: Macdonald, G.; Abbott, A.; Peterson, F., 1983. Volcanoes in the Sea. Honolulu, Hawaiʻi: University of Hawaiʻi Press.

Table 3. (Continued) Average Chemical Composition of Rock Types in Hawaiʻi (Wt. %)

Elemental Composition	Mugearite	Nephelinite	Ankaramite	Nepheline Basanite	Rhyodacite
SiO_2	51.9	38.7	44.1	44.3	66.0
TiO_2	2.6	2.7	2.7	2.6	0.7
Al_2O_3	16.6	10.8	11.2	12.8	15.5
Fe_2O_3	4.2	5.8	2.8	3.4	1.4
FeO	6.2	7.8	9.9	9.2	1.9
MnO	0.2	0.1	0.2	0.2	0.1
MgO	3.6	13.6	15.1	11.0	1.5
CaO	6.3	13.0	10.7	10.5	2.8
Na_2O	5.2	4.0	1.7	3.6	4.4

K_2O	2.0	1.1	0.5	1.0	3.3
P_2O_5	0.9	1.0	0.3	0.4	0.5

* The tholeiitic series comprises the following rocks, arranged in order from the most basic (magnesium- and iron-rich) to the most acidic (silica-rich): oceanite, tholeiitic olivine quartz basalt, rhyodacite. The alkalic series similarly consists of: ankaramite, alkalic olivine basalt, alkalic basalt, hawaiite, mugearite, trachyte. The nephelinites and basanites are even more strongly alkalic than the rocks of the main alkalic series, and form a by themselves. Source: Macdonald, G.; Abbott, A.; Peterson, F., 1983. Volcanoes in the Sea. Honolulu, Hawaiʻi: University of Hawaiʻi Press.

Table 4. Hawaiian Eruptive Products

Eruptive Stage	Rock Type	Eruption Rate	Volume (%)
Pre-Shield	Basanite	Low	-3
	Alkalic Basalt		
	Transitional Basalt		
Shield	Tholeiitic Basalt	High	95-98
	Picritic Tholeiitic Basalt		
Post-Shield	Alkalic Basalt	Low	-1
	Transitional Basalt		
	Ankaramite		
	Hawaiite		
	Mugearite		
	Benomoreite		
	Trachyte	Very Low	< 1
Rejuvenated	Alkalic Basalt		
	Basanite		
	Nephelinite		
	Nepheline Melilitite		

Source: Tectonics, Geochronology, and Origin of the Hawaiian-Emperor Chain (Claque & Dalrymple, 1989)

2.2 Groundwater Chemistry

Table 5. Average Elemental Composition of Surface, Ground, and Geothermal Water in Hawaii (mg/l)

Elemental Composition	Seawater	Groundwater	Geothermal Fluids	Rainwater

SiO_2	4.0	45.0	561.0	0.0
Na	10760.0	27.0	4420.0	4.5
K	399.0	3.0	910.0	0.4
Ca	412.0	10.0	177.0	0.9
SO_4	2712.0	13.0	15.4	1.8
Mg	1292.0	31.0	0.2	1.1
Cl	19353.0	34.0	7920.0	7.9

Source: Waller, D, 2015. Identification of Geothermal Resources in Hawai‘i Utilizing Aqueous Geochemistry

The chemistry of water in Hawai‘i’s geothermal systems largely indicate the geological, physical, and hydrological characteristics of the reservoir environment. The three fundamental processes that govern the chemical composition of water in Hawai‘i’s geothermal systems are: mixing of ascending hydrothermal fluids and cold circulatory water (groundwater and/or seawater), composition of source water (groundwater and/or seawater), and hydrothermal alteration of minerals and rocks (Druecker & Fan 1976) (Schuchmann, 2015). In Hawai‘i, apart from hot springs and steam vents that surround active volcanoes on the Island of Hawai‘i (Fowler et al., 1980), most geothermal systems lack surface manifestations. The lack of surface indicators limits the identification of prospective sample locations, however, chemical signatures in groundwater wells can reveal imperative information on subsurface conditions and processes that are not easily accessible through geological and geophysical means (Cox et al. 1979). This aqueous chemical signature can deduce the range of elements that may have been selectively dissolved in the groundwater while others precipitated out, resultant of physical processes and chemical reactions within the aquifer environment as reflected in the various Hawaiian water types (Table 4) (Plummer, Bexfield, & Anderholm, 2003). The significance of observing certain chemical signatures from groundwater wells can be a qualitative indication of exposure to subsurface heat.

2.3. Chemical Geothermal Indicators in Hawai‘i

There are many geothermal indicators, although, many have been applied to Hawaiian groundwater with minimal success, however, based on research, the chemical species that have been commonly associated with geothermal anomalies in Hawai‘i are: silica (SiO_2) content, chloride/magnesium (Cl/Mg) ratio, and sulfate/chloride (SO_4/Cl) ratio (Waller, 2015; Schuchmann, 2015; Cox and Thomas, 1979a). Chemical Geothermal Indicators also known as Groundwater Geothermal Indicators are an important geochemical tool for the detection and development of geothermal resources. During exploration, they are used to indicate subsurface heat by analysis of chemical composition of the groundwater. Central to the application of hydrogeothermal indicators in Hawai‘i, is basic knowledge of the chemical composition of the source rock and water, chemical reactions between source rock and water, and subsurface conditions that make the indicators effective (Waller, 2015). The concentration of dissolved solutes, behavior of chemical reactants, and the chemical composition of source water establish the framework of the chemical geothermal indicators in this study, however, the use of these indicators for geothermometry goes beyond the scope of this work.

2.3.1 Silica Concentration

One method used to indicate subsurface heat and mean aquifer temperature, is to measure the concentration of dissolved silica in groundwater (Hannah, Lautze et al., 2017a; Cox et al., 1979b). Silica is the second most abundant element found on earth, and in Hawaii is sourced by the composition of resident basalts. On average, silica concentrations of groundwater in Hawaii range from 0.2 to 85 ppm depending on the source water categorization (Table 3) (Davis, 1969; Cox and Thomas, 1979b). An increase in subsurface temperature in an aquifer region can be inferred by applying the linear relationship between the amount of dissolved silica and associated water temperature (Fournier & Rowe, 1966). In general, the dissolution of silica in aqueous solutions in a geothermal reservoir occurs as water interacts with rock at elevated temperatures. It is assumed, however, that chemical alteration caused by precipitation or dilution has not occurred and the reservoir is in equilibrium (Cox et al. 1979a). Although this an idealized situation because chemical equilibrium cannot be assumed in basaltic aquifers, furthermore, the dispersal of silicate minerals can be difficult to ascertain in most aquifers (Davis, 1969). Concentrations of dissolved silica that indicate an elevated subsurface heat anomaly warrant further geochemical test indications for validation.

Identifying regions of anomalous subsurface temperature in Hawaiʻi using dissolved silica concentrations have been moderately effective, however, validation of this qualitative indicator can be difficult to establish because it is influenced by a variety of factors (Cox et al., 1979a). In Hawaii, factors that can cause elevated concentrations of dissolved silica in groundwater are: the addition of agricultural phosphates (Fox et al. 1967), weathering processes, rates of recharge and irrigation (Cox et al. 1979b), burning of agricultural wastes, chemical composition of rock and soil type, reduction of soil pH, length of residence time (Davis 1969), and climatic variables. Generally, in shallow aquifers where dissolved silica reaches high concentrations, recharge from irrigation return flow and erosional processes commonly occur, and areas of lower concentrations can generally be attributed to shorter residence times and higher recharge rates (Cox et al. 1979b). Given that the concentration of silica can be affected by both natural and anthropogenic processes, the use of silica as a geothermal indicator requires caution. Although the effects of these factors have been documented, field data suggests reasonably consistent silica values for any given aquifer lithology in Hawaii (Davis, 1969). While the effect of temperature on silica concentrations can be substantial, it is often difficult to determine between thermal and non-thermal groundwater solely based on an aqueous thermal signature of silica.

Table 6. Average Silica Concentration in Surface, Ground, and Geothermal Water in Hawai'i

Silica Concentration (mg/l)	Water Category
561	Geothermal Water (Puna Area, Hawaii)
4	Seawater
45	Groundwater
0	Rainwater

Source: Adapted from Table 2 and (Lautze et al., 2017a; Waller, 2015)

2.3.2 Cl/Mg Ratio

The chloride/magnesium ion ratio has been a reliable distinguisher between thermal and non-thermal groundwater and can also be used to indicate subsurface heat (Cox and Thomas, 1979a). Located in the middle of the Pacific Ocean, a major dissolved constituent of groundwater in Hawaii is chloride, extant in the form of sea salt. The chloride ion is fairly non-reactive in groundwater and its concentration is relatively consistent despite thermal elevation. In contrast, the magnesium ion, in the presence of a thermal resource, is extremely susceptible to temperature dependent reactions, and can result in concentrations that are severely depleted in magnesium (Lautze et al., 2017a). On average, the concentration of chloride and magnesium in seawater is 19,353 mg/l and 1,292 mg/l, respectively, thus, chloride/magnesium ion ratio of seawater equates to ~ 15.0 (Resing & Sansone, 1999; Schuchmann, 2015). Most non-thermal groundwater and surface water in Hawaii, maintain a chloride/magnesium ion ratio in the range of 1-8 (Cox and Thomas, 1979b). Any aqueous reservoir demonstrating a chloride/magnesium ion ratio greater than seawater, can indicate exposure to a nearby thermal source (Waller, 2015). Therefore, this chemical signature in groundwater can be used as a geothermal indicator with relative success, however, this ratio can also be influenced by external variables.

Table 7. Typical Ratio of Chloride to Magnesium in Surface, Ground, and Geothermal Water in Hawaii

Ratio	Water Category
41904.8	Geothermal Water (Puna Area, Hawaii)
15.0	Seawater
1.1	Groundwater
7.2	Rainwater

Source: Adapted from Table 2 and (Lautze et al., 2017a; Waller, 2015)

2.3.3 SO_4/Cl Ratio

A similar geothermal indicator to the chloride/magnesium ion ratio is the sulfate/chloride ion ratio. As stated earlier, the average concentration of chloride in seawater is 19,353 mg/l and the average concentration for sulfate in seawater is 2,712 mg/l, thus, a standard seawater sulfate/chloride ion ratio is ~ 0.14 (Kroopnick, 1977). The sulfate/chloride ion ratio can signal a nearby subsurface heat anomaly in two ways: an ionic ratio that is greater or less than the standard for seawater (0.14). A sulfate/chloride ion ratio that is less than 0.14 occurs when an aqueous solution is heated above 200 degrees, the precipitation of gypsum transpires, and sulfate is depleted from the solution (Libes, 2011). A sulfate/chloride ion ratio that is greater than 0.14 generally occurs in areas of volcanic activity, where geothermal fluids have reached a boiling point, and steam has actively been released. When steam loss (boiling) occurs, hydrogen sulfide ascends with the steam and may be transferred to an adjoining water body. The hydrogen sulfide mixes with the cooler water, oxidizes, and the remaining solution has a sulfate/chloride ion ratio that is greater than 0.14 (Fournier & Truesdell, 1973). Although less common, an elevated ionic ratio may be difficult to assign a value because of the unknown amount of seawater mixing, therefore, an anomalous ratio above seawater should be independently analyzed.

Table 8. Typical Ratio of Sulfate to Chloride in Surface, Ground, and Geothermal Water in Hawai‘i

Ratio	Water Category
0.002	Geothermal Water (Puna Area, Hawaii)
0.140	Seawater
0.382	Groundwater
0.228	Rainwater

Source: Adapted from Table 2 and (Lautze et al., 2017a; Waller, 2015)

2.3.4 Temperature

While not an aqueous geochemical indicator, groundwater temperature profiles have been used throughout Hawaii to identify areas of subsurface heat (State of Hawaii, 1984). In Hawai‘i, unique hydrogeologic environments occur and divisions among aquifer waters are not always well defined, nevertheless, there are three basic groundwater types: dike-impounded, sedimentary and alluvial, and basal. These aquifer waters have associated temperatures that can range from 18℃ to 26℃ (Table 8), however, a well temperature of 27℃ and above does not automatically signify the presence of a subsurface heat anomaly (Cox et al. 1979a). A temperature anomaly can occur with the addition of thermal fluids from a neighboring geothermal source, although, several factors can cause an elevation in the temperature measurement. Factors that can influence temperature increase in groundwater include: surface and subsurface temperature oscillations, frictional flow, mixing of irrigation and/or saline water, altitude recharge fluids and the frequency of pumping (State of Hawaii, 1984). Caution must be applied when utilizing comparisons of well temperature and aqueous chemistry during analysis to prevent ambiguous interpretation of data.

Table 9. Types and Associated Average Temperatures of Aquifers in Hawai‘i

Aquifer Type	Temperature ℃	Indications
Dike Impounded	18 – 21	High Elevation Rainfall Recharge
Sedimentary and Alluvial	20 – 24	Mixing of High-Level Recharge and Lower Altitude Surface Recharge
Basal	22 – 26	Direct Surface Recharge

Source: Investigation of Geothermal Potential in the Waianae Caldera Area, Western Oahu, Hawai‘i (Cox et al., 1979)

3. METHODS

3.1 Well Identification

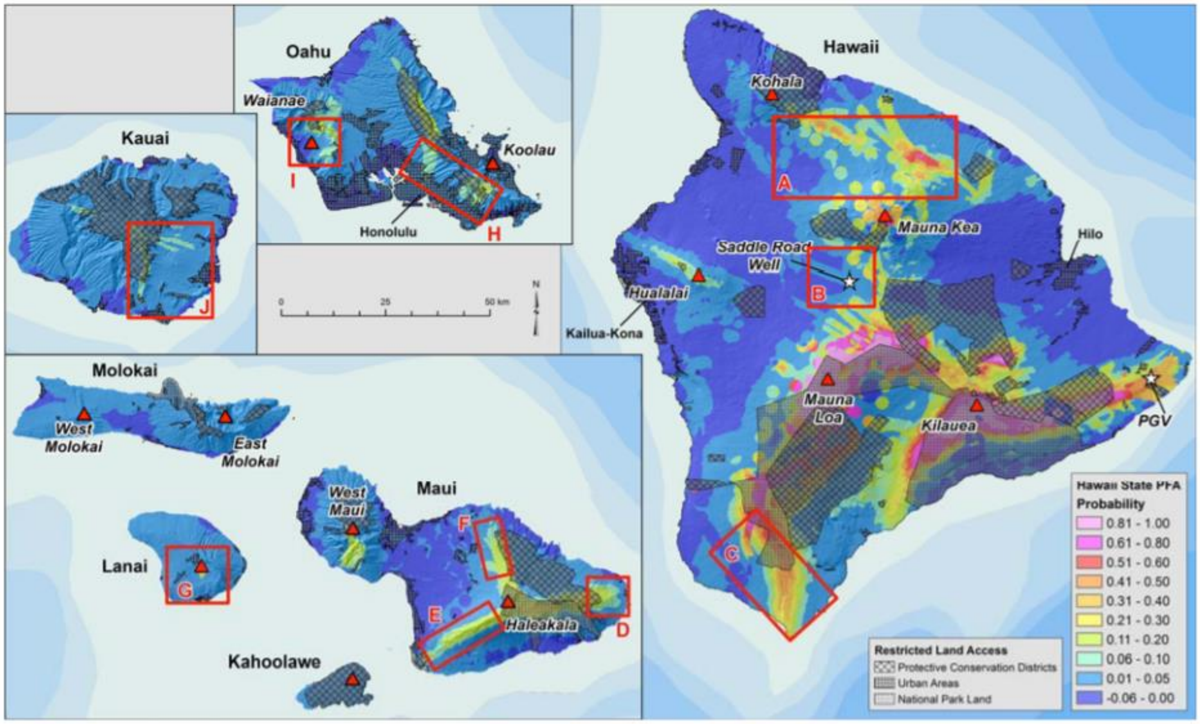


Figure 6. Geothermal Play Fairway Probability Analysis for the State of Hawai‘i. Probabilities of a geothermal resource are colored. Areas with restricted land access are shown in stippled and crosshatched patterns (e.g., National Parks lands, protective conservation districts, and urban areas). Red boxes outline areas proposed for Phase 2 study. Red triangles designate the calderas of the main shield volcanos. White stars mark the locations of the Saddle Road well and Puna Geothermal Ventures (PGV) (Lautze et al., 2017b).

Water samples were collected and analyzed in ten locations across the State of Hawai‘i that were identified in the Play Fairway Project as areas of geothermal resource (Fig.7). The Phase 1 prospect probability map was generated based on existing data, and areas were selected based on elevated subsurface heat, permeability, and fluid. These sample sites included a single sampling area on both Kauai and Lanai, two sampling areas on Oahu, and three areas on Maui and Hawai‘i Island. A total of 61 samples were collected: 60 from existing wells and 1 spring was sampled in an area were no wells exist (Mauna Kea, Hawaiʻi Island). The geographic location of each well sampled within the selected areas, was determined within a few meters with a hand-held global positioning system (GPS).

3.2 Sample Collection

Water samples were collected using standard methods that have been described in detail elsewhere (Bergfeld and others, 2013). Water temperature, specific conductance, pH, total dissolved solids (TDS), oxidation reduction potential (ORP), and dissolved oxygen (DO) were measured on site using a hand-held YSI Pro Plus Meter. A continuous flow of pumped water from the wellhead was directed into a plastic container housing the measuring probes. Data was collected and recorded on a field data sheet. Note that the temperature reported for each well sampled is that of the water temperature in the collection container, not the down-hole temperature. Briefly, water collected for chemical analysis was filtered on-site into plastic bottles using a hose/funnel apparatus and 0.45-micrometer (µm) filters. The bottle for cation analysis was acidified to pH 2 with nitric acid. Glass bottles were filled with unfiltered water for alkalinity determinations made at the end of the work day. All samples come from source water, therefore, selected samples were not chemically treated to meet drinking water standards.

3.3 Lab Analysis

Water samples were analyzed at three different University of Hawaiʻi laboratories: The Water Resource Research Center Analytical Chemistry Laboratory, the SOEST Laboratory for Analytical Biochemistry, and the Biogeochemical Stable Isotope Facility. Water samples were analyzed for major ions using an ion chromatograph at the Water Resource Research Center Environmental and Water Laboratory using the standard Environmental Protection Agency Method (Pfaaf, 1993; Hautman & Munch, 1997). At the SOEST Laboratory for Analytical

Biochemistry, analysis of samples for trace metals and silica were completed with the Varian Vista MPX ICP optical emission spectrometer following standard methods (Martin et al., 1992). Although not analyzed in this thesis, the Biogeochemical Stable Isotope Facility analyzed samples for oxygen ($^{18}\mathrm{O}$), deuterium (D), and carbon-13 ($^{13}\mathrm{C}$) isotopes. Isotopes of $^{13}\mathrm{C}$ were measured using an automated headspace sampling and continuous-flow mass spectrometry (Torres, Mix, & Rugh, 2005). The $^{18}\mathrm{O}$ and D isotopes are measured using a Picarro cavity ring down spectrometer (Godoy, Godoy, & Neto, 2012). Alkalinity of water samples were determined by Robert Whittier.

3.4 Quality Control: Charge Balance

All aqueous solutions must be electrically neutral and the use of the charge balance error in percent (CBE) was applied to all water samples to judge validity and quality. It is well documented that within a water sample, the number of positively charged ions in solution (cations) should balance the number of negatively charged ion (anions):

CBE = $\frac{\sum \mathrm{cations} - |\sum \mathrm{anions}|}{\sum \mathrm{cations} + |\sum \mathrm{anions}|} \times 100$) (Aqion, 2015).

An acceptable balance for routine water quality analysis is generally considered to be less than 5%, although, it is been recognized that average CBE values for ground and surface waters are between 1.55% to 9.34% (Fritz, 1994), hence, making CBE values of ± 10% satisfactory. Possible causes for electrical imbalances are: lab errors during analysis, sampling procedure error, the use of an unfiltered water sample, dissolved species not measured, and constitute precipitate in sample container (Aqion, 2015). Of the 61 groundwater samples obtained, only 53 met this criterion.

3.5 Criteria for Anomalous Indicators

The following criteria for anomalous indicators were determined, according to compiled historical data and research, as chemical signatures that could indicate subsurface heat (Table 9). While general in application, the chosen aqueous geothermal indicators: silica concentration, chloride/magnesium, sulphate/chloride, and elevated temperature, have had relative success in the complex aquifer environment of Hawaii. The average silica concentration of groundwater in Hawaii is less than 60 mg/l, concentrations ranging from (60 – 85) mg/l were considered to be altered by irrigation, and any concentration > 85 mg/l was considered anomalous. The standard chloride/magnesium ion ratio for non-thermal water in Hawai‘i is ≤ 8, ratios ranging from 12.9 – 15 were considered elevated, and any ratio above the standard chloride/magnesium ion ratio of seawater (15/1) was considered anomalous. The typical sulphate/chloride ion ratio can be indicative of subsurface heat at two different thresholds: any ratio less than the sulphate/chloride ion ratio seawater (0.14) and any ratio above 1. Finally, temperatures greater than 29℃ were considered anomalous, temperatures of (>27 – 29)℃ were considered elevated, and the temperatures of (22 – 27) ℃ is the standard temperature range of groundwater wells in Hawai‘i. Although acceptable water analyses have a charge balance error less than ± 5%, in this water chemistry analysis, all water samples with complete water chemistry data were analyzed, and only charge balances of less than ± 10% were considered during map generation and final analysis.

Table 10. Criteria for Anomalous Indicators

SiO_2 Concentration	
> 85 mg/l	Anomalous
(60 to 85) mg/l	Irrigation
(0 to 60) mg/l	Standard
Cl/Mg Ion Ratio	

> 15.0	Anomalous
12.9 to 15.0	Elevated
8.0	Standard
SO_4/Cl Ion Ratio	
< 0.14	Anomalous
> 1.0	Anomalous
0.14	Standard
Temperature ℃	
> 29°C	Anomalous
(>27 to 29)°C	Elevated
(22 to 27)°C	Standard

4. RESULTS

4.1 Results for O'ahu

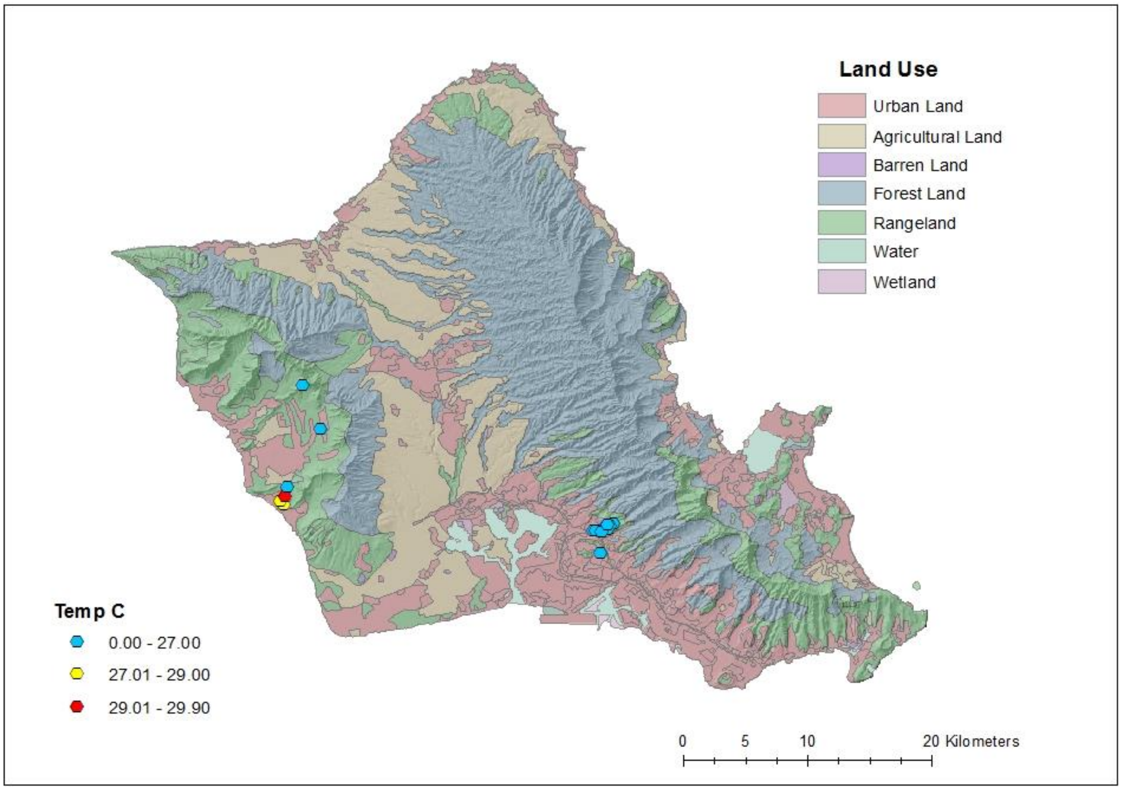


Figure 7. Well Temperature in Degrees Celsius (℃) for the Island of O'ahu. Land use is located to the right and colored. The range of temperature is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analy

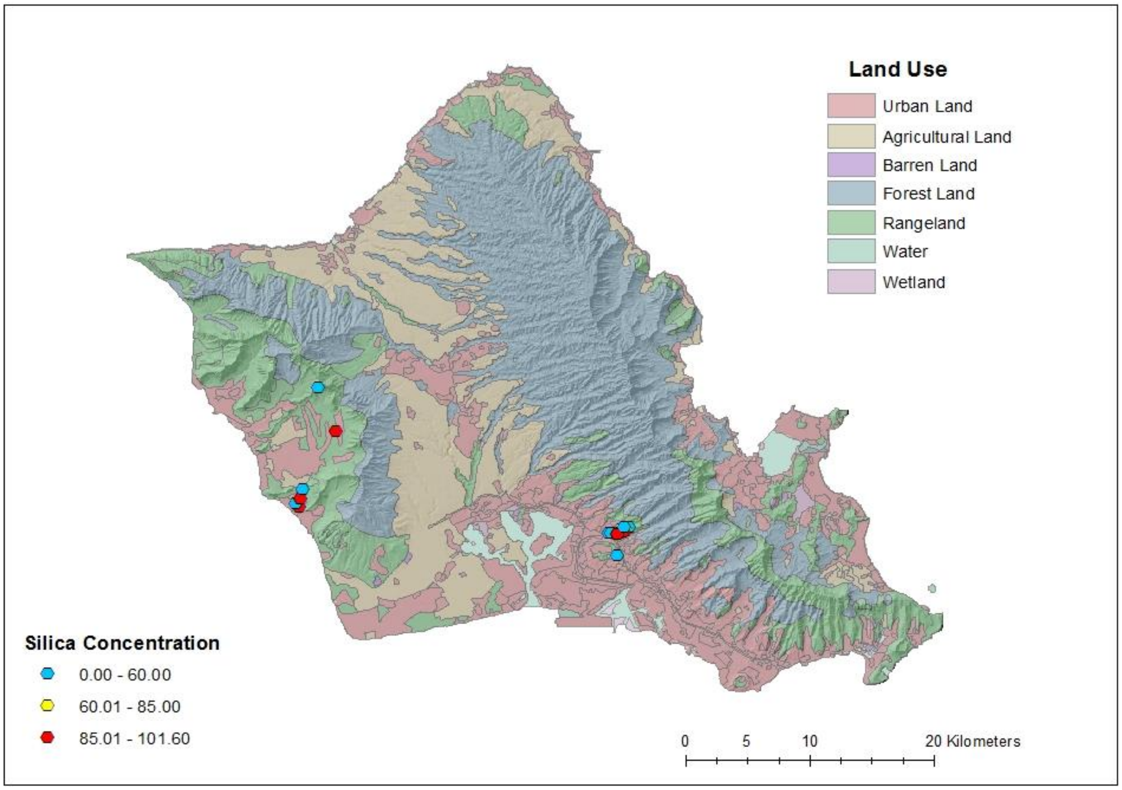


Figure 8. Silica Concentration (ppm) for the Island of O‘ahu. Land use is located to the right and colored. The range of silica concentration is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

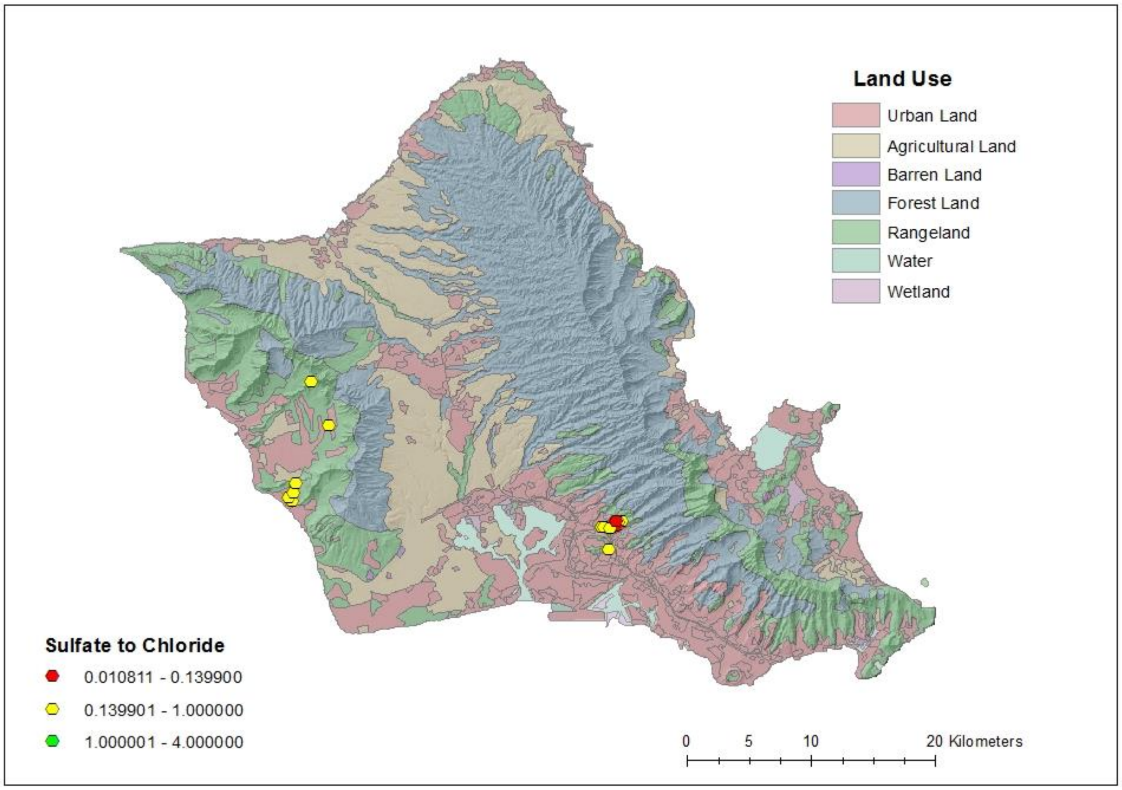


Figure 9. Sulfate to Chloride Ion Ratio for the Island of O'ahu. Land use is located to the right and colored. The sulfate/chloride ion ratio range is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

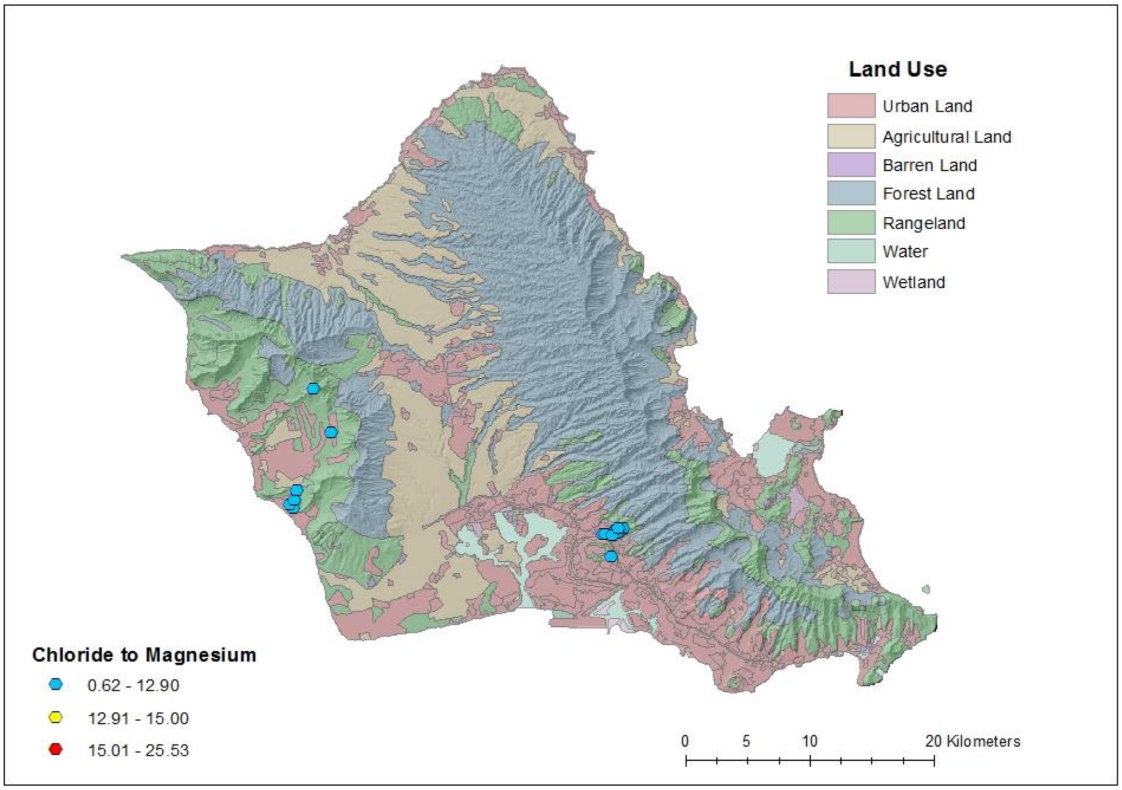


Figure 10. Chloride to Magnesium Ion Ratio for the Island of O‘ahu. Land use is located to the right and colored. The chloride/magnesium ion ratio is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

The Play Fairway Analysis (PFA) identified seven anomalous wells on the Island of O‘ahu. Four anomalous wells were located within the south shore Koolau sampling site and three wells were located within the Waianae sampling site. All of the anomalous wells in the Koolau sampling site were located in the Red Hill area, however, there were two separate locations within the Waianae sampling site that presented anomalies. Two anomalous wells were located in the PVT area and one anomalous well was located in the Lualualei area within the Waianae sampling location. Three of the anomalous Red Hill wells (RHMW03, RHMW02, and RHMW05) had a silica concentration anomaly, however, RHMW03 also exhibited an elevated well temperature , and RHMW02 and Halawa Deep Monitor at 851 feet indicated a sulphate/chloride ion ratio anomaly. All of the anomalous PVT wells (MW1, MW2, MW3, and MW4) displayed either an elevated well temperature or temperature anomaly, however, MW1 and MW3 also presented a silica concentration anomaly. Well number 3-2607-001 (Laulaulei) only presented a silica concentration anomaly.

4.2 Results for Kaua'i

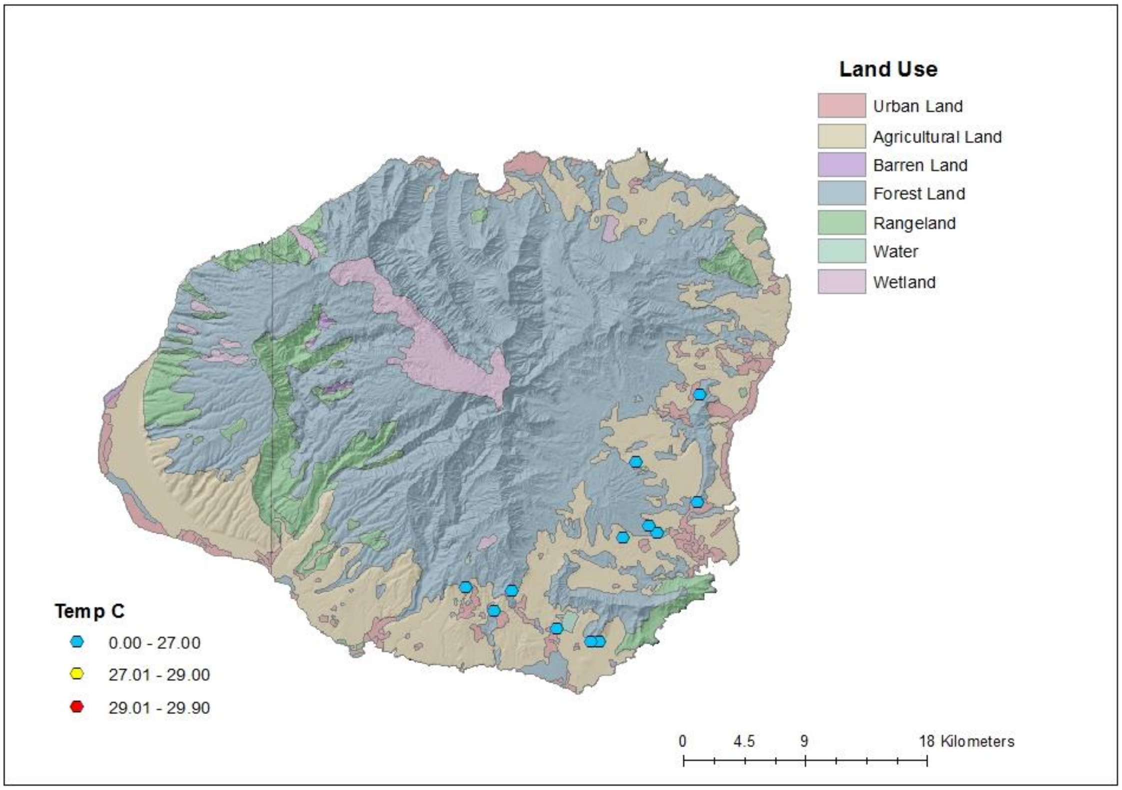


Figure 11. Well Temperature in Degrees Celsius (℃) for the Island of Kaua'i. Land use is located to the right and colored. The range of temperature is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

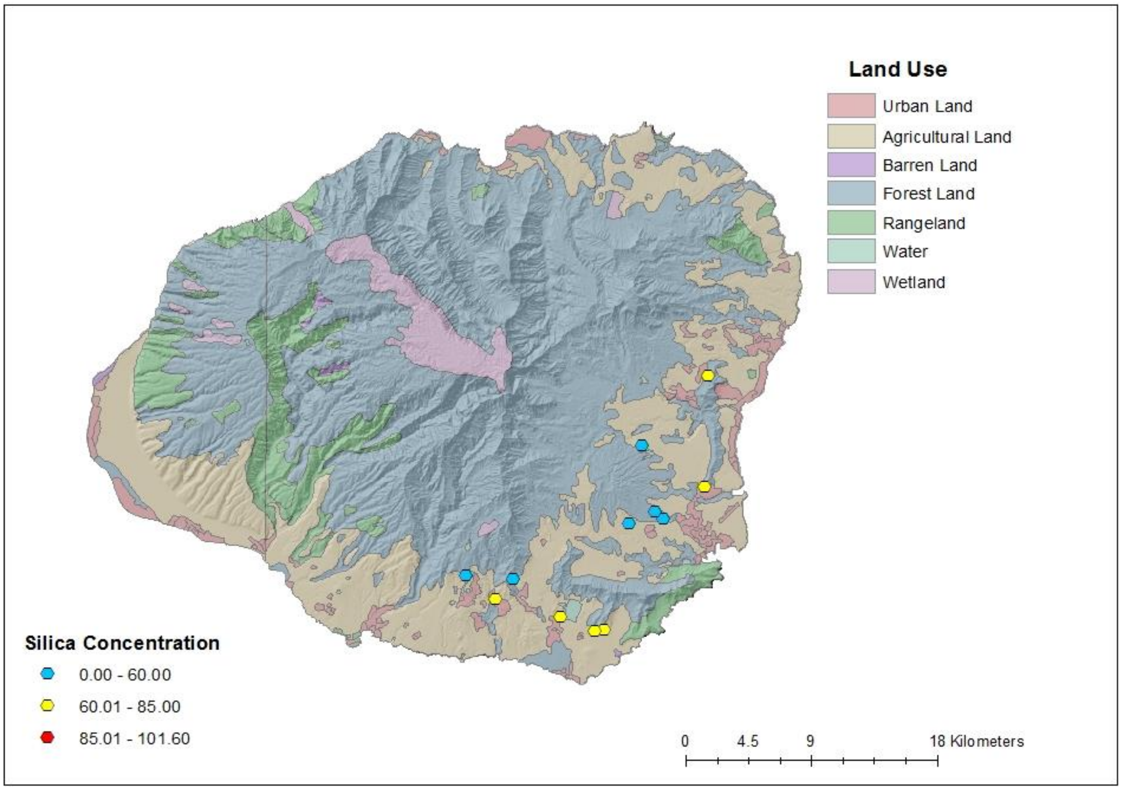


Figure 12. Silica Concentration (ppm) for the Island of Kaua‘i. Land use is located to the right and colored. The range of silica concentration is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

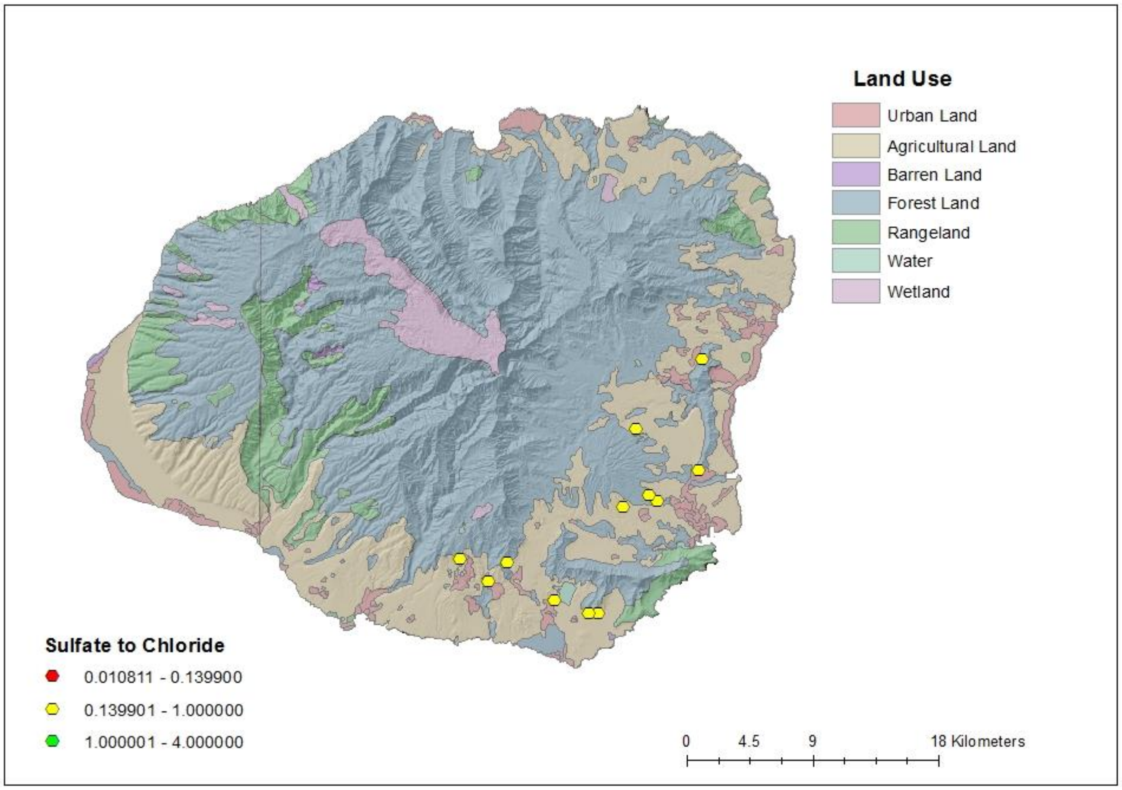


Figure 13. Sulfate to Chloride Ion Ratio for the Island of Kaua‘i. Land use is located to the right and colored. The sulfate/chloride ion ratio range is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

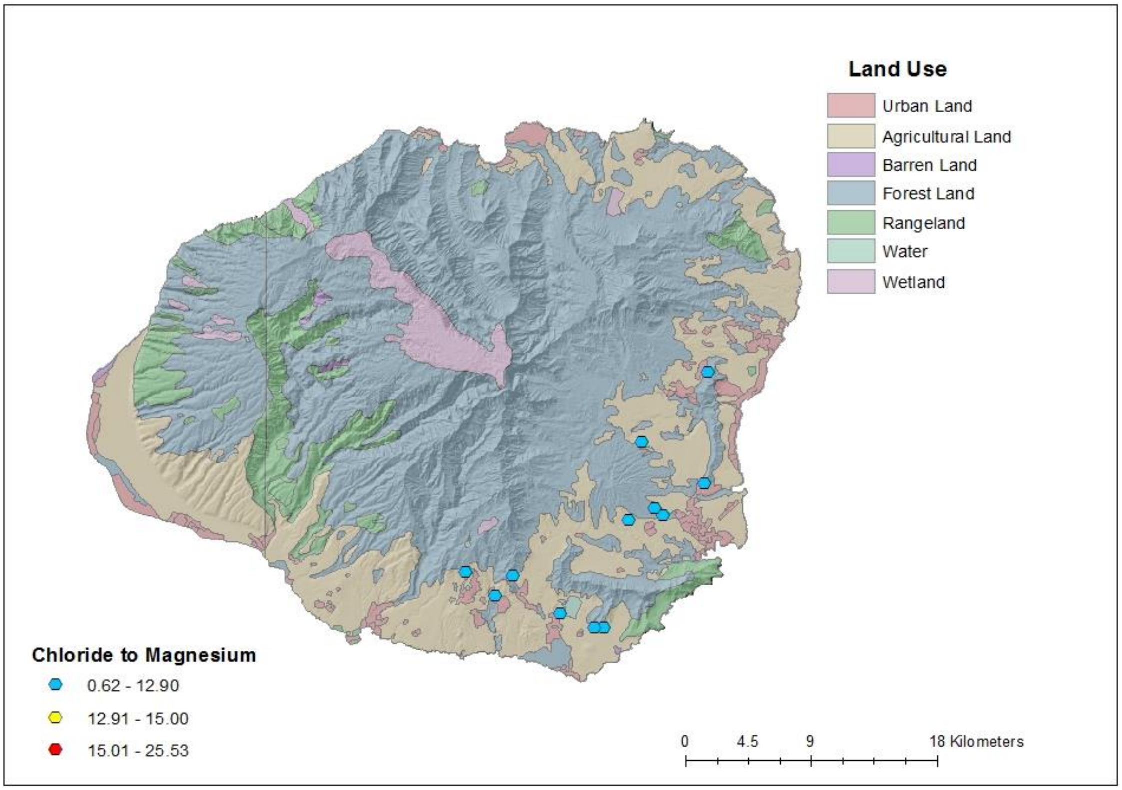


Figure 14. Chloride to Magnesium Ion Ratio for the Island of Kaua'i. Land use is located to the right and colored. The chloride/magnesium ion ratio is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

The Play Fairway Analysis (PFA) did not identify any anomalous wells on the Island of Kaua'i, based on the criteria previously stipulated for anomalous indicators.

4.3 Results for Maui

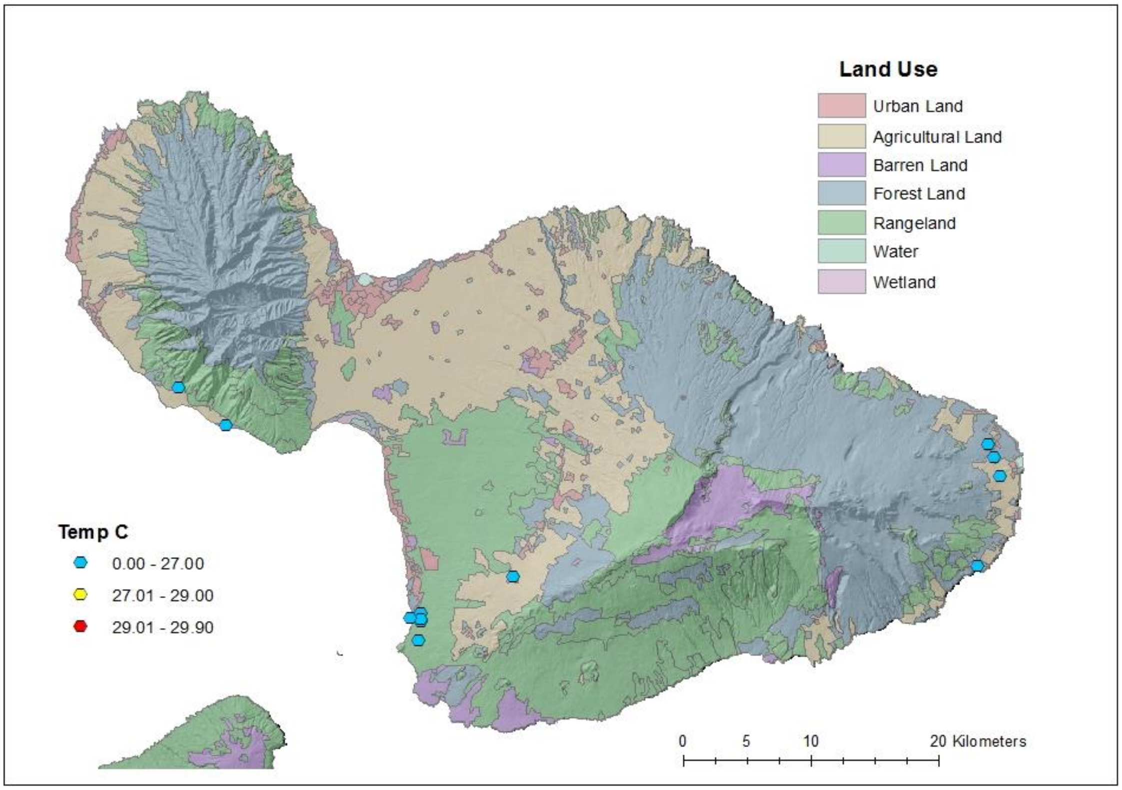


Figure 15. Well Temperature in Degrees Celsius (℃) for the Island of Maui. Land use is located to the right and colored. The range of temperature is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

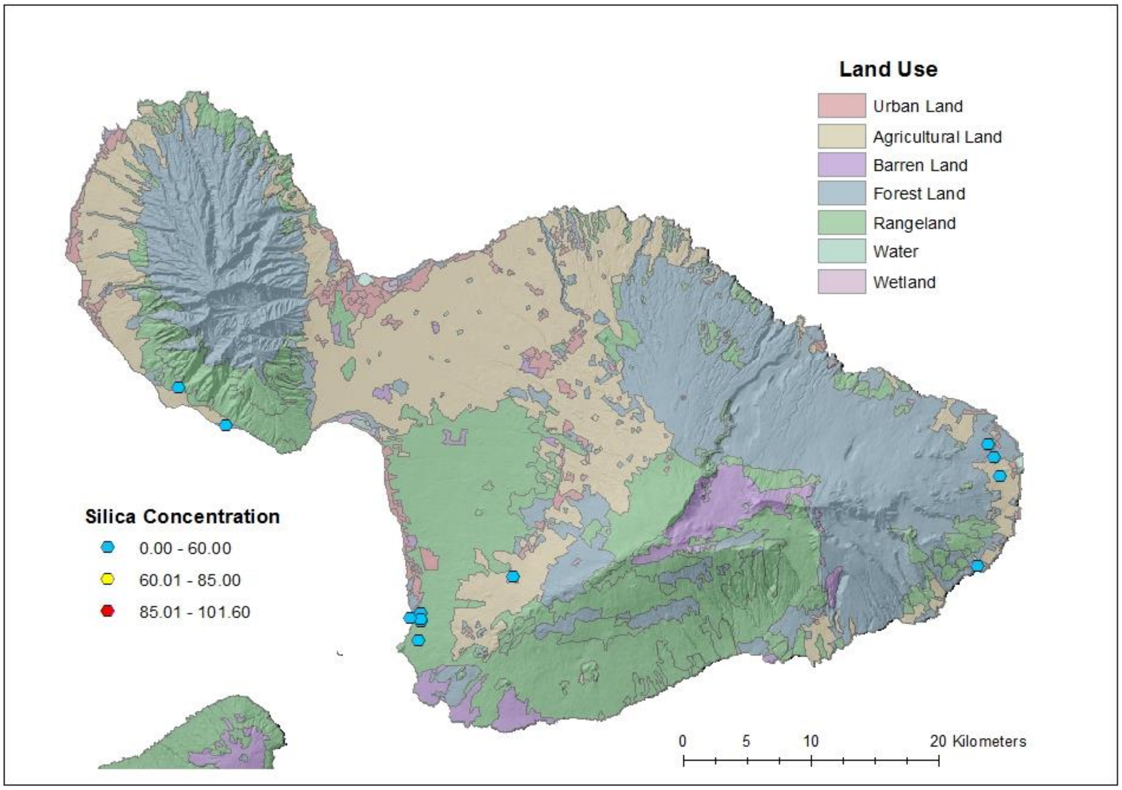


Figure 16. Silica Concentration (ppm) for the Island of Maui. Land use is located to the right and colored. The range of silica concentration is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

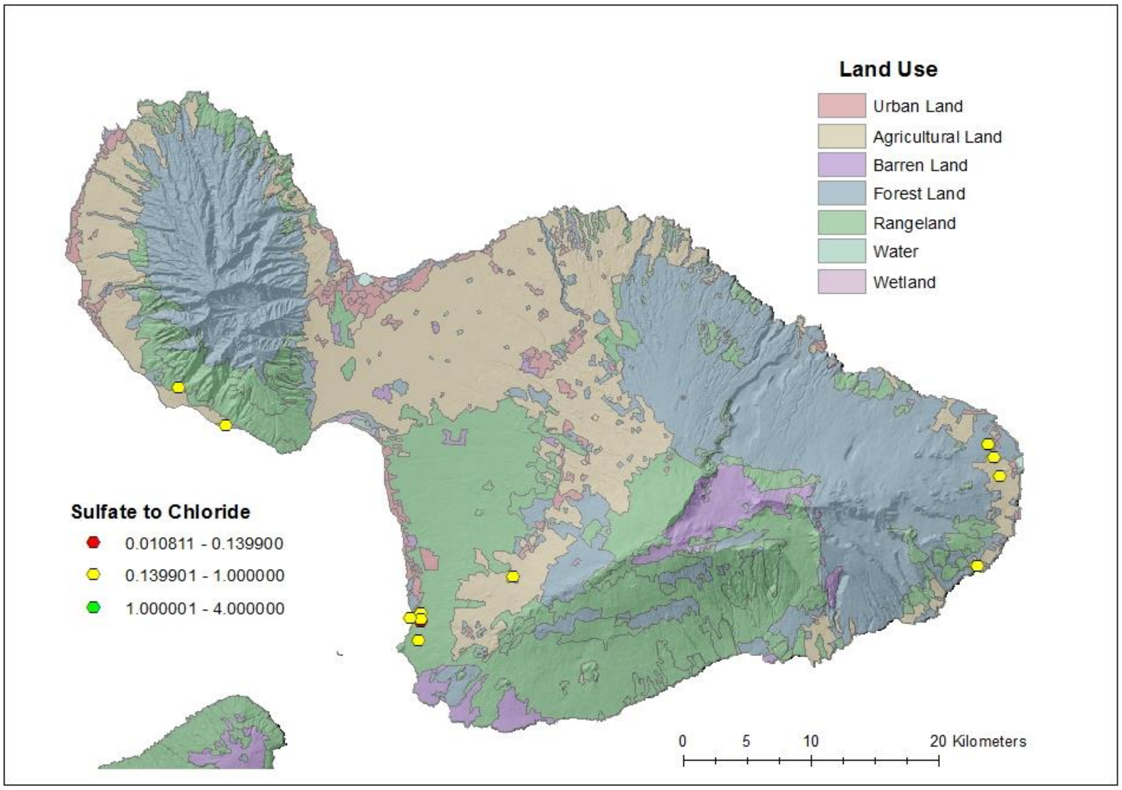


Figure 17. Sulfate to Chloride Ion Ratio for the Island of Maui. Land use is located to the right and colored. The sulfate/chloride ion ratio range is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

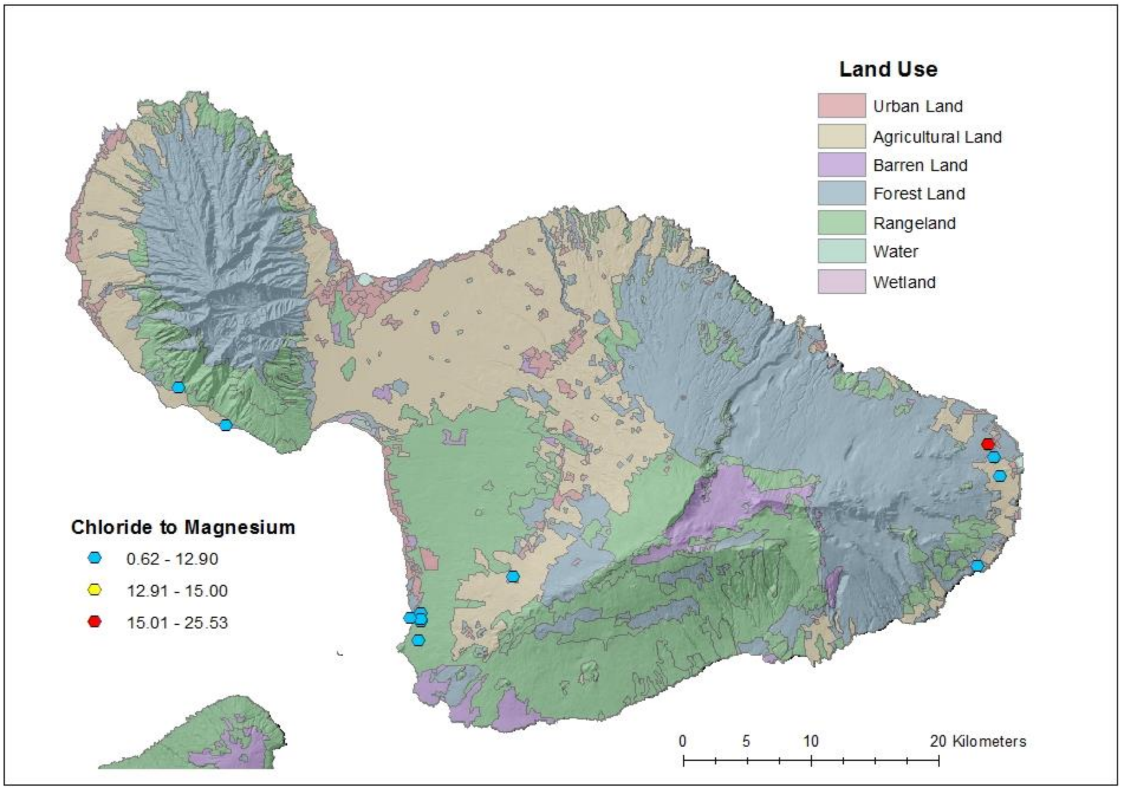


Figure 18. Chloride to Magnesium Ion Ratio for the Island of Maui. Land use is located to the right and colored. The chloride/magnesium ion ratio is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

The Play Fairway Analysis (PFA) identified one anomalous well on the Island of Maui. This well was located within the Haleakala east rift zone sampling site area. Well number 6-4600-003 (Wakiu B) indicated a chloride/magnesium ion ratio anomaly.

4.4 Results for Lānaʻi

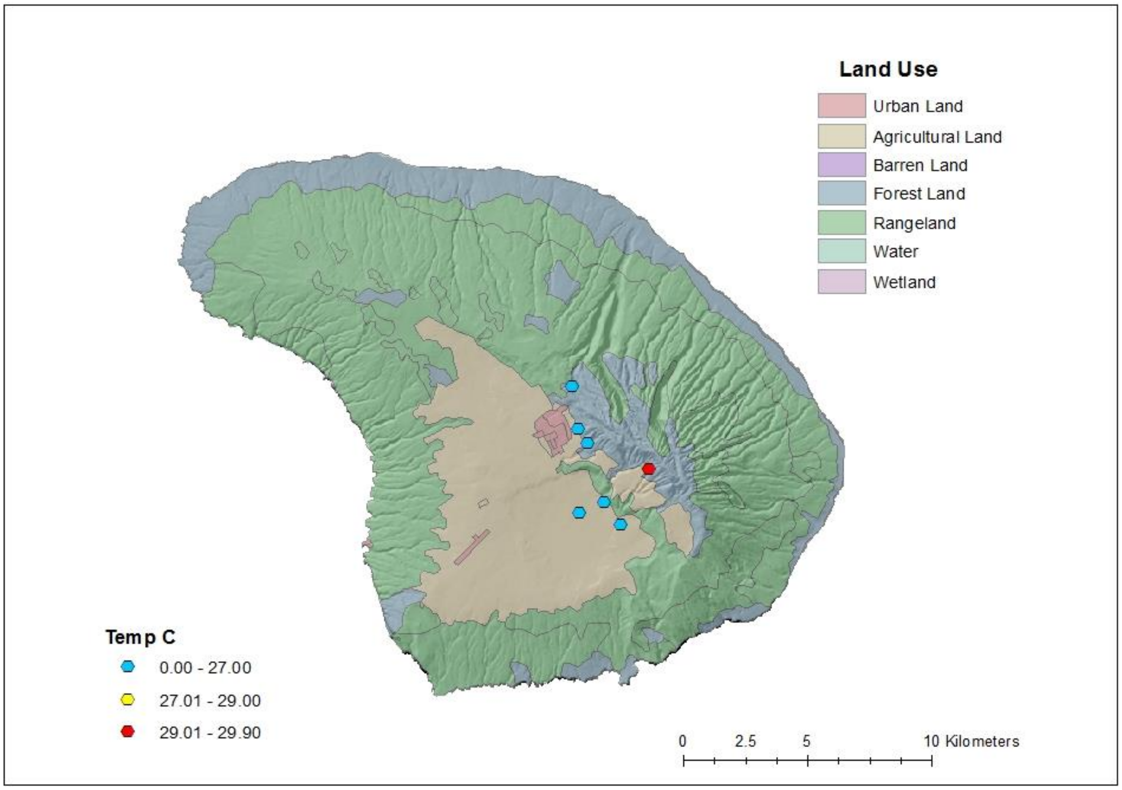


Figure 19. Well Temperature in Degrees Celsius (℃) for the Island of Lānaʻi. Land use is located to the right and colored. The range of temperature is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

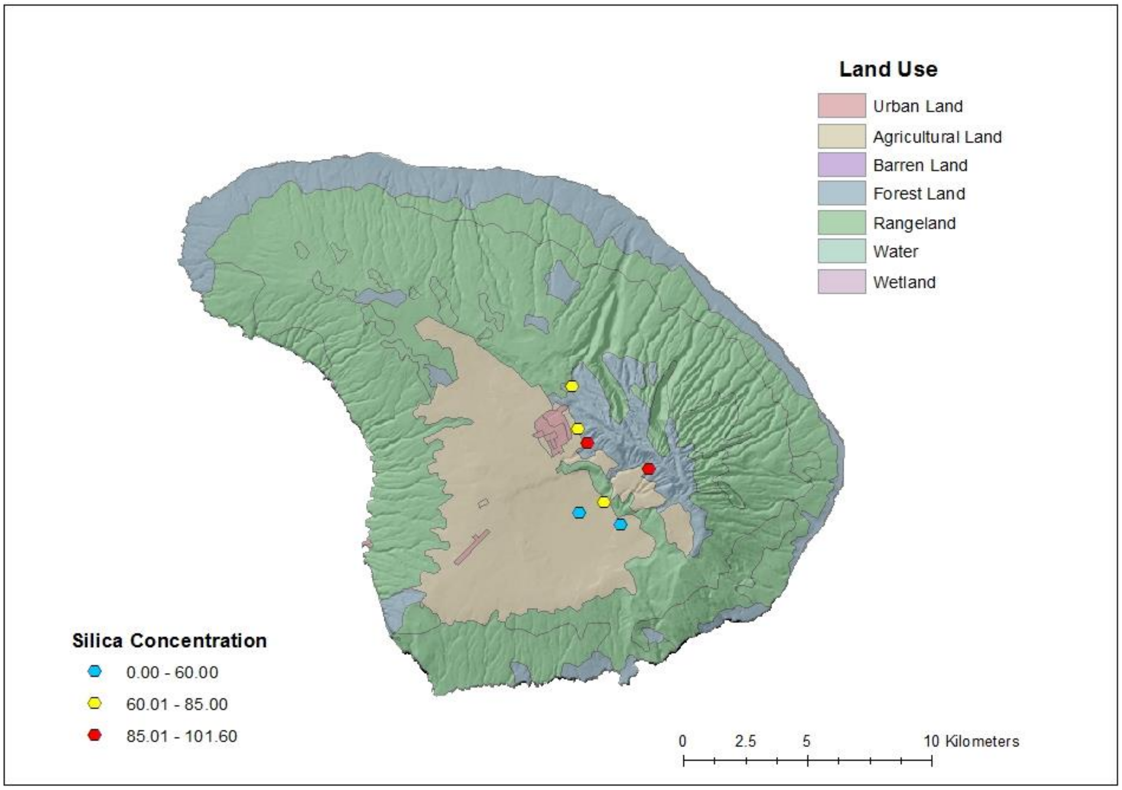


Figure 20. Silica Concentration (ppm) for the Island of Lānaʻi. Land use is located to the right and colored. The range of silica concentration is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

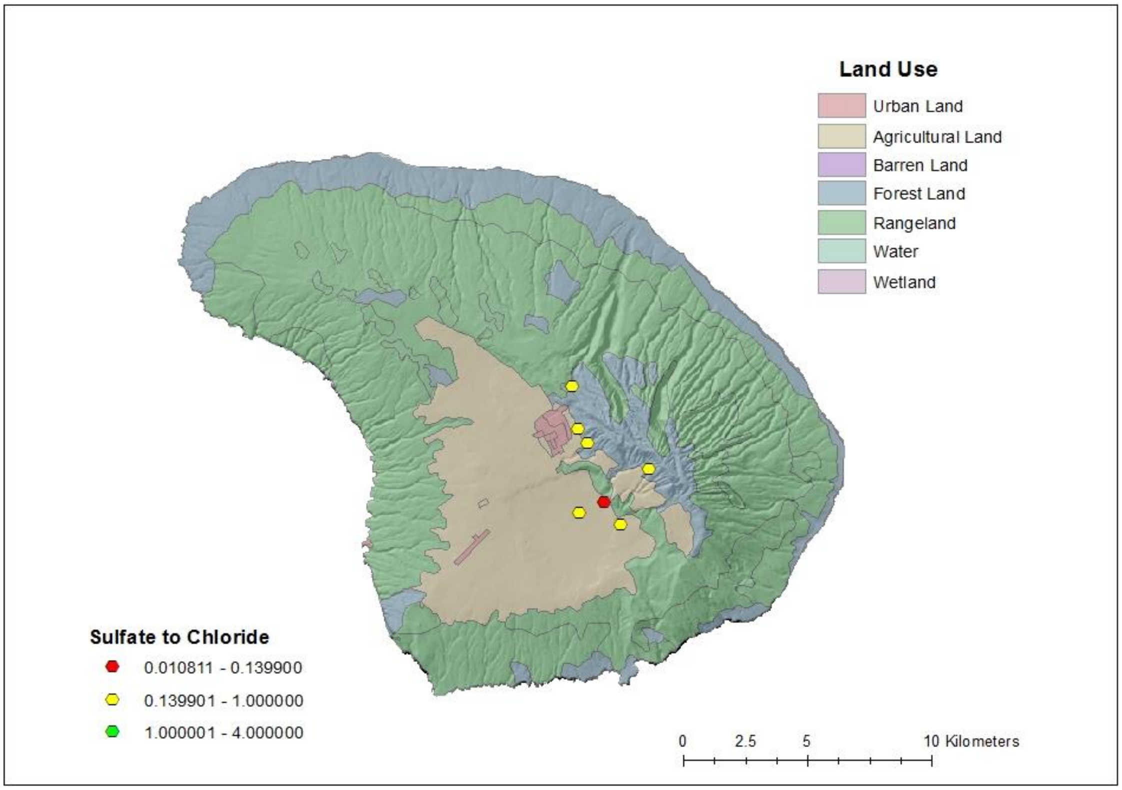


Figure 21. Sulfate to Chloride Ion Ratio for the Island of Lāna‘i. Land use is located to the right and colored. The sulfate/chloride ion ratio range is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

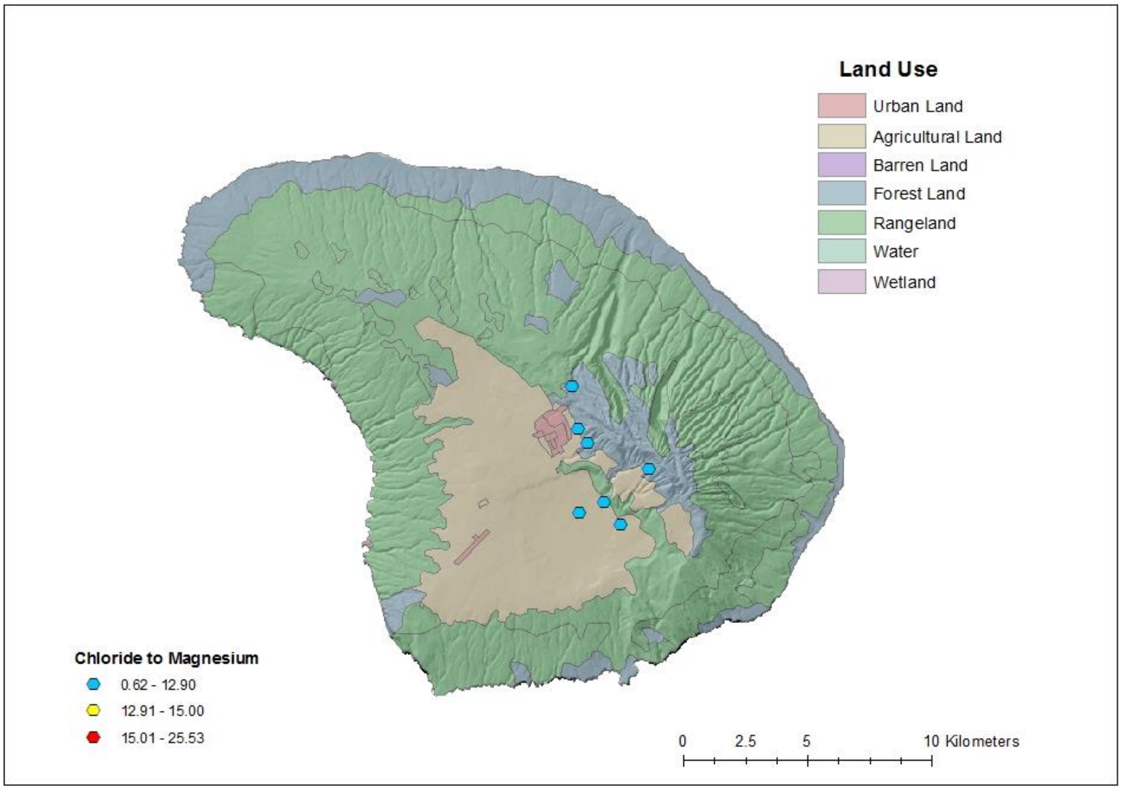


Figure 22. Chloride to Magnesium Ion Ratio for the Island of Lānaʻi. Land use is located to the right and colored. The chloride/magnesium ion ratio is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

The Play Fairway Analysis (PFA) identified three anomalous wells on the Island of Lānaʻi. All of anomalous wells were located in the Palawai Basin sampling site area. Two of the anomalous wells in the Palawai Basin area presented anomalies for silica concentration and well 5-4854-002 also had a temperature anomaly. One well (5-4753-001) had a sulfate/chloride ion ratio anomaly.

4.5 Results for Hawaii Island

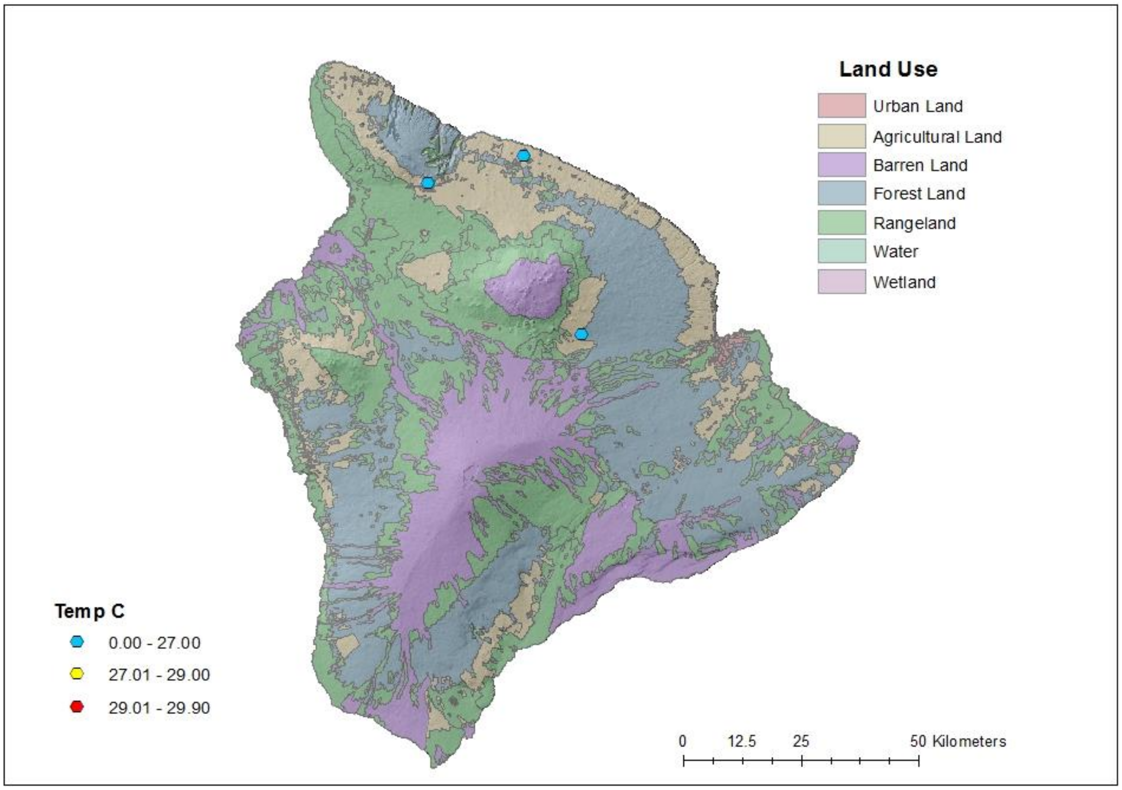


Figure 23. Well Temperature in Degrees Celsius (℃) for the Island of Hawai‘i. Land use is located to the right and colored. The range of temperature is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

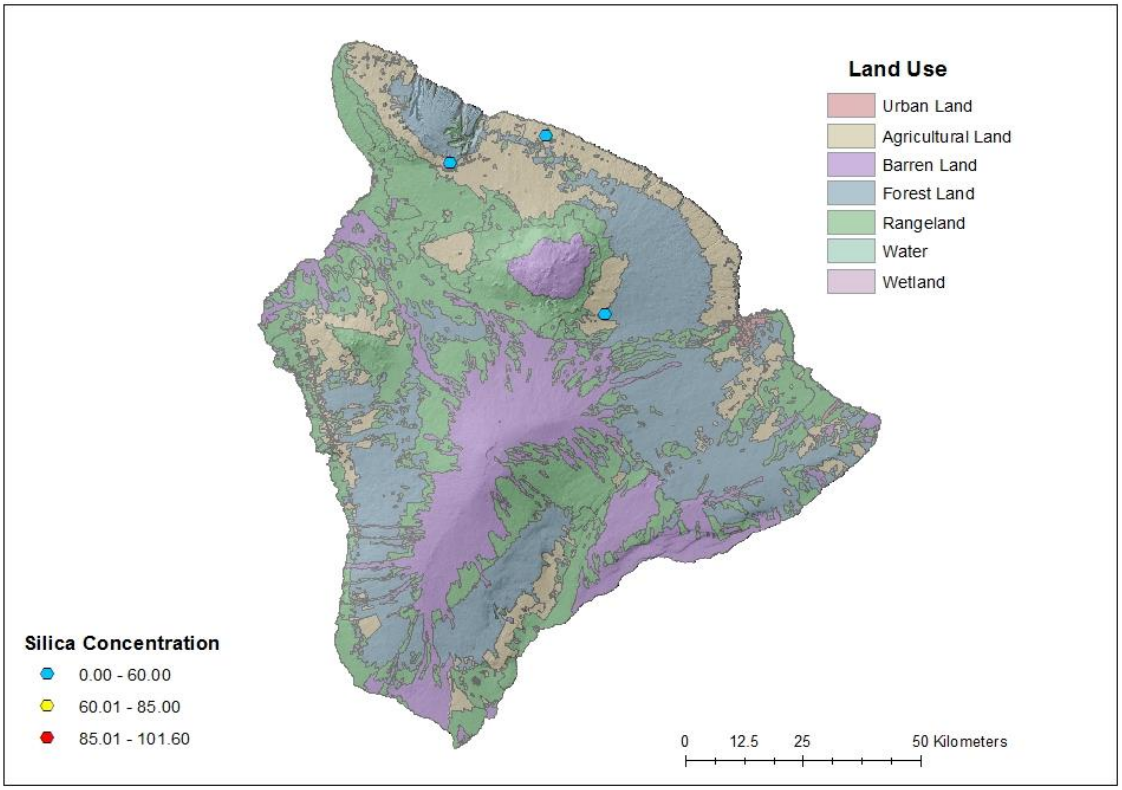


Figure 24. Silica Concentration (ppm) for the Island of Hawai‘i. Land use is located to the right and colored. The range of silica concentration is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

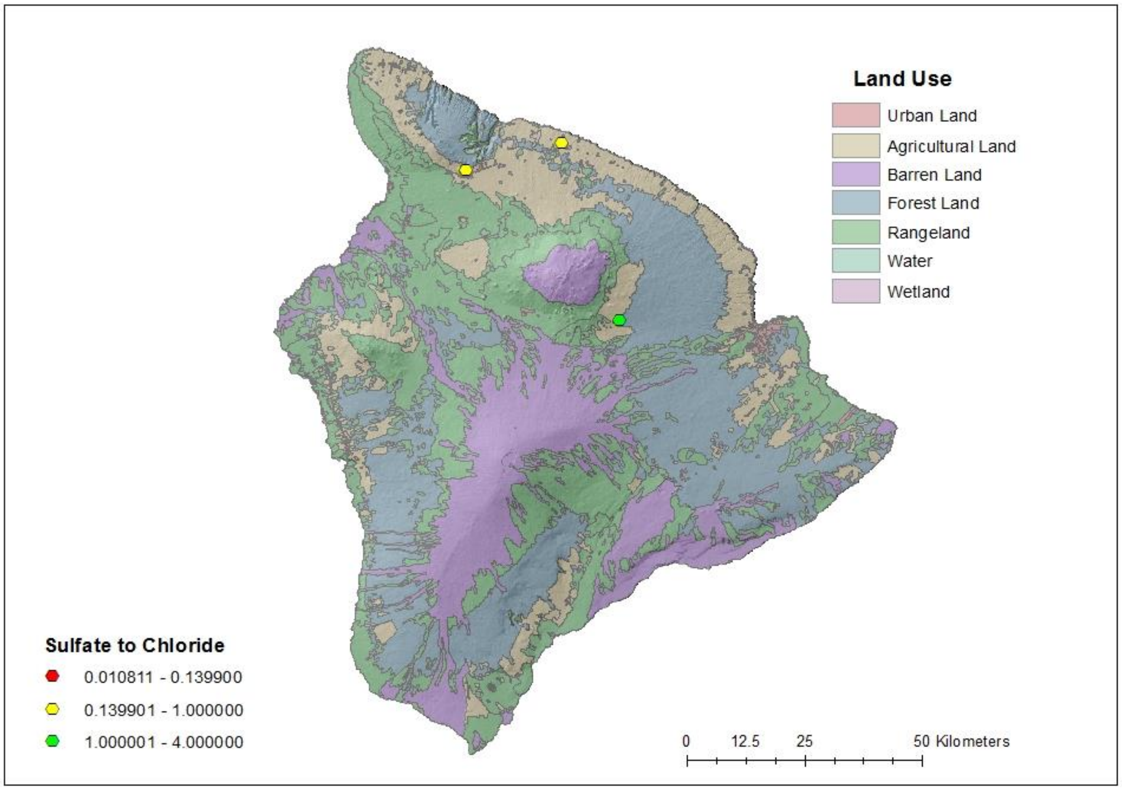


Figure 25. Sulfate to Chloride Ion Ratio for the Island of Hawai‘i. Land use is located to the right and colored. The sulfate/chloride ion ratio range is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

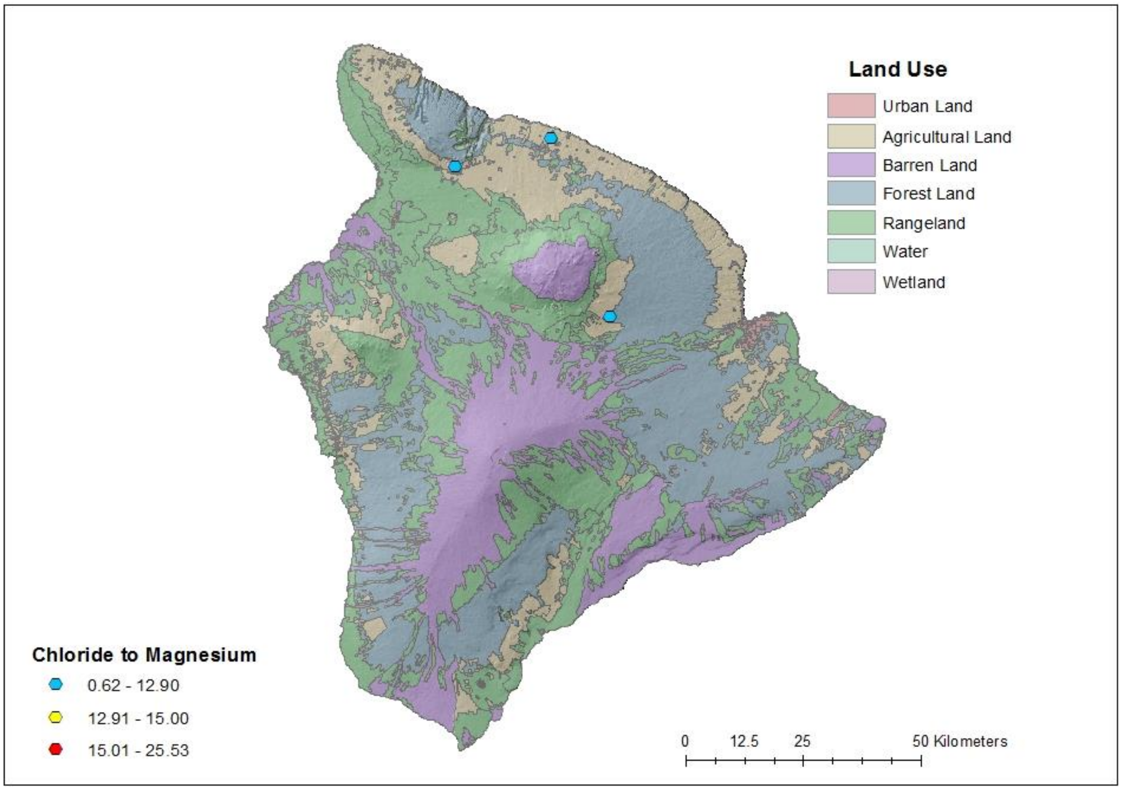
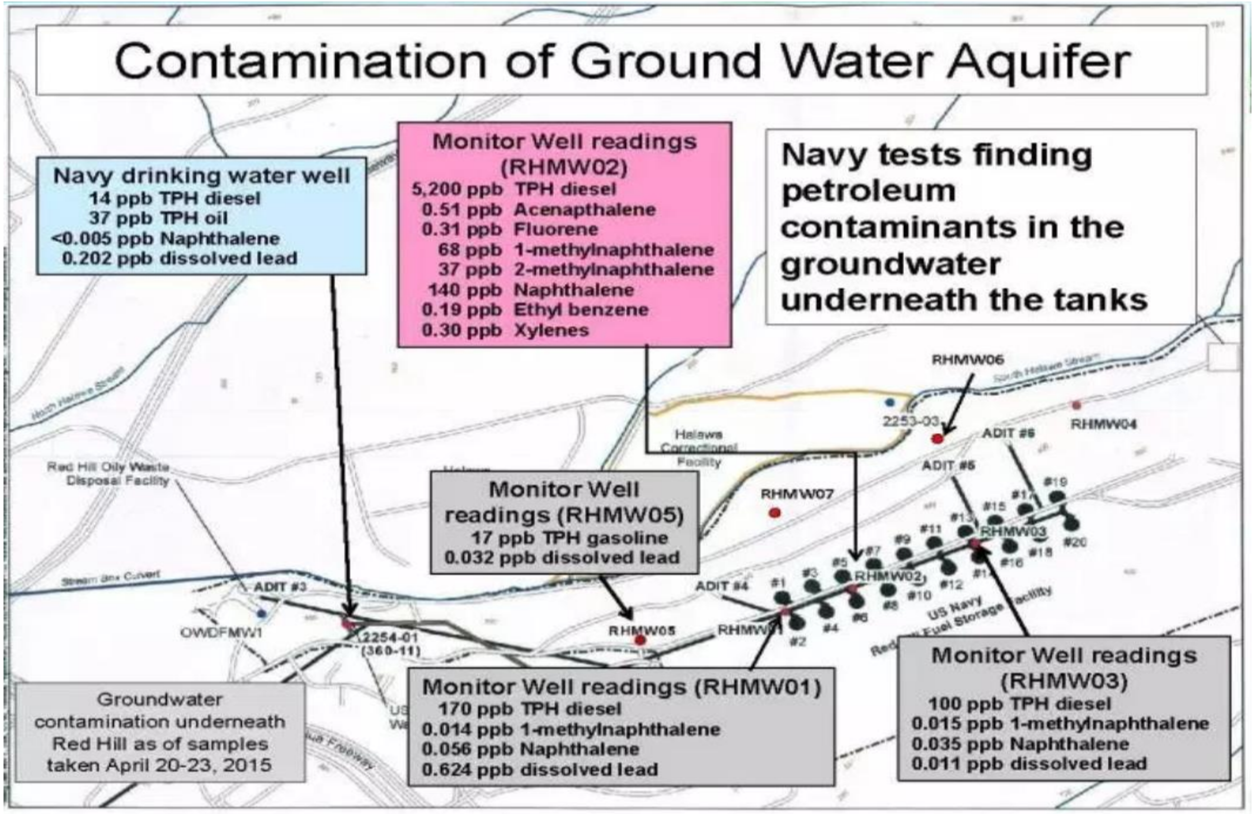


Figure 26. Chloride to Magnesium Ion Ratio for the Island of Hawai‘i. Land use is located to the right and colored. The chloride/magnesium ion ratio is located to the left and colored. Charge balance error values higher than 10% were not used for map composition or further analysis.

The Play Fairway Analysis (PFA) one anomalous well on Hawai‘i Island. This anomalous well on the Hawai‘i Island demonstrated a sulphate/chloride ion ratio anomaly.

5. DISCUSSION

5.1 Discussion for O‘ahu


Contamination of Ground Water Aquifer

Navy drinking water well
14 ppb TPH diesel
37 ppb TPH oil
<0.005 ppb Naphthalene
0.202 ppb dissolved lead

Monitor Well readings (RHMW02)
5,200 ppb TPH diesel
0.51 ppb Acenapthalene
0.31 ppb Fluorene
68 ppb 1-methylnaphthalene
37 ppb 2-methylnaphthalene
140 ppb Naphthalene
0.19 ppb Ethyl benzene
0.30 ppb Xylenes

Navy tests finding petroleum contaminants in the groundwater underneath the tanks

Monitor Well readings (RHMW05)
17 ppb TPH gasoline
0.032 ppb dissolved lead

Monitor Well readings (RHMW01)
170 ppb TPH diesel
0.014 ppb 1-methylnaphthalene
0.056 ppb Naphthalene
0.624 ppb dissolved lead

Monitor Well readings (RHMW03)
100 ppb TPH diesel
0.015 ppb 1-methylnaphthalene
0.035 ppb Naphthalene
0.011 ppb dissolved lead

Groundwater contamination underneath Red Hill as of samples taken April 20-23, 2015

Figure 27. Groundwater Contamination of Red Hill Wells and Associated Contaminants as Sampled on April 20 - 23, 2015
Source: Board of Water Supply, City and County of Honolulu (presentation given by Ernest Lau and Erwin Kawata)

Anomalies detected in the Red Hill region within the south shore Koolau sampling site of O‘ahu, displayed an unusual pattern, and although there is a possibility that these chemical indicators could be attributed to geothermal heat, it is highly unlikely. An alternative explanation could involve the possibility of both natural and anthropogenic contamination. All of the anomalous monitoring wells are located within the Red Hill Bulk Fuel Storage Facility. This storage facility is one of the largest military fuel facilities in the United States and based on Navy reports, records, and maintenance data (epa.gov, 2014; Board of Water Supply, (n.d.)), there have been documented fuel tank leaks and lapses in maintenance since this facility’s inception in 1940. A plausible explanation for the Red Hill anomalies could be the biodegradation of petroleum (organic) products and lead (inorganic) (Fig.27). It would not be unusual to observe a pattern like the one displayed by the anomalous wells since groundwater generally flows from a higher elevation to a lower elevation (Makua to Makai), however, it is difficult to predict the migration of a groundwater contaminant plume because of extenuating factors which include: precipitation rates, groundwater flow patterns, rock type, permeability, diffusion and hydrodynamic dispersion (Fetter, 2018). In addition, the wells are located in a highly developed area, next to active pumping, irrigation recharge and other anthropogenic variables, which could also lead to groundwater contamination of the aquifer. Other natural contaminants and erosional processes could also be a contributing factor to the spike in groundwater anomalies displayed. Chemical analyses of the samples also suggest the possibility of saltwater infiltration and display an observable anthropogenic signature.

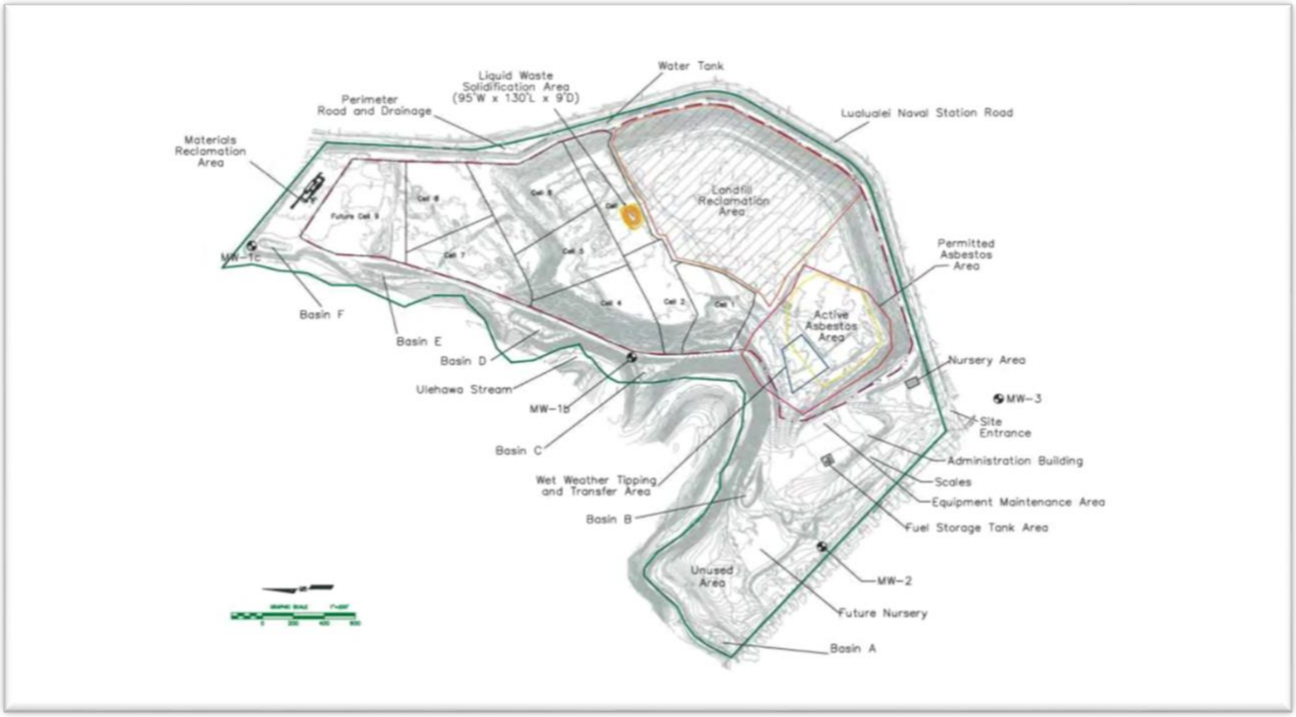


Figure 28. PVT Integrated Solid Waste Facility

Source: base map provided by Spencer B. Gross, Inc. Topography July 2014. Green lines indicate the property boundary and red dashed lines indicate refuse limits. PVT Land Company, LTD (A-Mehr, Inc., 2015)

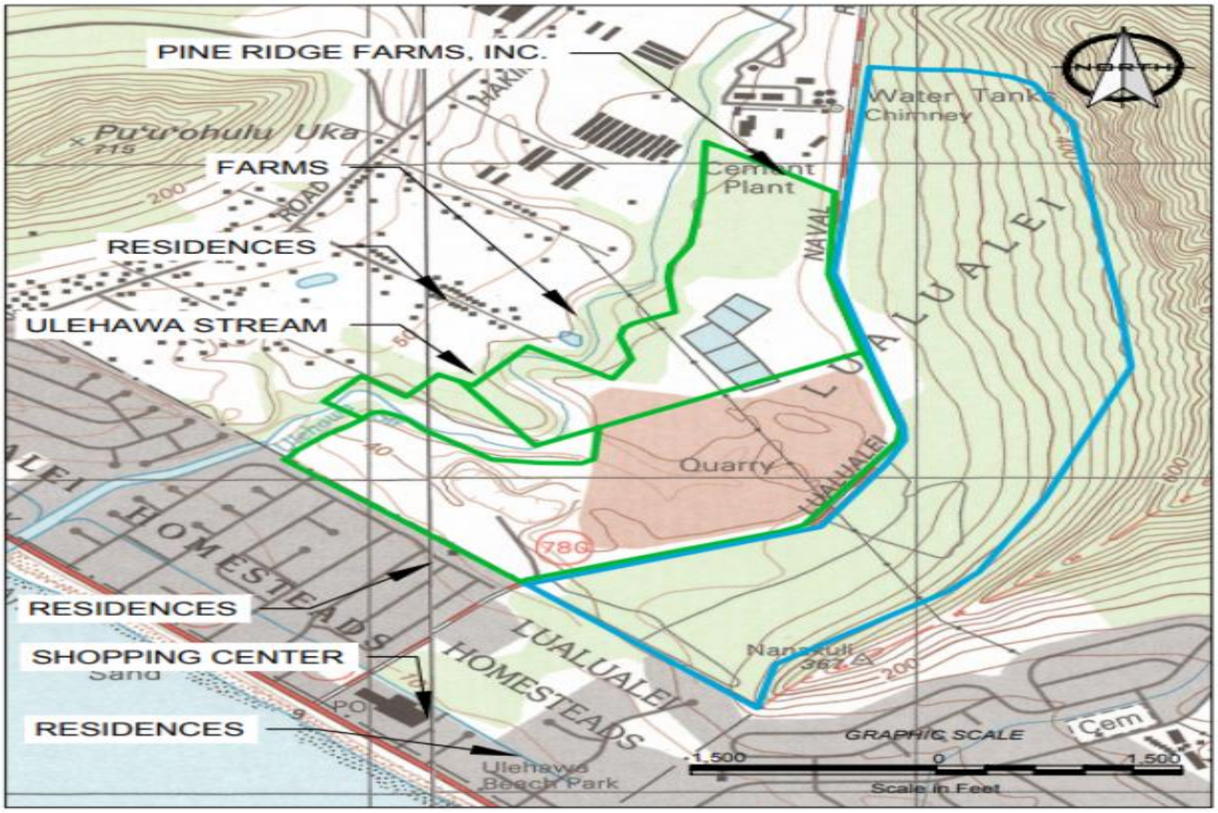


Figure 29. PVT Integrated Solid Waste Facility and Neighboring Parcels of Land and Associated Land Use
Source: base map provided by Juturna, LLC, May 2015. Solid green lines indicate PVT ISWMF Property Boundary and the solid blue lines indicate the Leeward Land Property Boundary. PVT Land Company, (A-Mehr, Inc., 2015)

In the PVT region of O‘ahu, a similar display of anomalies was detected in wells at the Waianae sampling location. Although, these chemical signatures could be an indication of subsurface heat, it is unlikely that water from these wells sustained heat-alteration from a nearby geothermal resource. Similar to the Red Hill wells, the PVT wells may be affected by neighboring contamination from external sources and contamination produced within the sampling site. The anomalous wells are located within the PVT Integrated Solid Waste Management Facility (PVT

ISWMF), which is a 200-acre operating landfill (Fig.28) that accepts wastes associated with construction, demolition, and other recyclable products (A-Mehr, Inc., 2015). Types of waste include: liquid waste, contaminated soils, construction and demolition waste, organic waste, product waste, asbestos contaminated waste, and coal ash waste (A-Mehr, Inc., 2015). A possible explanation for the PVT well anomalies could be inorganic and organic contamination of the groundwater aquifer. In addition, the facility is also located to adjacent parcels of land that may be associated with industrial, mining, residential, and agricultural waste and contamination (Fig.29). Chemical analyses of the samples also suggest the possibility of saltwater infiltration and display an observable anthropogenic signature. Injection wells are located on site and irrigation return flow, natural contaminants and weathering of source rock could also be a contributing factor in the groundwater site anomalies.

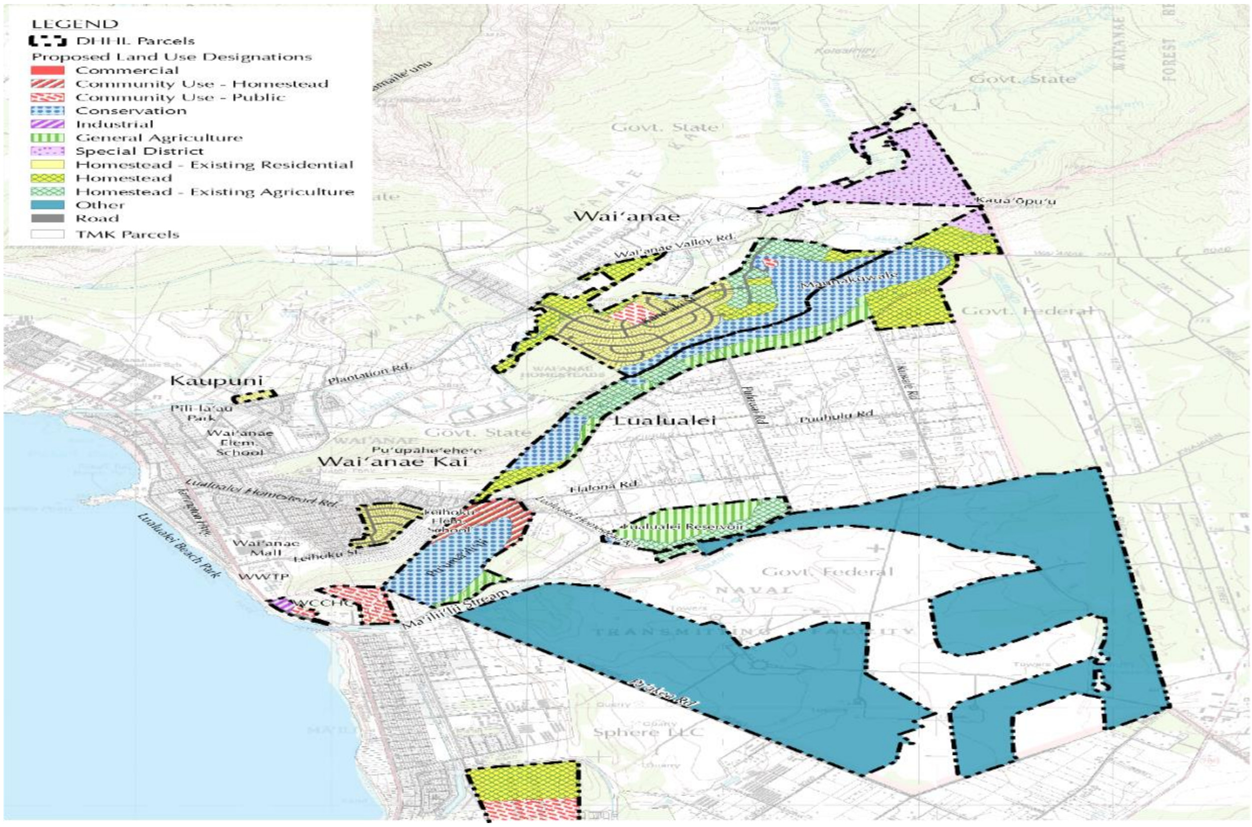


Figure 30. Proposed Land Use Designations of Waianae, Waianae Kai, and Lualualei Parcels of Land

Source: base map provided by PBR Hawaii & Associates, Inc. July 2013. Department of Hawaiian Homelands (www.dhhl.hawaii.gov)

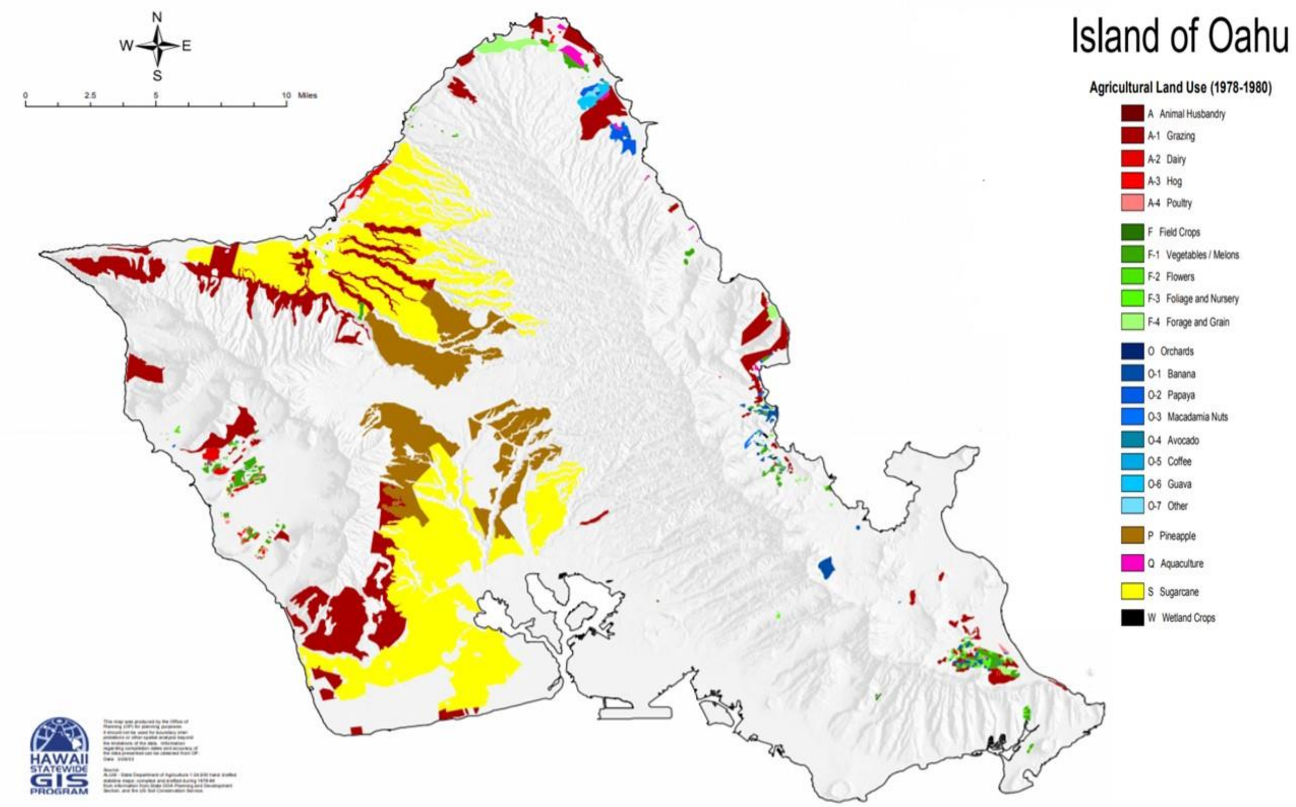


Figure 31. Agricultural Land Use in the State of O‘ahu
Source: base map provided by Hawaii Statewide GIS Program. March 2003. State of Hawaii Office of Planning (www. planning.hawaii.gov)

In the Lualualei region of O‘ahu, within the Waianae sampling site location, a single silica concentration anomaly was identified. In Hawaii, geothermal heat has been associated with elevated concentrations of dissolved silica, conversely, other non-thermal phenomena can also have a significant impact on groundwater silica concentrations (Cox & Thomas, 1979). As a result, additional geochemical test anomalies were warranted for validation, however, since there were no other positive test indications, confidence in this anomalous indicator alone is minimal. Chemical analysis of the sample does not indicate noticeable infiltration of saltwater but rather demonstrate an observable anthropogenic signature. An alternative explanation could be residual and current aquifer contamination from non-point source pollution. Distinct from the first two anomalous sampling sites, the Lualualei region does not have an obvious point source of pollution, but rather a history of land use that could shed light on likely candidates of contamination. During the 19th century, the Laulaulei region of O‘ahu was dominated by cattle ranching, agriculture, and sugarcane production, and while not as expansive, agricultural industries and animal farming still significantly impact this region today (Reith, 2009). Elevated levels of nitrate, sulfate, and phosphate could be from chemical fertilizers, human sewage, and animal waste and other fertilizers (EPA, n.d.). Associated with these industries are irrigation practices can also cause an anomalous silica concentration indication. In addition, this particular Lualualei well is located inland and not as close in proximity to the coast as the PVT wells, which might explain the lack of evidence for obvious saltwater intrusion or mixing. While the elevated silica concentration indication could be from residual heat from the old Waianae Caldera Complex, it does not seem likely based on the groundwater analysis.

5.2 Discussion of Maui

The hydrogeochemical analysis for the Haleaakalā east rift sampling location on the Island of Maui exhibited a single geothermal anomaly, nonetheless, due to the lack of other anomalous geothermal indications, the probability of a subsurface thermal resource is minimal. On the coastline of east Maui, near the city of Hana, the highest chloride to magnesium ion ratio in the assessment was detected. Chemical analysis of the sample implies the possibility of saltwater infiltration as demonstrated by the low sodium to chloride ion ratio, and contamination from agricultural practices as revealed by the low chloride to bromide ion ratio. An observable anthropogenic signature was not exhibited in the analysis. A groundwater tracer study completed on Maui in 2012, by principle investigator Dr. Craig R. Glenn, found that chloride to magnesium ion ratios varied within the same wells at different sampling dates. Some wells showed significant changes in ion ratio values and the subsequent assessment revealed two potential heat sources besides geothermal: warm effluent and exothermic reactions from organic matter decomposition (Glenn et al., 2013). While this study was not in the same area as the anomalous well, it does indicate that on the Island of Maui there are other potential heat sources that have affected the chloride to magnesium ratio in the past. Maui may have residual heat from a geothermal source, but an accurate determination cannot be made based on these test results. Further investigation is necessary.

5.3 Discussion of Lanai

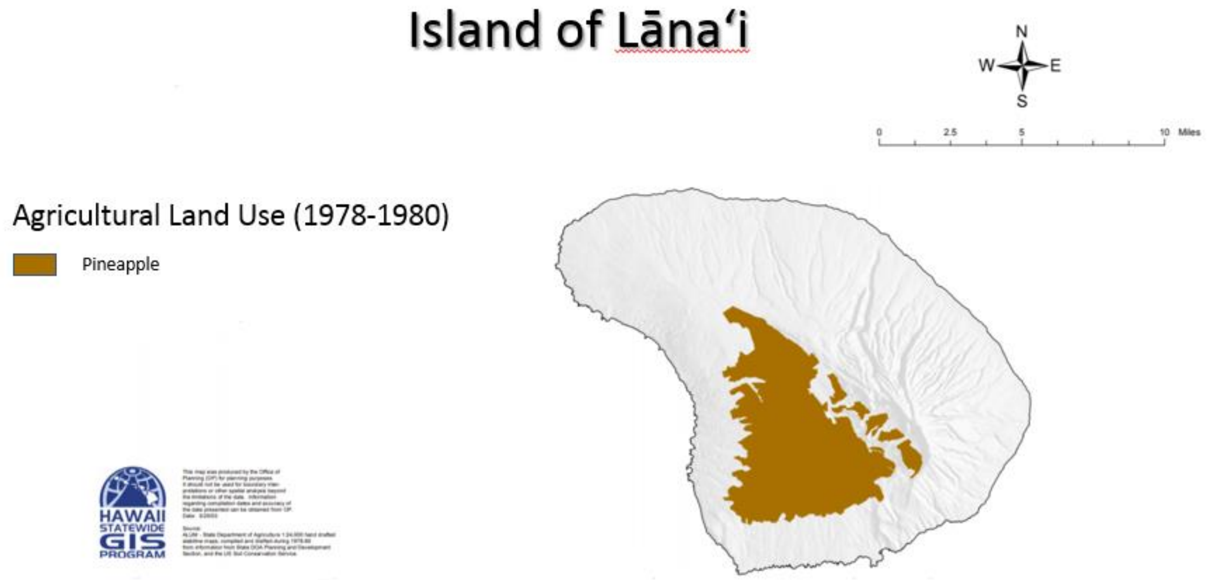


Figure 32. Agricultural Land Use in the State of Lānaʻi
Source: base map provided by Hawaii Statewide GIS Program. March 2003. State of Hawaii Office of Planning (www. planning.hawaii.gov)

On the Island of Lānaʻi, within the Palawai Basin sampling location, a display of anomalies comparable to those exhibited on the Island of Oʻahu, were detected. Positive anomalous indicators could be an indication of residual heat from the old caldera complex, however, similar to the reasons given for the Oʻahu sites, additional background information is necessary. Lānaʻi is one of the smaller Hawaiian Islands, lies within the rain shadow of Maui, has an arid climate, and minimal Tradewinds and precipitation (Juvik, Juvik, & Paradise, 1998). A majority of the island remains undeveloped barren land, however, at the peak of agricultural prosperity, the Island of Lānaʻi supplied over 75% of the world's pineapples (lanaichc.org). While commercial production of pineapple on the island has ceased, Lānaʻi has sustained over a hundred years of intensive agriculture, animal farming, and animal ranching, which to some level still continues today (Hobdy, 1993; Maly & Maly, 2007). The Palawai Basin is the location were much of the past and current agricultural use and development has taken place, and the site of one of the two groundwater sub-aquifers on the island (Maui County, 2016; Maly & Maly, 2007). Some of the possible alternative suggestions for non-thermal phenomena that could indicate positive anomalies are: inorganic and organic contamination from past and current land use practices: fertilizer application and storage, pesticide use and storage, animal storage, irrigation, and excess pumping of the aquifer. This information could indicate, probable, non-thermal reasons for the positive indicators, nevertheless, further chemical analyses of the anomalous samples are warranted.

Upon chemical analyses of the anomalous groundwater samples, certain trends were observed. Bromide is a trace element commonly found in seawater with an average concentration of 65 mg/l (Naily, 2018a; Sverdrup, Johnson, & Fleming, 1942) and can be affected by an increase in temperature, periods of drought, and water quality changes (Sawade et al., 2016). An elevated concentration of bromide observed in the anomalous samples suggest the possibility of saltwater influence, and that the samples could have been withdrawn from brackish water wells. In addition, the low sodium to chloride (Na/Cl) and chloride to bromide (Cl/Br) ion ratios also suggest that the groundwater wells have been contaminated by saltwater and possibly the effects of agriculture (Naily, 2018b). The samples also display an observable anthropogenic signature. Elevated levels of nitrate and sulfate suggests possible contamination of the groundwater through the application of fertilizers for agricultural crops and marine sea salts. Excess pumping, irrigation return flow, natural contaminants and weathering of source rock could also be a contributing factor in the groundwater site anomalies, however, these positive indications also meet the criteria for thermal anomalies.

The positive signals of an elevated subsurface temperature, an increase in silica concentration and a decrease in sulfate concentration could indicate that the thermal anomalies displayed within the samples could be caused by a nearby geothermal source. An increase in well temperature can not only be a subsurface thermal indication of residual heat from the old caldera complex, but can also induce chemical reactions within the source water. An increase in subsurface temperature in an aquifer can increase the amount of dissolved silica within the subsurface fluid as water interacts with rock at elevated temperatures. An increase in subsurface temperature in an aquifer can also decrease the concentration of sulfate and magnesium by, the precipitation and formation of secondary minerals, which could also lead to an anomalous ratio. It is assumed, however, that the reservoir is in equilibrium (Cox et al. 1979a). The summation of these processes could have been produced by a neighboring thermal resource on the Island of Lānaʻi, and may have caused the highest abundance of individual anomalous geothermal indicators, apart from having a high chloride to magnesium ion ratio. Interestingly, Lānaʻi is composed of a single parent rock consisting of primitive basalt and olivine ($(Mg,Fe)_2SiO_4$) basalt, which is highly enriched with olivine phenocrysts that contain more magnesium than iron (Mink & Lau, 1993; West et al., 1992). Since the parent rock has a higher abundance of magnesium, it is probable that water in the surrounding area could have a higher magnesium content, thus, affecting the chloride to magnesium ion ratio. The complexities of the data suggest further exploration is needed to determine if a subsurface thermal resource is present.

5.4 Discussion of Hawai'i Island

Anomalies in the one spring located on the Island of Hawai'i displayed a significantly elevated ion ratio of sulfate to chloride above 0.14. Having a sulfate to chloride ion ratio considerably higher than seawater is less common and generally occurs in areas of volcanic activity where steam is produced at depth. The mixing of heat-altered water with cooler oxygenated water upon accent can increase sulfate concentration. Generally, the chemical signature of waters exhibiting thermal alteration tend to be chloride deficient yet enriched with carbon dioxide and sulfate. While it appears that this sample meets the criteria, a sulfate to chloride ion ratio above 1.0 as a threshold for an anomalous indicator in this analysis could be insufficient to indicate direct geothermal heat. A threshold considerably higher than 1.0 might be necessary as evidenced by the number of historical wells that had ratios above 1.0 but no anomalous geothermal indicators. While there is known geothermal activity on the Island of Hawai'i, this anomalous signature threshold does not appear to indicate proximal geothermal heat. Having an elevated sulfate to chloride ion ratio is in stark comparison to known geothermal wells on the Island of Hawai'i, 8-2982-001 (Geothermal Test Well 3) and 8-2783-001 (Malama-Ki), both which have an ion ratio below 0.14. An alternative explanation could be excess atmospheric constituents of sea salt, volcanic emanations, and anthropogenic pollutants especially in the air over the open ocean (Kroopnick, 1977) or that thermally altered water may have traveled away from the potential thermal source. This seems like a probable explanation because this particular anomalous sample was taken from a spring on Mauna Kea. However, resultant sample data remains inconclusive and geothermal potential is minimal due to a lack of other anomalous geothermal indicators.

6. CONCLUSION AND FUTURE WORK

The Play Fairway Analysis detected various anomalies on four islands within the State of Hawaiʻi based on the criteria set within the project as potential indications of subsurface heat, and identified a potential geothermal source on the Island of Lānaʻi as evidenced by multiple anomalous indicators. The PFA was a successful exploration tool based on the assessment of groundwater geochemical data, highlighting wells displaying chemical signatures suggestive of a subsurface heat anomaly. However, positive indications of a subsurface heat anomaly based on this PFA could have an alternative non-thermal explanation. Given that these aqueous geochemical indicators can be affected by both natural and anthropogenic processes, further investigation is necessary to determine between thermal and non-thermal groundwater under Hawaiian conditions. Nonetheless, a sampling source location suggestive of geothermal heat was identified: Palawai Basin on the Island of Lānaʻi. The likelihood and sustainability of an abundant geothermal resource on Lānaʻi should be studied further with another exploratory technique such as drilling. Furthermore, continuous data collection and additional geophysical and geochemical surveys are necessary to not only increase the current knowledge of potential geothermal resources but to improve the overall understanding of the subsurface dynamics of Hawaii's unique groundwater systems. Thus, data collected could assist the Hawaiʻi State Legislature to address the state's energy demands through identification, exploration, and use of available geothermal sources.

On June 8, 2015, the State of Hawaiʻi became the first U.S. state to mandate that 100% of its electricity come from renewable sources by 2045 (State of Hawaiʻi, 2017). Globally, geothermal energy is already an established source of reliable renewable power and Hawaiʻi is one of the seven states with utility-scale geothermal capacity (www.eia.gov). Baseload geothermal power could also reduce the cost of transportation and fabrication of goods and services produced in Hawaiʻi, and assist the state in becoming an effective competitor in the global market (Yen & Iacofono, 1981). In addition, geothermal reservoirs are naturally replenished, impacts produced by power generation are minimal, and the release of main greenhouse gases are reduced when compared to traditional energy combustion sources (Komurcu et al. 2009). Hawaii's rate of penetration into the geothermal energy market could set the standard for regions with similar quandaries, promote sustainable energy use, and contribute useful information to the global geothermal community (Shupe, 1982). Furthermore, widespread volcanism and the presence of a variety of subsurface heat anomalies make Hawaiʻi an ideal location for the development and use of geothermal energy (Fowler et al., 1980; Shupe, 1973).

Over the past two decades, there has been a growing trend of both private and government industry interest towards the expansion and evaluation of geothermal resources in Hawaiʻi. The systematic investigation of new methods and approaches, validation of current techniques, and exploration of future projects regarding geothermal work in Hawaiʻi can significantly bridge deficiencies within the current pool of knowledge. While there has been sufficient progress in Hawaiʻi towards laying the groundwork for geothermal energy, future exploration efforts should consider these results as well as the economic, cultural, societal, and practical circumstances that can influence development sustainability (Lautze et al., 2017a). Additionally, recent technological advancements have lowered costs associated with resource exploration and exploitation. Ultimately, whether motivation for Hawaiʻi's alternative energy goal for the year 2045 is protection from fluctuations in the global energy market, environmental degradation, or resource depletion, it is within the best interest of the state to develop a self-sufficient energy resource (Shupe, 1973).

Table 11. Aqueous Geothermal Indicators: Chloride/Magnesium Ratio, Silica Concentration (ppm), Sulfate/Chloride Ratio, and Well Temperature (℃) for the Island of Oahu

Well ID	Well Name	Well Depth (ft)	Cl/Mg	SiO_2	SO_4/Cl	Temp ℃	CBE (%)
RHMW03	Red Hill	-	1.46	86.16	0.94	27.4	5.5
RHMW04	Red Hill	320.53	3.94	57.07	0.15	22.8	7.3
RHMW06	Red Hill	-	5.61	74.34	0.23	22.6	4.0
RHMWO7	Red Hill	-	5.22	76.17	0.17	22.9	4.1
RHMW08	Red Hill	-	8.96	45.60	0.47	24.0	3.0
OWDFMW1	Red Hill	-	4.32	51.37	0.30	25.8	2.1
RHMW 2254-01	Red Hill	-	5.66	49.10	0.17	21.8	1.5
RHMW02	Red Hill	-	1.44	91.26	0.01	23.5	4.2
RHMW05	Red Hill	-	11.61	86.47	0.31	23.8	3.7
3-2157-005	Ford Island Saltwater Well	-	13.65	35.25	0.14	21.7	(0.8)
3-2253-003 @ 276 ft	Halawa Deep Monitor	-	5.68	65.03	0.31	22.6	2.5
3-2253-003 @ 851 ft	Halawa Deep Monitor	-	6.71	39.23	0.13	22.7	1.1
MW1	PVT	-	9.41	90.21	0.17	28.4	3.8
MW2	PVT	-	6.79	46.29	0.37	27.9	8.5
MW3	PVT	-	9.69	101.60	0.21	29.9	3.1
MW4	PVT	-	9.34	52.18	0.21	26.8	3.8
3-2607-001	Lualualei Deep Well	-	3.82	97.28	0.20	24.0	8.3
3-2808-002	Lualualei Well	-	3.45	56.50	0.19	24.1	7.1
3-2154-001	Honolulu Intl. Country Club	-	4.53	45.98	0.21	20.9	5.9

*** Values highlighted in red indicate an anomaly, values highlighted in yellow indicate an elevation, and complete samples highlighted in blue have Charge Balance Error values higher than 10% were not used for map composition or analysis.**

Table 12. Aqueous Geothermal Indicators: Chloride/Magnesium Ratio, Silica Concentration (ppm), Sulfate/Chloride Ratio, and Well Temperature (℃) for the Island of Kaua‘i

Well ID	Well Name	Well Depth (ft)	Cl/Mg	SiO_2	SO_4/Cl	Temp ℃	CBE (%)
2-0124-03	Hanamaulu 4	467	1.22	45.82	0.22	24.9	9.3
2-0421-02	Wailua Homestead B	560	1.71	63.61	0.15	24.8	8.7
2-5425-15	Koloa F	377	2.62	68.30	0.22	23.9	8.7
2-5426-05	Koloa D	420	3.32	65.97	0.18	23.9	7.3
2-5427-03	Koloa E	511	2.29	62.09	0.21	23.5	9.6
2-5530-03	Lawai 1	695	1.96	63.17	0.27	23.2	8.6
2-5629-01	Piwai 2	775	2.10	54.04	0.20	23.2	8.0
2-5631-01	Kalaheo Deep Well 1	1125	2.00	46.89	0.17	NA	9.8
2-5823-01	Garlinghouse Tunnel	-	2.11	35.70	0.30	23.4	7.5
2-5923-07	Kilohana 1	200	2.45	36.89	0.42	23.6	9.9
2-5824-06	Puhi 3	346	2.23	24.76	0.25	23.6	10.5
2-5824-06	Puhi 4	500	2.32	36.22	0.69	23.2	6.0
2-5921-01	Kalepa Ridge	540	1.94	81.47	0.23	25.4	9.3

*** Values highlighted in red indicate an anomaly, values highlighted in yellow indicate an elevation, and complete samples highlighted in blue have Charge Balance Error values higher than 10% were not used for map composition or analysis.**

Table 13. Aqueous Geothermal Indicators: Chloride/Magnesium Ratio, Silica Concentration (ppm), Sulfate/Chloride Ratio, and Well Temperature (℃) for the Island of Maui

Well ID	Well Name	Well Depth (ft)	Cl/Mg	SiO_2	SO_4/Cl	Temp ℃	CBE (%)
6-3826-001	Seibu 2	222	6.96	43.88	0.14	21.4	2.8
6-3926-002	Makena 1	211	7.68	33.39	0.14	23.1	1.8
6-3926-003	Wailea 8	208	9.73	32.67	0.15	19.5	2.0
6-3926-011	Makena Surf	55	4.21	48.92	0.17	26.4	8.0
6-5317-001	Kaupakulua	1361	1.55	52.24	0.30	21.7	13.9
6-5417-004	JN & RS Well 1	875	2.45	41.51	0.21	20.5	7.8
6-4300-002	Hamoa 1	400	4.62	17.87	0.23	20.6	13.4
6-4600-003	Wakiu B	323	25.53	20.47	0.18	19.4	3.7
6-4701-001	Kaeleku	426	2.38	20.88	0.38	20.1	11.4
6-4937-001	Olowalu Shaft	-	5.17	47.78	0.51	23.0	3.6
6-4936-001	Olowalu Well	-	1.79	46.18	0.82	22.5	5.1
6-4100-002	Wallach	280	5.22	0.00	0.17	25.7	6.6
6-4559-001	Wananalua	440	8.29	0.00	0.16	21.0	7.1
6-4600-001	Wakiu	280	4.44	0.00	0.17	21.5	7.0
6-3926-005	Seibu 6	224	7.37	0.00	0.15	20.5	4.1

*** Values highlighted in red indicate an anomaly, values highlighted in yellow indicate an elevation, and complete samples highlighted in blue have Charge Balance Error values higher than 10% were not used for map composition or analysis.**

Table 14. Aqueous Geothermal Indicators: Chloride/Magnesium Ratio, Silica Concentration (ppm), Sulfate/Chloride Ratio, and Well Temperature (℃) for the Island of Lānaʻi

Well ID	Well Name	Well Depth (ft)	Cl/Mg	SiO_2	SO_4/Cl	Temp ℃	CBE (%)
5-4853-002	Lanai Well 1	1274	3.76	86.24	0.19	28.1	14.0
5-4952-002	Lanai Well 4	1178	2.75	52.89	0.19	18.9	8.4
5-5054-002	Lanai Well 6	1310	2.94	50.60	0.20	19.8	3.8
5-4954-002	Lanai Well 8	1490	2.61	67.89	0.20	22.9	9.2
5-4954-003	Lanai Well 3a	1216	2.37	68.51	0.18	22.7	8.7
5-4753-001	Lanai Well 15	972	3.97	79.50	0.13	25.8	1.5
5-4854-002	Lanai Well 14	950	4.14	96.04	0.18	29.8	3.4
5-4854-001	Lanai Well 9	-	4.02	99.16	0.18	NA	5.0

*** Values highlighted in red indicate an anomaly, values highlighted in yellow indicate an elevation, and complete samples highlighted in blue have Charge Balance Error values higher than 10% were not used for map composition or analysis.**

Table 15. Aqueous Geothermal Indicators: Chloride/Magnesium Ratio, Silica Concentration (ppm), Sulfate/Chloride Ratio, and Well Temperature (℃) for the Island of Hawaii

Well ID	Well Name	Well Depth (ft)	Cl/Mg	SiO_2	SO_4/Cl	Temp ℃	CBE (%)
8-6223-001	Paauilo Deepwell	-	1.47	37.98	0.39	21.8	13.6
8-6240-002	Waimea Deepwell	-	1.05	57.79	0.32	24.5	3.2
8-6528-001	Haina Well	-	4.11	45.44	0.17	22.4	1.8
11007	Spring on Mauna Kea	-	0.62	30.14	4.00	15.8	5.9
8-0545-001	Hawaiian Ocean View Estates Well	-	5.42	44.74	2.61	0.0	PHI
8-5239-001	Waikii 1	-	1.01	68.44	2.98	0.0	PHI

*** Values highlighted in red indicate an anomaly, values highlighted in yellow indicate an elevation, and complete samples highlighted in blue have Charge Balance Error values higher than 10% were not used for map composition or analysis. No pH values for 8-0545-001 or 8-5239-001.**

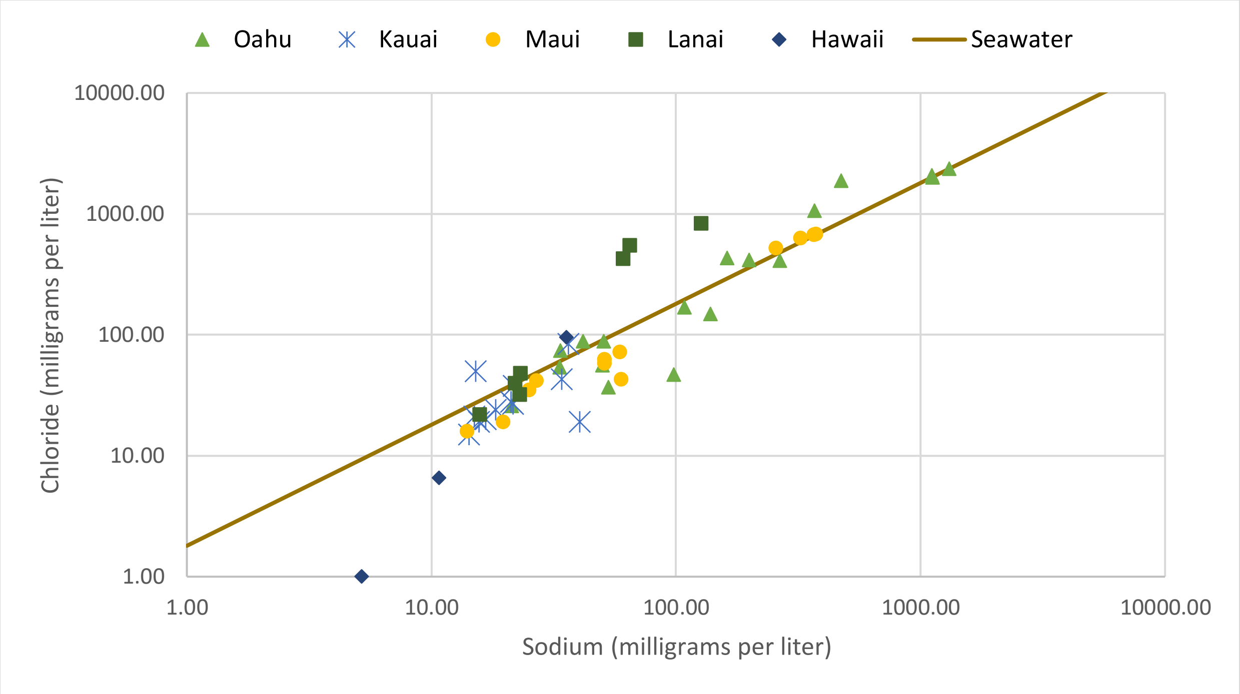


Figure 8. Concentration of Chloride relative to Sodium within Sample Analysis for Oahu, Kauai, Maui, Lanai and the Island of Hawaii. The ratio of Na/Cl in sea water is ~ 0.86 ratio, < 0.86 possible groundwater has been contaminated by seawater, and >1, indicates the groundwater could be contaminated by anthropogenic source (Naily, 2018b)

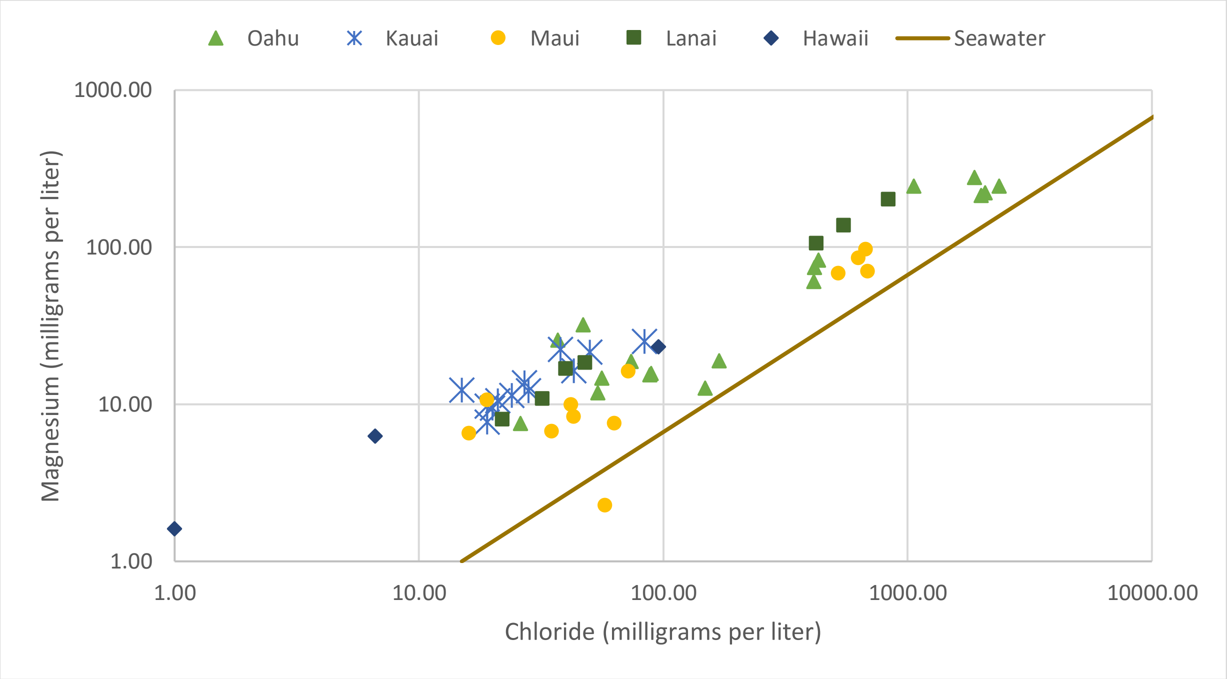


Figure 9. Concentration of Magnesium relative to Chloride within Sample Analysis for Oahu, Kauai, Maui, Lanai, and the Island of Hawaii. Seawater Concentration (1,292/19,353 → 0.07)

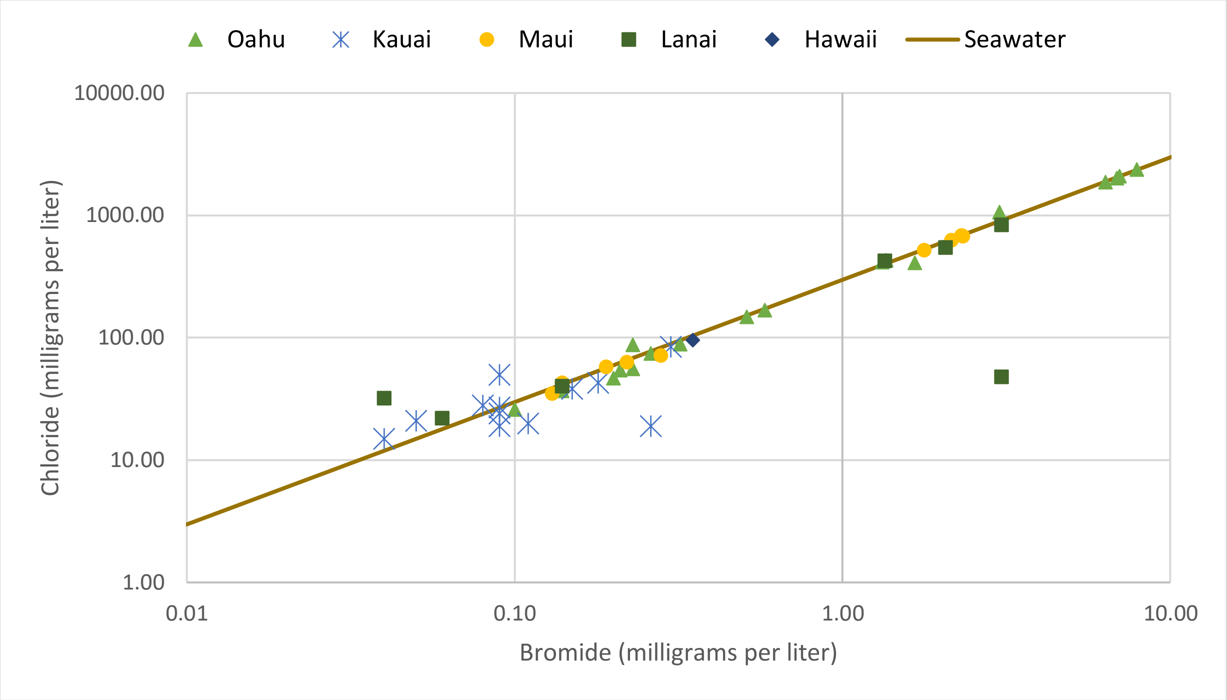


Figure 10. Concentration of Chloride relative to Bromide within Sample Analysis for Oahu, Kauai, Maui, Lanai and the Island of Hawaii. The ratio of Cl/Br in sea water is ~ 297, < 297 indicates hypersaline brine, >1000 indicates evaporate-dissolution, and is < 800 possibly from anthropogenic sewage or the effect of agriculture (Naily, 2018b)

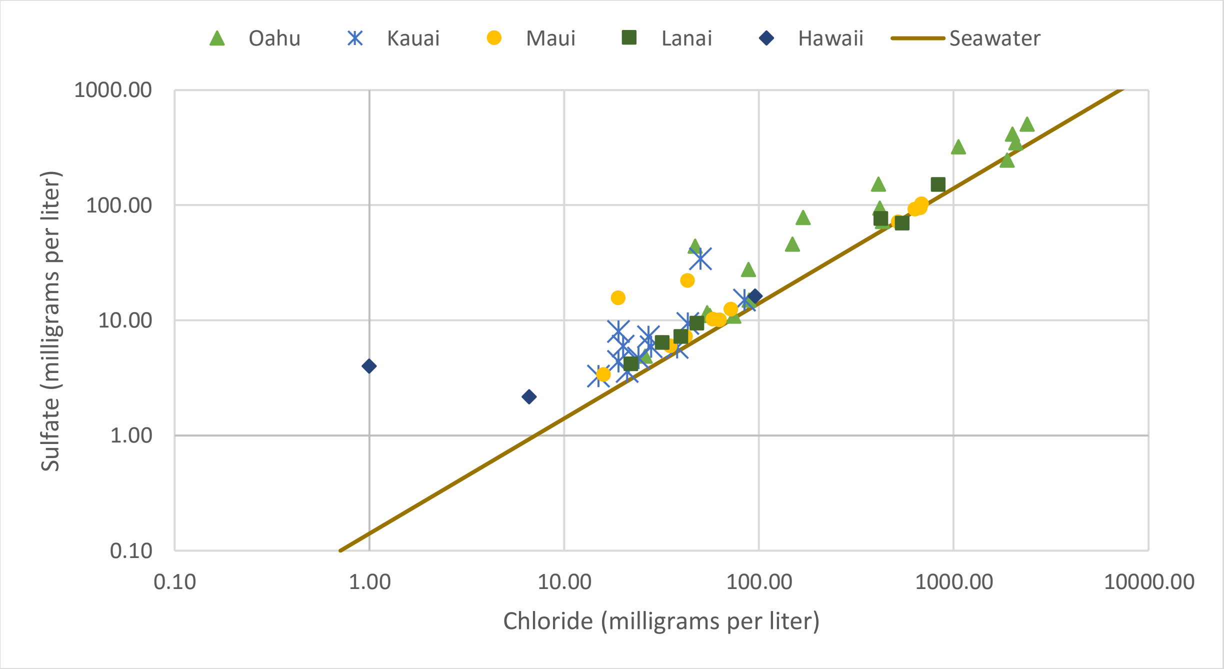


Figure 11. Concentration of Sulfate relative to Chloride within Sample Analysis for Oahu, Kauai, Maui, Lanai, and the Island of Hawaii. Seawater Concentration (2,712/19,353 → 0.14)

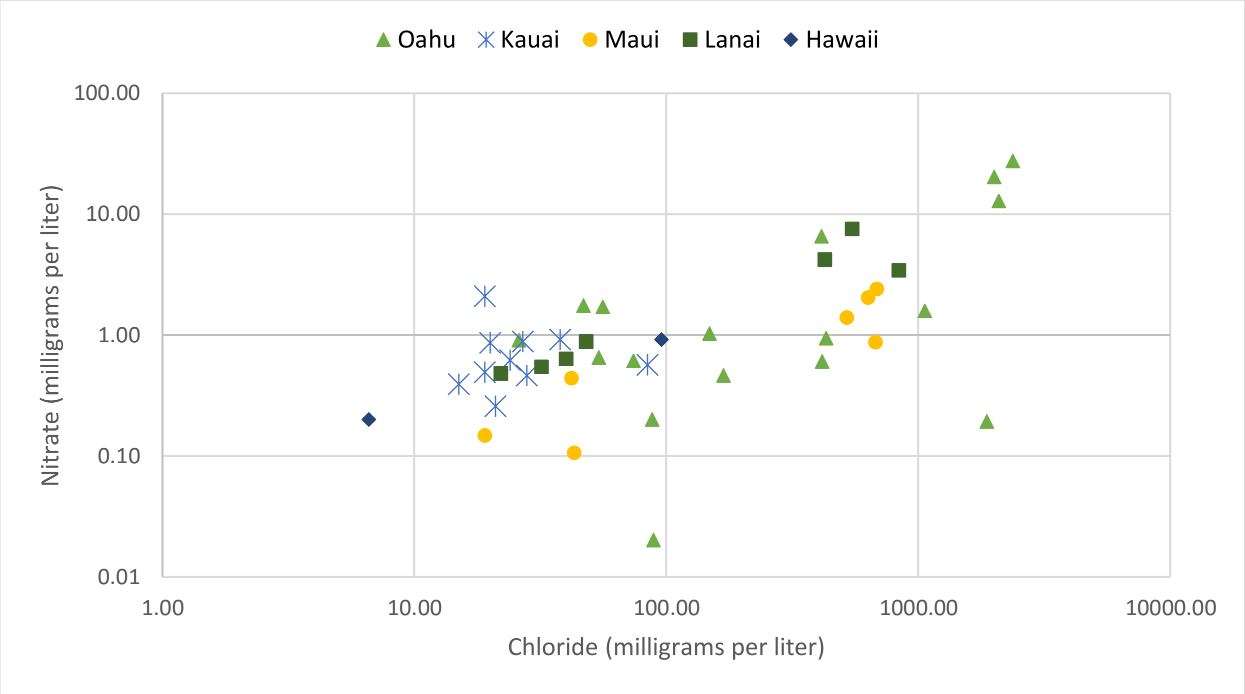


Figure 12. Concentration of Nitrate relative to Chloride within Sample Analysis for Oahu, Kauai, Maui, Lanai and the Island of Hawaii.

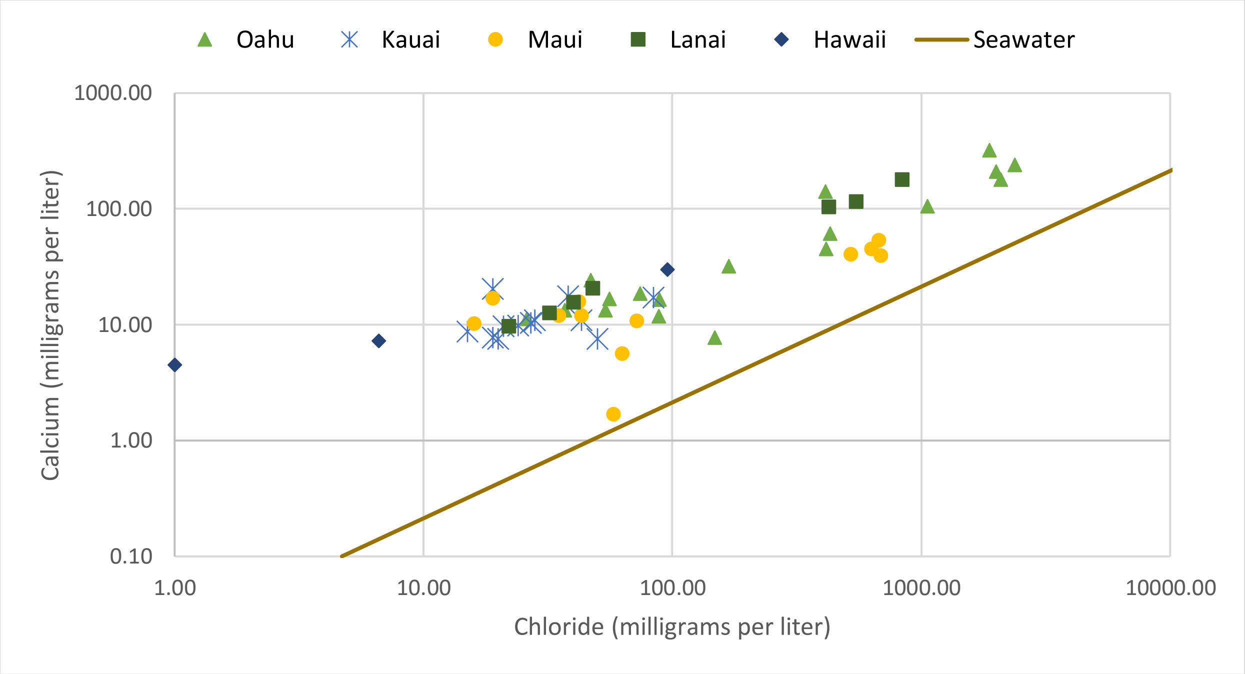


Figure 13. Concentration of Calcium relative to Chloride within Sample Analysis. Seawater Concentration (412/19,353 → 0.02)

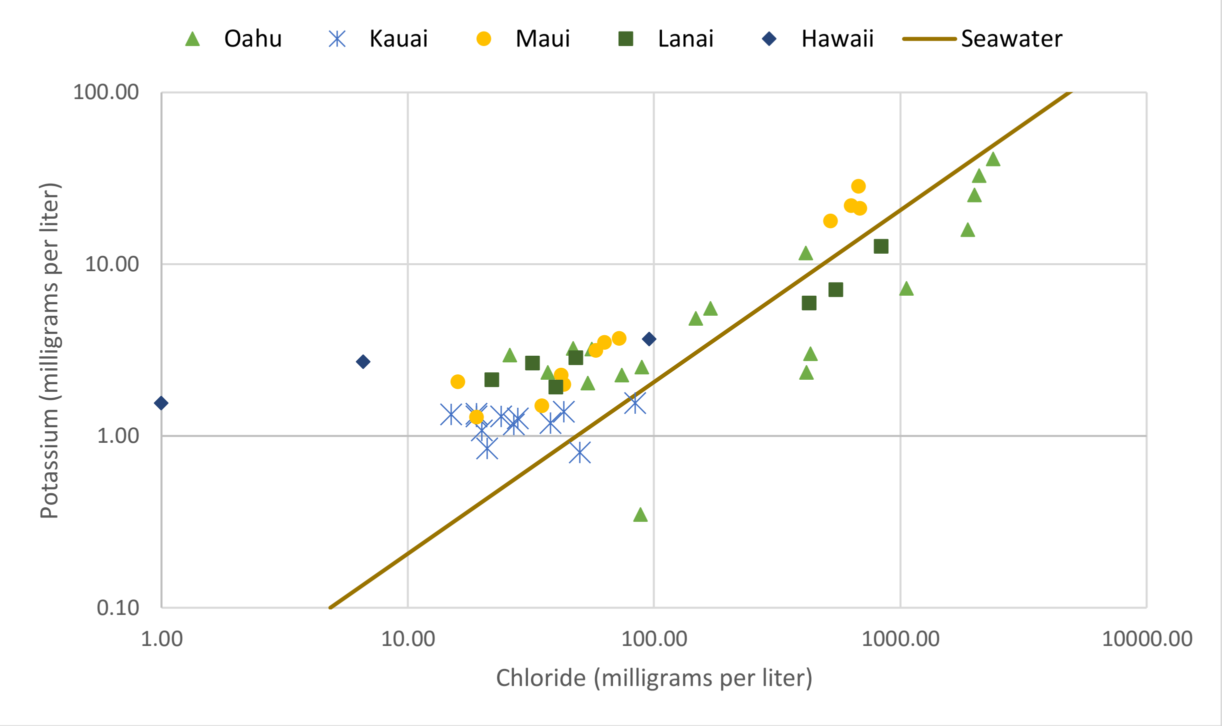


Figure 14. Concentration of Potassium relative to Chloride within Sample Analysis. Seawater Concentration (399/19,353 → 0.02)

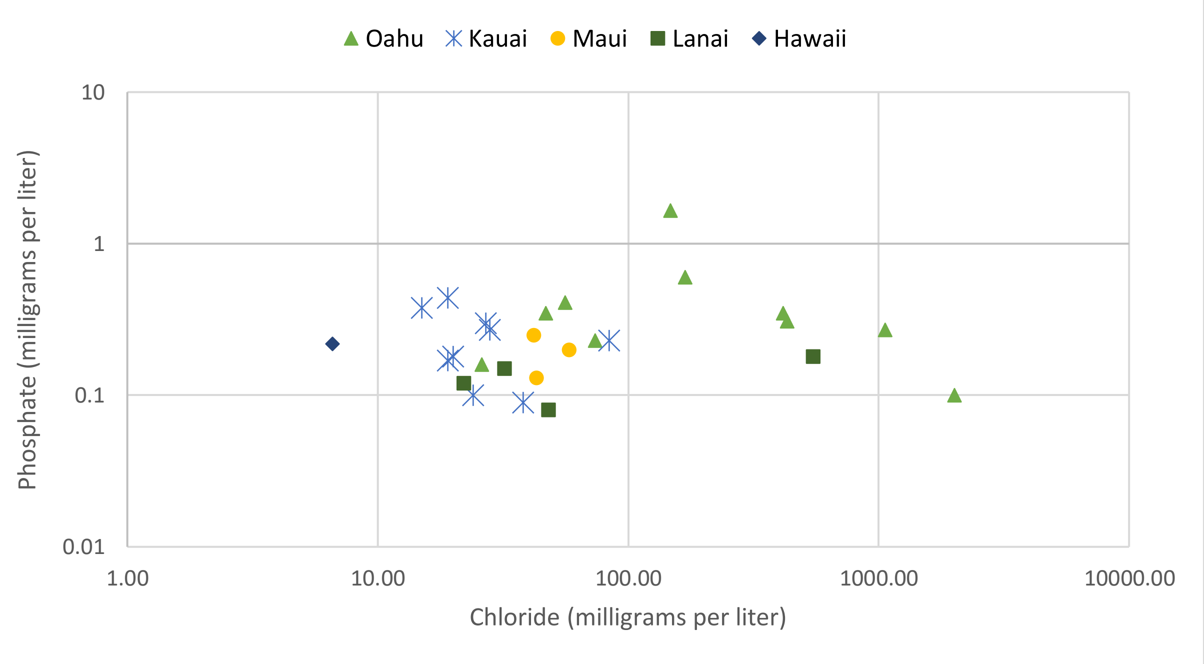


Figure 15. Concentration of Phosphate relative to Chloride within Sample Analysis

REFERENCES CITED

1. A-Mehr, Inc. (2015). PVT Integrated Solid Waste Management Facility Operations Plan. Retrieved November 30, 2018, from http://www.pvtland.com/wp-content/uploads/2015/06/PVT-ISWMF-EIS-Volume-II-Appendices_Reduced.pdf.

2. Aquion. (2015). Charge-Balance Error (CBE). Retrieved February 13, 2017, from http://www.aqion.de/site/92.

3. Board of Water Supply. (n.d.). Red Hill Documents. Retrieved November 29, 2018, from http://www.boardofwatersupply.com/news-events/news-and-updates/red-hill-documents.

4. Bergfeld, D., Lewicki, J. L., Evans, W. C., Hunt, A. G., Revesz, K., & Huebner, M. (2013). Geochemical investigation of the hydrothermal system on Akutan Island, Alaska, July 2012. US Geological Survey. Scientific Investigations. Rep, 5231, 20.

5. Clague, D., Sherrod, D., Poland, M., Takahashi, T., & Landowski, C. (2014). Growth and Degradation of Hawaiian Volcanoes. In Characteristics of Hawaiian Volcanoes, v. 1801, p. 97-146. United States Geological Survey. Reston, Virginia.

6. Cox, M., Sinton, J., Thomas, D., Mattice, M., Kauahikaua, J., Helstern, D., & Fan, P. (1979). Investigation of Geothermal Potential in the Waianae Caldera Area, Western Oahu, Hawaii.

7. Cox, M., Sinton, J., Thomas, D., Mattice, M., Kauahikaua, J., Helstern, D., & Fan, P. (1979). Investigation of Geothermal Potential in the Waianae Caldera Area, Western Oahu, Hawaii. Assessment of Geothermal Resources in Hawaii: Number 2 (No. HIG-79-8). University of Hawaii, Honolulu (USA). Hawaii Institute of Geophysics.

8. Cox, M., & Thomas, D. (1979). Cl/Mg Ratio of Hawaiian Groundwaters as a Regional Geothermal Indicator.

9. Cox, M., & Thomas, D. (1979). Chloride/Magnesium Ratio of Shallow Groundwaters as a Regional Geothermal Indicator in Hawaii. Assessment of Geothermal Resources in Hawaii: Number 3 (No. HIG-79-9). University of Hawaii, Honolulu (USA). Hawaii Institute of Geophysics.

10. Davis, S. (1969). Silica in Streams and Ground Water of Hawaii. University of Hawaii, Water Resources Research Center.

11. Dalrymple, G., Silver, E., & Jackson, E. (1973). Origin of the Hawaiian Islands: Recent Studies Indicate that the Hawaiian Volcanic Chain is a Result of Relative Motion Between the Pacific Plate and a Melting Spot in the Earth's Mantle. American Scientist, v. 61(3), p. 294-308.

12. Druecker, M., & Fan, P. (1976). Hydrology and Chemistry of Ground Water in Puna, Hawaii. Groundwater, v. 14(5), p. 328-338.

13. EPA, Environmental Protection Agency. (2014). The Red Hill Bulk Fuel Storage Facility in Hawaii. Retrieved November 29, 2018, from http://www.epa.gov/red-hill.

14. EPA, Environmental Protection Agency. (n.d.). Potential Well Water Contaminants and Their Impacts. Retrieved November 30, 2018, from http://www.epa.gov/privatewells/potential-well-water-contaminants-and-their-impacts.

15. Fetter, C. (2018). Applied Hydrogeology. Waveland Press.

16. Fournier, R., & Rowe, J. (1966). Estimation of Underground Temperatures from the Silica Content of Water from Hot Springs and Wet-Steam Wells. American Journal of Science, v. 264(9), p. 685-697.

17. Fournier, R., & Truesdell, A. (1973). An Empirical Na-K-Ca Geothermometer for Natural Waters. Geochimica et Cosmochimica Acta, v. 37(5), p. 1255-1275.

18. Fowler, N., Thomas, D., & Yen, W. (1980). Geothermal Energy.

19. Fox, R., Silva, J., Younge, O., Plucknett, D., & Sherman, G. (1967). Soil and Plant Silicon and Silicate Response by Sugar Cane 1. Soil Science Society of America Journal, v. 31(6), p. 775-779.

20. Fritz, S. (1994). A Survey of Charge-Balance Errors on Published Analyses of Potable Ground and Surface Waters. Groundwater, v. 32(4), p. 539-546.

21. Godoy, J., Godoy, M., & Neto, A. (2012). Direct Determination of δ (D) and δ (^{18}O) in Water Samples Using Cavity Ring Down Spectrometry: Application to Bottled Mineral Water. Journal of Geochemical Exploration, v. 119, p. 1-5.

22. Glenn, C., Whittier, R., Dailer, M., Dulaiova, H., El-Kadi, A. I., Fackrell, J., Kelly, J., Waters, C., & Sevadjian, J. (2013). Lahaina Groundwater Tracer Study-Lahaina, Maui, Hawaii.

23. Grose, L., Keller, G., Tasci, M., & Butler, D. (1975). Geothermal Energy in the Pacific Region. Appendix A: Exploration for a Geothermal System in the Lualualei Valley, Oahu, Hawaii. Appendix B: Exploration on Adak Island Alaska. Colorado School of Mines. Golden, Colorado.

24. Hautman, D., & Munch, D. (1997). Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography. United States Environmental Protection Agency: Ohio.

25. Hobdy, R. (1993). Lana'i a Case study: The Loss of Biodiversity on a Small Hawaiian Island.

26. Ito, G., Frazer, N., Lautze, N., Thomas, D., Hinz, N., Waller, D., Whittier R., & Wallin, E. (2017). Play Fairway Analysis of Geothermal Resources Across the State of Hawaii: 2. Resource Probability Mapping. Geothermics, v. 70, p. 393-405.

27. Juvik, S., Juvik, J., & Paradise, T. (Eds.). (1998). Atlas of Hawai'i. University of Hawaii Press.

28. Kroopnick, P. (1977). The SO_4: Cl Ratio in Oceanic Rainwater. Pacific Science, v. 32(1), p. 91-106.

29. Langenheim, V., & Clague, D. (1987). The Hawaiian-Emperor Volcanic Chain. Part, 2, p. 55-84.

30. Lautze, N., Thomas, D., Hinz, N., Apuzen-Ito, G., Frazer, N., & Waller, D. (2017). Play Fairway Analysis of Geothermal Resources across the State of Hawaii: 1. Geological, Geophysical, and Geochemical Datasets. Geothermics, v. 70, p. 376-392.

31. Lautze, N., Thomas, D., Waller, D., Frazer, N., Hinz, N., & Apuzen-Ito, G. (2017). Play Fairway Analysis of Geothermal Resources Across the State of Hawaii: 3. Use of Development Viability Criterion to Prioritize Future Exploration Targets. Geothermics, v. 70, p. 406-413.

32. Libes, S. (2011). Introduction to Marine Biogeochemistry. Academic Press.

33. Macdonald, G., Abbott, A., & Peterson, F. (1983). Volcanoes in the Sea: The Geology of Hawaii. University of Hawaii Press.

34. Macdonald, G., & Hubbard, D. (1968). Volcanoes of the National Parks in Hawaii.

35. Maly, K., & Maly, O. (2007). E Ike Hou Ia Lanai-To Know Lanai Once Again: A Historical Reference and Guide to the Island of Lanai. Lanai Culture & Heritage Center.

36. Martin, T., Brockhoff, C., Creed, J., & Long, S. (1992). Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. Methods for Determination of Metals in Environmental Samples. CRC Press Inc., Boca Raton, p. 33-91.

37. Maui County. (2016). Lanai Community Plan: Ordinance No. 4343, Bill No. 67.

38. Mink, J., & Lau, L. (1993). Aquifer Identification and Classification for Lāna‘i.

39. Naily, W. (2018a). Cl/Br Ratio to Determine Groundwater Quality. In IOP Conference Series: Earth and Environmental Science, v. 118(1), p. 012020. IOP Publishing.

40. Naily, W. (2018b). Ratio of Major Ions in Groundwater to Determine Saltwater Intrusion in Coastal Areas. In IOP Conference Series: Earth and Environmental Science, v. 118(1), p. 012021. IOP Publishing.

41. Pfaff, J. (1993). Method 300.0 Determination of Inorganic Anions by Ion Chromatography. United States Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, 28.

42. Plummer, L., Bexfield, L., & Anderholm, S. (2003). How Ground-Water Chemistry Helps Us Understand the Aquifer. United States Geological Survey Circular, v. 1222, p. 92-93.

43. Rieth, Timothy. (2009). An Archaeological Inventory Survey of the Former Voice of America Site, Mā‘ili, Lualualei Ahupua‘a, Wai‘anae District, O‘ahu. International Archaeological Research Institute, Inc.

44. Resing, J., & Sansone, F. (1999). The Chemistry of Lava–Seawater Interactions: The Generation of Acidity. Geochimica et Cosmochimica Acta, v. 63(15), p. 2183-2198.

45. Sawade, E., Fabris, R., Humpage, A., & Drikas, M. (2016). Effect of Increasing Bromide Concentration on Toxicity in Treated Drinking Water. Journal of Water and Health, v. 14(2), p. 183-191.

46. Schuchmann, H. (2015). Prospecting Geothermal Resources in Hawaii: Application of GIS Mapping and Water Chemistry (Undergraduate Thesis, University of Hawaii).

47. Shupe, J. (1973). Geothermal Power for Hawaii-Phase I. Geothermics, v. 2(3-4), p. 101-104.

48. Shupe, J. (1982). Energy Self-Sufficiency for Hawaii. Science, v. 216(4551), p. 1193-1199.

49. State of Hawaii, Department of Land and Natural Resources, Division of Water and Land Development. (1984). Assessment of Available Information Relating to Geothermal Resources in Hawaii.

50. Sverdrup, H., Johnson, M., & Fleming, R. (1942). The Oceans: Their Physics, Chemistry, and General Biology, v. 7. New York: Prentice-Hall.

51. Thomas, D., Cox, M., Erlandson, D., & Kajiwara, L. (1979). Potential Geothermal Resources in Hawaii: A Preliminary Regional Survey. Phase I, Final Report (No. HIG-79-4). University of Hawaii, Honolulu (USA). Hawaii Institute of Geophysics.

52. Thomas, D. (1982). Final Report for State of Hawaii DPED Allotment, Advice No. 166 and DPED Contract 1102, Hawaii Geothermal Assessment Program.

53. Thomas, D. (1986). Geothermal Resources Assessment in Hawaii. Geothermics, v. 15(4), p. 435-514.

54. Torres, M., Mix, A., & Rugh, W. (2005). Precise $\delta^{13}C$ Analysis of Dissolved Inorganic Carbon in Natural Waters Using Automated Headspace Sampling and Continuous-Flow Mass Spectrometry. Limnology and Oceanography: Methods, v. 3(8), p. 349-360.

55. Waller, D. (2015). Identification of Geothermal Resources in Hawaii Utilizing Aqueous Geochemistry (Master Thesis, University of Hawaii).

56. West, H., Garcia, M., Gerlach, D., & Romano, J. (1992). Geochemistry of Tholeiites from Lanai, Hawaii. Contributions to Mineralogy and Petrology, v. 112(4), p. 520-542.

57. Yen, W., & Iacofano, D. (1981). Geothermal Energy for Hawaii: A Prospectus.

58. Ziegler, A. (2002). Hawaiian Natural History, Ecology, and Evolution. University of Hawaii Press.