A HYDROGEOCHEMICAL EXAMINATION OF WEST HAWAIʻI'S WATER CYCLE

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAIʻI AT MĀNOA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

EARTH AND PLANETARY SCIENCES

April 2022

By

Diamond K. Tachera

Dissertation Committee:

Nicole Lautze, Chairperson
Henrietta Dulai
Scott Rowland
Donald Thomas
Giuseppe Torri
Kimberly Burnett

Keywords: groundwater, groundwater flow, recharge, precipitation, stable isotopes of water, $\delta^{18}O$, $\delta^{2}H$, dissolved ions, aquifer management, Hawaiʻi Island, community engagement

Acknowledgements

First and foremost, thank you to the West Hawaiʻi community without whom this research would not have been possible: Hui Aloha Kīholo, The Nature Conservancy, Rebecca Most, Barbara Seidel, Keith Olson, Pamela Madden, the Natural Energy Laboratory of Hawaiʻi Authority, Mana Purdy, the Queen Liliʻuokalani Trust, David Chai, Hualālai Resort, University of Hawaiʻi Pālamanui Campus, Tommy and Nina Segovia, Nāmaka Whitehead, Billy Lee, Keala Kanakaʻole, Colin Onaka, Kamehameha Schools, Hui Kuahiwi, Gregory Chun, Ardele Kershaw, Huʻehuʻe Ranch, Paul Ponthieux, Henk Rogers, Puʻu Waʻawaʻa Ranch, Britt Craven, Palani Ranch, Department of Land and Natural Resources Division of Forestry and Wildlife, Brian Shiro, Michaela Musilova, University of Hawaiʻi HI-SEAS, Fritz Klasner, Mike Yabe, Office of Maunakea Management, Aidan Colton, the Mauna Loa Observatory, Rick Strojny, Napuʻu Water, Puʻu Waʻawaʻa Ranch, Kimber Deverse, David Kadowaki, Hawaiʻi Water Service, Daniel Gudgel, Gene Quiamas, West Hawaiʻi Landfill, Jason Trim, Makani Golf Club, Darren Okimoto, Joshule JJ Johnston, William O'Neil Jr., and the Hawaiʻi County Department of Water Supply. Thank you to Jeremy Kimura, Bob Chenet, Patrick Casey, Neal Fujii, Ryan Imata, Nick Ing from the State of Hawaiʻi Commission on Water Resource Management for their continued collaboration.

Thank you to my advisor, Dr. Nicole Lautze, and committee members Dr. Henrietta Dulai, Dr. Scott Rowland, Dr. Donald Thomas, Dr. Giuseppe Torri, and Dr. Kim Burnett for your mentorship and patience as I navigate my journey through academic research. I appreciate your time in reviewing and co-authoring papers, and your support as I grow my confidence in writing. Thank you to Honour Booth, Daniel Dores, Henrietta Dulai, Kiana Frank, Kekuʻiapōiula Keliipuleole, Tristan McKenzie, Brytne Okuhata, Kexin Catherine Rong, Chris Shuler, Taylor Viti, Natalie Wallsgrove, and Sheree Watson for their assistance with sampling and data analysis.

Thank you to the UH Lab, KCC STEM Center, NHSEMP, SOEST Maile Mentoring Bridge Program, G&G undergrad lounge crew, POST 719D snack buddies, UCAR Next Generation Fellowship mentors and friends, Rising Voices Center of Indigenous and Earth Sciences ʻohana, and Department of Earth Sciences Huliāmahi JEDI ʻohana. Thank you for the in-person and virtual hugs over the years, the continued words of encouragement during this journey, and the teachings both in the classroom and in life. Thank you for always cheering me on and lifting me up when times got tough.

Thank you to the Department of Earth Sciences (formerly known as Geology & Geophysics) for all of the fun field trips, cool rock labs, and interesting conversations about our Earth. It has been so amazing to be mentored by so many role models who are passionate about their work and continue to mentor students along the way. Walking these halls over the last 9 years have been some of the best in my life. And thank you for allowing us to build the scaffolding of JEDI efforts in Huliāmahi, to move towards a diverse, equitable, and inclusive work and learning environment.

Mahalo piha to the kūpuna who built the foundations of the kanaka science that I hope to perpetuate and carry forward, for the aloha of the ʻāina and wai that flow through my veins. Mahalo for teaching me, for sharing your knowledge, and for guiding me on this journey even when I question "why" or "how". Mahalo nui to the keiki to come, who will follow in the footsteps of their kūpuna and continue to work for a better future. Mahalo for sharing this honua with your kūpuna, as we borrow it from you on our journey through life.

Finally, thank you to my friends and family for your continued love and support: to mom and dad for the greatest amount of patience and hugs that a child could ever want, to grandma for being the biggest cheerleader of all time, to papa who watches over us from the heavens and keeps us in good health and spirit, to the rest of the family for always feeding me and the family holiday parties that I look forward to every year. A special thank you to Bodie - my study buddy, alarm clock, ankle biter - the unexpected bundle of fluff that fell out of a tree and into my life in the most fantastic, loving way.

This project was funded by the NSF Hawaiʻi EPSCoR Program through the National Science Foundation's Research Infrastructure Improvement award (RII) Track-1: ʻIke Wai: Securing Hawaiʻi's Water Future Award # OIA-1557349. Additional funding for student support was provided by NSF GEO #2022937, NSF EAR #2047313, and a Geoscience Alliance award. The views expressed are those of the author(s) and do not necessarily reflect the views of any of the agencies listed.

Abstract

Groundwater, sourced from precipitation, is the main source of drinking water in the State of Hawaiʻi. Understanding Hawaiʻi's groundwater system is critical to understanding future water security. With increasing development, decreasing rainfall, and sea level rise, the uncertainty of Hawaiʻi's water resource security is a growing concern. The overarching goal of this dissertation is to address the source, flow, and interconnectivity of Hawaiian aquifer systems. This dissertation identified relationships between precipitation and groundwater using stable isotopic compositions of water, flow and connectivity of groundwater aquifers using relative abundances of geochemical parameters, and the relationship between geochemical abundances and spatial distribution.

The second chapter evaluates the isotopic and chemical compositions of rainfall from central to leeward Hawaiʻi Island. The study collected cumulative rainfall samples at regular intervals over a 28-month period from 20 stations spanning a range of elevations across this region, and determined average isotopic and dissolved ion compositions in those samples. The study period included an extreme weather event (Hurricane Lane), a major volcanic eruption at Kīlauea in 2018, and the nearly complete cessation of long-term volcanic emissions following that eruptive event. Consistent with previous literature, results show long-term variability through the establishment of an enhanced local meteoric water line (LMWL) for West Hawaiʻi. Additionally, results of stable isotope compositions and bulk ion deposition highlight how extreme events, such as volcanic eruptions and hurricanes, can affect the chemistry of precipitation. The results from this study can be used to better quantify and characterize precipitation, which is the ultimate source of Hawaiʻi's groundwater.

Groundwater chemistry studies utilize the occurrence of dissolved ions and other geochemical parameters to determine source, quality, flow, and interconnectivity of aquifers. In groundwater chemistry studies focused on island and coastal environments, a salinity correction is routinely applied, which subtracts the fraction of ocean water from a mixed fresh- and salt-water system in order to focus on fresh-water processes. The third chapter identifies challenges associated with accurate identification of the ocean water fraction in groundwater in a location where dissolved ion contribution can occur through processes that include seawater intrusion, seaspray deposition, wastewater, and hydrothermal reactions. Further exacerbating this challenge is the complex subsurface hydrogeologic environment of West Hawaiʻi Island. The simplistic end-member values for fresh and ocean water currently used in salinity corrections proved challenging for this region. Instead, the study finds the use of end-members chosen from within probable groundwater flow paths produces better results (less frequent over corrections). In addition, this study finds that alkalinity analyses cause higher charge balance errors in groundwater with lower ion concentrations. Charge balance errors may be a good check of quality for datasets, but are not definitive in determining whether a dataset is viable for further geochemical analyses.

The fourth chapter uses the geochemical datasets and analyses from previous chapters to better understand areas of recharge as well as the interconnectivity of groundwater aquifers in West Hawaiʻi. The research utilized two methods to calculate groundwater recharge elevations: point-source and fully-integrated recharge. The utilization of two methods constrained the possible range of recharge elevations from Hualālai, Mauna Kea, and Mauna Loa volcanoes. In many cases, the recharge from Hualālai volcano is not isotopically depleted enough to account for the isotopic compositions of groundwater found in the Hualālai aquifer systems. More depleted recharge from Mauna Loa or Mauna Kea volcanoes are additionally needed to account for the isotopically-depleted groundwater. In addition, recharge crosses current aquifer management boundaries used for groundwater resources.

The final chapter explores inequalities in funding structures for scientific research. The current academic and research systems are rooted in colonization and continue to perpetuate the exploitation of Indigenous lands and peoples. As the geoscience field works towards a more diverse, equitable, and inclusive environment, leadership from funding agencies must recognize the burden of broader impacts on Indigenous scientists, and the additional devaluing of community engagement and other labor necessary for equitable scientific research practices. Enacting steps for accountability and encouraging best practices in community-driven research are two ways that, as a scientific community, we can raise our standards of ethical research and develop reciprocity and respect, and repair relationships.

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Chapter 1. INTRODUCTION

1.1 Water in Hawaiʻi

Ola i ka wai a ka ʻōpua– *there is life in the water from the clouds* (Pukui, 1983). Kānaka ʻōiwi (Native Hawaiians) have understood their relationship with the land, water, and surrounding ecosystems for generations. Moʻolelo (stories) and ʻōlelo noʻeau (wise proverbs) tell us the stories and experiences of the past, passing down the observations and knowledge of our kūpuna (ancestors). For example, wai (water) was such a vital and precious resource that other Hawaiian words are rooted in wai: waiwai (wealth) and kānāwai (law). The ahupuaʻa (land management) system designated land boundaries from mauka (mountain) to makai (sea), with every ahupuaʻa containing enough resources to sustain each community. Ola i ka wai a ka ʻōpua is a testament to the observation of my kūpuna: that there is a cycle and connection between all waters, and the water resources that feed our bodies and land are sourced from precipitation.

Groundwater is the main source of drinking water in the State of Hawaiʻi. Every Hawaiian Island, however, has its own challenges regarding water resources. Even within an island, groundwater resource issues may vary based on specific location. For example, the low-lying industrial area of Māpunapuna (Oʻahu) is experiencing impacts from sea level rise because although it is not a coastal area, sea level rise is causing the water table to rise closer to the ground surface, and will flood streets during high tides. Other challenges relate to the overuse of groundwater. In Kailua-Kona (Hawaiʻi Island), extensive pumping of shallow groundwater is causing salinization and seawater intrusion in some areas.

To best manage groundwater usage across the State, the Hawaiʻi State Legislature established the State Water Code in the late 1980s, thus establishing the Commission on Water Resource Management (CWRM). Through the State Water Code, CWRM protects and manages fresh waters in Hawaiʻi by designating surficial aquifer boundaries. Within each aquifer, a sustainable yield (pumping limit) is assigned based on the estimated amount of available groundwater. However, the characterization of groundwater aquifers - source, volume, connectivity - is still poorly understood. Understanding Hawaiʻi's groundwater system is critical to ensuring future water security with the threat of climate change. With increasing development, decreasing rainfall, and sea level rise, the uncertainty of Hawaiʻi's water resource security is a growing concern.

1.2 Dissertation organization and significance

This dissertation uses stable isotopic compositions of water and relative abundances of geochemical parameters to address the source, flow, and interconnectivity of aquifer systems in West Hawaiʻi (Hawaiʻi Island). Historically, Hawaiʻi Island's complex subsurface geology - such as the basal and high-level divide - has created many challenges in understanding groundwater aquifer systems (Oki, 1999). With increasing anthropogenic impacts and the threat of climate change, the uncertainty of Hawaiʻi's groundwater sustainability is a growing concern.

Chapter 2, *Characterization of the isotopic composition and bulk ion deposition of precipitation from Central to West Hawaiʻi Island between 2017 and 2019*, evaluates the isotopic and chemical compositions of rainfall from central to leeward Hawaiʻi Island. The study collected cumulative rainfall samples at regular intervals over a 28-month period from 20 stations spanning the entire range of elevations in this region and determined average isotopic and dissolved ion compositions in those samples. The study period included an extreme weather event (Hurricane Lane), a major volcanic eruption at Kīlauea in 2018, and the nearly complete cessation of what had been > 30 years of volcanic emissions following that eruptive event. Consistent with previous literature, stable isotopes of water results show long-term variability through the establishment of an enhanced local meteoric water line (LMWL) for West Hawaiʻi. Additionally, results of stable isotopic compositions and bulk ion deposition highlight how extreme events can affect the chemistry of precipitation. The results from this study can be used to better quantify and characterize precipitation, which is the ultimate source of Hawaiʻi's groundwater.

Chapter 3, *Flow dependent salinity corrections in West Hawaiʻi aquifers*, identifies challenges associated with accurate calculation of the ocean water fraction in groundwater in a location where dissolved ion contribution can occur through processes that include seawater intrusion, seaspray deposition, wastewater releases, and hydrothermal reactions. Groundwater chemistry studies utilize the occurrence of dissolved ions and other geochemical parameters to determine source, quality, flow, and interconnectivity of aquifers. In groundwater chemistry studies focused on island and coastal environments, a salinity correction is routinely applied, which subtracts the fraction of ocean water from a mixed fresh- and salt- water system, in order to focus on fresh-water processes. In West Hawaiʻi Island, however, the complex subsurface hydrogeology complicates routine salinity correction methods. The simplistic end-member values of pure fresh and pure ocean water currently used in salinity corrections proved challenging for this region. Instead, this study finds the use of end-members chosen from within probable groundwater flow paths produces better results (less frequent overcorrections), and finds that alkalinity analyses cause higher charge balance errors in groundwater with lower ion concentrations.

Chapter 4, *Identifying groundwater source, flow, and interconnectivity in West Hawaiʻi*, uses the geochemical datasets and analyses from previous chapters to better understand areas of recharge and the interconnectivity of groundwater aquifers in West Hawaiʻi. The research utilizes two methods to calculate groundwater recharge elevations: point-source and fully-integrated recharge. The utilization of two methods constrained the possible range of elevations of recharge from Hualālai, Mauna Kea, and Mauna Loa volcanoes. In many cases, the recharge from Hualālai volcano is not isotopically depleted enough to account for the isotopic compositions of groundwater found in the Hualālai aquifer systems. More depleted recharge from Mauna Loa or Mauna Kea volcanoes are additionally needed to account for the isotopically-depleted groundwater. In addition, recharge crosses current aquifer management boundaries used for groundwater resources.

Chapter 5, *Reframing funding strategies to build reciprocity*, is an opinion piece published in Eos as part of my UCAR Next Generation Diversity and Inclusion Fellowship. This paper explores the inequalities experienced by people of color (POC) in the geoscience fields. In addition, the short timelines of funding grants perpetuates the inequalities further with local and Indigenous communities who assist researchers with data collection and share Indigenous knowledges. The paper proposes reframing funding structures that will build reciprocity and repair relationships between the academic and Indigenous communities who participate in scientific research.

Chapter 6 summarizes the main findings of Chapters 2 through 4. It also discusses potential future work for the West Hawaiʻi region, and ways to further explore the complex interactions between water, geology, and the local community.

1.3 West Hawaiʻi study region

The National Science Foundation's Established Program to Stimulate Competitive Research (EPSCoR) *ʻIke Wai* project is focused on two areas: Pearl Harbor aquifer located in central Oʻahu, and Hualālai aquifer sector located in western Hawaiʻi Island. The Hualālai aquifer sector, composed of the Kīholo and Keauhou aquifer systems, as well as the surrounding aquifers, are the focus of this dissertation. *ʻIke Wai* aimed to address five main questions in West Hawaiʻi, with strong emphasis on source, flow, and connectivity:

1. What is the degree of connectivity between the high level and basal aquifers?
2. What are the sources of water that pass through the Hualālai aquifer?
3. How does the Hualālai volcano's rift zone affect groundwater flow and quality within the Hualālai aquifer?
4. In the Keauhou aquifer, what is the nature of the geologic structures as linked to subsurface water storage?
5. What is the submarine groundwater discharge volume and distribution along the coastal boundary of the aquifer and what are the water quality metrics (salinity, nutrient levels, etc.) relevant to the coastal ecosystems?

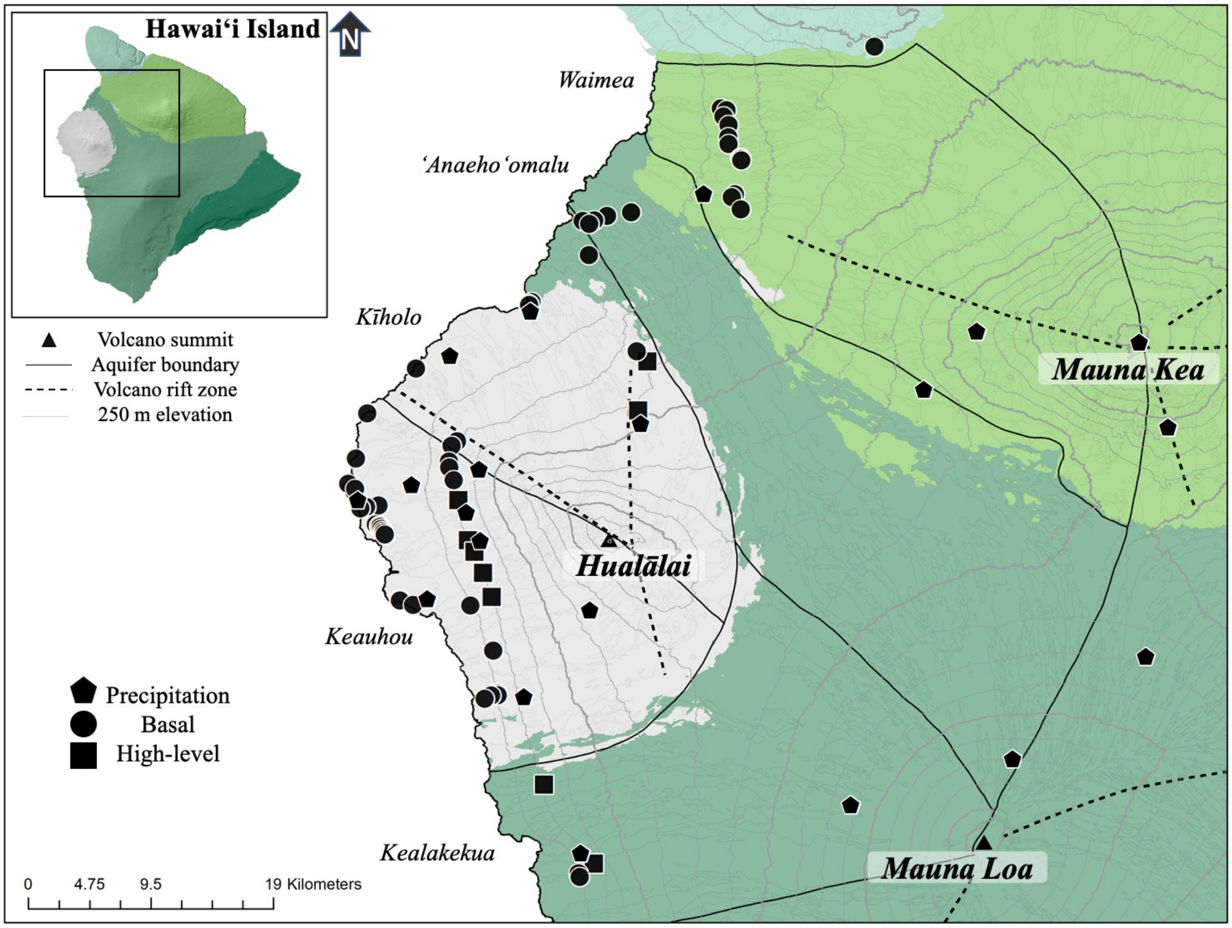

Figure 1.1. West Hawai‘i study region map. Circles represent basal groundwater sample sites, squares represent high-level groundwater sites, and pentagons represent precipitation collector sites. Solid black lines outline the five aquifers in the region: Waimea, ‘Anaeho‘omalu, Kīholo, Keauhou, and Kealakekua. Basemap colors represent surface flows of volcanoes: Kohala, Mauna Kea, Hualālai, and Mauna Loa. Dotted lines represent approximate locations for rift zones of each volcano. Black triangles indicate the summits of Hualālai, Mauna Kea, and Mauna Loa volcanoes. Gray lines show the 250 m elevation contours.

To address these questions, *‘Ike Wai* assembled a muti-disciplinary team of researchers. Geochemical, geophysical, microbial, economic, and modeling techniques were used in conjunction with community ‘ike (Hawaiian knowledge). The project also translated Hawaiian language newspapers that mention water features within the study region. These five questions, along with other concerns, were brought up by community stakeholders such as ranchers and land managers. As a stakeholder driven project, *'Ike Wai* was committed to integrating community concerns about natural resource management into research goals, and including ‘ike kūpuna (ancestral knowledge) of past management techniques to address future concerns related to climate change and overuse of groundwater resources. This dissertation addresses the 1) source of groundwater through stable isotope values of water, and 2) flow and connectivity through stable isotopes of water and dissolved ion concentrations.

1.4 Stable isotopes of water

Kinetic fractionation of stable isotopes of hydrogen and oxygen in a water molecule arises from a phase change between vapor and liquid, and this fractionation allows hydrologists to examine variations in Earth's water cycle. Stable isotopes of water are often used as natural tracers in hydrologic studies because it is assumed that the isotopic composition ($\delta^{18}O$ and δD) remains the same as the composition at which it fell to the ground are precipitation, without any (or minimal) changes during the recharge infiltration process (i.e. Scholl et al., 1996). Isotopic ratios are reported as the ratio R of ^{18}O to ^{16}O or ^{2}H to ^{1}H divided by the ratio of a standard:

$$\delta = ((R_{sample}/R_{standard})-1) \times 1000$$

where R_{sample} is $^{18}O/^{16}O$ (or $^{2}H/^{1}H$) of the sample, and $R_{standard}$ is $^{18}O/^{16}O$ (or $^{2}H/^{1}H$) of a standard, typically Standard Mean Ocean Water (SMOW) and reported in per mil (‰).

SMOW is the global standard used to compare all isotopic compositions of water. The current standard, created by the International Atomic Energy Agency (IAEA) is called VSMOW2 (a second iteration of VSMOW) where V stands for Vienna (International Atomic Energy Agency, 2017). Ocean water provides a good standard for water isotopic evaluations because 97% of Earth's water resides in the ocean, and globally has very small variations ($\delta^{18}O$ = 0±1‰ and $\delta^{2}H$ = 0±5‰; Sharp, 2017). As ocean water is the principal source of atmospheric water vapor, the ocean makes an ideal standard by which to compare water isotope values.

The Global Meteoric Water Line (GMWL) is a linear trend-line that relates $\delta^{18}O$ and δD, and describes the majority of precipitation that falls on Earth. It was described by Craig (1961) as:

$$\delta D = 8\ \delta^{18}O + 10$$

Global isotopic distributions are dominantly controlled by temperature. Colder temperatures inland and at high altitudes prevent an air mass from easily holding onto moisture in comparison to warmer, coastal regions at lower altitudes. The effects of temperature on isotopic variation can be described by four controlling factors (Figure 1.2): 1) the distance or continentality effect, 2) the latitude effect, 3) the altitude effect, and 4) the amount effect (Sharp, 2017).

As an air mass rains out water, the heavier isotopes (^{18}O and ^{2}H) fall out first in a process called Rayleigh fractionation. Resultantly, the residual air mass has a lighter isotopic composition. The formation of precipitation and removal of heavier isotopes from the system prevents back exchange between the two phases, leaving the new parent mass isotopically lighter (Sharp, 2017). This rain-out effect is globally caused by the four controlling factors previously listed: distance, latitude, altitude, and amount. Local Meteoric Water Lines (LMWL) can be derived for smaller-than-global scales, and differ from the GMWL due to factors such as variations in source of evaporation, temperature, and amount of rainfall. These effects will be investigated in rainfall isotopic trends, in order to relate groundwater isotopic compositions to recharge elevations.

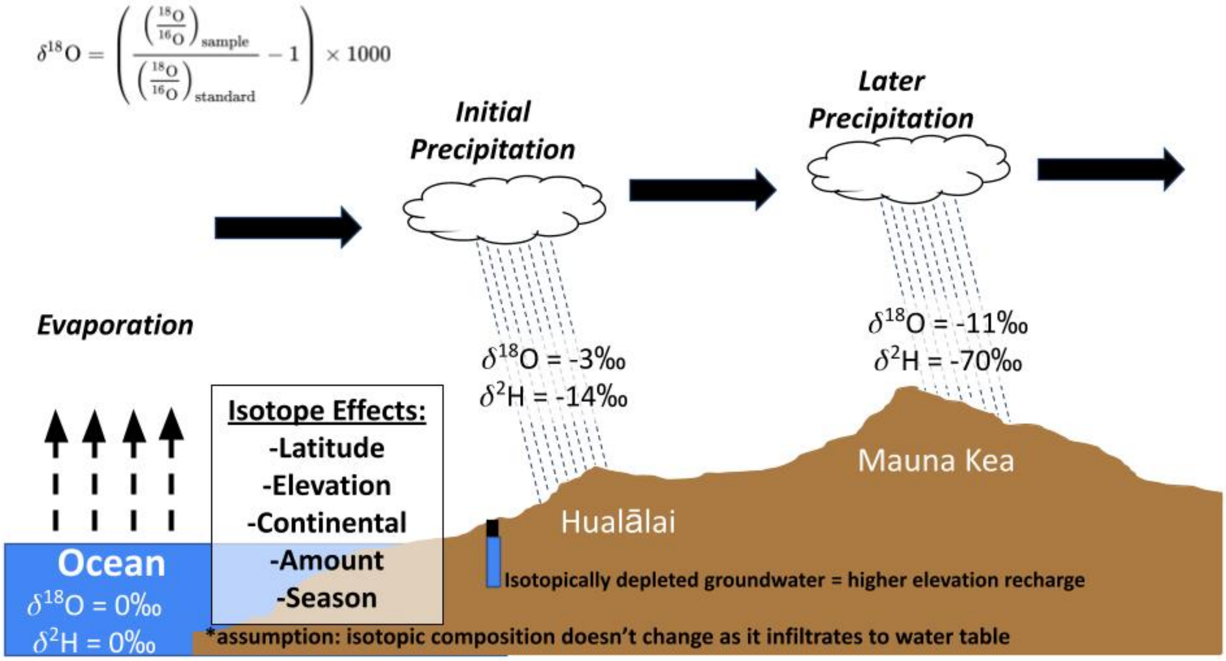

Figure 1.2. Diagram for stable isotopes of water in the West Hawai'i region. A simplistic depiction of stable isotopes of water in precipitation in the West Hawai'i study region. As vapor in an air mass condenses and produces precipitation, the isotopic compositions (δ^{18}O and δD) of the clouds and precipitation change with space and time through a process called Rayleigh fractionation. This study assumes the stable isotopes of water (δ^{18}O and δD) remain the same as the composition at which it fell to the ground surface, without any changes during the infiltration process, allowing it to serve as a tracer of source, flow, and interconnectivity of groundwater aquifers.

Chapter 2. CHARACTERIZATION OF THE ISOTOPIC COMPOSITION AND BULK ION DEPOSITION OF PRECIPITATION FROM CENTRAL TO WEST HAWAI‘I ISLAND BETWEEN 2017 AND 2019

Published as: Tachera, D. K., Lautze, N. C., Torri, G., and Thomas, D. M. (2021). Characterization of the isotopic composition and bulk ion deposition of precipitation from Central to West Hawai‘i Island between 2017 and 2019. Journal of Hydrology: Regional Studies, v. 34. doi: 10.1016/j.ejrh.2021.100786

Abstract

The current study evaluates the isotopic and chemical compositions of rainfall from central to leeward Hawai‘i Island, an area characterized by the interactions of Pacific tradewind flow with two 4,000-meter high mountains as well as one of the largest natural emitters of sulfur dioxide on the planet. Our study collected cumulative rainfall samples at regular intervals over a 28-month period from 20 stations spanning a range of elevations across this region and determined average isotopic and dissolved ion compositions in those samples. The study period included an extreme weather event (Hurricane Lane), a major volcanic eruption at Kīlauea in 2018, and the nearly complete cessation of long-term volcanic emissions following that eruptive event. Consistent with previous literature, results show long-term variability through the establishment of an enhanced local meteoric water line (LMWL) for West Hawai‘i. We hypothesize the two LMWL represent ends of a spectrum, due to the variability in atmospheric and climate processes in this region. Additionally, results of stable isotope compositions and bulk ion deposition highlight how extreme events, such as volcanic eruptions and hurricanes, can affect the chemistry of precipitation. Sulfate concentrations in bulk precipitation decreased by a mean of 70% ($p = 0.032$) after the 2018 Kīlauea eruption ceased. The results from this study can be used to better quantify and characterize precipitation, which is the ultimate source of Hawai‘i’s groundwater.

2.1 Introduction

Groundwater is the main source of potable water in the State of Hawai‘i. To better understand the spatial distribution of groundwater recharge on Hawai‘i Island, we look to the source - precipitation. Understanding the source of Hawai‘i’s groundwater is critical to future water security. Questions including the degree of connectivity between aquifers, and the sustainability of groundwater withdrawal, continue to puzzle hydrogeologists and draw concerns from growing communities and water managers across the State, including West Hawaiʻi. Complex subsurface geologic structures in West Hawaiʻi Island are inferred, which require further investigation (Oki, 1999; Tillman et al., 2014; Kelly and Glenn, 2015; Attias et al., 2020). Building upon other studies (e.g., Fackrell et al., 2020), we investigate the variable chemistry of precipitation from Central to West Hawaiʻi Island given its link to source, storage, and flow of groundwater.

This research is part of the National Science Foundation, EPSCoR Track 1 ʻIke Wai project. A key science goal of ʻIke Wai was to investigate groundwater recharge, storage, and flow within an ocean island volcanic environment. ʻIke Wai collected, and is currently analyzing, new geophysical, microbiological, and geochemical data in the West Hawaiʻi study region. The objective of this paper specifically, is to investigate isotopic and bulk ion deposition variability in precipitation across an extended region of Central and West Hawaiʻi Island. Here we present results from precipitation samples collected at 20 sites on an approximately quarterly basis between August 2017 and November 2019 (Figure 2.1). During the 28-month sampling period, Kīlauea Volcano experienced a large-volume East Rift Zone eruption from early May to September 2018 that, at its conclusion, terminated a ~35 year period of nearly continuous eruptive activity at Kīlauea. Hurricane Lane impacted the State of Hawaiʻi and specifically Hawaiʻi Island in late August 2018. These events allowed us the rare opportunity to investigate the impact of volcanic gases (also known as vog) and a hurricane, respectively, on the precipitation chemistry.

The stable isotopes of water, ^{18}O and ^{2}H (also referred to as deuterium or D), have been used around the world to identify the source and flow trajectories of water. The global meteoric water line (GMWL) is a linear trendline that describes the majority of precipitation that falls on Earth by relating $\delta^{18}O$ and δD as $\delta D = 8\ \delta^{18}O + 10$ (Craig, 1961). Two main factors that control the isotopic composition of precipitation are the temperature of condensation and the amount of rainout from the air mass (Dansgaard, 1964). Seasonal variations in $\delta^{18}O$ and δD precipitation values at tropical latitudes can be attributed to the source of moisture and to the amount effect, as well as elevation and types of convection (Torri et al., 2017). These variations remain fairly constant at tropical latitudes due to their consistent annual climatic patterns (Dansgaard, 1964). A first publication on the stable isotope variations in Hawaiʻi rainfall was by Friedman and Woodcock (1957), and focused on East Hawaiʻi Island. More recent work in Hawaiʻi has been conducted in the Kīlauea Region of Hawaiʻi Island, on Haleakalā on Maui, on the island of Oʻahu, and in West Hawaiʻi Island (Scholl et al., 1996; Scholl et al., 2002; Tillman et al., 2014; Fackrell et al., 2020; Dores et al., 2020). This research expands on the work of Fackrell et al. (2020) in West Hawaiʻi. Between October 2012 and December 2014, Fackrell et al. (2020) collected and analyzed isotopic compositions of precipitation recovered at six-month collection intervals from eight sites and produced a local meteoric water line (LMWL) for the West Hawaiʻi region. Using the LMWL in conjunction with groundwater data, their study determined recharge elevations to develop new conceptual models for groundwater flow paths. One of their conclusions is the suggestion that precipitation from high elevations on Mauna Kea and Mauna Loa volcanoes recharge the Hualālai aquifers. However, no data were collected from the high-elevation regions, demonstrating the need for an expanded investigation in order to more fully comprehend the complex hydrogeology of West Hawaiʻi.

Precipitation studies focusing on chemical composition, pH, and the effects of Kīlauea gases on acid rain have been conducted on Hawaiʻi Island for more than six decades (Eriksson, 1957; Miller and Yoshinaga, 1981; Harding and Miller, 1982; Nachbar-Hapai et al., 1989; Siegel et al., 1990; Scholl and Ingebritsen, 1995). Similar coastal and volcanic studies of wet and bulk (wet + dry) deposition of major ions in precipitation have been conducted around the world, such as in Mexico (Cerón et al., 2005), Korea (Lee et al., 2000), and Italy (Aiuppa et al., 2006). A study by Zuo et al. (2020) used rainfall and vog emission observations in a numerical model to demonstrate that increased aerosols from Kīlauea Volcano have reduced rainfall for the downwind regions of Hawaiʻi Island.

Although challenging to collect, we contend that long-term precipitation geochemistry data over a broad area of Hawaiʻi Island are needed to develop a LMWL that is able to characterize the isotopic composition of rainfall recharge and its evolution to local groundwater. This paper provides the most comprehensive such dataset to date.

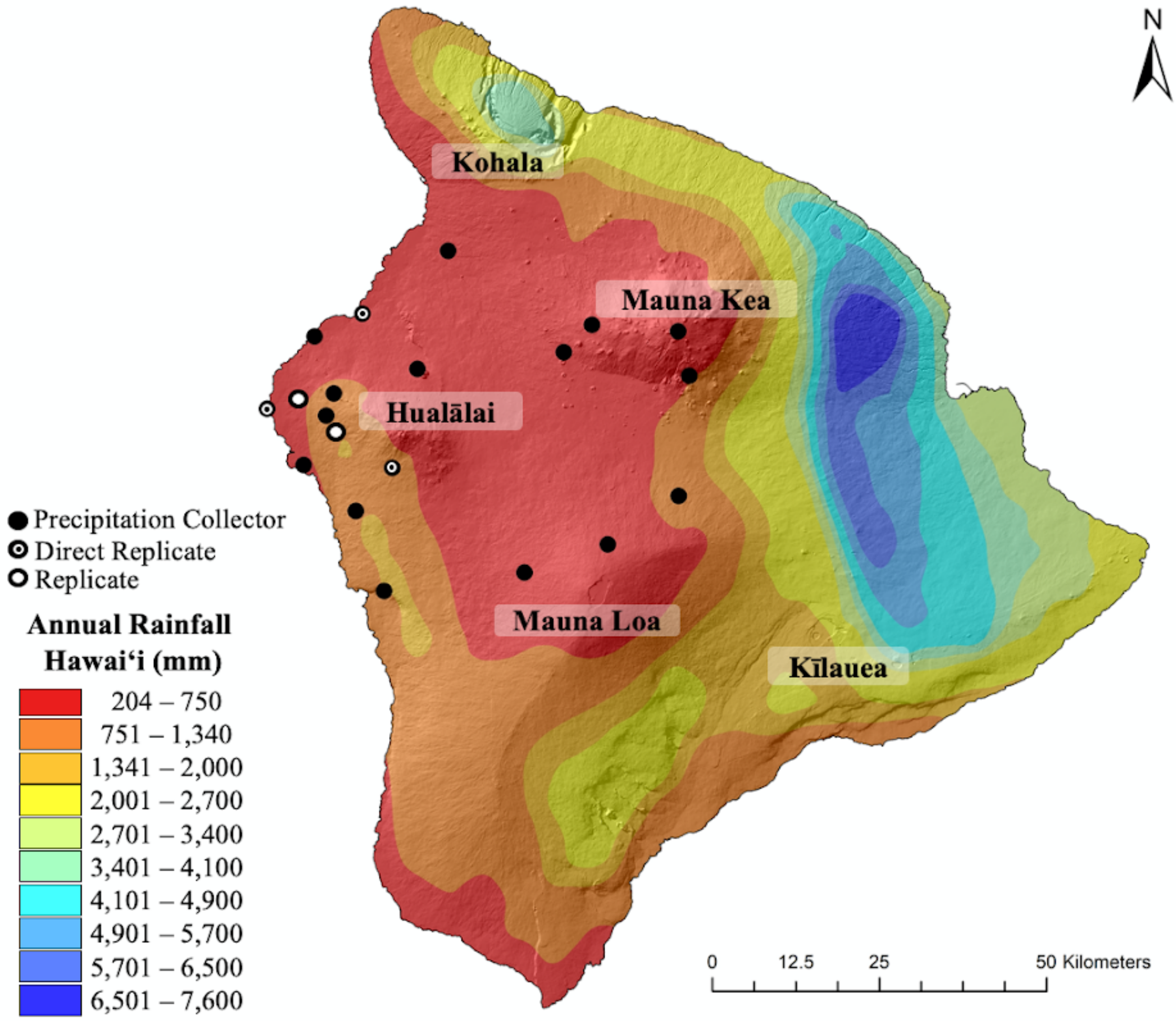

Figure 2.1. Precipitation collectors. Twenty precipitation collectors (black points) were deployed throughout the West Hawai‘i study area, extending into Central Hawai‘i Island on Mauna Kea and Mauna Loa volcanoes. Five replicated sites from the Fackrell et al. (2020) study are shown, three as direct replicates and two replicates to within two kilometers and 100 meters elevation. The base map shows average annual rainfall contours for Hawai‘i Island (Giambelluca et al., 2013); the five volcanoes of Hawai‘i Island are labeled.

2.2 Material and methods

2.2.1 Study site

There are three volcanoes located within the West Hawaiʻi study region: Hualālai, Mauna Kea, and Mauna Loa (Figure 2.1). Hualālai volcano is the western-most volcano on Hawaiʻi Island, standing at an elevation of 2,523 meters above mean sea level (amsl). Although the age of Hualālai versus Mauna Kea has been debated over time (Moore and Clague, 1992), the most recent research identifying the superposition of shore breaks supports that Hualālai is older (Taylor, 2019). Mauna Loa is one of the most voluminous volcanoes on the planet, rising to 4,169 meters amsl. Mauna Kea is slightly taller, standing at 4,207 meters amsl. Hualālai and Mauna Loa are considered volcanically active, and all three volcanoes have surface lava flows that extend to the coast within the study area.

The study area experiences a diverse range of climates. Mean annual air temperatures range from 22-24°C in coastal regions to 4-6°C in the high summit regions of Mauna Loa and Mauna Kea (Giambelluca et al., 2014). Due to Hualālai's placement in the rain shadow of Mauna Kea and Mauna Loa, trade wind-derived orographic precipitation does not reach this region. Instead, land-breeze sea-breeze patterns are experienced almost daily. Annual rainfall averages for Hawaiʻi Island range from 204 mm to 2,750 mm (Giambelluca et al. 2013). The Kona coffee region of Kailua-Kona has a unique pattern of rainfall, with a band of higher rainfall at mid-elevations (300 m-500 m amsl) (Figure 2.1). Airflow travels from the eastern side of Hawaiʻi Island (Kīlauea) around the southern tip and back up the western slopes of Mauna Loa, causing a persistent band of clouds and rain almost daily (Giambelluca et al., 2013). Afternoon land breezes typically enhance the cloud belt. West Hawaiʻi experiences more intense rain events during the summer months, in contrast with much of the rest of the State of Hawaiʻi, which experiences the most rain in the winter (Leopold, 1949). Precipitation above the trade wind inversion, found at around 2,000 meters, decreases steeply with elevation, resulting in a dry environment that receives rain dominantly from extra-tropical and subtropical storms (Giambelluca et al., 2013).

Kīlauea is the eastern-most volcano on Hawaiʻi Island and has, until recently, been in a state of nearly continuous eruption for more than 35 years. Volcanic gases emitted by Kīlauea are dominantly carbon dioxide (CO_2), sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and hydrogen halides (HF, HCl, HBr) and are distributed throughout Hawaiʻi by varying weather systems (Sutton and Elias, 2014). From 1983 to 2018, eruptive activity occurred along Kīlauea's East Rift Zone as well as at the summit, where a lava lake at Halemaʻumaʻu crater produced heavy gas plumes between 2008 and 2018 (Neal and Anderson, 2020). Kīlauea erupted on its Lower East Rift Zone (LERZ) between late May to September 2018, draining the lava lake, causing a more than 10-fold increase in gas emissions and, at the conclusion of that event, bringing a cessation in eruptive activity for the first time in decades (Williams et al., 2020).

2.2.2 Sampling methods

Twenty rain collectors were deployed throughout the study site. Three of our sites exactly replicated, and two were located within two kilometers and 100 meters elevation of, Fackrell et al. (2020) sites. Such replicated sites are denoted by single and double asterisks, respectively (Table 1). Samples were collected on an approximately quarterly basis to assess seasonal trends in rainfall, including cumulative volume during the sampling intervals, isotopic composition ($\delta^{18}O$ and δD), and ion chemistry. Two models of rain collectors were used in this study (Figure 2.2): 1) NovaLynx Rain and Snow Gauges, which have a 20 cm diameter funnel and are secured in a tripod stand that is bolted to cement platforms, and 2) a hand-made design based on that of previous studies (Scholl et al. 1996; Fackrell et al., 2020), which uses a 5-gallon HDPE bucket with a 101.6 or 152.4 mm diameter funnel protruding from the bucket lid. These bucket-style rain collectors were secured to common potting stands, which were secured into the ground with metal stakes. A 1-cm thick layer of mineral oil was poured into both styles of collectors to prevent rainwater from evaporating. The NovaLynx Gauges were deployed at the UH88 Telescope on the summit of Mauna Kea and at the Mauna Loa Observatory research facility. The hand-made design was deployed at the other 18 sites.

Figure 2.2. Precipitation collector designs. (a) A NovaLynx Rain and Snow Gauge, deployed at the Mauna Loa Observatory. (b) A bucket-style rain collector, deployed at Humuʻula.

At the time of each sample collection, the weather conditions, temperature, and total volume of water was recorded following methods described in Fackrell et al. (2020). The volumes presented in Appendix A Table A.1 are the measured total volume of precipitation in each collector for each sampling interval (co-located rain gauges were not used). Of the total volume, a 500 mL sample in a HDPE bottle was taken for further analyses; the rest was poured out at the site. A 0.2 µm MilliporeSigma Sterile Syringe Filter was used to remove any biological material or mineral oil from the 500 mL sample. Each 500 mL sample was then partitioned into two 60 mL HDPE bottles and refrigerated until sample analysis was conducted, which was typically within two to six weeks of sample collection. One 60 mL bottle was used for major ions and the other for $\delta^{18}O$ and δD analyses.

2.2.3 Analytical methods

Stable isotopes were analyzed by the Biogeochemical Stable Isotope Facility at the University of Hawaiʻi at Mānoa. Stable isotope analyses for $\delta^{18}O$ and δD were performed using a Picarro L2130-i wavelength scanned cavity ring down spectroscopy (WS-CRDS) following similar methods as Godoy et al. (2012) relative to V-SMOW. Within our dataset, the minimum standard deviation for $\delta^{18}O$ and δD was 0.01 (‰), and the maximum standard deviation was 0.07 (‰) and 0.59 (‰) for $\delta^{18}O$ and δD, respectively. Major ion analyses for cations (Na, K, Mg, Ca) and anions (F, Cl, Br, SO_4) were performed by the Water Resources Research Center laboratory at the University of Hawaiʻi at Mānoa using a dual Dionex ICS-1100 Ion Chromatograph following the US EPA Method 300.1 for determining inorganic ions in drinking water (Hautman and Munch, 1997). Sample precision at one standard deviation based on duplicate sample pairs indicate variances of ±0.342 µM (F), ±28.36 µM (Cl), ±0.28 µM (Br), ±18.96 µM (SO_4), ±24.78 µM (Na), ±5.47 µM (NH_4), ±1.40 µM (K), ±13.22 µM (Mg), and ±16.45 µM (Ca).

2.3 Results and discussion

2.3.1 Short-term trends in stable isotopes

The accumulated precipitation (mm), $\delta^{18}O$ (‰) and δD (‰) results for each sampling period are presented in Figure 2.3 to show the variability in the precipitation rate over time at each site. Of the 20 rain collectors, 9 were visited immediately after Hurricane Lane to collect a hurricane-specific sample. The volume-weighted averages (VWA) of $\delta^{18}O$ and δD values of all the samples collected at each site are shown in Figure 2.4 and Table 2.1. In Figure 2.3, the samples are separated as follows: seven "low"-elevation sites below 500 meters relative to mean sea level (msl), seven "mid"-elevation sites between 500 and 2,000 meters msl, and six "high"-elevation sites above 2,000 meters msl. Low-elevation sites are distinguished from those above 500 m because they exhibit similar trends in rainfall (mm) and isotopic composition (Figure 2.5). High-elevation sites are separated out because they are above the trade wind inversion that typically occurs at around 2,000 meters and therefore experiences different patterns of rainfall (Giambelluca et al., 2013). The shaded region in Figure 2.3 represents the Kīlauea LERZ eruption from May to September 2018.

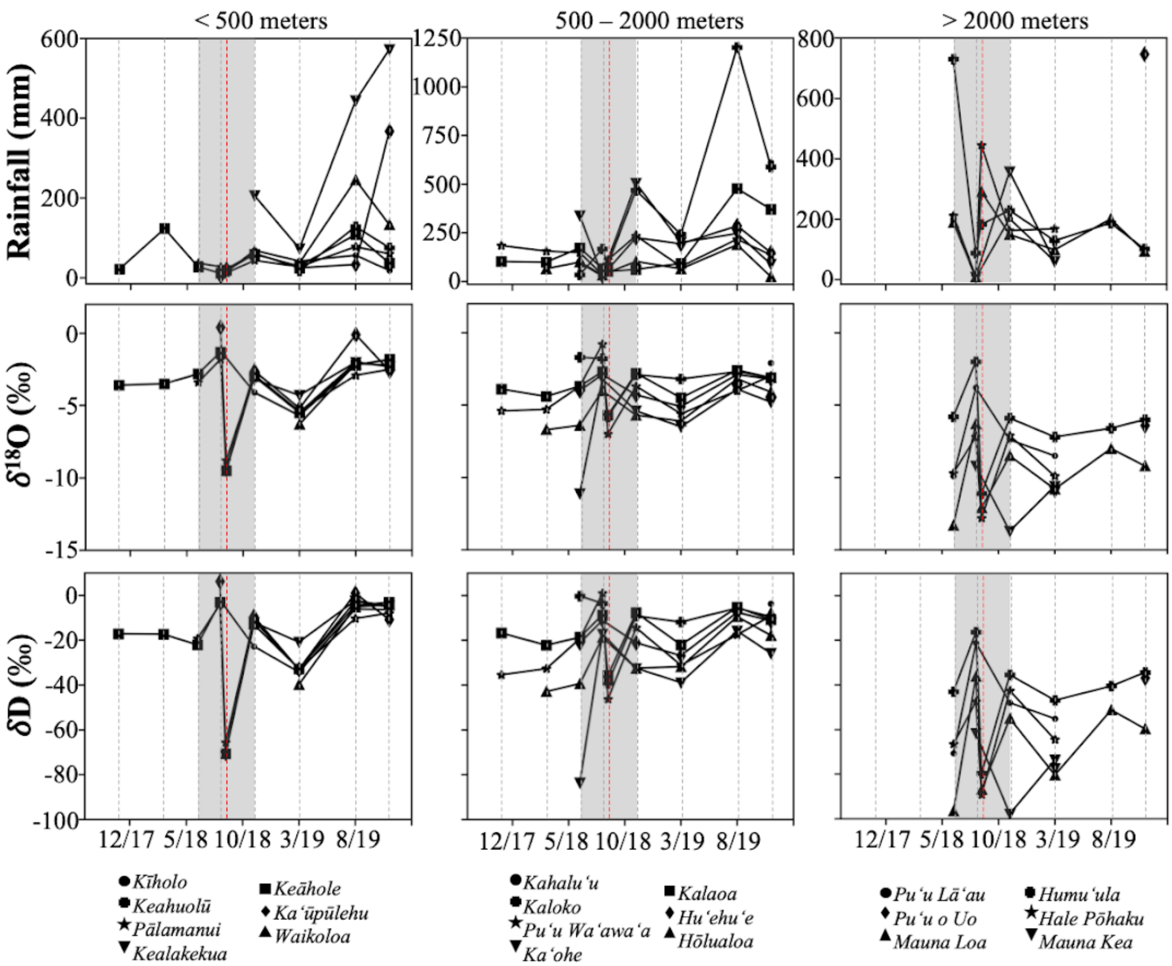

Figure 2.3. Time-series of rainfall and stable isotopic composition. Precipitation (mm), $\delta^{18}O$ (‰), δD (‰) values for precipitation sites sampled between August 2017 and November 2019. The precipitation sites are broken up into three columns: low elevation sites-less than 500 meters (n=7), mid elevation sites-500 to 2,000 meters (n=7), and high elevation sites-above 2,000 meters (n=6). The first row shows the precipitation accumulated (in mm), the second row shows the $\delta^{18}O$ isotopic composition (‰), and the bottom row shows the δD isotopic composition (‰). The shaded region represents the duration of the 2018 Kīlauea eruption. Dashed vertical lines represent each sample collection, and the red vertical dashed line represents the Hurricane Lane event and sample collection.

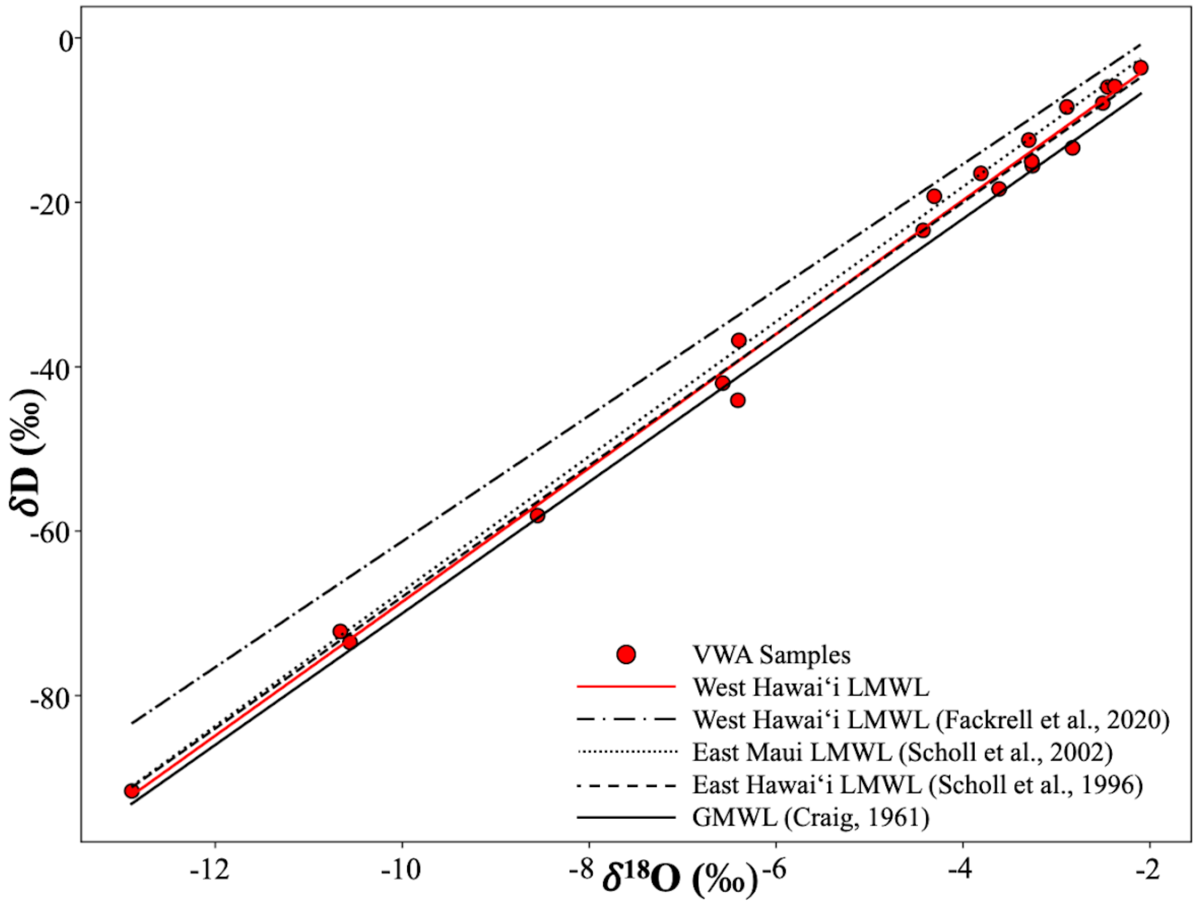

Figure 2.4. Local meteoric water lines of Hawai‘i. Volume-weighted averages for the twenty sites, shown as red points. Various local meteoric water lines (LMWL) are displayed: the West Hawai‘i LMWL conducted by this study as a solid red line, the West Hawai‘i LMWL defined by Fackrell et al. (2020) as a black dot-dash line, the East Maui LMWL defined by Scholl et al. (2002) as a black dotted line, the East Hawai‘i LMWL defined by Scholl et al. (1996) as a black dashed line, and the global meteoric water line (GMWL) defined by Craig (1961) as a solid black line.

Table 2.1. Precipitation collector site information and VWA results. Replicated sites from the Fackrell et al. (2020) study are denoted with an asterisk, sites within 2 kilometers and approximately 100 meters elevation denoted with two asterisks. Latitude and longitude are in decimal degrees. Elevation is reported in meters relative to mean sea level. *n* is the number of individual samples collected for each site. Cumulative precipitation reports the total precipitation for the study period (8/2017 - 11/2019) in mm. Stable isotopic compositions $\delta^{18}O$ and $\delta^{2}H$ are reported as volume-weighted averages for the study period (8/2017 - 11/2019) in per mil (‰).

Site information						08/2017 - 11/2019 totals		
Site	**Latitude**	**Longitude**	**Elevation (m)**	**Funnel Size (mm)**	***n***	**Cumulative Precipitation (mm)**	**VWA δ18O (‰)**	**VWA δ2H (‰)**
*Kīholo	19.85	-155.92	3	101.6	5	189	-3.6	-18.3
*Keāhole	19.72	-156.05	5	101.6	9	437	-3.2	-15.5
Keahuolū	19.65	-156.00	12	152.4	3	221	-2.3	-5.8
Ka‘ūpūlehu	19.82	-155.98	17	101.6	6	514	-2.8	-13.3
**Pālamanui	19.73	-156.01	140	152.4	7	287	-3.2	-15.0
Waikoloa	19.93	-155.79	250	101.6	3	416	-2.5	-7.9
Kealakekua	19.47	-155.89	430	152.4	4	1296	-2.4	-5.9
Kahalu‘u	19.58	-155.93	520	152.4	1	612	-2.1	-3.6
Kalaoa	19.71	-155.97	540	101.6	9	1495	-3.2	-12.3
**Kaloko	19.69	-155.96	660	101.6	7	2789	-2.8	-8.3
Hu‘ehu‘e	19.74	-155.96	730	152.4	6	975	-3.8	-16.4
Pu‘u Wa‘awa‘a	19.77	-155.84	780	101.6	9	1298	-4.4	-23.4
*Hōlualoa	19.64	-155.88	1380	152.4	8	2237	-4.3	-19.2
Ka‘ohe	19.79	-155.63	1620	101.6	6	1410	-6.5	-41.9
Pu‘u Lā‘au	19.83	-155.59	2270	101.6	4	464	-8.5	-58.1

Humuʻula	19.60	-155.47	2430	101.6	7	1651	-6.4	-44.0
Puʻu o Uo	19.50	-155.69	2615	152.4	1	747	-6.4	-36.8
Hale Pōhaku	19.76	-155.45	2840	101.6	5	1000	-10.6	-72.1
Mauna Loa	19.53	-155.57	3400	203.2	7	1033	-10.5	-73.5
Mauna Kea	19.82	-155.47	4200	203.2	3	488	-12.8	-91.5

Observed quarterly cumulative rainfall at low-elevation sites was less than 250 mm until after the cessation of the 2018 Kīlauea eruption. The rainfall during the eruption period of May to September 2018 was particularly low, as summer is typically the rainy season in West Hawaiʻi. At these low elevations, isotopic variability throughout the study period is observed with the most depleted isotopic compositions collected during Hurricane Lane. The remaining depleted samples were collected during the dry, winter season possibly indicating that, rather than local storms produced by daily heating, larger storm systems contribute to the rainfall in this region during these months, as was also noticed by Dores et al. (2020).

At mid-elevations, quarterly cumulative rainfall generally peaked at ~500 mm, with one outlier (Kaloko) collecting over 1,000 mm in a sample period. Similar to the low-elevation sites, rainfall remained relatively low throughout the summer of 2018 until the cessation of the Kīlauea eruption. Isotopic variability is observed, with Hurricane Lane not making much of an impact at mid-elevations. Isotopic variability is observed at these elevations, but the impact of Hurricane Lane on isotopic values is more muted here than seen at the lower elevation sites. Similarly, relative seasonal variations in isotopic compositions at the mid-elevations are less than seen at the lower elevations.

At high-elevation sites, quarterly cumulative rainfall appears to be higher during the 2018 Kīlauea eruption, however sampling at Puʻu Lāʻau, Hale Pōhaku, and Mauna Kea ended early in March 2019. Also, due to the central location of many of the high-elevation sites on Hawaiʻi Island, it is likely that these sites are influenced by weather systems that pass over the island, particularly larger more organized systems like cold fronts or Kona lows. High-elevation sites observed the most isotopically depleted compositions overall and the strongest isotopic variability. Similar to the low- and mid-elevation sites, the winter season is observed to have the most depleted samples besides those collected during Hurricane Lane, possibly due to the influence of larger storm systems that originate at higher latitudes that travel toward the islands (e.g., Dores et al., 2020).

The West Hawai‘i local meteoric water line was calculated by determining the linear regression through the VWA of $\delta^{18}O$ and δD for all sites, and is described as $\delta D = 8.14\ \delta^{18}O + 12.83$ ($r^2 = 0.99$). The LMWL from this study is nearly identical to the East Hawai‘i LMWL, $\delta D = 8.0\ \delta^{18}O + 12$, defined by Scholl et al. (1996) and differs from the LMWL defined for the West Hawai‘i region by Fackrell et al. (2020), $\delta D = 7.65\ \delta^{18}O + 15.25$ (Figure 2.4). The variability between the LMWL is discussed further in Section 3.2.

The $\delta^{18}O$ (‰) isotope-elevation relationship is shown in Figure 2.5. The linear regression is defined as $\delta^{18}O = -0.0017\ h – 2.54$ for low- and mid-elevation sites (lapse rate = -0.17‰/100m), and $\delta^{18}O = -0.0030\ h – 0.33$ for high-elevation sites (lapse rate = -0.30‰/100m), where h is the elevation of each site in meters relative to msl. The isotope-elevation relationships observed are similar to those found by Scholl et al. (1996) for trade-wind (below 2,000 meters) and high-elevation (above 2,000 meters) areas. Comparing these regressions and lapse rates to previous studies worldwide, Poage and Chamberlain (2001) compiled 68 studies from around the world and determined a global lapse rate of -0.28 ‰/100 meters; Paternoster et al. (2008) found a similar lapse rate of -0.17‰/100m for Mt. Vulture, Italy; Kong and Pang (2016) found a positive lapse rate of 0.12‰/100m for the Tianshan Mountains. The $\delta^{18}O$ lapse rates observed, which are on the low end of the global $\delta^{18}O$ lapse rates, are likely a function of temperature lapse rates and the sources of moisture.

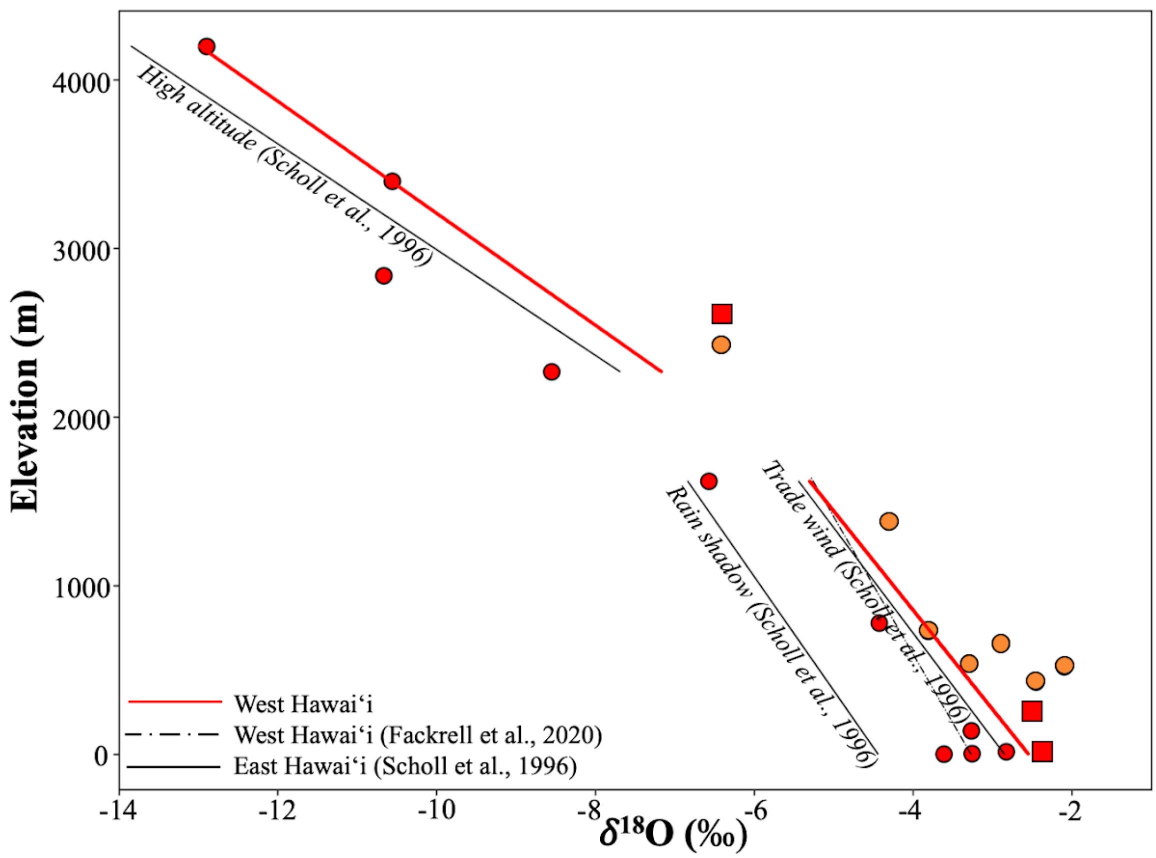

Figure 2.5. VWA δ^{18}O-elevation relationship. Regressions are drawn through the samples below and above the approximately 2,000 meter inversion zone for the West Hawai‘i dataset. Sites are colored red and orange based on the rainfall zones, 204-750 mm and 751-1,340 mm respectively. Three sites that are enriched relative to the regressions but are within the lowest annual rainfall zone (Figure 2.1) are shown as squares. Isotope-elevation relationships observed by Scholl et al. (1996) for Kīlauea region and Fackrell et al. (2020) for the West Hawai‘i region are shown for reference.

There does not appear to be a strong relationship between elevation and isotopic composition below an elevation of 1,000 meters. All of the sites deployed in the lowest annual rainfall zone (Figure 2.1) have VWA values that are isotopically depleted relative to the calculated regression lines (Figure 2.5). The exceptions are three sites (Keahuolū, Waikoloa, and Pu‘u o Uo, Figure 2.5 as squares), which are enriched relative to the regression lines despite being located in the lowest annual rainfall zone. It is important to note, however, that these sites collected precipitation for under one year. Previous studies in Hawaiʻi determined that elevation effects were difficult to observe below the inversion layer (Dores et al., 2020). The lowest annual rainfall zone likely only receives rainfall during extratropical and subtropical storm events, which would therefore have already depleted $\delta^{18}O$ isotopic compositions resulting in depleted $\delta^{18}O$ samples compared to the regression lines (Gedzelman and Lawrence, 1990; Good et al., 2014; Dütch et al., 2016).

Precipitation sites that are enriched relative to the linear regression, with the exception of the three mentioned just above, fall within the orange (751-2,000 mm) annual rainfall zone (Figure 2.1). Given that rainfall in the orange zone has been interfacing with the land as it travels from the windward to leeward side of the island, it is possible that there may be isotopic enrichment of the water at the base of the cloud (Scholl et al., 2002; Scholl et al., 2007). Another explanation for the observed enrichment is that more of the rainfall here occurs in frequent, lower intensity rain events that are related to the diurnal wind cycles and thus is not as depleted - due to the amount effect - as precipitation from infrequent storms that contribute more to the lower elevation red zone. These hypotheses could explain the enrichment of samples above the regression line, however more data are necessary to provide a conclusive answer.

2.3.2 Comparison of stable isotopes across studies

There is a distinct difference between the LMWL produced by the data of Fackrell et al. (2020) versus this study (Figure 2.6), which potentially addresses the discrepancy of ^{18}O enrichment in groundwater samples observed in previous studies (Tillman et al., 2014; Kelly and Glenn, 2015). Figure 5 of Fackrell et al. (2020) shows that the salinity-corrected groundwater-sample-group averages plot with an offset to the right of the West Hawaiʻi LMWL, described as $\delta D = 7.65\ \delta^{18}O + 15.25$, indicating an ^{18}O enrichment in groundwater relative to precipitation. They propose four hypotheses for this difference: 1) variability in precipitation δD and $\delta^{18}O$ values during the study period compared to a long-term average, 2) some degree of preferential evaporation of D and ^{18}O during infiltration, 3) hydrothermal water-rock interactions in high-temperature regions of the groundwater system, or 4) a combination of these effects. Five of the eight precipitation collectors deployed by Fackrell et al. (2020) were replicated to within 1.5 km, three of which were identical placements. Fackrell et al. (2020) concluded that rainfall sourced at higher elevations, possibly from the slopes of Mauna Kea or Mauna Loa, are recharging into the Hualālai aquifers. In order to test this conclusion, we strategically placed precipitation collectors at higher elevations.

We computed combined VWA for the five replicated sites, which resulted in better characterization of the groundwater data presented in previous literature (Tillman et al., 2014; Kelly and Glenn, 2015; Fackrell et al., 2020). The 2012-2014 sampling period of Fackrell et al. (2020) remained relatively neutral, however the 2017-2019 study period experienced both a La Niña from October 2017 to March 2018 and an El Niño from October 2018 to June 2019 (NOAA Climate Prediction Center). Previous work in Hawaiʻi observed lower than normal rainfall during El Niño, which can be further exacerbated by the influence of the Pacific Decadal Oscillation (PDO) (Chu and Chen, 2005; Giambelluca et al., 2013; Frazier and Giambelluca, 2017; Elison Timm et al., 2020). Changes in the atmospheric circulation, resulting in strong surface westerly anomalies, have been observed to reduce trade wind rainfall in Hawaiʻi (e.g., Chu and Chen, 2005). We hypothesize that the two LMWL represent ends of a spectrum, due to such variability in atmospheric and climate processes in this region. However, specific investigations into the cause of such variability is beyond the scope of this project.

Long-term variations, such as those shown above, have not been previously observed, and highlight the need for long-term sampling in order to accurately characterize rainfall for groundwater recharge studies. To our knowledge, the longest collection of isotope data in Hawaiʻi was conducted by the International Atomic Energy Agency, through the Global Network of Isotopes in Precipitation (GNIP). Through this project, data for only a few years (1962-1969) and from a single station was collected. We hope, however, that the results presented here will serve as motivation for the creation of long-term monitoring of water isotopes in Hawaiʻi.

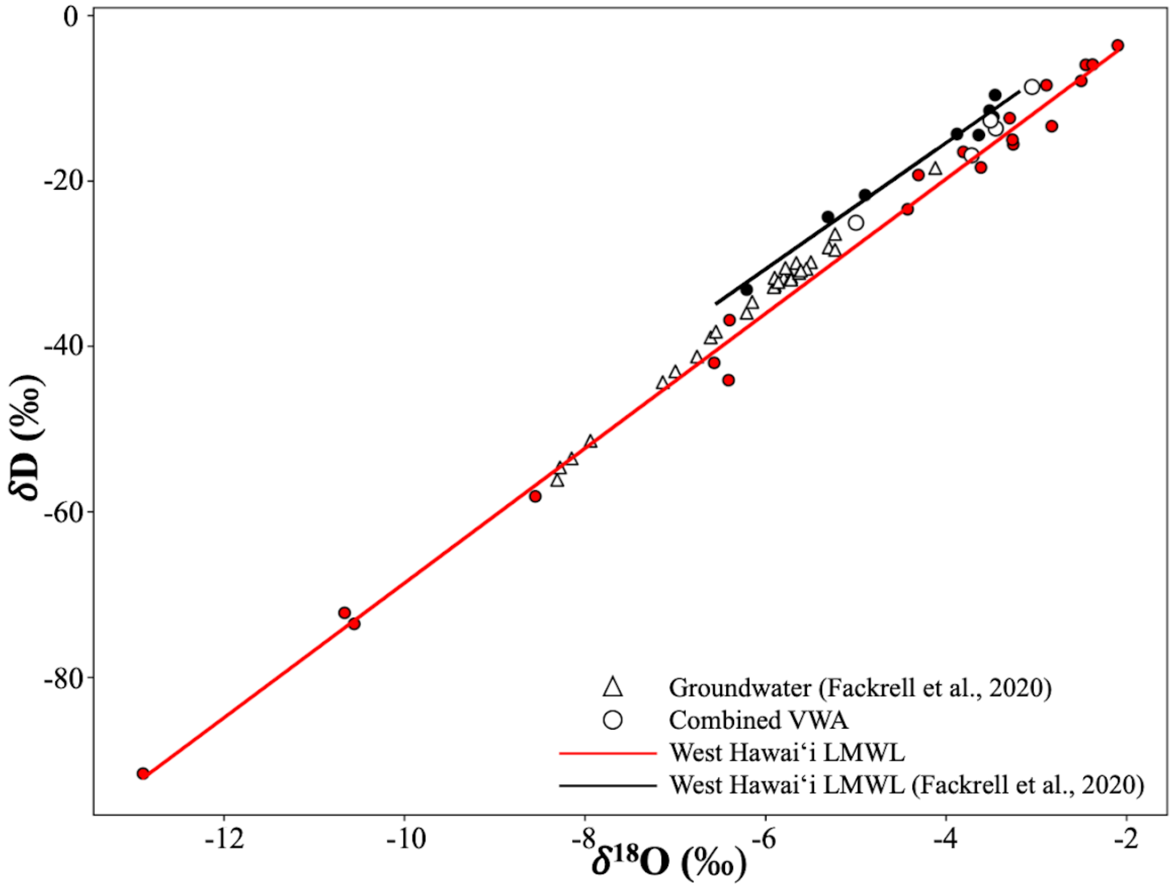

Figure 2.6. Comparison of local meteoric water lines. Comparison of the local meteoric water line (LMWL) defined by Fackrell et al. (2020) in black, the LMWL defined by this study in red, a combined VWA of overlapping sites in white circles, and groundwater collected and analyzed by Fackrell et al. (2020) as white triangles.

2.3.3 Variability of ions in precipitation

The investigation into bulk deposition for the West Hawai'i study area, specifically chloride and sulfate concentrations (Figure 2.7), is to explore whether our results are similar to those of previous studies that observed increased aerosols downwind of a volcano contributing to the development of acid rain (Eriksson, 1957; Miller and Yoshinaga, 1981; Harding and Miller, 1982; Nachbar-Hapai et al., 1989; Siegel et al., 1990; Scholl and Ingebritsen, 1995), however direct comparison is difficult due to the large spatial difference between the focus of the previous studies on East Hawaiʻi and ours in West Hawaiʻi. Major ion concentrations as bulk (wet + dry) deposition for each sampling trip are reported in Appendix A Table A.1.

Quarterly cumulative rainfall in low- and mid-elevations was relatively low (less than 250 mm) for each sampling period prior to, and during, the 2018 Kīlauea LERZ eruption (Figure 2.7). After the eruption ended in September 2018, precipitation amounts increased to 500 mm or higher. The low rainfall observations during the Kīlauea eruption, particularly below the inversion layer, corroborate those of Zuo et al. (2020), who present rainfall and gas emission data in parallel with a numerical model suggesting reduced rainfall during periods of increased aerosols.

Spikes in chloride and sulfate concentrations (μM) were observed during two periods: 1) June 2018 to August 2018 and 2) November 2018 to March 2019. The first spike coincided with the 2018 Kīlauea eruption, which caused heavy vog in West Hawaiʻi. Low rainfall (less than 250 mm precipitation) was also observed at all sites during this time, despite coinciding with the typical wet season for West Hawaiʻi. The second spike was observed in only a few sites and was more pronounced for chloride than sulfate. Again, quarterly cumulative rainfall measurements did not exceed ~250 mm for all sites, however November to March is the expected dry season for West Hawaiʻi. Previous studies have also observed higher major ion concentrations during periods of lower rainfall (e.g., Lee et al., 2000).

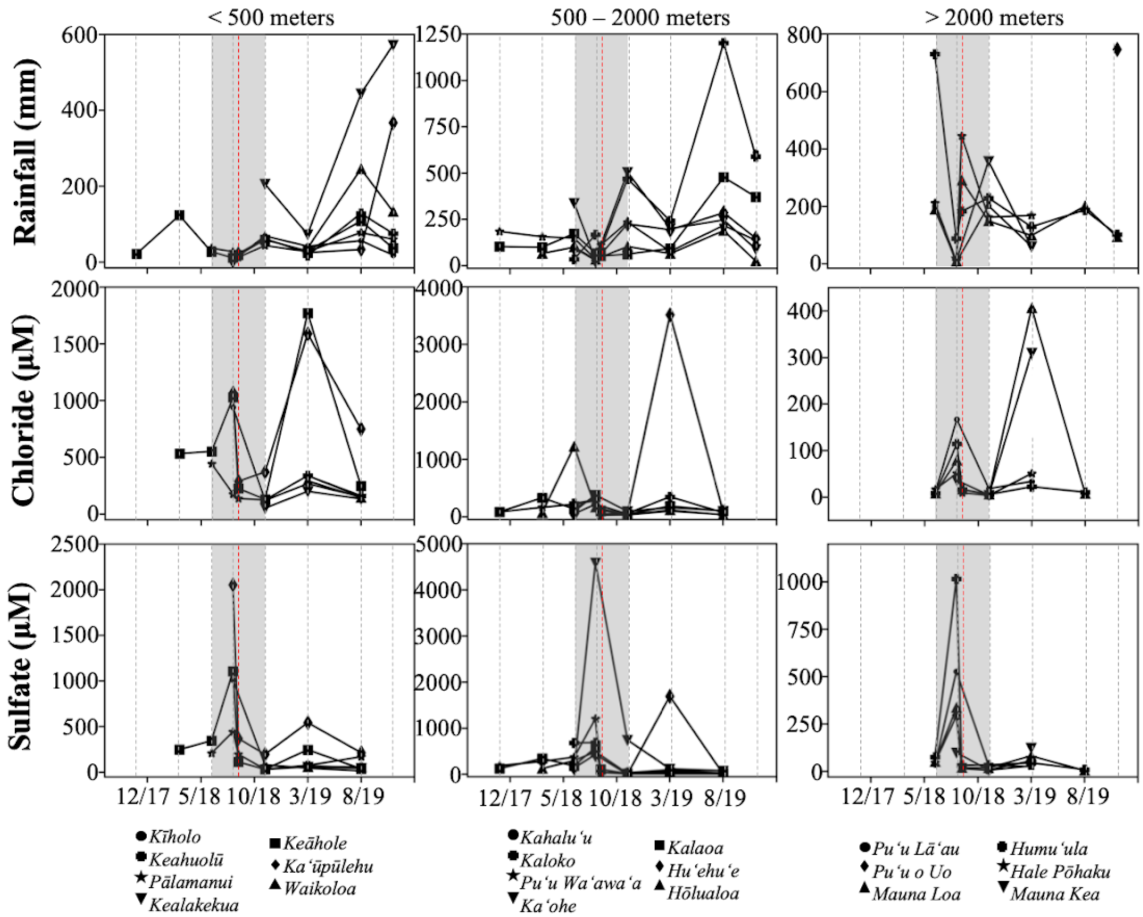

Figure 2.7. Time-series of rainfall, chloride, and sulfate concentrations. Precipitation (mm), chloride (µM), and sulfate (µM) concentrations for precipitation sites sampled between August 2017 and August 2019. Shaded region represents the 2018 Kīlauea East Rift Zone eruption period. Dashed vertical lines represent each sample collection, and the red vertical dashed line represents the Hurricane Lane event and sample collection.

2.3.4 Event-based impacts on precipitation

Two events during our study period affected the chemistry of precipitation: 1) the lower East Rift Zone (LERZ) eruption of Kīlauea Volcano from May to September 2018, and 2) Hurricane Lane, which dissipated into a tropical storm upon approach to the Hawaiian Islands in August 2018. To better understand the impacts of these events on the ion concentrations in rainfall, we compared chloride and sulfate concentrations to sodium concentrations (Figure 2.8 and 2.9). Stable isotopic compositions were also investigated (Figure 2.10).

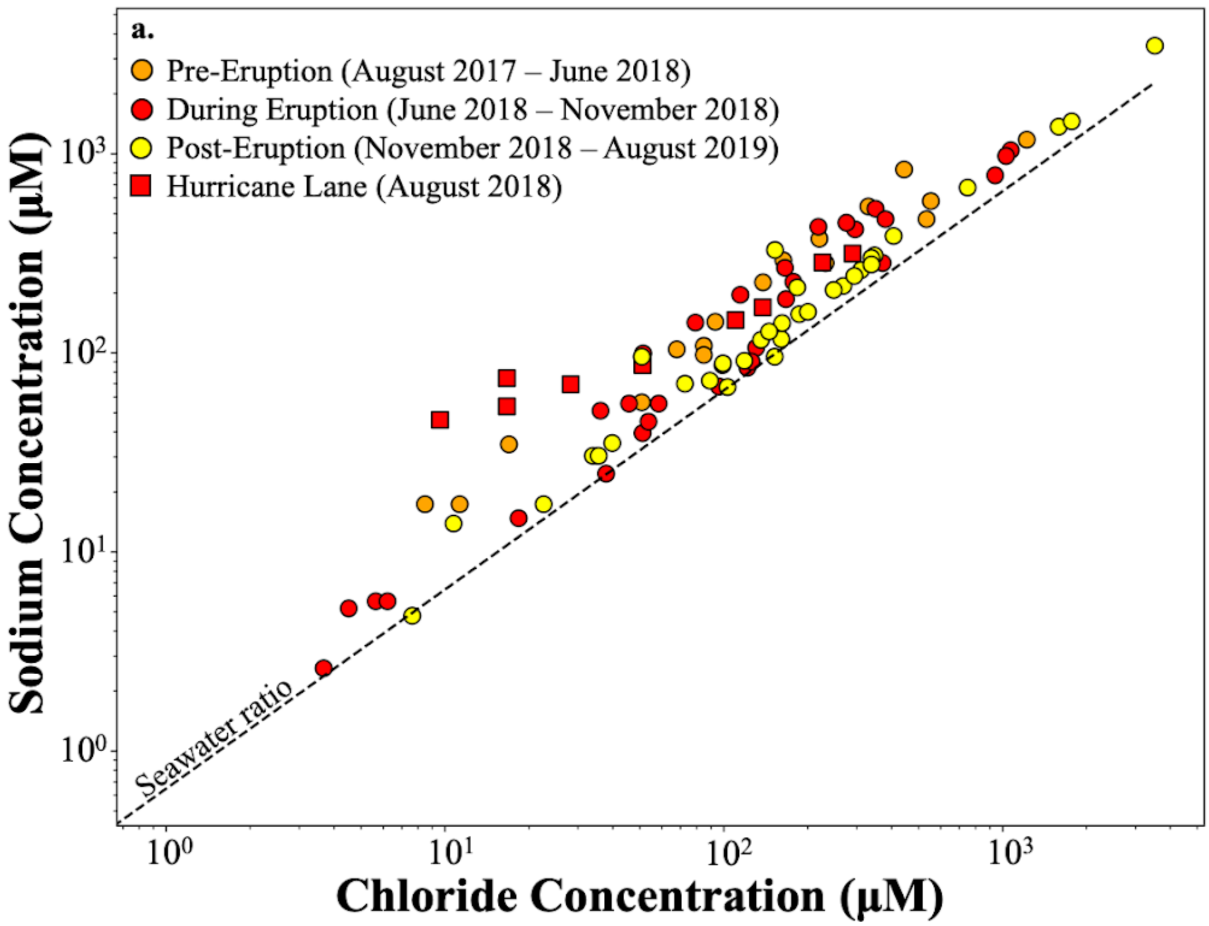

Figure 2.8: Pre-, during, and post-eruption comparison of chloride concentrations. Chloride compared to sodium concentrations (μM), with the seawater ratio. Points are colored as: before the 2018 Kīlauea eruption (orange), during the eruption (red), and after the eruption ended (yellow). Hurricane Lane samples are plotted as red squares (red, as sampled during the eruption). Data are shown on a log-log scale.

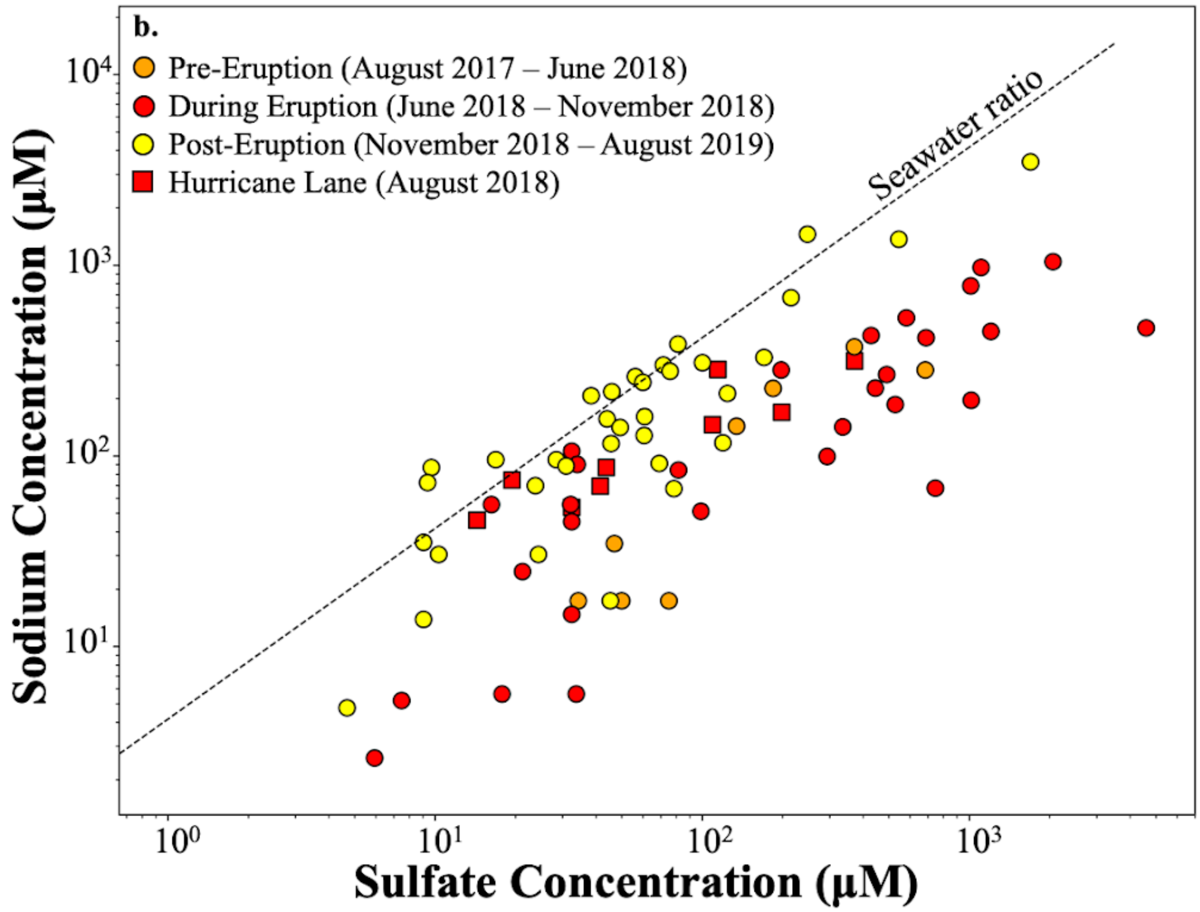

Figure 2.9: Pre-, during, and post-eruption comparison of sulfate concentrations. Sulfate compared to sodium concentrations (µM), with the seawater ratio. Points are colored as: before the 2018 Kīlauea eruption (orange), during the eruption (red), and after the eruption ended (yellow). Hurricane Lane samples are plotted as red squares (red, as sampled during the eruption). Data are shown on a log-log scale.

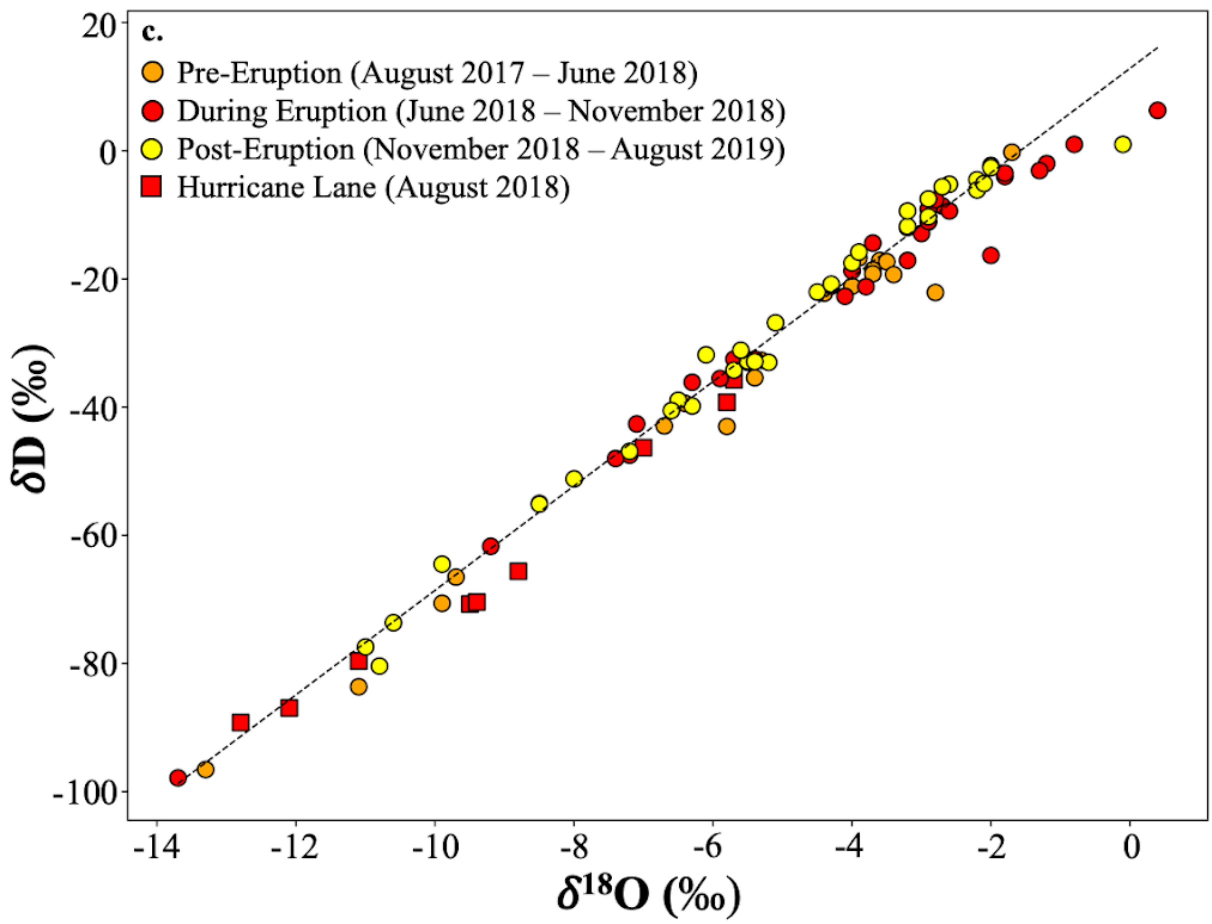

Figure 2.10: Pre-, during, and post-eruption comparison of isotopic compositions. Isotopic composition (‰) with the local meteoric water line. Points are colored as: before the 2018 Kīlauea eruption (orange), during the eruption (red), and after the eruption ended (yellow). Hurricane Lane samples are plotted as red squares (red, as sampled during the eruption).

The observed chloride concentrations approximated those of seawater, with the largest deficiencies occurring at lower concentrations, particularly the samples collected during Hurricane Lane (Figure 2.8). This may be attributed to the low chloride and sodium concentrations approaching the detection limits, as similar observations were made in previous studies (e.g., Scholl and Ingebritsen, 1995). Crustal dust could also cause the sodium concentrations to increase relative to chloride (Keene et al., 1986; Scholl and Ingebritsen, 1995), however indicators like Al and Fe were not collected during this study therefore we are unable to determine if the higher abundance of sodium is due to this deposition. Chloride concentrations do not appear to be affected by the 2018 Kīlauea eruption, as the spread of pre-, during-, and post-eruption samples were similar. A Welch's t-test performed on pre-during ($p = 0.535$), during-post ($p = 0.151$) and pre-post ($p = 0.349$) groups concluded there is no statistical difference between the samples.

Sulfate concentrations exceeded the seawater ratio even at the start of our sampling due to the long-term Pu‘u ‘Ō‘ō eruption of Kīlauea Volcano, which began in 1983 and terminated just prior to the start of the 2018 Kīlauea LERZ eruption (Figure 2.9). Between March 2014 and December 2017, daily summit and East Rift Zone sulfur dioxide emission rates were between 1,227 and 9,970 metric tonnes per day (t/d), averaging 4,783 t/d (Elias et al., 2018). This emission rate dramatically increased during the 2018 Kīlauea lower East Rift Zone eruption. Preliminary analyses from the U.S. Geological Survey indicate that sulfur dioxide gas emissions averaged more than 50,000 tons per day and during some periods exceeded 100,000 tons per day (Williams et al., 2020). During the 2018 Kīlauea eruption, Hurricane Lane impacted the State of Hawai‘i in August 2018, during which sulfate concentrations also exceeded the seawater ratio. The Lane samples also display the lowest sulfate concentrations observed during the eruption. After the cessation of the 2018 Kīlauea eruption, sulfate concentrations decreased approximately 70% to yield chloride ratios approaching those in seawater. A Welch's t-test performed on the sulfate concentrations concluded that there is a statistical difference between during-post groups ($p = 0.032$, $\alpha = 0.05$), however there is no statistical difference between pre-during ($p = 0.118$) and pre-post ($p = 0.159$) groups.

Downwind of the volcano, ammonium sulfate is typically observed due to the reaction of terrigenous and volcanic ammonia and the sulfate compounds in the atmosphere (Cornell et al., 2001). Appendix A Table A.1 reports the ammonium concentrations observed during this study, demonstrating that the highest concentrations of ammonium ions during our study period were recorded during the 2018 Kīlauea eruption.

Stable isotopic compositions before, during, and after the eruption are spread throughout the range of samples (Figure 2.10). Rainfall during the hurricane was less than 200 mm at low- to mid-elevations, and was between 200 to 400 mm at high-elevations. Although the rainfall amounts were not notable at low elevations, samples collected during Hurricane Lane observed the most depleted isotopic compositions observed during our study period for this elevation interval. A Welch's t-test performed on the isotopic compositions shows that there is no statistical difference between the pre-during ($p = 0.686$), during-post ($p = 0.781$), and pre-post ($p = 0.511$) groups.

2.4 Conclusions

Samples of precipitation were collected at 20 sites from Central to West Hawaiʻi between August 2017 and November 2019. The isotopic composition and bulk ion deposition of such samples were measured and compared to previous studies conducted on Hawaiʻi Island and Maui to better characterize the source of groundwater in Central to West Hawaiʻi Island. Significant findings support our assertion that long-term precipitation data are crucial when developing a LMWL for Hawaiʻi. These findings include:

- The local meteoric water line established during this study is similar to those for East Hawaiʻi and East Maui, as well as the global meteoric water line. It differs from the local meteoric water line established in the previous West Hawaiʻi study by Fackrell et al. (2020). Combined VWA for replicated sites produce averages that better characterize the groundwater isotopic compositions observed in previous studies. Long-term studies are needed to better understand the variations observed in the meteoric water lines spanning a near-decade long sampling of these sites.
- The $\delta^{18}O$ isotope-elevation relationship established for West Hawaiʻi is similar to the trade wind (for low- and mid- elevations) and high-elevation relationships observed in East Hawaiʻi. Depletion in VWA $\delta^{18}O$ is observed in sites within low annual rainfall areas (less than 750 mm) relative to the isotope-elevation regression. These sites possibly experience rainfall mainly during extratropical and subtropical storms, which already have depleted $\delta^{18}O$ compositions. Enrichment in VWA $\delta^{18}O$ is observed for sites in the rain band, which wraps around the southern tip of Hawaiʻi Island and flows up the leeward slopes of Mauna Loa and Hualālai.

Additional results provide insight into extreme events, which can impact the chemical composition of precipitation. These findings include:

- During periods of low rainfall (less than 250 mm), as well as the 2018 Kīlauea eruption, all sites observed increased concentrations of sulfate and chloride. Precipitation at low- and mid- elevation sites remained low during the 2018 Kīlauea eruption, supporting previous research that an increase in aerosols decreases rainfall downwind of the volcano.
- Sulfate concentrations increased during the Kīlauea eruption, however chloride concentrations did not. Welch's t-tests demonstrated a statistical difference only between sulfate concentrations observed during and after the eruption ended ($p = 0.032$), and no statistical difference between the rest of the samples.

This paper provides a foundation to follow-on work including: (1) incorporation of the data presented herein with new groundwater chemistry data in order to investigate the recharge zones, interconnectivity, and storage of West Hawai‘i aquifers; and (2) analyses of the effects of sea salt aerosol deposition on ecological processes and water quality. Continued collection of bulk deposition, particularly in the current quiet period of Kīlauea Volcano, would aid in understanding the importance and impacts of volcanic emissions on rainfall rates and compositions. Multi-decadal sampling, although challenging, will be crucial to determining the variability of stable isotopes in precipitation.

Chapter 3. FLOW DEPENDENT SALINITY CORRECTIONS IN WEST HAWAIʻI AQUIFERS

Diamond K. Tachera, Nicole C. Lautze, Henrietta Dulai, Donald M. Thomas

Abstract

Groundwater chemistry studies utilize the occurrence of dissolved ions and other geochemical species to determine source, quality, flow, and interconnectivity of aquifers. In groundwater chemistry studies focused on island and coastal environments a salinity correction is routinely applied, which subtracts the fraction of ocean water from a mixed fresh- and salt- water system, in order to focus on fresh-water processes. This study identifies challenges associated with accurate identification of the ocean water fraction in groundwater in a location where dissolved ion contribution can occur through processes that include seawater intrusion, seaspray deposition, wastewater, and hydrothermal reactions. Exacerbating this challenge is the complex subsurface hydrogeologic environment of West Hawaiʻi Island. The simplistic end-member values for fresh and ocean water currently used in salinity corrections proved insufficient for this region. Instead, we find the use of end-members chosen from within probable groundwater flow paths produces better results (less frequent over corrections). In addition, this study finds that alkalinity analyses cause higher charge balance errors in groundwater with lower ion concentrations. Charge balance errors may be a good check of quality for datasets, but are not definitive in determining whether a dataset is viable for additional geochemical analyses.

3.1 Introduction

Groundwater studies utilize the concentrations and species of dissolved ions to elucidate the source, flow, and quality of water as well as the interconnectivity of aquifers. Spatially and temporally heterogeneous inputs of ions to a fresh groundwater aquifer occur via their naturally variable concentrations in precipitation and ocean water, as well as input from wastewater (e.g. Park et al., 2005), seaspray (e.g. Whipkey et al., 2000), mineral dissolution and geothermal (e.g. Thomas, 1985), among other influences. The final ion concentration in groundwater is also influenced by subsurface geologic structures, which can affect the ability of groundwater to flow and mix across aquifer regions. In continental coastal and ocean island environments, seawater intrusion is a natural process that affects the ion concentrations in groundwater. This has implications for water resources, but also for the characterization of freshwater chemistry. In order to exclusively consider the freshwater component of groundwater chemistry in locales where seawater mixing is likely to occur, groundwater researchers frequently apply a salinity correction to remove the seawater fraction of a mixed sample (Clark and Fritz, 1997).

For example, previous studies on Hawaiʻi Island have utilized salinity corrections to unmix the stable isotope compositions of water samples (δ^{18}O and δD), with the goal of determining their apparent ages (Kelly and Glenn, 2015) and recharge elevations (Fackrell et al., 2020) of groundwater. These studies followed standard practice in Hawaiʻi by using salinity measurements or chloride concentrations to achieve the corrections, as chloride has a near-zero concentration in fresh groundwater due to the scarcity of chloride in basalt rocks. The salinity correction uses author-specified end-member values for fresh- and ocean-water to calculate the fraction of each water type in a given sample. However, determining the ion contribution of seawater in groundwater can be challenging in hydrogeologically complex systems such as the Hawaiian Islands where, among other processes, seaspray, wastewater, geothermal reactions, mineral dissolution, and deep seawater intrusion pathways may contribute to the ion budgets of groundwater.

It is this complexity that also creates a challenge for water management in this area. In the 1990s, development in the West Hawaiʻi region of Kailua-Kona created increased demand for water resources. During this period of development, roughly 10 groundwater wells were drilled at elevations greater than 1,500 feet, some of which, for the first time, intersected an unexpected high-level water resource (Bauer, 2003). Over the last few decades, research on Hawaiʻi Island has demonstrated that the hydrogeology in this area is very complex and still poorly understood (Oki, 1999; Stolper et al., 2009; Kelly and Glenn, 2015; Izuka et al., 2018; Attias et al., 2020; Fackrell et al., 2020; Attias et al., 2021a).

Improving our understanding of this region was a goal of the NSF EPSCoR ʻIke Wai project. ʻIke Wai aimed to characterize the sources of water that pass through this region, the degree of connectivity among aquifers, how subsurface features affect flow and storage, and the volume, distribution, and quality of submarine groundwater discharge (SGD) along the coast. ‘Ike Wai employed various techniques including microbiological, geophysical, and geochemical data collection and analysis, as well as economic and numerical modeling of groundwater aquifers (Attias et al., 2020; Attias et al., 2021a; Bremer et al., 2021). As part of this project, geophysical investigations offshore of Hualālai Volcano found large-scale submarine freshwater reservoirs beneath the seafloor, as well as alternating fresh and saline saturated basalt zones (Attias et al., 2020). A new conceptual model by Attias et al. (2021a), which builds on previous studies such as Oki (1999) and Taylor (2019), suggests that there is a multilayer system that allows low permeability layers to act as both a confining and perching formations. These studies demonstrate that Hawai‘i’s subsurface geology can be more complex than the traditional Gyben-Herzberg lens model assumes (e.g. Oki, 1999; Rotzoll et al., 2010), and provides for the ability of seawater to intrude into coastal aquifers through various shallow and deep pathways. It has been critical to determine the source, flow path, and degree of mixing of groundwater in these aquifers to better understand resource sustainability.

The research presented here builds on the previous work in this region, with the goal of better utilizing geochemical data to unmix fresh and saltwater components and address questions of resource quality and sustainability. Overall, this paper demonstrates that it is far from straightforward to perform a salinity correction in a complex hydrogeologic environment with multiple ion inputs, in particular because it is not possible to identify accurate ocean and freshwater end-member chemical compositions.

3.2 Materials and methods

3.2.1 Study site

3.2.1.1 Geology

Hualālai is the western most volcano on Hawai‘i Island, standing at 2,523 meters above sea level (masl) with a subaerial volume estimated at about 600 km^3 (Moore et al., 1987). There are three rift zones (Figure 3.1): (1) the prominent northwest rift zone, 2 to 4 km wide and extending from the summit to the ocean and offshore; (2) the north rift zone, 5 km wide and about 10 km in length; and (3) the south-southeast rift zone, 3 to 5 km wide and about 13 km in length. In general, rift zones are treated as impermeable structures in hydrologic modeling, because dense dike systems that underlie them are expected to have very low permeability and thus not allow for cross-dike groundwater flow (Izuka et al., 2018).

Volcanic eruptions of Hualālai are characterized by pāhoehoe and ʻaʻā lava flows, ash and pyroclastic deposits, faults, dikes, and lava tubes (Moore et al., 1987). Previous studies suggest interfingering of lavas from Hualālai and Mauna Loa (Stearns and Macdonald, 1946) and Hualālai, Mauna Kea, and Mauna Loa in the saddle between these three volcanoes (Wolfe et al., 1997; Izuka et al., 2018). The most recent eruptions from Hualālai volcano ended around 1800-1801 A.D. and are known as the Kaʻūpūlehu and Huʻehuʻe eruptions (Kauahikaua et al., 2002). The permeability of volcanic rocks is highly variable and depends on the morphology, emplacement, thickness, and degree of weathering (Oki, 1999).

Coastal aquifers in Hawaiʻi that lack nearshore confining layers (sediments, soil horizons, etc.), experience groundwater and seawater mixing, as well as effects from tidal forcing (Rotzoll et al., 2008). A case study on Maui suggested that asymmetric and asynchronous tides cause fluctuations within groundwater aquifers with exponentially decreasing amplitudes with distance from the coast (Rotzoll et al., 2008; Rotzoll, 2010). Other studies suggest that sea level rise will cause coastal-plain flooding as groundwater aquifers inundate low-lying regions (Rotzoll and Fletcher, 2012; Vitousek et al., 2017). Such studies demonstrate that adequate salinity corrections are needed both laterally and vertically across the state in order to understand the degree of mixing and source of dissolved ions in groundwater systems.

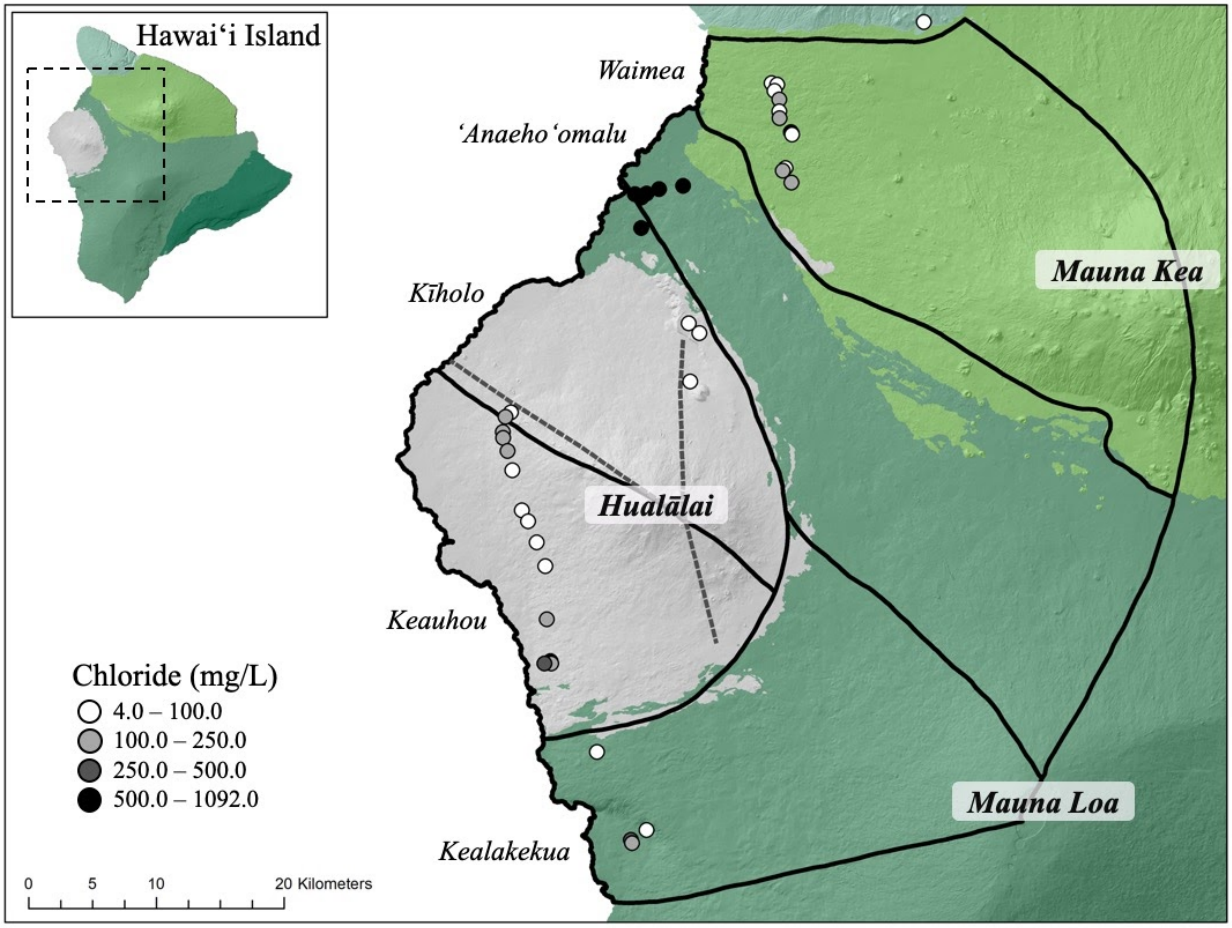

Figure 3.1. Study area. Background colors represent the surface lava flows from the five volcanoes on Hawai‘i Island. Black solid lines represent aquifer boundaries delineated by the Commission on Water Resource Management, State of Hawai‘i. Rift zones of the Hualālai volcano are shown as gray dashed lines. Chloride concentrations (mg/L) of sampled sites are shown as circles, where white is low chloride concentrations and black is high concentrations.

3.2.1.2 Groundwater

Groundwater in West Hawai‘i is classified by groundwater head levels (Oki, 1999). Basal (head < 12 meters amsl) refers to the freshwater lens in coastal areas that floats on salty groundwater and seawater. High-level water (head > 12 meters amsl) refers to impounded freshwater, confined or unconfined, likely disconnected from the ocean by impermeable structure(s) or layer(s) of some sort. Three possible conceptual models explaining the occurrence of high-level water along the western flanks of Hawaiʻi were proposed by Oki (1999): 1) a buried dike system, 2) buried faults, and/or 3) buried lava flows. Aquifer systems are designated by the Commission on Water Resources Management to provide a consistent basis for managing groundwater resources, including calculating sustainable yields, and are defined by topographic and historical surficial boundaries (State of Hawaiʻi, 1990), essentially without regard to subsurface hydrogeology. There are five aquifers in our study area: Waimea, ʻAnaehoʻomalu, Kīholo, Keauhou, and Kealakekua (Figure 3.1).

An alternative model for these confining formations is offered by the observations resulting from several continuously cored boreholes that have been drilled on Hawaiʻi Island. The Hawaiʻi Scientific Drilling Project (HSDP) completed a well to a depth of 3,508 mbsl in Hilo, Hawaiʻi in 2007; that well encountered a sequence of weathered soil and ash layers at the transition from Mauna Loa rocks into the underlying Mauna Kea edifice that were interpreted to be a confining formation for a deep, artesian freshwater aquifer within the lower units (Paillet and Thomas, 1996; Thomas et al., 1996; Stolper et al., 2009). More recent core drilling on West Hawaiʻi encountered a sequence of confined aquifers under artesian pressures of up to 10 Mpa (Thomas and Haskins, 2015), where the confining layers were composed of ash-rich sequences or intervals of tephra and clastics that were consistent with pyroclastic deposits. These findings suggest that the confining layers responsible for the high level aquifers on Hualālai may be associated with weathered soils, ash, or other, broadly distributed, less permeable, materials buried within the stratigraphic sequence, rather than any of the geologic features suggested by Oki (1999).

3.2.1.3 Climate

Hualālai’s location in the rain shadow of Mauna Kea and Mauna Loa deprives this region of trade wind-derived orographic precipitation; instead a land-breeze sea-breeze pattern occurs almost daily. The Kailua-Kona coffee region experiences a higher band of rainfall at mid-elevations (300 m-500 m amsl) as airflow travels from the eastern side around the island’s southern tip and back up the western slopes of Mauna Loa (Giambelluca et al., 2013). South of the rift zone, the on-shore off-shore cycle of rainfall causes a difference in the chemistry of precipitation from that north of the rift zone, as microclimates have a large impact on the chemistry of precipitation (Tachera et al., 2021).

Stable isotope analyses of water (^{18}O and ^{2}H) have been previously used on Hawaiʻi Island to better understand the source of groundwaters by calculating estimated recharge elevations (Scholl et al., 1996; Fackrell et al., 2020). Around the world, the global meteoric water line (GMWL) and local meteoric water lines (LMWL) help to establish long-term trends in hydroclimatic processes (Craig, 1961; Dansgaard, 1964). The flux of water in the water cycle can be observed by the partitioning of ^{18}O and ^{2}H through Rayleigh distillation (Clark and Fritz, 1997). Investigations into sources and processes that affect isotopic compositions of groundwater require the use of salinity corrections to separate the recharge-derived groundwater from the seawater fractions that may be mixing with the freshwater present in the aquifer.

3.2.2 Sampling techniques

The water samples discussed in this paper were collected on a quarterly basis between May 2017 and March 2019. Sites were chosen based on accessibility and availability of pumping wells running at that time. Given the large spatial distribution of the study region, a variety of basal, high-level, and thermally-influenced wells were chosen to represent the extremes of water compositions in West Hawaiʻi. Ocean water samples were also taken from three Natural Energy Laboratory of Hawaiʻi Authority (NELHA) ocean water pipes ranging in depths: shallow ocean 21 m, mid-level 674 m, and deep ocean 900 m (Natural Energy Laboratory of Hawaii Authority, 2020). A range of depths were sampled in order to evaluate the varying chemistry within a vertical profile of the ocean, given the uncertainty of the source depths from which ocean water is circulating into the island below the fresh groundwater.

At each field location, we measured the water temperature (°C), dissolved oxygen (% saturation and mg/L), specific conductivity (μS/cm), salinity, and pH using a multiparameter probe (YSI Professional Plus Multiparameter Instrument Model 6050000 and 605790-4). Any apparent color or odor was also noted. Samples were collected in triple-rinsed 10-L Cubitainers, which were kept in coolers on ice until processed in the laboratory as follows. Before filtration, a portion of each sample was taken in two 250 mL HDPE bottles for nutrient and alkalinity analysis. Within 5 hours of collection, each sample was filtered using a Thermo Scientific™ Nalgene™ reusable filter holder with receiver and a vacuum pump. All samples were filtered through both 0.8 µm and 0.2 µm pore-sized hydrophilic polypropylene membrane filters to remove microbial components. After filtering, water was partitioned for geochemical analyses in a 40-mL glass bottle with septum for stable isotopes ($\delta^{18}O$ and δD), and two 60-mL HDPE bottles for major ion and trace metal analyses. All samples were refrigerated until the time of laboratory analyses, which occurred within two weeks to one month of the sample collection.

3.2.3 Analytical methods

Stable isotopes were analyzed by the Biogeochemical Stable Isotope Facility at the University of Hawai‘i at Mānoa. Stable isotope analyses for $\delta^{18}O$ and δD were performed using a Picarro L2130-i wavelength scanned cavity ring down spectroscopy (WS-CRDS) following similar methods as Godoy et al. (2012). Analyses of cations (Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}) and anions (F^{-}, Cl^{-}, Br^{-}, $SO4^{2-}$) were performed by the Water Resources Research Center (WRRC) laboratory at the University of Hawai‘i at Mānoa using a dual Dionex ICS-1100 Ion Chromatograph following the US EPA Method 300.1 for determining inorganic ions in drinking water (Hautman and Munch, 1997). Analyses of trace metals (As, B, Ba, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Re, Si, Sr, U, V, and Zn) were also performed by the University of Hawai‘i at Mānoa WRRC laboratory using a Thermo Scientific iCAP 6300 Duo inductively coupled plasma optical emission spectrometer (ICP OES) following the EPA 200.7 method (Martin et al., 1994). Nutrient analyses for ammonium (NH_4^{+}), nitrate + nitrite ($NO_3^{-} + NO_2^{-}$), silicate (H_4SiO_4), orthophosphate (PO_4^{3+}), total nitrogen (TN) and total phosphorus (TP) were performed with a four channel Astoria Pacific A2 segmented-flow auto-analyzer. Alkalinity (HCO_3^{-}) analyses were performed at the Natural Energy Laboratory of Hawai‘i Authority (NELHA) Water Quality Laboratory following both the Hach (#8203) and Standard Methods (#2320 B) for titration (Rice et al., 2012). Median values of dissolved ions and isotopes are reported in Table 3.1 and Table 3.2, and all relative standard deviations and all geochemical parameters described in this section are reported in Appendix B.

3.3 Results

3.3.1 Raw data

Individual groundwater samples collected during the study period of May 2017 to March 2019 from wells spanning the five aquifer systems (Figure 3.1) demonstrated a range of dissolved ions and isotopic compositions, with temporal variations that generally fell within the relative standard deviation (Appendix B). Average groundwater ion concentration values were also calculated for wells that were visited multiple times over the duration of the project (Table 3.1 and 3.2).

Groundwater samples are commonly considered to be freshwater if the chloride concentration is < 250 mg/L (e.g. Oki et al., 1999), however nine wells were, on average, above this threshold. Of such wells, three have been or are currently used for potable groundwater while the remaining six were used for irrigation. The ionic strength of the samples ranged from 0.0018 M to 0.051 M. Isotopic compositions for $\delta^{18}O$ and δD ranged from -9.1 (‰) to -3.4 (‰) and -62.2 (‰) to -11.7 (‰), respectively, indicating a diverse range of recharge elevations to these groundwater systems (Fackrell et al., 2020; Tachera et al., 2021). The observed groundwater pH was, on average, ~7.8, as typical of groundwater systems in Hawaiʻi; groundwater in the vicinity of the rift zone of Hualālai volcano was slightly lower, falling between 6.55 to 7.45.

Table 3.1. Site identification and averaged in-situ data. Well ID is designated by the State of Hawai‘i Commission on Water Resource Management. Longitude and latitude are reported in decimal degrees. Sample type, high-low divide, and CWRM Aquifer are additional identifiers for each site. pH, temperature (°C), specific conductivity (µS/cm), and dissolved oxygen (% and mg/L) are collected in the field and reported as averaged values for the 43 groundwater and 3 ocean water samples during the study period of May 2017 to March 2019.

Index	Sample Name	Well ID	Longitude	Latitude	Sample Type	High-Low Divide	CWRM Aquifer	pH	Temp (°C)	Specific Conductance (µS/cm)	Salinity	Dissolved Oxygen (%)	Dissolved Oxygen (mg/L)
	Relative Standard Deviation												
1	Parker Ranch Deepwell	8-6239-002	-155.66	20.03	production well	Low	Waimea	7.9	23.0	153	0.1	91.0	7.8
2	Lalamilo C Deepwell	8-5946-003	-155.78	19.99	production well	Low	Waimea	7.9	26.2	568	0.3	97.0	8.4
3	Lalamilo A Deepwell	8-5946-001	-155.77	19.99	production well	Low	Waimea	7.9	26.1	460	0.2	82.3	5.7
4	Lalamilo B Deepwell	8-5946-002	-155.77	19.98	production well	Low	Waimea	7.8	26.2	496	0.2	79.3	6.1
5	Parker #2 Deepwell	8-5846-002	-155.77	19.98	production well	Low	Waimea	7.9	26.7	703	0.3	90.4	4.6
6	Parker #3 Deepwell	8-5846-003	-155.77	19.97	production well	Low	Waimea	7.8	26.7	433	0.2	96.8	6.6
7	Parker #4 Deepwell	8-5746-001	-155.77	19.96	production well	Low	Waimea	7.9	27.1	738	0.4	84.8	5.3
8	Waikoloa 1	8-5745-001	-155.76	19.95	production well	Low	Waimea	8.0	26.5	312	0.1	96.2	6.5
9	DW-7	8-5745-004	-155.76	19.95	production well	Low	Waimea	8.0	26.5	288	0.1	80.5	5.2
10	Parker 5	8-5745-001	-155.76	19.95	production well	Low	Waimea	8.2	26.5	304	0.1	75.3	5.9
11	Parker 4	8-5745-002	-155.76	19.95	production well	Low	Waimea	8.0	26.7	350	0.2	87.6	5.2
12	Waikoloa 3	8-5546-002	-155.77	19.93	production well	Low	Waimea	7.9	28.2	512	0.2	72.4	5.5
13	Waikoloa 2	8-5546-001	-155.77	19.93	production well	Low	Waimea	7.9	28.6	660	0.3	78.5	4.7
14	Waikoloa DW-6	8-5545-001	-155.76	19.92	production well	Low	Waimea	8.0	28.5	726	0.3	77.2	4.9
15	Resort Irr 2	8-5552-001	-155.84	19.92	production well	Low	Anaehoomalu	7.9	24.7	2522	1.3	90.5	7.4

16	Waikoloa Irr 3	8-5551-001	-155.86	19.92	production well	Low	Anaehoomalu	8.0	24.1	2184	1.1	96.5	6.5
17	Resort 1	8-5452-003	-155.87	19.91	production well	Low	Anaehoomalu	8.0	23.9	2921	1.5	96.7	7.1
18	Nursery	8-5452-001	-155.88	19.91	production well	Low	Anaehoomalu	7.9	23.5	3795	2.0	99.1	7.0
19	Fifty-One FT STP	8-5452-002	-155.88	19.91	production well	Low	Anaehoomalu	7.9	24.2	3421	1.8	76.6	5.9
20	West Hawaii Landfill	8-5352-001	-155.88	19.89	production well	Low	Kiholo	8.0	22.4	4161	2.2	105.7	8.8
21	Makani Golf Course	8-4950-001	-155.84	19.82	production well	Low	Kiholo	8.0	22.9	556	0.3	110.8	9.4
22	Puu Lani	8-4850-001	-155.83	19.81	production well	High	Kiholo	8.1	23.5	421	0.2	94.2	7.1
23	Puu Waawaa	8-4650-001	-155.84	19.78	production well	High	Kiholo	8.2	23.7	280	0.1	90.9	6.9
24	Huehue Ranch 5	8-4558-002	-155.98	19.76	production well	Low	Kiholo	7.1	23.7	1803	0.9	67.3	4.3
25	Huehue Ranch 3	8-4558-001	-155.98	19.76	production well	Low	Kiholo	7.1	20.3	1536	0.7	37.0	3.9
26	Huehue Ranch 4	8-4459-002	-155.98	19.75	production well	Low	Keauhou	6.6	23.7	1422	0.7	58.7	5.7
27	Huehue Ranch 2	8-4459-001	-155.98	19.74	production well	Low	Keauhou	6.9	21.9	1335	0.6	60.6	4.5
28	Kau (Makalei) Deepwell	8-4458-002	-155.98	19.73	production well	Low	Keauhou	7.3	24.3	1389	0.7	100.1	7.2
29	Kalaoa Deepwell	8-4358-001	-155.98	19.72	production well	High	Keauhou	7.8	23.3	304	0.1	84.7	7.6
30	Palani Ranch Deepwell	8-4158-003	-155.97	19.69	production well	High	Keauhou	8.0	22.0	228	0.1	90.0	7.2
31	Honokohau Deepwell	8-4158-002	-155.96	19.68	production well	High	Keauhou	7.8	21.9	234	0.1	93.6	7.2
32	Queen Liliuokalani Trust (Keahuolu) Deepwell	8-4057-001	-155.96	19.67	production well	High	Keauhou	7.9	20.9	160	0.1	99.5	8.3
33	Keopu Deepwell	8-3957-001	-155.95	19.65	production well	High	Keauhou	7.9	21.3	155	0.1	98.0	7.3
34	Holualoa Deepwell	8-3657-001	-155.95	19.61	production well	Low	Keauhou	7.9	20.6	928	0.4	100.7	9.1
35	Kahaluu A Deepwell	8-3557-001	-155.95	19.58	production well	Low	Keauhou	7.9	20.6	614	0.3	92.6	7.0

36	Kahaluu C Deepwell	8-3557-003	-155.95	19.58	production well	Low	Keauhou	7.9	20.3	335	0.1	100.1	7.0
37	Kahaluu B Deepwell	8-3557-002	-155.95	19.58	production well	Low	Keauhou	8.0	20.3	980	0.5	113.9	8.3
38	Kahaluu D Deepwell	8-3557-004	-155.95	19.58	production well	Low	Keauhou	7.5	20.2	940	0.4	98.5	6.8
39	Kahaluu Shaft	8-3557-005	-155.95	19.58	production well	Low	Keauhou	7.8	20.3	1499	0.7	91.3	7.7
40	Halekii Deepwell	8-3155-002	-155.92	19.52	production well	High	Kealakekua	7.8	21.4	139	0.1	104.5	6.4
41	Keei D Deepwell	8-2753-003	-155.88	19.46	production well	High	Kealakekua	7.8	18.7	133	0.1	115.2	8.8
42	Keei A Deepwell	8-2753-001	-155.89	19.46	production well	Low	Kealakekua	7.7	19.6	1638	0.8	100.4	6.7
43	Keei B Deepwell	8-2753-002	-155.89	19.45	production well	Low	Kealakekua	7.4	19.2	1139	0.5	94.6	7.1
44	Ocean End Member 21m	--	--	--	ocean	--	--	8.0	26.3	60927	40.9	111.7	
45	Ocean End Member 674m	--	--	--	ocean	--	--	7.5	6.2	61603	40.6	27.5	
46	Ocean End Member 900m	--	--	--	ocean	--	--	7.4	5.1	60858	35.2	58.7	

Table 3.2. Averaged, raw dissolved ion and stable isotope of water values. Averaged, raw (un-corrected) data for 43 groundwater and 3 ocean water samples during the study period of May 2017 to March 2019. Fluoride (F^-), chloride (Cl^-), bromide (Br^-), sulfate (SO_4^{2-}), sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}) are reported as averaged raw values in mg/L. Stable isotopes of water $\delta^{18}O$ and δ^2H are reported in per mil (‰). Relative standard deviations are reported for the geochemical parameters. Charge balance error, ocean water fraction, and ionic strength are calculated from the observed raw values.

Index	Sample Name	Fluoride (mg/L)	Chloride (mg/L)	Bromide (mg/L)	Sulfate (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	$\delta^{18}O$ (‰)	δ^2H (‰)	Charge Balance Error (%)	Ocean Water Fraction	Ionic Strength
	Relative Standard Deviation	4.94%	4.55%	4.70%	4.58%	2.68%	2.44%	3.38%	5.9%	0.78	0.46			
1	Parker Ranch Deepwell	0.09	8.00		3.10	12.00	2.70	7.50	10.90	-3.5	-11.9	5.5	0.00	0.002
2	Lalamilo C Deepwell	0.24	95.60	0.43	24.70	64.90	6.22	19.81	15.08	-5.4	-28.8	5.5	0.00	0.007
3	Lalamilo A Deepwell	0.26	73.00	0.28	21.30	54.00	5.23	18.40	14.46	-5.4	-28.7	6.5	0.00	0.006
4	Lalamilo B Deepwell	0.25	76.90	0.29	22.80	54.50	5.45	19.23	14.86	-5.6	-29.9	6.0	0.00	0.006
5	Parker #2 Deepwell	0.28	112.00	0.50	27.70	76.40	6.31	22.95	16.70	-5.7	-30.9	6.8	0.01	0.008
6	Parker #3 Deepwell	0.26	49.35	0.24	19.32	42.30	4.92	16.31	13.03	-5.7	-30.9	6.8	0.00	0.005
7	Parker #4 Deepwell	0.28	124.40	0.50	31.60	83.20	6.70	23.00	16.00	-5.8	-31.9	5.1	0.00	0.008
8	Waikoloa 1	0.32	27.85	0.07	16.40	32.05	4.01	14.40	11.12	-5.7	-30.5	6.9	0.00	0.004
9	DW-7	0.33	26.40	0.10	16.40	33.00	4.00	14.55	10.40	-5.7	-31.4	8.1	0.00	0.004
10	Parker 5	0.33	28.00	0.10	16.60	34.00	4.00	12.90	9.90	-5.7	-30.9	6.1	0.00	0.004
11	Parker 4	0.27	30.00	0.11	17.47	34.80	4.20	14.50	10.89	-5.8	-31.6	7.5	0.00	0.004
12	Waikoloa 3	0.33	68.00	0.30	30.60	63.50	6.02	19.06	12.70	-6.9	-42.1	5.2	0.00	0.007
13	Waikoloa 2	0.36	116.00	0.40	38.00	87.00	7.00	27.10	16.56	-7.1	-43.4	6.8	0.01	0.009
14	Waikoloa DW-6	0.35	128.20	0.50	41.00	97.40	8.05	27.20	15.38	-7.6	-48.2	5.4	0.01	0.010
15	Resort Irr 2	0.52	679.00	2.50	132.00	398.00	18.00	64.60	28.60	-8.9	-61.0	2.8	0.02	0.034

16	Waikoloa Irr 3	0.64	568.40	2.10	116.86	340.60	15.90	59.14	21.60	-8.9	-61.1	3.4	0.03	0.029
17	Resort 1	0.63	730.95	2.80	136.65	441.50	19.46	73.16	23.85	-8.9	-60.8	4.1	0.04	0.036
18	Nursery	0.64	1001.15	4.30	175.35	601.35	25.35	97.06	28.60	-8.6	-59.2	4.3	0.05	0.048
19	Fifty-One FT STP	0.75	1092.00	3.60	190.60	640.50	27.50	90.25	38.30	-8.7	-59.2	2.4	0.06	0.051
20	West Hawaii Landfill	0.80	991.10	3.90	176.30	595.70	27.20	98.51	30.10	-7.9	-53.1	4.5	0.05	0.048
21	Makani Golf Course	0.65	65.60	0.30	60.86	65.85	4.25	14.50	20.63	-8.1	-53.8	5.5	0.00	0.002
22	Puu Lani	0.81	41.00	0.18	48.80	53.60	3.86	10.53	17.39	-7.9	-51.2	5.2	0.00	0.007
23	Puu Waawaa	0.64	21.00	0.10	25.40	34.50	2.92	7.80	11.41	-8.0	-52.3	5.6	0.00	0.004
24	Huehue Ranch 5	1.54	84.50	0.37	314.40	165.40	9.40	138.40	48.30	-5.0	-25.0	6.5	0.00	0.038
25	Huehue Ranch 3	1.36	171.00	0.40	242.00	98.00	9.00	152.80	43.80	-4.9	-24.1	5.7	0.01	0.035
26	Huehue Ranch 4	0.71	161.40	0.48	103.90	112.90	12.43	121.05	41.84	-5.2	-28.0	4.5	0.01	0.023
27	Huehue Ranch 2	0.72	200.00	0.96	69.00	114.00	11.00	100.00	45.98	-4.8	-24.8	5.1	0.01	0.020
28	Kau (Makalei) Deepwell	0.76	238.80	0.93	64.65	129.70	13.42	76.03	42.39	-5.1	-25.8	5.0	0.01	0.019
29	Kalaoa Deepwell	0.42	9.80		28.53	31.45	5.27	11.40	12.38	-6.7	-40.2	5.7	0.00	0.005
30	Palani Ranch Deepwell	0.49	8.50		22.15	26.50	4.00	8.60	11.45	-7.0	-42.9	6.6	0.00	0.004
31	Honokohau Deepwell	0.39	7.80		20.02	25.70	4.17	7.76	10.10	-6.9	-42.3	4.6	0.00	0.003
32	Queen Liliuokalani Trust (Keahuolu) Deepwell	0.24	6.50		10.05	16.70	3.30	6.00	10.13	-5.5	-29.6	9.0	0.00	0.002
33	Keopu Deepwell	0.23	6.10	0.02	9.97	16.10	3.53	6.20	10.30	-5.2	-27.0	8.9	0.00	0.002
34	Holualoa Deepwell	0.16	224.00	0.73	36.45	130.00	7.65	24.05	26.00	-4.1	-18.9	5.6	0.01	0.012
35	Kahaluu A Deepwell	0.28	138.00	0.40	27.40	82.00	4.50	14.55	21.45	-5.3	-28.4	5.7	0.01	0.008

36	Kahaluu C Deepwell	0.23	56.40	0.20	16.60	38.00	3.05	8.30	13.30	-5.3	-28.4	5.1	0.00	0.004
37	Kahaluu B Deepwell	0.24	251.80	0.90	42.94	148.15	5.96	23.90	26.24	-5.3	-28.3	5.5	0.01	0.013
38	Kahaluu D Deepwell	0.19	242.00	1.10	41.80	144.00	6.00	23.80	25.10	-5.2	-28.0	6.0	0.01	0.013
39	Kahaluu Shaft	0.20	389.00	1.40	61.40	206.80	8.00	36.20	40.10	-5.1	-27.3	4.0	0.02	0.019
40	Halekii Deepwell	0.25	4.60		15.00	17.00	2.10	3.70	8.61	-5.9	-32.6	8.7	0.00	0.002
41	Keei D Deepwell	0.23	4.00		10.50	13.00	1.79	3.80	8.19	-5.3	-27.9	10.0	0.01	0.002
42	Keei A Deepwell	0.21	401.00	1.54	66.00	233.00	9.00	41.70	24.10	-4.5	-21.4	5.5	0.02	0.020
43	Keei B Deepwell	0.13	245.00	1.50	39.30	147.00	6.00	23.80	16.50	-4.6	-22.7	4.8	0.01	0.012
44	Ocean End Member 21m		19484.00	75.63	2749.60	11117.90	386.80	1597.97	314.96	0.3	2.6	--	--	0.8408
45	Ocean End Member 674m		19747.00	75.70	2769.60	11035.00	387.00	1582.19	319.14	0.0	0.0	--	--	0.8428
46	Ocean End Member 900m		20055.00	71.25	2865.30	11385.00	391.10	1552.90	300.70	0.0	-0.2	--	--	0.8575

3.3.2 Charge balance error

Based on thermodynamic laws, the charge balance of natural aqueous solutions in equilibrium is expected to be neutral, where the total number of positive charges carried by cations must equal the total number of negative charges carried by anions (Drever, 1997). Groundwaters that have low ionic strength are prone to charge balance errors greater than 10% due to uncertainties in ion concentration measurements, however charge balance errors are frequently presented in groundwater studies to represent the quality of the analyses performed (Fritz, 1994). A charge balance error within 2% is an ideal threshold to aim for, with 5% typically the reasonable goal for datasets to be presented as valid (e.g. Fritz, 1994).

In this study ionic charge balance errors were calculated using the following (Freeze and Cherry, 1979):

$$CBE = (\sum cations - |\sum anions|) / (\sum cations + |\sum anions|) * 100 \qquad \text{Eq. 3.1}$$

where ∑cations represents the sums of the major cations (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) and |∑anions| represents the absolute value of the sum of major anions (Cl^{-}, SO_4^{2-}, HCO_3^{-}). Charge balance errors range from 2.38% to 9.56% with an average of 5.78% and standard deviation of 1.57% (Figure 3.2). Samples with an ionic charge balance error less than +/- 5% (meaning they have an “allowable” or “acceptable” charge balance error) have a higher ocean-water fraction therefore higher ionic strength, as discussed further in Section 3.4.2.

High elevation wells with low ionic strength have lower concentrations of chloride and sulfate and are more likely to be dominated by bicarbonate in the charge balance calculations, whereas lower elevation wells are dominated by chloride and sulfate concentrations due to seawater influence. Guidelines for alkalinity analysis suggest completing the analysis in the field or within 24 hours of collection (Rice et al., 2012). Due to challenging field conditions in this study, water samples were collected for alkalinity analysis and stored in refrigerators until analyses could be performed. In most cases, the samples were analyzed within a few days, some within a few weeks.

We suspect that alkalinity introduces the majority of the charge balance error for the low ionic strength samples because of the longer than optimal time between sample collection and analysis, as well as random errors in the analysis of alkalinity itself. Therefore, bicarbonate concentrations may play a significant role in whether a sample is "charge balanced" and has higher than 5% error. Because of this uncertainty, samples that have an ionic charge imbalance greater than +/- 5% were flagged, however were still used further in our analysis.

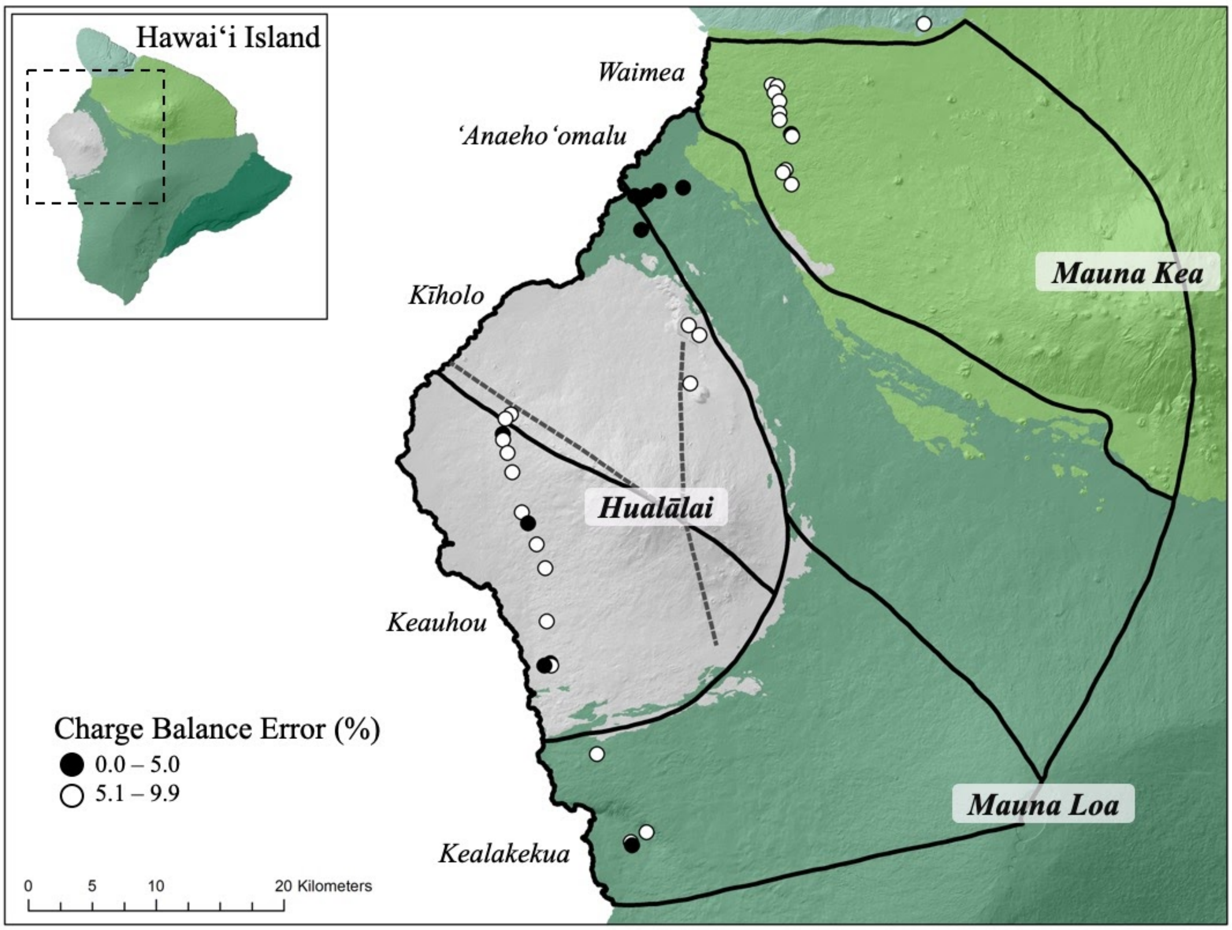

Figure 3.2. Charge balance error distribution across the study region. Aquifer boundaries delineated by the Commission on Water Resource Management (CWRM) State of Hawai'i are shown as black outlines. Hualālai rift zones are shown as gray dashed lines. Charge balance errors are colored as sites falling within the acceptable +/- range of 5% (black) and over +/- 5% (white).

3.4 Discussion

3.4.1 Groundwater flow paths inferred by geochemistry

Since, presumably, the major source of salt in the coastal aquifer is from seawater intrusion, first we turn to an ion analysis commonly applied to water resource studies in which seawater intrusion is likely to occur (Figure 3.3). The hydrochemical facies evolution (HFE) diagram was designed to investigate and interpret the hydrochemistry of seawater intrusion in coastal aquifers (e.g. Gimenez-Forcada, 2010; Gimenez-Forcada, 2019). It utilizes groundwater cation (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anion (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-) data to calculate percentages of major ions implicated in the hydrochemical processes related to the dynamics of sea water intrusion (Gimenez-Forcada, 2010). The facies are calculated as a function of the percentage of cations (Ca^{2+} and Na^+) and anions (HCO_3^- or SO_4^{2-} and Cl^-) with respect to the sums of cations and anions. Freshening waters plot above the conservative mixing line (CML), and intruded waters below. This type of hydrochemical plotting is designed to identify stages of salinity advance or withdrawal in a coastal aquifer system. Although there is no observable seasonal variation in compositions during the study period, the HFE-Diagram clearly suggests a pattern of spatial distribution of coastal seawater intrusion, or at least differences of major ion balances in different parts of the aquifers.

Potential flow paths were distinguished within the groundwater samples by determining the spatial distribution and groupings of the raw, uncorrected geochemical data. Utilizing the HFE and Piper diagrams, five distinct groups of wells were identified: rift zone (red), north of the rift zone coastal (yellow), north of the rift zone (green), south of the rift zone high-level (blue), and south of the rift zone coastal (yellow) (Figures 3.3 and 3.4). These groups and their corresponding groundwater chemistry demonstrate that geochemical evolution along a flow path can vary based on the geographic location and distance from the coastline of the groundwater well.

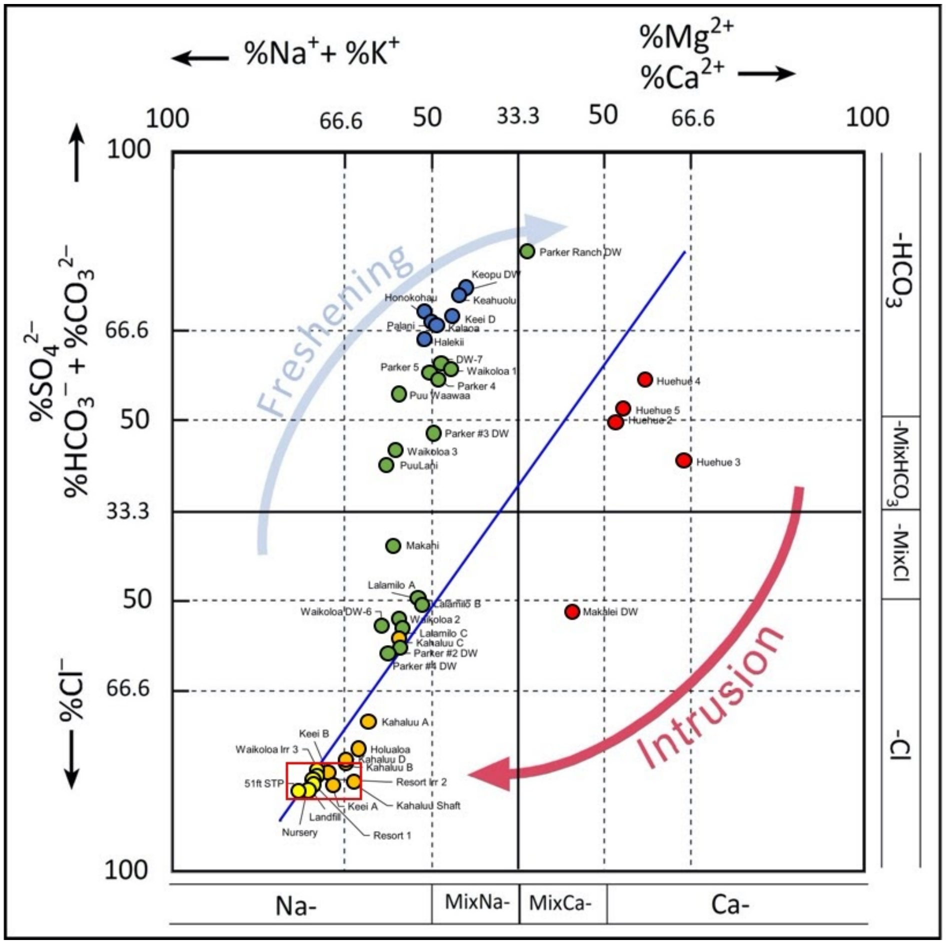

Figure 3.3. Hydrochemical facies diagram of groundwater samples. Groundwater wells are colored by location: rift zone (red), south of the rift zone basal (orange), north of the rift zone coastal (yellow), north of the rift zone (green), and south of the rift zone high-level (blue). Red box indicates the 9 wells that are above the 250 mg/L chloride threshold.

The dominant facies in the four quadrants in the HFE diagram are sodium and magnesium for cations, and bicarbonate and chloride for anions. While the diagram in its classic interpretation suggests freshening, we can interpret the clustering of a group of wells in the Ca^{2+}/Mg^{2+} and HCO_3^--dominated quadrants based on their location with respect to the Hualālai western rift zone. Rift zone wells (shown as red points in Figure 3.3) including Huʻehuʻe Ranch and Kau (Mākālei) Deepwell, plot in the upper right quadrant. This is likely due to the higher dissolved ion concentrations, excluding chloride, that result from hydro-geothermal water rock reactions at play here; this inference is supported by the interpretation of Fackrell et al. (2020).

Another cluster of wells appears near the seawater corner of the plot (bottom left) including north of the rift zone and south of the rift zone coastal wells. The red box around the bottom-most wells denote the 9 wells that exceed the 250 mg/L chloride threshold. The coastal wells (orange and yellow) are expected to plot on or near the intruded side of the plot, as they have been heavily utilized for groundwater withdrawal, which may have contributed to seawater intrusion or up-coning of the underlying transition zone (e.g. Swain, 1973). Because these wells are drawing from the basal aquifer within a few kilometers of the shoreline, a shallow salinity transition zone extends kilometers inland.

High-level wells south of the rift zone (blue) and about half of the inland wells north of the rift zone (green) plot on the Na^+/K^+ dominated side of the figure. High-level wells (blue) are located between 4 to 8 kilometers inland, whereas the wells inland and north of the rift zone are located 5 to 16 kilometers from the shoreline. The high-level wells south of the rift zone are located on the inland side of the impermeable feature in which Oki (1999) described three possible conceptual models. Previous studies have attempted to discern whether this high-level groundwater is connected to the basal aquifer, however further research is needed to discern this (Tillman et al., 2014; Kelly and Glenn, 2015; Fackrell et al., 2020). Inland wells north of the rift zone are split between the HCO_3^- (upper) and Cl^- (lower) quadrants of the diagram. There is no discernable spatial or geographic pattern as to why this split occurs, further investigations into land use and subsurface geology are needed.

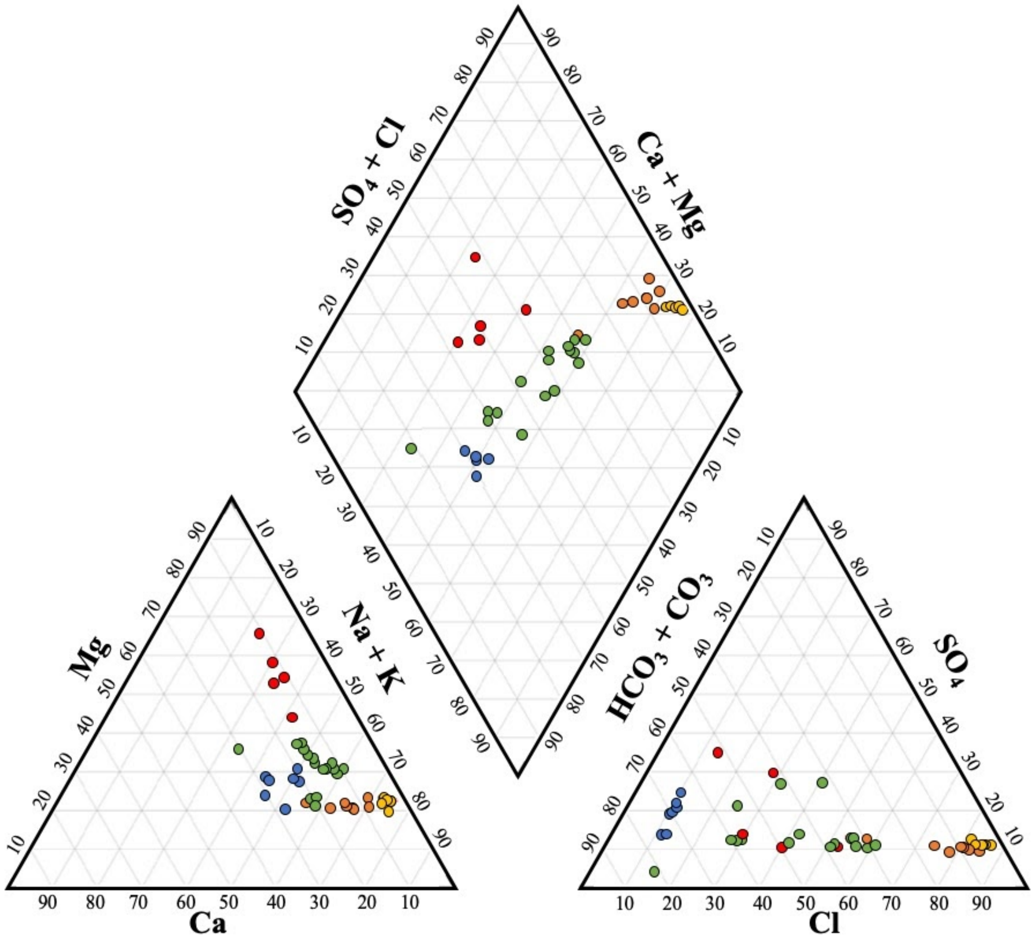

Figure 3.4. Piper diagram of groundwater samples. Wells are colored by location, same as HFE diagram: rift zone (red), south of the rift zone basal (orange), north of the rift zone coastal (yellow), north of the rift zone (green), and south of the rift zone high-level (blue).

HFE diagrams are used to illustrate seawater intrusion relationships but plotting data on a classical Piper diagram provides additional dimensions for analysis. The use of Piper diagrams (Figure 3.4) helps further visualize the relative proportions of the major ions, but not their absolute concentrations (Drever, 1997). Groundwater geochemistry plotted on a Piper diagram, specifically in the diamond-shaped plot and the cation plot (bottom left), shows similar groupings to the HFE diagram. Again, groundwater around the rift zone plots in a clear cluster. Other geographically and hydrogeologically distinct groups can be identified and clustered mostly based on their geographical locations. South of the rift zone basal, and north of the rift zone coastal wells group together, likely due to the high concentrations of chloride in these samples. The anion plot (bottom right) shows more mixing of the rift zone wells with the rest of the samples due to the variations in sulfate concentrations.

The conclusions drawn from these figures, which rely on ion proportions, are that (1) there are clear groupings with different groundwater chemical characteristics, and (2) a uniform salinity-correction approach would not be appropriate.

3.4.2 Salinity corrections

Globally, salinity corrections are applied to groundwater samples where seawater mixing is likely to occur - to remove the seawater fraction of a mixed sample (Clark and Fritz, 1997). The purpose of the salinity correction is to identify the geochemistry of the groundwater-fraction of a water sample, in order to assess the potential source, flow, and quality of groundwater, so as to characterize the freshwater chemistry and inform water resource management. Calculations for salinity corrections employ end-member values, chosen to represent the ends of the spectrum for freshwater and ocean water within the study region.

There has been no conventional way of choosing the end-members for a salinity correction. Instead, individual research projects choose end-member chemistries that best suit their hydrogeologic setting. Along these lines, previous research in Hawaiʻi is not consistent with respect to the end-member chemistry chosen for freshwater and seawater. At times, a very simplistic approach is taken or the end-member chemistry applied in the correction is not specified. For example, Kelly and Glenn (2015) and Fackrell et al. (2020) utilize a freshwater end-member salinity value as 0 ppt for simplicity. This is not realistic given that there is a non-zero contribution of dissolved ions to groundwater recharge, as demonstrated by Tachera et al. (2021). The Hydrochemical Facies diagram (Figure 3.3) also suggests that various Na^+/K^+ or Ca^{2+}/Mg^{2+} dominated water masses are present in the aquifers, which renders the use of a single, fresh end-member inappropriate.

In order to account for seawater mixing, salinity corrections were applied to the groundwater samples, in order to effectively unmix the seawater fraction from the freshwater component. In all calculations of salinity corrections, the following equations were used with varying freshwater and ocean-water end-members. First, the fraction of ocean water was calculated:

$$F_{ow} = (Cl_{sample} – Cl_{fw})/(Cl_{ow} – Cl_{fw}) \qquad \text{Eq. 3.2}$$

where F_{ow} is the fraction of ocean water, and Cl is the chloride concentration of the sample ($_{sample}$), freshwater ($_{fw}$) end-member, and ocean water ($_{ow}$) end-member (Clark and Fritz, 1997). Most commonly the salinity as measured in the field with a multiparameter sonde is used for this correction, however we used the chloride concentration to be more ion specific in the corrections. The chosen end-member values are discussed in more detail in section 4.2.

There are multiple needs for a salinity correction. Here, we illustrate its application via the prior-mentioned $\delta^{18}O$ and δD isotopes of water, nutrients, and metals. We include discussion of issues related to use of the conventional salinity correction. To calculate the isotopic composition of the freshwater fraction in the sample, for either $\delta^{18}O$ and δD in water, equation 3.3 was used:

$$\delta_{fw} = (\delta_{sample} – F_{ow} \times \delta_{ow})/(1 – F_{ow}) \qquad \text{Eq. 3.3}$$

where δ_{sample} is the isotopic value of the sample, F_{ow} is the fraction of ocean water calculated previously, and δ_{ow} is the isotopic composition of the ocean water end-member (Scholl et al., 1996).

In order to account for seawater mixing in major ions, trace metals, and nutrient concentrations in groundwater samples, the following correction is used (Hunt & Rosa, 2009):

$$C_{fw} = C_{sample} + (C_{sample} - C_{ow}) \times (Cl^-_{sample} - Cl^-_{fw})/(Cl^-_{ow} - Cl^-_{sample}) \qquad \text{Eq. 3.4}$$

where C is the ion concentration and Cl^- is the chloride concentration, as above in place of salinity.

3.4.2.1 Unreliable salinity corrections

We attempted salinity corrections with the data presented above in multiple ways. The first attempt was to use the simplest end-member values of 0 ppt and 35 ppt salinity for the fresh-and ocean-water end-members, respectively. This resulted in over corrections (producing negative values) of the major ions, trace metals, and nutrients datasets.

The second attempt investigated a non-zero salinity end-member for freshwater because the freshwater end-member value of 0 ppt seemed unreasonable based on previous research (e.g. Lee et al., 2000; Tachera et al., 2021). The average salinity of high-level groundwater was used as the freshwater end-member. The ocean water end-member was also changed, calculated from the average of the three sea-water depth samples (shallow ocean at 21 m depth, mid-level at 674 m depth, and deep at 900 m depth) collected during the sampling period. This attempt also resulted in over corrections.

A third attempt was again to use an average of high-level groundwater for the freshwater end-member, however using an ocean water end-member value following Fackrell et al. (2020), who used different end-members for north and south of the rift zone. Fackrell et al. (2020) used the shallow ocean sample north of the rift zone, and an average of shallow and deep ocean samples south of the rift zone, in accordance with their hypothesis that seawater circulation within the aquifer system south of the rift zone is different from that north of the rift zone. Again, in our calculations this resulted in over corrections for some samples.

3.4.2.2 Flow-path dependent salinity corrections

Ultimately, we chose to use dissolved ion data from precipitation along the flow path as the freshwater end-member from our recent research in the study region (Tachera et al., 2021). The calculation of ocean end-member values using both the shallow (21 m depth) and mid-level (674 m depth) ocean samples resulted in significantly fewer over corrections. Salinity-corrected groundwater values are reported in Appendix C.

The freshwater end-member value was calculated from precipitation collected within the upper reaches of a probable flow path to the sampled groundwater well (Tachera et al., 2021), as the average chloride concentration sampled. Precipitation was chosen to represent the freshwater end-member because of the uncertainty of the origin and flow path of the high-level groundwater samples. We contend that precipitation is the best representation for the freshwater fraction, as it is the water that is recharging the aquifers. Ocean water end-member values were calculated as a range, using both shallow and deep sea water samples, given the hypothesis that seawater circulates within the aquifers south of Hualālai's rift zone (Oki, 1999; Fackrell et al., 2020; Attias et al., 2020).

3.5 Conclusions

We present a new, flow-path specific method to calculate salinity corrections, and apply this method to groundwater samples collected in West Hawai‘i from May 2017 to March 2019. This method utilizes end-member values for precipitation and ocean-water within the probable flow path to (or for) each groundwater sample, with the precipitation values determined from field data collection during the same time period (Tachera et al, 2021). This method provided better results (lower error) than previously-published methods of calculating the correction, for example utilizing generic end-members such as 0 ppt for freshwater.

Charge balance error cannot always be used to indicate the quality of datasets. As demonstrated in this study, alkalinity analyses can introduce significant error. Groundwaters that are low in ionic concentration, like the high-level wells in West Hawai‘i, frequently result in charge balance errors larger than +/- 5% because of the dominating alkalinity geochemistry. In coastal waters, chloride and sulfate dominate the ion chemistry. Two potential problems result from alkalinity analyses: (1) the time between sample collection and sample analysis, and (2) random errors associated with sample collection and analysis.

Appropriate salinity corrections are crucial to groundwater management, because it is a necessary step in the characterization of groundwater aquifer chemistry. Seawater intrusion is a natural process that affects groundwater salinity in coastal environments. In Hawai‘i, and elsewhere around the world, salinity corrections are required to separate out the ocean water fraction from the freshwater fraction, to better understand the degree of seawater inundation and anthropogenic contamination. Especially in settings like West Hawai‘i where the hydrogeology is very complex, it is crucial to use proper end-members for these corrections. This study demonstrates that utilizing end-members from within flow paths allows for better characterization of groundwater systems that can be temporally and spatially heterogeneous.

Chapter 4. IDENTIFYING GROUNDWATER SOURCE, FLOW, AND INTERCONNECTIVITY IN WEST HAWAIʻI

Diamond K. Tachera, Nicole C. Lautze, Henrietta Dulai, Kimberly M. Burnett, Scott K. Rowland, Donald M. Thomas

Abstract

West Hawaiʻi is a region with complex hydrogeology that has been studied intently over the past decades for reasons including: 1) the discovery of high-level groundwater following a period of intense development in the 1990s; and 2) recent requests to designate a protected groundwater management area. This paper links previously published precipitation chemistry from the West Hawaiʻi region with 96 groundwater well and anchialine pond samples, to address key outstanding questions related to the source, flow, and connectivity. Groundwater samples were analyzed for major ion, trace metal, and stable isotopes of water (oxygen and hydrogen) chemistry, which serve as natural tracers in the environment. Groundwater recharge elevations were calculated using the stable isotope compositions of precipitation and groundwater following two methods: point-source and fully-integrated recharge. The implementation of two methods constrained the possible range of recharge elevations to Hualālai, Mauna Kea, and Mauna Loa volcanoes. In the northern study region, isotopic compositions indicate that groundwater flows across aquifer boundaries which are based on surface geology. In many cases, the isotopic compositions of samples from within the Hualālai aquifer sector indicate groundwater recharges from elevations greater than that of Hualālai's summit. Therefore, recharge is sourced from the flanks of Mauna Kea and/or Mauna Loa. In contrast, isolated groundwater flow is observed around the Hualālai rift zone due to a sharp change in groundwater isotopic compositions over a short distance. These findings illustrate the complex hydrogeology within West Hawaiʻi, and highlight that current groundwater management boundaries do not represent the nuanced and complex subsurface in the West Hawaiʻi region.

4.1 Introduction and background

Groundwater is the main source of drinking water in the State of Hawaiʻi, providing about 99% of Hawaiʻi's domestic water and 50% of freshwater used in the State (Gingerich and Oki, 2000). With increasing urban development, population, and tourism, it is critical to understand water availability, which depends on its quality in aquifers. In order to properly manage the resource and preserve the health and sustainability of groundwater in Hawaiʻi, improved understanding is needed regarding: (1) the source region where rainfall enters the ground as recharge, (2) groundwater flow paths from mauka (mountain) to makai (sea), and (3) the interconnectivity and mixing of groundwater across aquifers.

In the late 1980s, the Hawaiʻi State Legislature established the State Water Code and the Commission on Water Resource Management (CWRM). Through the State Water Code, CWRM protects and manages fresh waters in Hawaiʻi. If groundwater in a particular area is deemed at risk, the CWRM can designate a Groundwater Management Area (GWA), which requires all water users in the area to submit a permit application that specifies their withdrawal rate of groundwater and justifies its usage (Chapter 171, Hawaiʻi Revised Statutes (HRS)).

Determining the source, flow, and interconnectivity of aquifers has direct implications for water resource management. Ideally, a water management authority would set groundwater withdrawal rates such that in any given time period, the rate of withdrawal would not exceed the net rate of natural recharge minus discharge, and would account for any linked groundwater-dependent ecosystems associated with corresponding rates of stream flow and submarine groundwater discharge (SGD). Such sustainable management requires accurate knowledge of the inputs and outputs to a system, including the degree of connectivity among units. However, the complexity of geologic subsurface structures in West Hawaiʻi (and elsewhere in Hawaiʻi) complicates our understanding of subsurface processes, including sustainable groundwater withdrawal estimation. CWRM utilizes groundwater and transport models RAM and RAM2 to estimate sustainable yields (Mink, 1980; Mink, 1981; Liu, 2006). These models rely on management units that are not based on subsurface hydrology, but rather surface geology and analytical convenience. Sustainable yield (SY) as described here (see Elshall et al., 2020 for other definitions) is the allowable net draft associated with a minimum equilibrium head of an aquifer or hydrologic unit (Liu, 2006). Key input parameters of both the RAM and RAM2 models are head level and rates of recharge and discharge. Without an accurate understanding of these basic parameters for each groundwater management unit of interest, it is impossible to determine an accurate sustainable yield. Understanding the source, flow, and interconnectivity of aquifers in West Hawaiʻi is a crucial first step to improving sustainable groundwater management, and the health and longevity of linked groundwater dependent ecosystems in this area. Furthermore, these goals are required by law in the Hawaiʻi State Water Code (Chapter 174C, Hawaiʻi Revised Statutes (HRS)).

Globally, geochemical parameters including chloride concentration and stable isotopes of water (^{18}O and ^{2}H) are used to investigate properties such as the source, flow, and interconnectivity of groundwaters. The stable isotopes of water help determine the source and flow paths of water. The amount of rainout from the air mass and temperature of condensation are factors controlling the isotopic composition of precipitation (Dansgaard, 1964). An important assumption of previous, as well as this work, is that as recharge filters into the subsurface, its isotopic composition is unaffected by the infiltration process in low temperature settings (Drever, 1997). Chloride concentrations can elucidate interconnectivity among aquifers and saltwater intrusion due to the low abundance of chloride in basalt rocks in Hawaiʻi (Macdonald et al., 1983).

Groundwater-related research in the West Hawaiʻi region has been ongoing over the last few decades. In the 1990s, increased development in the Kailua-Kona region led to much higher demands for water, and the discovery of a high-level water resource around 4 km inland from the coast (Oki, 1999; Bauer, 2003). Increased development and changing land use in the mauka region has also caused concern regarding decreased water quality and availability for coastal ecosystems (i.e. Tillman et al., 2014; Brauman et al., 2015). Concerns about conserving water for non-consumptive public trust uses became so prevalent that in 2013, the National Park Service petitioned to designate the Keauhou aquifer as a groundwater management area (National Park Service, 2013).

Previous research has started to uncover the source, flow, and interconnectivity of groundwater on Hawaiʻi Island. For example, Fackrell et al. (2020) investigated the recharge regions and elevations of Hualālai groundwaters in West Hawaiʻi, and showed that at least some of the rainfall had to have fallen at elevations higher than that of Hualālai's summit. Tachera et al. (2021) highlighted the dynamic effects of weather and climate patterns on isotopic compositions of rainfall, a data set frequently used to identify elevations of recharge (Dansgaard, 1964; Tachera et al., 2021). In addition, numerous geophysical studies have focused on the relatively young, complex subsurface hydrogeology of West Hawaiʻi (Kauahikaua et al., 1985; Kauahikaua et al., 2000; Dimova et al., 2012; Attias et al., 2020; Attias et al., 2021a).

Submarine groundwater discharge (SGD) is an important hydrogeologic process, both in quality and quantity, because it transports both nutrients and contaminants to nearshore ecosystems that are key economic and sustainable resources for local communities (Duarte et al., 2010; Pongkijvorasin et al., 2010; Wada et al., 2021). Aerial mapping surveys using thermal infrared imagery have identified vast areas of cold, nutrient-rich freshwater discharge along the West Hawaiʻi coast (i.e. Johnson et al., 2008). Recent research conducted at Kīholo Bay, located along the coast of the Kīholo aquifer, demonstrates the linkage between SGD flow rates with groundwater levels and precipitation events, with a signature delay on the order of weeks to months (McKenzie et al., 2021).

Despite decades of research, questions still remain about the hydrogeology of West Hawaiʻi. The NSF EPSCoR ʻIke Wai project was a multidisciplinary approach to hydrologic research. The team collaboratively investigated the (1) degree of connectivity between the high-level and basal aquifers, (2) the sources of water that pass through the Hualālai aquifers, (3) how Hualālais rift zones affect groundwater quality and flow, (4) the nature of the geologic feature in the Keauhou aquifer and its impact on subsurface water storage, and (5) the quality, volume, and distribution of submarine groundwater discharge along the coast. The results of this hydrological and geochemical study attempt to describe the West Hawaiʻi hydrogeology as a whole, in order to provide more information to assist with regulatory considerations toward ensuring sustainable use of the region's fresh groundwater.

4.2 Materials and methods

4.2.1 Study site

4.2.1.1 Hydrogeology

Hawaiʻi Island has relatively young geology. The most recent eruptive events for Hualālai volcano ended by 1800-1801, with the Kaʻūpūlehu and Huʻehuʻe eruptions (Kauahikaua et al., 2002). Other recent eruptions in the study region originated from Mauna Loa. In the past 179 years, Mauna Loa volcano has erupted 33 times, averaging an eruption every 5 years (Trusdell, 2012). The 1859 eruption from the northwest flank generated paired ʻaʻā and pāhoehoe flows that ultimately reached the coast and covered part of the Kīholo fishpond and other historic sites in the area (Rowland and Walker, 1990; Riker et al., 2009). The relatively young surface geology combined with very low weathering rates in this region results in a porous surface, allowing recharge to rapidly enter the groundwater system (e.g., Mink and Lau, 2006). In addition, this young geology has not had enough time to develop a major confining layer along the coast as observed on other Hawaiian Islands (i.e. caprock on Oʻahu; e.g., Izuka et al., 2018). Therefore, surface water is rare in the West Hawaiʻi study region, and SGD along the coast contributes millions of gallons of freshwater to the nearshore environment daily (e.g., Johnson et al., 2008).

The subsurface geology of West Hawaiʻi Island is likely to be very complex. Within the study region, there are overlapping lava flows from four of Hawaiʻi Island's volcanoes: Kohala, Mauna Kea, Hualālai, and Mauna Loa (Figure 4.1). There are also rift zones, which typically exhibit low permeabilities due to the concentration of near-vertical dikes in the subsurface (e.g., Hunt, 1996; Gingerich and Oki, 2000; Izuka et al., 2018).

In the Keauhou aquifer, an additional subsurface structure commonly referred to as the "high-low divide" has proved challenging to interpret for many years. Groundwater levels in the Keauhou aquifer range from 0 to 12 meters above mean sea level (amsl) in the basal aquifer, and over a distance of < 2 km the head in wells increases to 12 to 140 meters amsl (i.e., the high-level aquifer; Oki, 1999; Figure 4.1). Three scenarios were proposed for the subsurface structure that creates the observed steep hydraulic head gradient: (1) a buried dike system, (2) buried faults, and/or (3) buried lava flows (Oki, 1999). Recent geophysical research in West Hawaiʻi by Attias et al. (2020; Figure 5), consistent with the Oki (1999) scenario of buried lava flows, suggests groundwater flow can be vertically segregated by low-permeability ash and soil layers that impede percolation of recharge and instead enter the ocean at various depths as submarine groundwater discharge. This suggests that the depth to which a groundwater well is drilled will determine which freshwater layer is encountered, and perhaps also the elevation of recharge that dominates that freshwater body. Additional findings suggest that lava tubes can serve as preferential pathways for groundwater flow, allowing for potential connection from mauka to makai (e.g., Attias et al., 2021b).

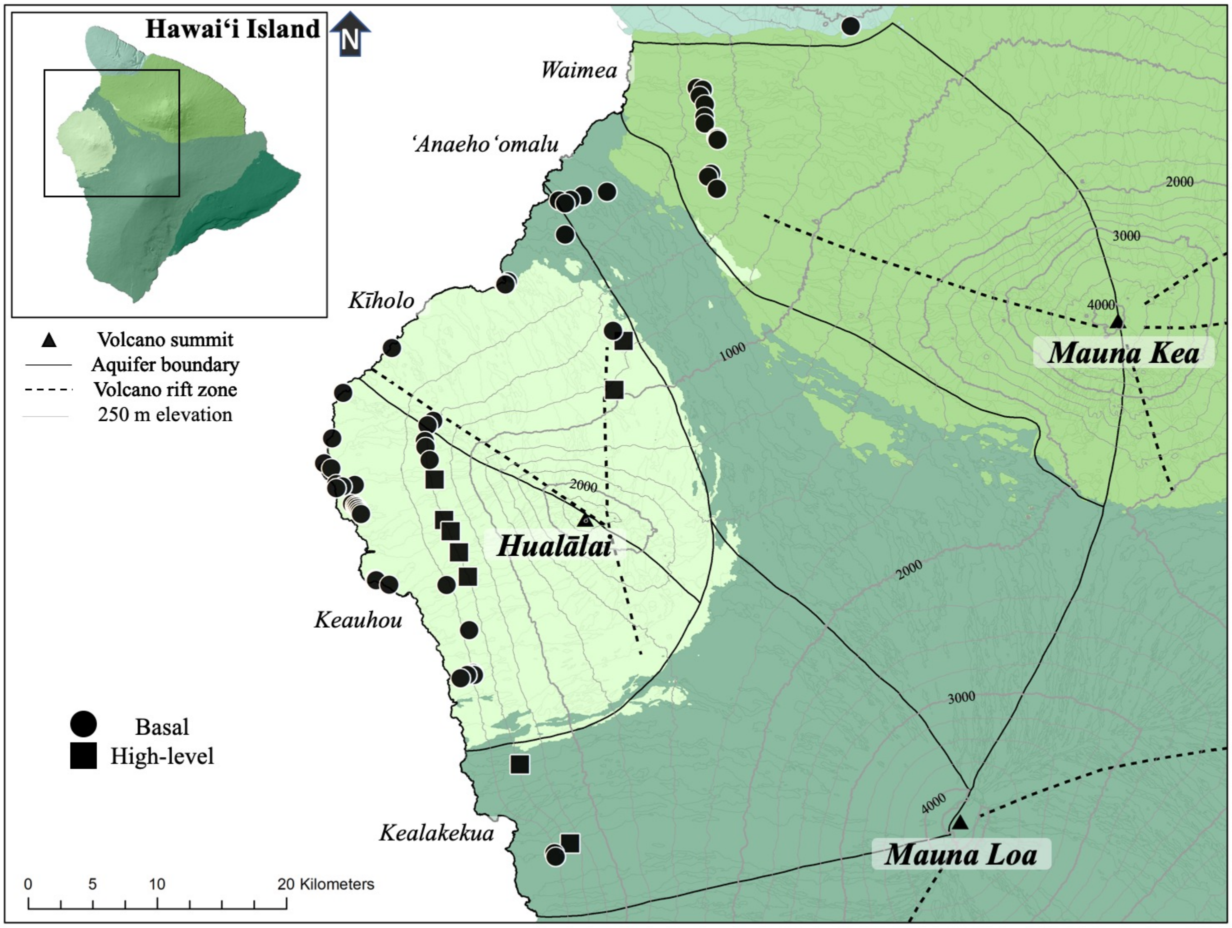

Figure 4.1. West Hawaiʻi study area. Points represent production wells, monitoring wells, irrigation wells, ponds, and basal groundwater sample sites. Squares represent high-level groundwater sites. Solid black lines outline the five aquifers in the region: Waimea, ʻAnaehoʻomalu, Kīholo, Keauhou, and Kealakekua. Basemap colors represent surface flows of volcanoes: Kohala, Mauna Kea, Hualālai, and Mauna Loa. Dotted lines represent approximate locations for rift zones of each volcano. Black triangles indicate the summits of Hualālai, Mauna Kea, and Mauna Loa.

4.2.1.2 Climate

The study region extends from the coastline of Kailua-Kona to the summit of Mauna Kea and nearly to the summit of Mauna Loa (Figure 4.1). Due to its position in the rain shadow of Mauna Kea and Mauna Loa, the West Hawaiʻi region experiences unique weather patterns as compared to the rest of the State. Hawaiʻi's tradewinds do not reach West Hawaiʻi, instead land-breeze sea-breeze patterns are typical (Giambelluca et al., 2013). The trade wind inversion is at approximately 2,000 meters amsl; precipitation above this decreases considerably with increasing elevation (Giambelluca et al., 2013), and is dominantly from extra-tropical and subtropical storms.

Previous research, spanning nearly a decade, has also highlighted long-term changes in climate patterns for West Hawaiʻi. Precipitation samples collected in similar locations in West Hawaiʻi during two periods 2012-2014 and 2017-2019, observed significantly different stable isotope compositions of water and produced differing local meteoric water lines (Fackrell et al., 2020; Tachera et al., 2021). In addition, groundwater isotopic compositions collected during both periods were better characterized by a volume-weighted average of both periods, demonstrating that groundwater represents an accumulation of the dynamically differing weather patterns experienced in this region over time.

4.2.2 Methods

4.2.2.1 Sampling methods

Precipitation samples were collected on an approximately quarterly basis from twenty sites (Tachera et al., 2021). A 1 cm-thick layer of mineral oil was poured into all collectors to prevent rainwater from evaporating. Each sample was partitioned into two 60 mL HDPE bottles, one for major ion analysis and the other for stable isotope ($\delta^{18}O$ and δD) analysis. The groundwater samples were collected on a quarterly basis between May 2017 and March 2019 (Tachera et al., in prep). Given the large area of the study region, a variety of wells (basal, high-level, thermally-influenced) were chosen to represent the expected variety of compositions of water in West Hawaiʻi (Figure 4.1). All samples were refrigerated until the time of laboratory analyses, which occurred between two weeks to one month after sample collection.

4.2.2.2 Analytical methods

Stable isotopes of water, $\delta^{18}O$ and δD, were analyzed following methods of Godoy et al. (2012) using a Picarro L2130-i wavelength scanned cavity ring down spectroscopy (WS-CRDS). Analyses of cations (Na, K, Mg, Ca) and anions (F, Cl, Br, SO4) were performed using a dual Dionex ICS-1100 Ion Chromatograph following the US EPA Method 300.1 for determining inorganic ions in drinking water (Hautman and Munch, 1997). Analyses of trace metals (As, B, Ba, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Re, Si, Sr, U, V, and Zn) were performed using a Thermo Scientific iCAP 6300 Duo inductively coupled plasma optical emission spectrometer (ICP OES) following the EPA 200.7 method (Martin et al., 1994). Nutrient analyses for ammonium (NH_4^+) nitrate + nitrite ($NO_3^- + NO_2^-$), silicate (H_4SiO_4), orthophosphate (PO_4^{3-}), total nitrogen (TN) and total phosphorus (TP) were performed with a four channel Astoria Pacific A2 segmented-flow auto-analyzer. Alkalinity (HCO_3^-) analyses were performed following both the Hach (#8203) and Standard Methods (#2320 B) for titration (Rice et al., 2012).

4.2.2.3 Recharge elevation calculations

The local meteoric water line (LMWL) determined by Tachera et al. (2021), $\delta D = 8.14\ \delta^{18}O + 12.83$ ($r^2 = 0.99$), was used to correlate the isotopic composition $\delta^{18}O$ values of groundwater to elevations of rainfall. Below 2,000 meters the $\delta^{18}O$-elevation relationship is $\delta^{18}O = -0.0017h - 2.54$, and above 2,000 meters is $\delta^{18}O = -0.0030h - 0.33$, where h is the elevation of each site in meters relative to msl. Recharge elevations were calculated using two methods: fully-integrated and point-source. Similar to previous research, fully-integrated recharge assumes that rainfall along a flow path fully integrates (or mixes) to a maximum elevation at which the mixture is isotopically identical to the salinity-corrected groundwater sample (Scholl et al., 1996; Fackrell et al., 2020). The calculation was performed for each site:

$$\delta^{18}O_{\text{sample}} = \frac{\sum_{\text{int}=1}^{n} \left(\delta^{18}O\right) n (R) n}{\sum_{\text{int}=1}^{n} (R) n}$$

where $\delta^{18}O_{sample}$ is the $\delta^{18}O$ isotopic composition of the salinity-corrected groundwater sample (Tachera et al., in prep). Following previous studies, intervals of 250 meters amsl elevation were used in this analysis (Fackrell et al., 2020).

Point-source recharge assumes that rainfall does not integrate along a flow path from point of recharge to discharge (or pumping). Instead, recharge enters the groundwater aquifer at the specified elevation, does not mix with any other recharge along the flow path, and is pumped out or discharged at the sampling site. By applying these two methods, this study was able to constrain the range of possible elevations at which groundwater recharge occurred, with fully-integrated recharge a minimum and point-source recharge a maximum.

4.3 Results and discussion

4.3.1 Source of groundwater

For each location, the averages of the salinity-corrected $\delta^{18}O$ values of water are shown in Figure 4.2 and Figure 4.3, and presented in Table 4.1. Averaging is justified in this case where multiple samples were collected during the study period because the seasonal variability observed is less than the analytical error (Appendix B). Literature values are plotted to demonstrate the minimal seasonal and long-term variability (Tillman et al., 2014; Kelly and Glenn, 2015; Fackrell et al., 2020). The local meteoric water lines established by previous research are also plotted in Figure 4.2 (Fackrell et al., 2020; Tachera et al., 2021).

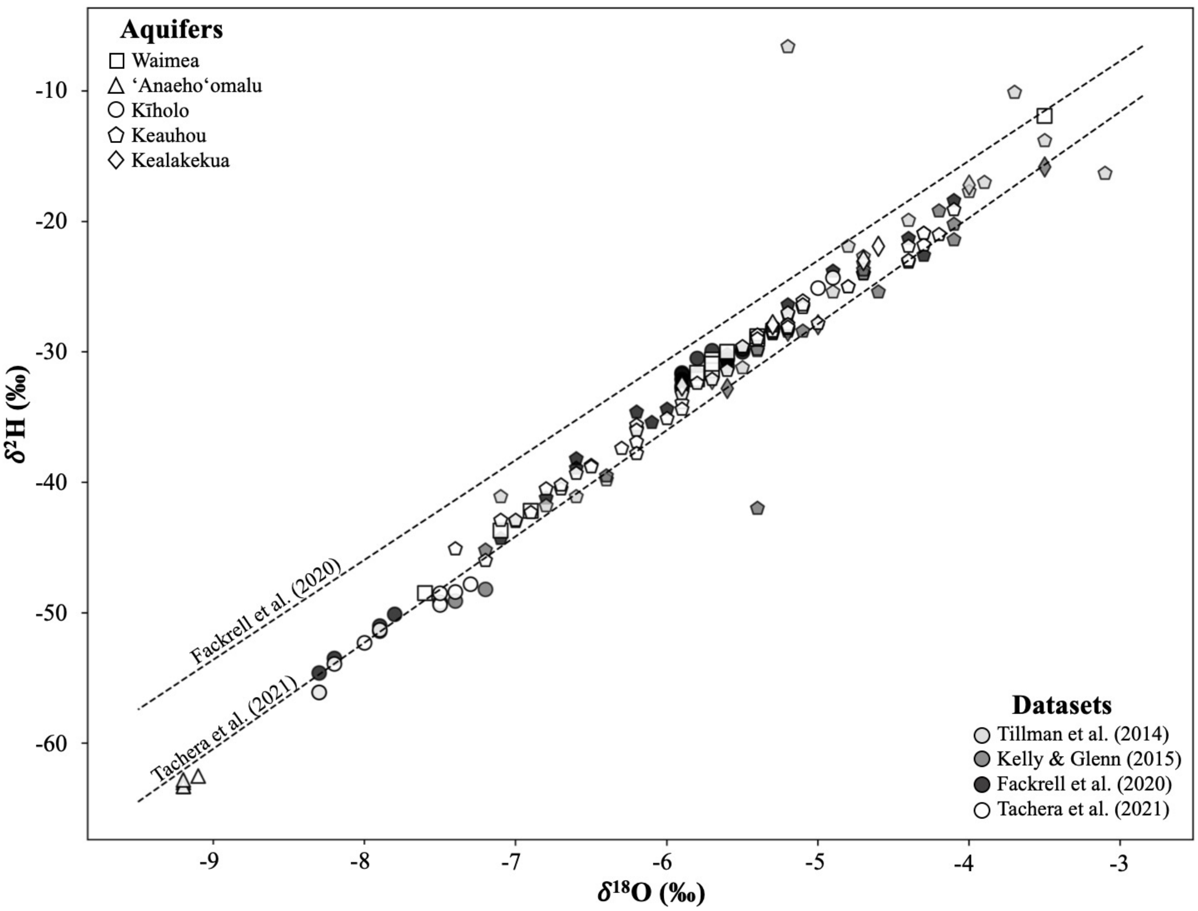

Figure 4.2. Salinity-corrected groundwater isotopic compositions. Including Fackrell et al. (2020) in black points, Tillman et al. (2014) in light gray, Kelly and Glenn (2015) in dark gray, and current dataset in white. Symbol shapes indicate aquifers: Waimea (square), ʻAnaehoʻomalu (triangle), Kīholo (circle), Keauhou (pentagon), and Kealakekua (diamond). Local meteoric water lines have been established for West Hawaiʻi by Fackrell et al. (2020) and Tachera et al. (2021).

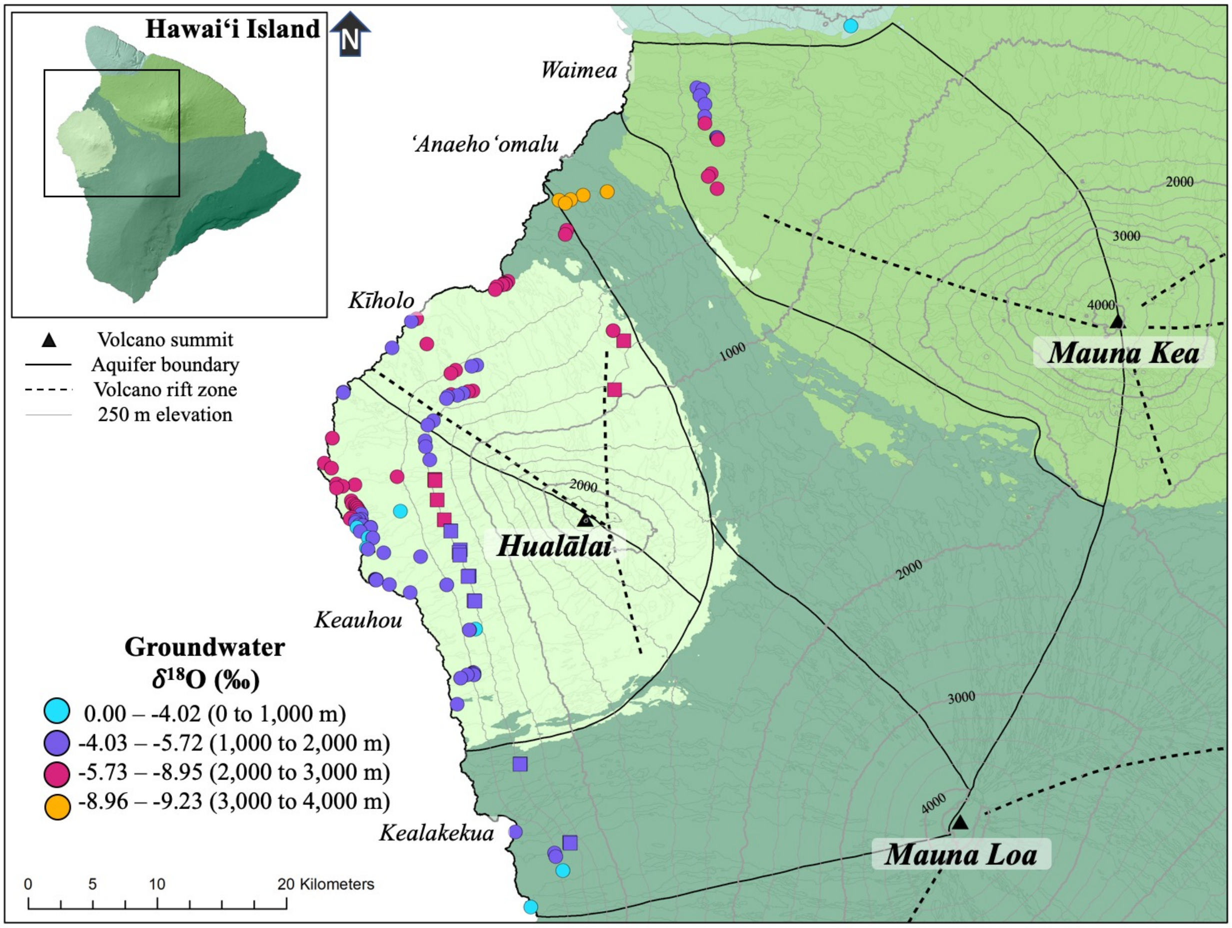

Figure 4.3. Isotopic compositions of groundwater in West Hawai'i. Salinity-corrected basal groundwater sites are presented as circles, high-level groundwater sites as squares, for the current research as well as previous studies (Tillman et al., 2014; Kelly and Glenn, 2015; Fackrell et al., 2020). $\delta^{18}O$ values of water are colored according to the recharge elevation ranges as calculated by Tachera et al. (2021): blue = 0 ‰ to -4.02 ‰ (0-1,000 m); purple = -4.03 ‰ to -5.72 ‰ (1,000-2,000 m); magenta = -5.73 ‰ to -8.95 ‰ (2,000-3,000 m); orange = -8.96 ‰ to -12.71 ‰ (3,000-4,250 m).

Table 4.1. Site identification, in-situ data, and stable isotopes of water values. Well ID is designated by the State of Hawai'i Commission on Water Resource Management. Longitude and latitude are reported in decimal degrees. Sample type, high-low divide, and CWRM Aquifer are additional identifiers for each site. pH, temperature (°C), specific conductivity (µS/cm), and dissolved oxygen (% and mg/L) are collected in the field and reported as averaged values. Averaged, salinity-corrected stable isotopes of water $\delta^{18}O$ and δ^2H are reported in per mil (‰). Ocean water fraction, and ionic strength are calculated from the observed raw stable isotopes of water ($\delta^{18}O$ and δ^2H) values.

Well Name	Well ID	Longitude	Latitude	Sample Type	High-Low Divide	CWRM Aquifer	pH	Temperature (°C)	Specific Conductivity (µS/cm)	Salinity	Dissolved Oxygen (%)	Dissolved Oxygen (mg/L)	$\delta^{18}O$ (‰)	δ^2H (‰)	Ocean Water Fraction
Parker Ranch Deepwell	8-6239-002	-155.66	20.03	production well	Low	Waimea	7.85	23	153.4	0.06	91	7.84	-3.50	-11.90	0.00
Lalamilo C Deepwell	8-5946-003	-155.78	19.99	production well	Low	Waimea	7.855	26.15	567.85	0.26	97	8.38	-5.43	-28.95	0.00
Lalamilo A Deepwell	8-5946-001	-155.77	19.99	production well	Low	Waimea	7.9	26.1	460	0.2	82.3	5.7	-5.42	-28.81	0.00
Lalamilo B Deepwell	8-5946-002	-155.77	19.98	production well	Low	Waimea	7.83	26.2	496	0.23	79.3	6.08	-5.62	-30.03	0.00
Parker #2 Deepwell	8-5846-002	-155.77	19.98	production well	Low	Waimea	7.89	26.7	2	0.34	90.4	4.58	-5.73	-31.09	0.01
Parker #3 Deepwell	8-5846-003	-155.77	19.97	production well	Low	Waimea	7.815	26.65	433.2	0.2	96.8	6.62	-5.66	-30.93	0.00
Parker #4 Deepwell	8-5746-001	-155.77	19.96	production well	Low	Waimea	7.91	27.1	738	0.35	84.8	5.32	-5.84	-32.12	0.01
Waikoloa 1	8-5745-001	-155.76	19.95	production well	Low	Waimea	8.015	26.5	312.25	0.14	96.2	6.45	-5.66	-30.59	0.00
DW-7	8-5745-004	-155.76	19.95	production well	Low	Waimea	7.99	26.5	287.7	0.12	80.5	5.19	-5.71	-31.44	0.00

Parker 5	8-5745-001	-155.76	19.95	production well	Low	Waimea	8.19	26.5	303.8	0.128	75.3	5.87	-5.71	-30.94	0.00
Parker 4	8-5745-002	-155.76	19.95	production well	Low	Waimea	7.97	26.7	350.1	0.15	87.6	5.23	-5.81	-31.65	0.00
Waikoloa 3	8-5546-002	-155.77	19.93	production well	Low	Waimea	7.87	28.2	512	0.233	72.4	5.5	-6.92	-42.24	0.00
Waikoloa 2	8-5546-001	-155.77	19.93	production well	Low	Waimea	7.93	28.6	660	0.3	78.5	4.73	-7.14	-43.66	0.01
Waikoloa DW-6	8-5545-001	-155.76	19.92	production well	Low	Waimea	7.97	28.5	726	0.33	77.2	4.89	-7.65	-48.52	0.01
Resort Irr 2	8-5552-001	-155.84	19.92	irrigation well	Low	Anaehoomalu	7.94	24.7	2522	1.28	90.5	7.38	-9.23	-63.28	0.03
Waikoloa Irr 3	8-5551-001	-155.86	19.92	irrigation well	Low	Anaehoomalu	8.03	24.1	2184	1.091	96.5	6.46	-9.17	-62.99	0.03
Resort 1	8-5452-003	-155.87	19.91	irrigation well	Low	Anaehoomalu	8.04	23.9	2920.5	1.505	96.65	7.12	-9.20	-63.30	0.04
Nursery	8-5452-001	-155.88	19.91	irrigation well	Low	Anaehoomalu	7.905	23.5	3794.5	1.995	99.05	7.01	-9.08	-62.53	0.05
Fifty-One FT STP	8-5452-002	-155.88	19.91	irrigation well	Low	Anaehoomalu	7.875	24.15	3420.5	1.778	76.55	5.93	-9.23	-62.85	0.06
West Hawaii Landfill	8-5352-001	-155.88	19.89	irrigation well	Low	Kiholo	8.02	22.4	4161	2.21	105.7	8.78	-8.34	-56.07	0.05
Back spring		-155.92	19.86	pond	Low	Kiholo	7.68	20.8	5211	2.815	104.05	9.8	-7.51	-49.16	0.07
Mouth ocean		-155.92	19.86	pond	Low	Kiholo	7.915	24.2	29469.5	18.275	119.65	8.65	-7.49	-49.42	0.47
Inside mouth channel		-155.92	19.85	pond	Low	Kiholo	7.67	22.4	8341.5	4.655	102.9	9.4	-7.52	-48.52	0.10

Big Bridge		-155.92	19.85	pond	Low	Kiholo	7.515	21.85	6840	3.77	92.7	8.65	-7.37	-48.40	0.09
Kitchen corner inlet		-155.92	19.85	pond	Low	Kiholo	7.43	21.6	7512.5	4.18	93.35	8.58	-7.30	-47.82	0.08
Makani Golf Course	8-4950-001	-155.84	19.82	production well	Low	Kiholo	8.01	22.85	556	0.27	110.8	9.35	-8.18	-53.93	0.00
Puu Lani	8-4850-001	-155.83	19.81	production well	High	Kiholo	8.145	23.55	420.9	0.195	94.2	7.14	-7.92	-51.25	0.00
Kekaha Kai - Kua Bay		-156.01	19.81	pond	Low	Kiholo	8.04	24.7	14615	8.49	121.8	6.23	-5.29	-28.07	0.19
Kekaha Kai - Kaelehuluhulu		-156.04	19.78	pond	Low	Keauhou	7.73	25.7	25651	15.63	98.3	7.13	-4.99	-27.82	0.40
Kekaha Kai - Small Pool		-156.04	19.78	pond	Low	Keauhou	7.5	29.3	21222	12.52	106.4	7.62	-5.20	-28.21	0.31
Puu Waawaa	8-4650-001	-155.84	19.78	production well	High	Kiholo	8.15	23.65	280.45	0.125	90.85	6.9	-8.01	-52.35	0.00
Huehue Ranch 5	8-4558-002	-155.98	19.76	production well	Low	Kiholo	7.11	23.7	1803	0.886	67.3	4.33	-5.02	-25.08	0.00
Huehue Ranch 3	8-4558-001	-155.98	19.76	production well	Low	Kiholo	7.08	20.3	1536	0.744	37	3.89	-4.94	-24.30	0.01
NELHA Well #12B	8-4463-007	-156.05	19.75	monitoring well	Low	Keauhou	8.01	23.09	16724	9.99	92.2	6.88	-5.71	-32.08	0.28
NELHA Well #12A	8-4463-006	-156.05	19.75	monitoring well	Low	Keauhou	7.84	22.13	34761	22.14	36.6	2.65	-6.69	-40.47	0.64
NELHA Well #12	8-4463-005	-156.05	19.75	monitoring well	Low	Keauhou	7.8	21.795	41867	27.51	24.35	0	-7.18	-46.00	0.79
Huehue Ranch 4	8-4459-002	-155.98	19.75	production well	Low	Keauhou	6.63	23.7	1422	0.68	58.7	5.73	-5.24	-28.21	0.01

Huehue Ranch 2	8-4459-001	-155.98	19.74	production well	Low	Keauhou	6.94	21.9	1335	0.64	60.6	4.5	-4.85	-25.04	0.01
Kau (Makalei) Deepwell	8-4458-002	-155.98	19.73	production well	Low	Keauhou	7.305	24.3	1389	0.68	100.1	7.19	-5.11	-26.11	0.01
NELHA A1		-156.06	19.73	pond	Low	Keauhou	7.99	24.05	24473	14.99	106.3	9.27	-6.18	-35.59	0.41
NELHA Well #3B	8-4363-023	-156.05	19.73	monitoring well	Low	Keauhou	7.93	23.7	46441	8.43	0	5.88	-5.87	-33.91	0.22
NELHA Well #3A	8-4363-022	-156.05	19.73	monitoring well	Low	Keauhou	7.96	23.54	13983	8.22	0	6.35	-5.95	-34.36	0.23
NELHA Well #3	8-4363-021	-156.05	19.73	monitoring well	Low	Keauhou	7.77	20.9	41362	26.14	0	2.94	-7.36	-45.06	0.76
Kalaoa Deepwell	8-4358-001	-155.98	19.72	production well	High	Keauhou	7.78	23.3	304	0.121	84.7	7.59	-6.65	-40.16	0.00
NELHA A2		-156.05	19.72	pond	Low	Keauhou	7.775	23.04	19629.5	11.775	113.2	5.33	-5.99	-35.08	0.31
NELHA Well #1	8-2979-011	-156.03	19.72	monitoring well	Low	Keauhou	7.76	20.8	18815	11.33	91.65	4.83	-6.24	-36.87	0.32
NELHA Well #9B	8-4262-006	-156.04	19.71	monitoring well	Low	Keauhou	7.76	19.21	23788	15.06	116.1	5.99	-6.23	-36.02	0.43
NELHA Well #9A	8-4262-005	-156.04	19.71	monitoring well	Low	Keauhou	7.71	17.56	32393	20.36	127.4	6.09	-6.81	-40.53	0.59
NELHA Well #9	8-4262-004	-156.04	19.71	monitoring well	Low	Keauhou	7.76	16.47	36316	22.95	129.3	6.48	-7.08	-42.92	0.67
NELHA A3		-156.05	19.71	pond	Low	Keauhou	7.785	21.6	23994	14.69	111.1	5.6	-5.85	-33.19	0.38
Kohanaiki #1	8-4262-001	-156.04	19.70	irrigation well	Low	Keauhou	7.93	19.9	16252	9.68	79.5	6.7	-6.52	-38.74	0.28

Kohanaiki #2	8-4262-002	-156.03	19.70	irrigation well	Low	Keauhou	7.835	21.05	15408	9.135	99.7	10.18	-5.77	-32.41	0.27
Kohanaiki #3	8-4161-004	-156.03	19.70	irrigation well	Low	Keauhou	7.95	20.7	14961	8.85	98.2	8.43	-6.56	-39.28	0.27
Kohanaiki #4	8-4161-005	-156.03	19.70	irrigation well	Low	Keauhou	7.87	20.7	14385	8.25	104.4	8.71	-6.30	-37.37	0.23
Kohanaiki #5	8-4161-006	-156.03	19.70	irrigation well	Low	Keauhou	7.92	19.8	14591	8.61	91.6	6.95	-6.18	-37.81	0.21
Kohanaiki #6	8-4161-007	-156.03	19.70	irrigation well	Low	Keauhou	7.745	19.5	14772.5	8.315	114.25	9.3	-6.46	-38.82	0.27
Kohanaiki #7	8-4161-008	-156.03	19.70	irrigation well	Low	Keauhou	7.815	21	15522	8.45	100.55	10.23	-5.64	-31.43	0.24
Kohanaiki A2				pond	Low	Keauhou	7.46	24.1	21682	11.54	126	13.44	-5.35	-30.37	0.34
Kohanaiki A30				pond	Low	Keauhou	7.72	25.2	20880	12.72	101.4	7.2	-5.62	-32.02	0.33
Kohanaiki A43				pond	Low	Keauhou	8.055	23.85	21527	13.15	101.35	7.6	-6.39	-38.03	0.37
Kohanaiki A5				pond	Low	Keauhou	8.05	24.6	20664	12.58	116	8.99	-6.17	-36.56	0.37
Kohanaiki A69				pond	Low	Keauhou	7.59	25.1	23339	14.23	92.5	9.14	-5.16	-31.19	0.41
Kohanaiki A172				pond	Low	Keauhou	8.23	28.2	22907	13.62	119.2	18.05	-5.24	-31.62	0.39
Kohanaiki A121				pond	Low	Keauhou	7.98	26.75	22360	11.255	123.1	11.68	-0.23	-1.97	0.43
Kohanaiki A139				pond	Low	Keauhou	8.21	27.35	27118	16.905	162.7	14.35	-6.07	-36.41	0.48
Kohanaiki A48				pond	Low	Keauhou	7.74	24.5	18130	7.74	64	4.98	-4.13	-20.90	0.19
Kohanaiki A46				pond	Low	Keauhou	7.11	22.85	16091	9.585	66.8	6.68	-4.50	-24.28	0.25
Kohanaiki A77				pond	Low	Keauhou	7.85	22.9	22503	13.8	113.1	8.65	-6.12	-36.23	0.39

Kohanaiki A120				pond	Low	Keauhou	8.2	24.2	24153	14.9	158.9	12.16	-6.03	-35.88	0.43
Palani Ranch Deepwell	8-4158-003	-155.97	19.69	production well	High	Keauhou	7.975	22	228.1	0.0925	89.95	7.22	-6.95	-42.91	0.00
Honokohau Deepwell	8-4158-002	-155.96	19.68	production well	High	Keauhou	7.825	21.9	233.9	0.12	93.55	7.23	-6.90	-42.30	0.00
Queen Liliuokalani Trust (Keahuolu) Deepwell	8-4057-001	-155.96	19.67	production well	High	Keauhou	7.93	20.9	159.8	0.075	99.5	8.29	-5.50	-29.60	0.00
Keopu Deepwell	8-3957-001	-155.95	19.65	production well	High	Keauhou	7.92	21.3	155.45	0.06	98	7.33	-5.15	-27.00	0.00
QLT A1		-156.02	19.65	pond	Low	Keauhou	7	25.65	22926	13.955	64.1	3.53	-4.31	-20.92	0.38
QLT A32		-156.02	19.65	pond	Low	Keauhou	6.885	24.4	23102	14.2	24.15	1.82	-4.39	-23.05	0.46
QLT A4S		-156.02	19.65	pond	Low	Keauhou	7.055	25.6	26155	16.05	57.25	1.43	-4.29	-21.80	0.41
QLT A36		-156.02	19.65	pond	Low	Keauhou	7.09	27.15	24843.5	15.37	42	2.7	-4.19	-20.97	0.39
QLT A30				pond	Low	Keauhou	7.7	25.4	19166	11.59	86.6	6.61	-4.12	-20.27	0.37
QLT A5		-156.02	19.65	pond	Low	Keauhou	7.765	26.9	30472.5	19.02	68.85	4.32	-4.43	-22.99	0.51
QLT A8		-156.02	19.65	pond	Low	Keauhou	7.225	25.1	24359	14.92	81.5	5.4	-4.36	-21.87	0.41
QLT Maka Eo		-156.01	19.65	pond	Low	Keauhou	7.64	21.45	22039.5	13.395	109.95	6.51	-4.30	-20.91	0.39
Keopu 2	8-3858-002	-155.97	19.64	monitoring well	Low	Keauhou	8.375	21.8	440	0.205	85	7.52	-5.10	-26.65	0.00
Keopu 1	8-3858-001	-155.97	19.64	monitoring well	Low	Keauhou	10.77	21.3	1980	0.98	17.6	1.53	-5.07	-26.39	0.03
Holualoa Deepwell	8-3657-001	-155.95	19.61	production well	Low	Keauhou	7.85	20.55	927.5	0.43	100.65	9.13	-4.15	-19.09	0.01

Kahaluu A Deepwell	8-3557-001	-155.95	19.58	production well	Low	Keauhou	7.92	20.6	613.95	0.274	92.6	6.95	-5.29	-28.56	0.01
Kahaluu C Deepwell	8-3557-003	-155.95	19.58	production well	Low	Keauhou	7.85	20.3	334.5	0.147	100.1	6.97	-5.31	-28.48	0.00
Kahaluu B Deepwell	8-3557-002	-155.95	19.58	production well	Low	Keauhou	7.95	20.3	980	0.456	113.9	8.33	-5.37	-28.69	0.01
Kahaluu D Deepwell	8-3557-004	-155.95	19.58	production well	Low	Keauhou	7.52	20.2	940	0.436	98.5	6.79	-5.27	-28.37	0.01
Kahaluu Shaft	8-3557-005	-155.95	19.58	production well	Low	Keauhou	7.82	20.3	1499	0.72	91.3	7.71	-5.21	-27.90	0.02
Kahaluu DW1 (96m)	8-3457-004	-155.96	19.58	monitoring well	Low	Keauhou	8.49	21.7	3110	1.6	16.7	1.45	-5.31	-28.00	0.25
Kahaluu DW1 (115m)	8-3457-004	-155.96	19.58	monitoring well	Low	Keauhou	8.27	22.3	38350	24.64	21.6	1.55	-5.39	-28.96	0.65
Kahaluu DW	8-3457-004	-155.96	19.58	monitoring well	Low	Keauhou	8.8	23.9	4560	2.43	0	0	-5.25	-28.06	0.04
Halekii Deepwell	8-3155-002	-155.92	19.52	production well	High	Kealakekua	7.82	21.4	138.5	0.054	104.5	6.37	-5.90	-32.60	0.00
Keei D Deepwell	8-2753-003	-155.88	19.46	production well	High	Kealakekua	7.79	18.7	132.7	0.054	115.2	8.78	-5.30	-27.90	0.00
Keei A Deepwell	8-2753-001	-155.89	19.46	production well	Low	Kealakekua	7.68	19.6	1638	0.83	100.4	6.66	-4.60	-21.90	0.02
Keei B Deepwell	8-2753-002	-155.89	19.45	production well	Low	Kealakekua	7.425	19.15	1138.5	0.535	94.6	7.12	-4.66	-23.02	0.01

Table 4.2. Averaged salinity-corrected dissolved ion and nutrient data. Dissolved common ions fluoride (F^-), chloride (Cl^-), sulfate (SO_4^{2-}), lithium (Li^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}) are reported as averaged salinity-corrected data in µM. Nutrients nitrate + nitrite ($NO_3^- + NO_2^-$), ammonia + ammonium ($NH_3 + NH_4^+$), total phosphorus (TP), total nitrogen (TN), alkalinity, and bicarbonate (HCO_3^-) are reported as averages in µM. Relative standard deviations are reported for the geochemical parameters in Appendix B.

Well Name	Fluoride (µM)	Chloride (µM)	Sulfate (µM)	Lithium (µM)	Sodium (µM)	Potassium (µM)	Magnesium (µM)	Calcium (µM)	Silica (µM)	Phosphate (µM)	$NO_3^- + NO_2^-$ (µM)	$NH_3 + NH_4^+$ (µM)	Total Phosphorus (µM)	Total Nitrogen (µM)	Alkalinity (mg/L)	HCO_3^- (mg/L)
Parker Ranch Deepwell	4.74	225.67	70.55		374.54	66.06	288.61	269.65	853.87	3.37	20.28	0.46	4.02	78.18	63.98	78.06
Lalamilo C Deepwell	12.69	2696.76	360.36		503.36	112.12	501.99	340.17	956.39	2.97	89.49	0.18	2.54	126.16	79.82	97.38
Lalamilo A Deepwell	13.74	2059.24	353.35		589.97	98.10	519.52	333.39	930.96	2.82	90.73	0.17	2.94	138.68	81.87	99.88
Lalamilo B Deepwell	13.21	2169.25	383.16		514.74	101.78	540.69	341.90	959.92	2.67	92.31	0.09	2.91	134.92	81.87	99.88
Parker #2 Deepwell	14.82	3159.38	382.16		597.44	106.16	576.47	374.45	977.66	2.65	91.93	0.16	2.55	137.49	83.81	102.25
Parker #3 Deepwell	13.72	1392.10	395.38		667.58	102.07	512.49	306.78	969.13	2.77	94.12	0.10	2.72	136.82	82.92	101.16
Parker #4 Deepwell	14.83	3509.17	449.89		585.72	109.93	536.80	352.08	959.35	2.61	95.62	0.19	2.68	133.00	83.79	102.23
Waikoloa 1	16.60	785.61	398.52		754.81	89.45	506.09	267.28	959.63	2.58	91.63	0.22	2.71	121.01	84.46	103.04
DW-7	17.39	744.71	404.88		832.16	90.06	517.13	249.99	968.13	2.78	90.68	0.17	3.00	133.58	83.96	102.43
Parker 5	17.39	789.84	404.11		836.02	89.25	443.79	236.87	877.11	2.61	92.47	0.21	2.44	136.62	81.95	99.98
Parker 4	14.23	846.26	422.51		821.23	93.37	503.00	260.82	987.22	2.58	98.35	0.16	2.60	145.42	83.95	102.42
Waikoloa 3	17.43	1918.19	683.14		1223.79	122.81	576.37	292.75	1022.93	2.63	95.29	0.06	2.77	145.21	102.96	125.61
Waikoloa 2	19.06	3272.21	704.41		1056.31	123.81	747.54	370.86	995.00	2.79	89.11	0.25	2.65	132.35	102.92	125.56
Waikoloa DW-6	18.54	3616.36	744.96		1207.40	144.68	710.71	336.52	1016.52	2.31	77.56	0.19	2.35	116.72	110.96	135.37
Resort Irr 2	28.35	19153.74	1194.77	0.77	621.43	122.74	399.66	457.85	869.06	1.90	38.21	1.17	2.45	78.90	62.10	75.77
Waikoloa Irr 3	34.69	16033.85	1202.97	0.88	874.42	124.56	550.42	321.27	881.75	2.01	46.78	0.20	2.03	91.53	64.48	78.67

Resort 1	34.44	20619.18	1111.14	0.72	1248.77	134.46	584.45	314.25	904.48	1.94	48.30	0.03	2.01	98.96	64.03	78.11
Nursery	35.50	28241.18	1145.72	0.43	1524.77	150.56	668.13	328.86	914.06	2.64	56.05	0.13	2.31	105.35	65.36	79.74
Fifty-One FT STP	41.81	30803.95	1231.49	0.33	946.98	160.67	49.93	547.99	864.30	2.82	50.93	0.29	5.97	101.53	65.64	80.08
West Hawaii Landfill	44.35	27957.69	1222.91	0.44	1527.90	205.69	766.34	372.37	858.08	2.44	72.50	0.10	2.26	127.69	71.71	87.49
Back spring	51.56	36320.17	771.38	0.12	2143.47	166.66	687.01	382.23	824.89	2.36	71.90		2.32	171.41	69.36	84.62
Mouth ocean	112.19	257007.05	2303.51	1.23	2016.57	0.00	639.91	0.00	849.75	2.82	65.42	1.05	3.72	273.45	76.62	93.48
Inside mouth channel	55.28	57801.13	883.95	0.85	3562.96	173.35	957.56	414.61	817.72	2.45	68.08	1.13	2.45	177.20	76.22	92.99
Big Bridge	50.75	48095.91	887.80	0.44	2284.10	151.69	787.02	408.03	807.55	2.38	70.05	0.27	2.30	177.45	73.17	89.27
Kitchen corner inlet	55.99	43375.18	1032.61	0.62	1699.23	140.50	724.89	392.33	866.54	2.66	75.56	0.42	2.29	173.83	76.84	93.74
Makani Golf Course	34.32	1850.49	1633.06	1.09	1343.82	77.63	390.32	491.52	736.70	1.51	63.70		1.68	157.31	76.87	93.79
Puu Lani	42.72	1156.56	1362.63	1.41	1420.13	80.18	309.57	419.84	729.10	2.24	87.57	0.18	1.99	125.20	78.93	96.29
Kekaha Kai - Kua Bay	69.27	107562.76	8595.37	5.86	9060.25	449.22	9150.26	277.67	1111.12	2.25	142.07	0.56	2.00	182.52	465.87	568.37
Kekaha Kai - Kaelehuluhulu		217689.70	1182.64	0.00	0.00	259.36	2290.32	1279.14	1185.97	5.43	55.07	2.72	4.76	143.62	141.80	173.00
Kekaha Kai - Small Pool	47.97	170186.18	1422.02	0.00	5762.50	311.20	1406.07	742.23	1114.74	4.87	35.40	3.54	3.99	148.46	132.91	162.15
Puu Waawaa	33.72	592.38	718.84	1.42	1084.10	66.20	264.39	278.15	757.78	1.09	36.68	0.19	1.75	76.56	68.46	83.52
Huehue Ranch 5	81.30	2383.64	9584.72	7.17	5802.72	212.22	5518.87	1185.71	1153.06	7.31	77.66	0.15	7.35	119.56	487.08	594.24
Huehue Ranch 3	72.12	4823.70	6968.51	2.75	709.31	158.56	5845.98	1042.71	1080.61	11.61	67.11	0.24	9.01	100.84	366.84	447.54
NELHA Well #12B	53.73	156699.58	0.00		2507.93	137.20	0.00	97.58	1055.67	5.22	81.16	0.21	4.44	145.58	89.04	108.62

NELHA Well #12A		353201.69	1084.84	0.00	0.00	0.00	4.01	0.00	1553.15	6.90	83.93	0.33	4.76	229.69	63.86	77.90
NELHA Well #12		432045.13	3911.49	0.00	0.00	140.83	0.00	0.00	1668.91	9.77	81.53	0.26	5.22	334.96	51.58	62.93
Huehue Ranch 4	37.63	4552.89	2670.34	2.76	1601.81	251.73	4560.40	996.86	1577.13	10.70	46.53		9.09	101.71	456.33	556.72
Huehue Ranch 2	38.24	5641.75	1405.71	1.27	685.29	195.53	3564.11	1087.34	1153.43	9.05	55.21	0.21	9.03	102.65	360.15	439.39
Kau (Makalei) Deepwell	40.18	6736.25	1098.46	1.24	402.09	238.42	2441.72	983.26	1219.01	6.86	45.31	0.18	6.52	81.31	246.40	300.61
NELHA A1		223102.96	879.37	0.00	49236.47	89.72	0.00	565.03	902.77	5.94	185.77	1.04	5.29	309.69	101.86	124.27
NELHA Well #3B		122313.12	392.64	0.00	0.00	0.00	131.35	548.90	899.48	4.09	133.25	0.15	3.46	189.72	75.86	92.55
NELHA Well #3A	33.56	127418.90	155.74	0.00	3129.08	48.31	0.00	350.11	902.21	4.16	139.04	0.17	3.40	183.96	75.36	91.94
NELHA Well #3		420507.76	4815.22	0.00	0.00	0.00	0.00	0.00	1631.95	5.03	115.78	0.73	4.60	365.17	38.28	46.70
Kalaoa Deepwell	21.85	276.45	873.14		1272.79	132.86	456.15	307.28	870.39	4.04	68.67	0.28	4.09	116.25	93.00	113.45
NELHA A2	56.35	169844.85	0.00	0.00	17833.77	21.51	276.83	244.04	870.73	4.59	225.31	0.12	4.18	273.73	70.71	86.26
NELHA Well #1		175909.73	1391.65	0.00	785.50	11.71	2159.98	780.72	943.26	4.31	122.90	0.05	3.74	186.93	71.43	87.14
NELHA Well #9B		238118.48	1524.14	0.00	6066.50	0.00	1882.97	943.51	955.71	4.69	179.35	0.17	3.95	257.46	72.91	88.95
NELHA Well #9A		325444.29	975.05	0.00	0.00	0.00	0.00	0.00	1033.45	6.28	179.84	0.21	5.22	320.99	75.34	91.91

NELHA Well #9	132.76	371001.41	1472.67	2.45	0.00	0.00	0.00	223.31	1138.19	8.00	217.35	0.33	5.26	386.86	70.86	86.45
NELHA A3		210409.03	640.90	0.00	14845.55	0.00	1430.37	0.00	921.95	4.52	177.69	0.57	4.23	254.95	68.41	83.46
Kohanaiki #1	53.48	154894.22	0.00	0.00	25189.21	39.42	0.00	0.00								
Kohanaiki #2	28.30	151057.83	24.88	0.00	9485.76	0.00	0.00	568.57	794.62	4.84	104.42	0.54	4.08	140.20	61.86	75.47
Kohanaiki #3	98.29	149478.14	0.00		23988.52	32.33	0.00	0.00								
Kohanaiki #4	31.32	124851.90	576.28	0.00	0.00	0.00	0.00	316.10	828.11	4.00	106.40	0.33	3.55	153.83	69.79	85.15
Kohanaiki #5	35.45	117275.04	131.01	0.03	5696.57	185.04	724.48	307.51	872.54	3.94	122.30	0.91	3.59	226.23	74.43	90.81
Kohanaiki #6	17.60	147066.29	203.50	0.00	150.36	0.00	0.00	356.01	850.49	3.98	112.28	0.12	3.64	194.19	71.96	87.79
Kohanaiki #7	36.45	133067.70	337.99	0.00	1570.15	42.99	323.80	372.85	884.53	4.72	104.95	0.19	4.05	175.06	62.93	76.77
Kohanaiki A2	53.83	189675.60	0.00	0.00	19399.82	0.00	0.00	572.10	765.95	2.55	113.92	7.64	2.17	185.76	66.63	81.29
Kohanaiki A30	44.97	183074.75	0.00	0.00	10091.35	86.90	0.00	100.09	760.54	2.39	80.01	5.92	2.17	168.21	74.28	90.63
Kohanaiki A43	23.90	204795.49	431.42	0.00	13148.55	0.00	0.00	1036.54	788.66	2.89	90.69	3.93	2.33	143.10	70.80	86.37
Kohanaiki A5	54.85	201664.32	0.00		34036.48	0.00	0.00	0.00								

Kohanaiki A69	30.97	222849.08	829.95	0.00	0.00	0.00	0.00	0.00	734.34	1.28	44.26	7.75	1.27	145.20	61.52	75.05
Kohanaiki A172	58.33	212496.47	1862.41	0.00	0.00	0.00	0.00	520.84	724.32	0.64	50.35	4.38	0.76	146.95	68.93	84.09
Kohanaiki A121	44.37	236812.41	320.05		50367.97	0.00	0.00	0.00	808.87	2.37	86.46	5.51	3.14	216.57	44.99	54.89
Kohanaiki A139	85.38	265105.78	863.63	0.00	22320.20	0.00	0.00	1669.40	823.65	0.54	13.81	8.92	0.47	133.96	72.59	88.56
Kohanaiki A48	31.08	103012.69	3.30	0.67	0.00	154.32	0.00	338.71	603.41	1.91	73.64	2.26	2.17	154.79	49.34	60.20
Kohanaiki A46	17.55	137729.20	342.65	0.00	0.00	56.38	2358.33	1497.55	628.51	2.81	79.46	3.56	4.76	151.05	56.31	68.70
Kohanaiki A77		215684.06	35.19	0.00	0.00	0.00	3934.27	2942.53	807.66	1.45	89.58	8.29	1.06	163.24	74.22	90.55
Kohanaiki A120		236925.25	1774.35		0.00	0.00	3132.91	3099.57	803.51	1.32	1129.13	4.40	0.94	1372.46	69.56	84.87
Palani Ranch Deepwell	25.80	239.77	679.78		1089.65	101.03	345.29	284.70	798.32	4.43	70.68	0.33	4.52	102.06	75.99	92.71
Honokohau Deepwell	20.53	220.03	616.39		1072.19	105.60	312.87	251.29	847.64	3.89	80.22	0.05	4.06	228.88	76.00	92.72
Queen Liliuokalani Trust (Keahuolu) Deepwell	12.63	183.36	311.09		712.91	84.13	245.03	252.54	762.98	3.96	86.44	0.34	3.90	123.79	56.00	68.32
Keopu Deepwell	11.84	172.07	310.35		696.72	90.21	254.61	256.94	761.94	3.86	78.47	0.16	3.89	111.10	57.00	69.54
QLT A1	23.40	209806.77	0.00	0.00	135.66	97.39	0.00	163.72	783.84	24.82	173.85	6.85	19.83	445.77	55.57	67.79
QLT A32	44.04	250850.49	0.00	0.30	23730.85	0.00	0.00	157.26	1062.40	37.43	134.45	9.18	26.44	230.08	45.29	55.25

QLT A4S	30.88	226504.94	0.00	0.00	3512.78	132.56	0.00	112.22	778.77	20.47	113.75	10.16	17.20	246.48	48.99	59.77
QLT A36		212870.24	0.00	0.00	4224.44	171.00	647.31	301.31	856.43	20.69	177.10	5.49	17.77	365.66	56.64	69.10
QLT A30	46.50	201354.02	0.00	0.00	36581.24	16.41	0.00	0.00								
QLT A5	29.76	282382.23	0.00	0.00	2694.00	79.20	0.00	0.00	795.41	12.44	37.77	7.60	11.73	182.40	49.16	59.98
QLT A8	51.69	225156.56	0.00	0.00	768.64	43.21	0.00	111.04	838.31	19.53	154.90	8.40	14.97	339.03	44.19	53.92
QLT Maka Eo	25.96	215424.54	0.00	0.00	2240.85	0.00	0.00	0.00	819.06	4.63	261.92	0.80	3.54	350.54	49.60	60.51
Keopu 2	14.74	169.25	282.37		673.42	74.98	259.37	298.91	723.68	4.45	71.31	0.29	12.16	86.59	50.01	61.01
Keopu 1	16.84	17179.13	8.67		0.00	160.47	0.00	2952.77	41.15	0.29	0.69	59.87	8.44	78.32	36.52	44.55
Holualoa Deepwell	8.52	6318.76	191.47		315.93	87.34	265.95	568.20	721.07	3.85	80.27	0.35	3.90	108.64	53.30	65.02
Kahaluu A Deepwell	14.84	3892.81	287.86		362.49	49.83	163.77	486.32	751.52	4.90	339.16	2.05	4.64	278.95	42.00	51.24
Kahaluu C Deepwell	12.14	1590.97	309.19		473.62	53.99	181.45	313.44	776.08	4.52	87.26	0.16	4.34	116.90	41.82	51.02
Kahaluu B Deepwell	12.79	7102.96	272.93		416.80	29.40	165.05	563.85	758.50	4.63	85.10	0.19	4.37	145.94	41.56	50.70
Kahaluu D Deepwell	10.12	6826.52	280.48		480.18	35.45	194.50	538.65	772.12	4.85	82.71	0.21	4.67	116.43	41.09	50.13
Kahaluu Shaft	10.74	10973.20	245.92		0.00	11.74	210.19	864.02	786.66	4.35	89.60	0.20	4.14	135.53	40.51	49.42
Kahaluu DW1 (96m)	21.10	138504.94	0.00	0.00	0.00	0.00	0.00	1808.38	179.80	1.42	4.71	17.61	17.48	131.28	22.12	26.99
Kahaluu DW1 (115m)		356417.49	0.00	0.00	0.00	0.00	3170.82	7542.24	727.31	2.34	15.71	17.70	32.67	258.72	17.48	21.32

Kahaluu DW	7.16	24583.92	0.00		0.00	0.00	21.48	879.29								
Halekii Deepwell	13.16	129.76	461.24		701.88	52.95	147.13	214.24	789.66	4.19	72.69	0.15	4.22	116.72	41.99	51.23
Keei D Deepwell	12.11	112.83	323.49		542.75	45.32	153.26	203.99	763.97	4.61	51.81	0.15	4.39	91.42	38.00	46.36
Keei A Deepwell	11.28	11311.71	319.91		300.10	29.47	385.65	450.58	799.03	4.08	128.32	0.13	4.09	174.47	35.34	43.11
Keei B Deepwell	6.93	6911.14	169.52		431.43	31.76	169.95	318.65	795.84	4.78	81.77	0.06	4.21	123.32	36.51	44.54

Stable isotopic compositions of water are assumed to remain unaffected by the processes of infiltration and flow, and therefore can be used to estimate recharge elevations (e.g., Drever, 1997; Scholl et al., 1996; Fackrell et al., 2020). In a conservative model, the isotopic composition of groundwater can be related to its recharge elevation as fully-integrated recharge along a flow path, which provides a minimum elevation (section 4.2.2.3). To account for the isotopically depleted groundwaters observed in the coastal regions, recharge from the higher-elevation slopes of Hualālai, Mauna Kea, and Mauna Loa are required (Figure 4.3). For example, the coastal ʻAnaehoʻomalu groundwaters are the most isotopically depleted in the study region, with calculated recharge elevations greater than or equal to 3,000 meters amsl. Given that Hualālai's summit elevation is 2,521 meters amsl, this indicates source recharge in the ʻAnaehoʻomalu aquifer from the slopes of Mauna Kea. This dataset cannot rule out the possibility that isotopically-depleted recharge originates from the slopes of Mauna Loa, however we assume Mauna Kea is more likely given its vicinity to the groundwater sites.

The majority of groundwater samples from this study plot between the two local meteoric water lines of Fackrel et al. (2020) and Tachera et al. (2021), with the highest deviation from this trend observed in isotopically depleted samples. As discussed previously, groundwater in West Hawaiʻi represents a cumulative average of isotopically variable precipitation observed in the region, as highlighted by the differing local meteoric water lines established during different time periods (Fackrell et al., 2020; Tachera et al., 2021). The deviation of isotopically depleted samples indicates that higher elevation recharge from Mauna Kea volcano may also experience varying weather and climate conditions, likely due to the inversion layer at approximately 2,000 meters amsl.

Additional isotopically-depleted groundwaters recharged from elevations between 2,000 and 3,000 meters amsl are observed in the Kīholo aquifer near the Hualālai rift zone and the Keauhou aquifer, including samples taken from coastal sites (Figure 4.3). Previous studies found that the isotopic composition of water observed along the coast indicates a connection between the high-level and basal aquifers (Tillman et al., 2014; Kelly and Glenn, 2015; Fackrell et al., 2020). However, more recent research proposes a multi-layer model within which the recharge elevation calculation is dependent on sample depth (Attais et al., 2020; Attias et al., 2021a). The isotopic compositions of groundwaters in the northern section of the Kīholo aquifer indicate that recharge is sourced from elevations between 2,000 meters and 3,000 meters amsl. Specifically, the Puʻu Lani, Puʻu Waʻawaʻa, and Makani Golf Course isotopic values require recharge from elevations higher than the summit of Hualālai volcano, suggesting that recharge from Mauna Kea contributes to groundwater in the northern part of Kīholo aquifer.

4.3.2 Flow and interconnectivity

Geochemical results indicate interconnectivity of groundwater in some locations, and barriers to flow in others. A transitional isotopic gradient is observed in northern West Hawaiʻi aquifers, where samples are isotopically-enriched in the Waimea aquifer and isotopically-depleted in the ʻAnaehoʻomalu coastal aquifer (Figure 4.4). Because lava flows from the Kohala Volcano underlie the Waimea aquifer (Bauer, 2003), Waimea aquifer samples likely receive recharge from the low elevation slopes of Kohala Volcano, which results in isotopically-enriched groundwater. The isotopically-depleted groundwaters in the ʻAnaehoʻomalu aquifer indicate waters are sourced from the upper slopes of Mauna Kea, as the calculated recharge elevations range from 3,000 to 4,000 m amsl.

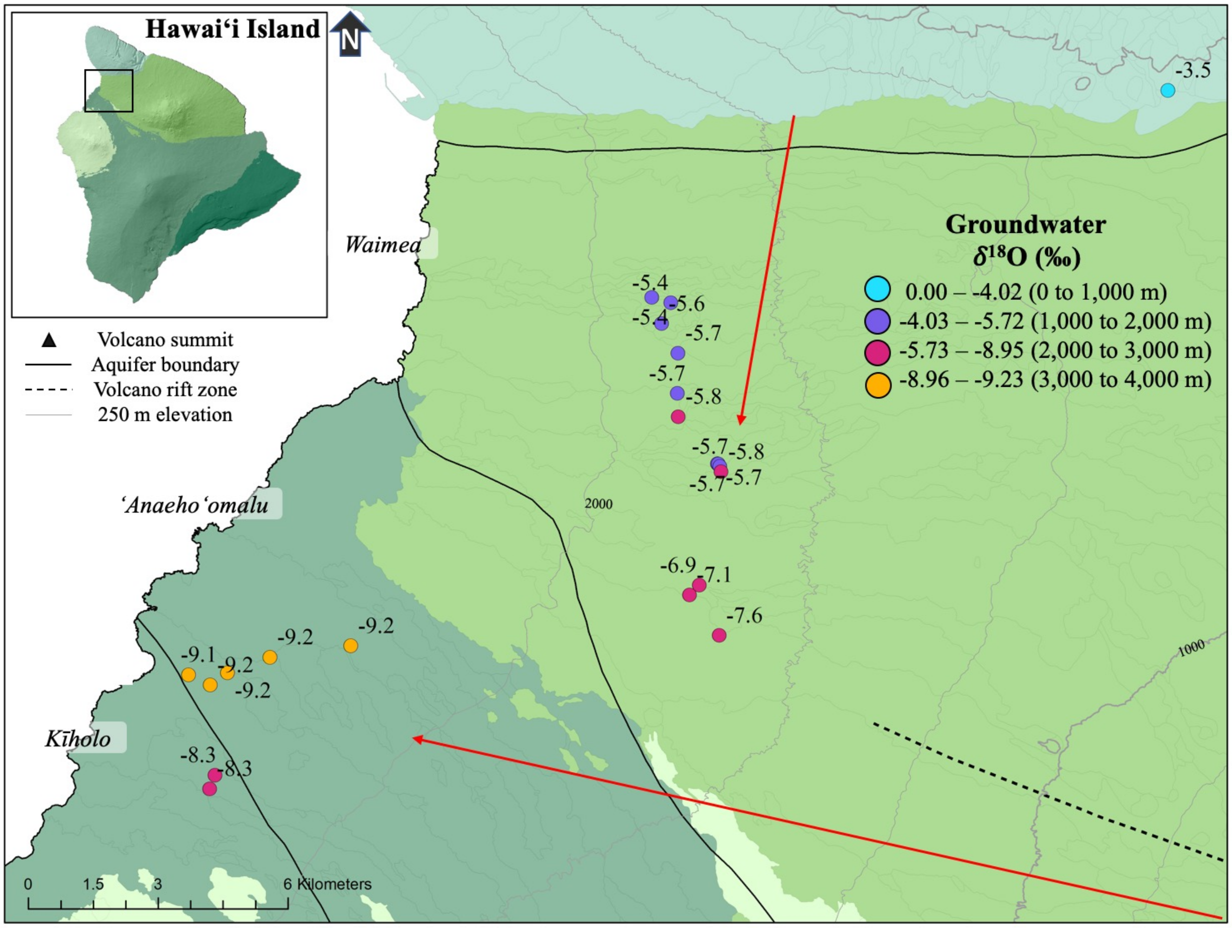

Figure 4.4. Isotopic compositions of groundwater in the northern part of the study region. Groundwater compositions in the northern section of the study region demonstrate a gradient from isotopically enriched in the north to isotopically depleted in the south. Samples are colored based on corresponding isotopic elevation ranges, delineated by recharge elevations calculated by Tachera et al. (2021): blue = 0 ‰ to -4.02 ‰ (0-1,000 m); purple = -4.03 ‰ to -5.72 ‰ (1,000-2,000 m); magenta = -5.73 ‰ to -8.95 ‰ (2,000-3,000 m); orange = -8.96 ‰ to -12.71 ‰ (3,000-4,250 m). Red arrows indicate flow from Kohala and Mauna Kea that allow for mixing in the northern part of the study region.

Either impermeable subsurface geological structure(s) that impede lateral groundwater flow, or very permeable structures that allow very rapid down-gradient flow with little lateral mixing are indicated by significant differences in isotopic compositions over short distances. One example is in the Kīholo aquifer, just north of Hualālai's northwest rift zone (Figure 4.5). A series of groundwater samples in a transect from mauka to makai are isotopically depleted, demonstrating recharge elevations between 2,000 meters to 3,000 meters amsl (i.e., unlikely to be on Hualālai). A parallel transect of samples only 500 m to the south indicates recharge from between 1,000 meters to 2,000 meters amsl (likely on Hualālai; Figure 4.5). Another example is in the Keauhou aquifer where a transect from mauka to makai with isotopically-derived recharge elevation ranges between 2,000 to 3,000 meters amsl lies only 500 m north of a transect of wells with recharge elevations in the 1,000 to 2,000 m amsl range (Figure 4.5). These sharp transitions in isotopic compositions across lines perpendicular to down-gradient flow directions between neighboring wells may indicate isolated flow.

Permeable structures with sharp boundaries, such as lava tubes may explain these isolated chemically distinct waters. Recent geophysical research suggests that the subsurface geology in the Hualālai aquifer consists of abundant permeable features, such as lava tubes, particularly along the coast (Attias et al., 2020; Attias et al., 2021a; Attias et al., 2021b). These high permeability subsurface structures are important transport mechanisms for freshwater resources to the coast (i.e., Prouty et al., 2017).

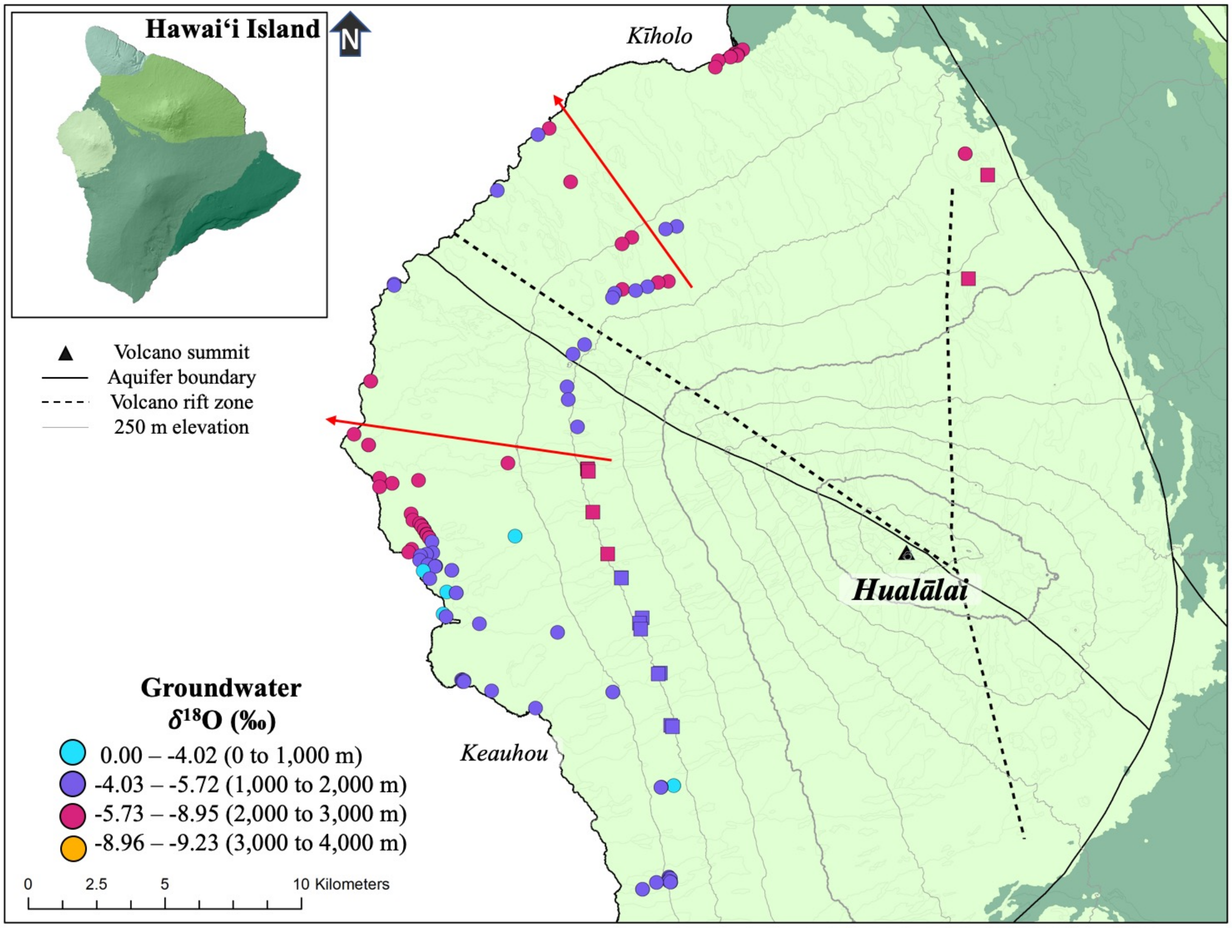

Figure 4.5. Isotopic compositions of groundwater in Hualālai aquifer sector. Salinity-corrected basal groundwater sites are presented as circles, high-level groundwater sites as squares, for the current research as well as previous studies (Tillman et al., 2014; Kelly and Glenn, 2015; Fackrell et al., 2020). δ^{18}O values of water are colored according to the recharge elevation ranges as calculated by Tachera et al. (2021): blue = 0 ‰ to -4.02 ‰ (0-1,000 m); purple = -4.03 ‰ to -5.72 ‰ (1,000-2,000 m); magenta = -5.73 ‰ to -8.95 ‰ (2,000-3,000 m); orange = -8.96 ‰ to -12.71 ‰ (3,000-4,250 m). Red arrows indicate isolated mauka to makai flow, as demonstrated by the sharp boundaries of groundwater samples.

Dissolved salinity-corrected ions, such as sulfate (SO_4^{2-}), potassium (K^+), bicarbonate (HCO_3^-), and silica (SiO_2), are in higher abundances along the Hualālai rift zone (Tachera et al., in prep). Given that bicarbonate (Figure 4.6A) and silica (Figure 4.6B) are derived from the dissolution of basalt rocks (e.g., Thomas, 1985), the higher abundances in these specific locales may indicate thermal influences causing an increase in dissolution of basalt. It may also indicate longer residence time in the subsurface from source of recharge to the point of discharge due to the low permeability of the dike complex.

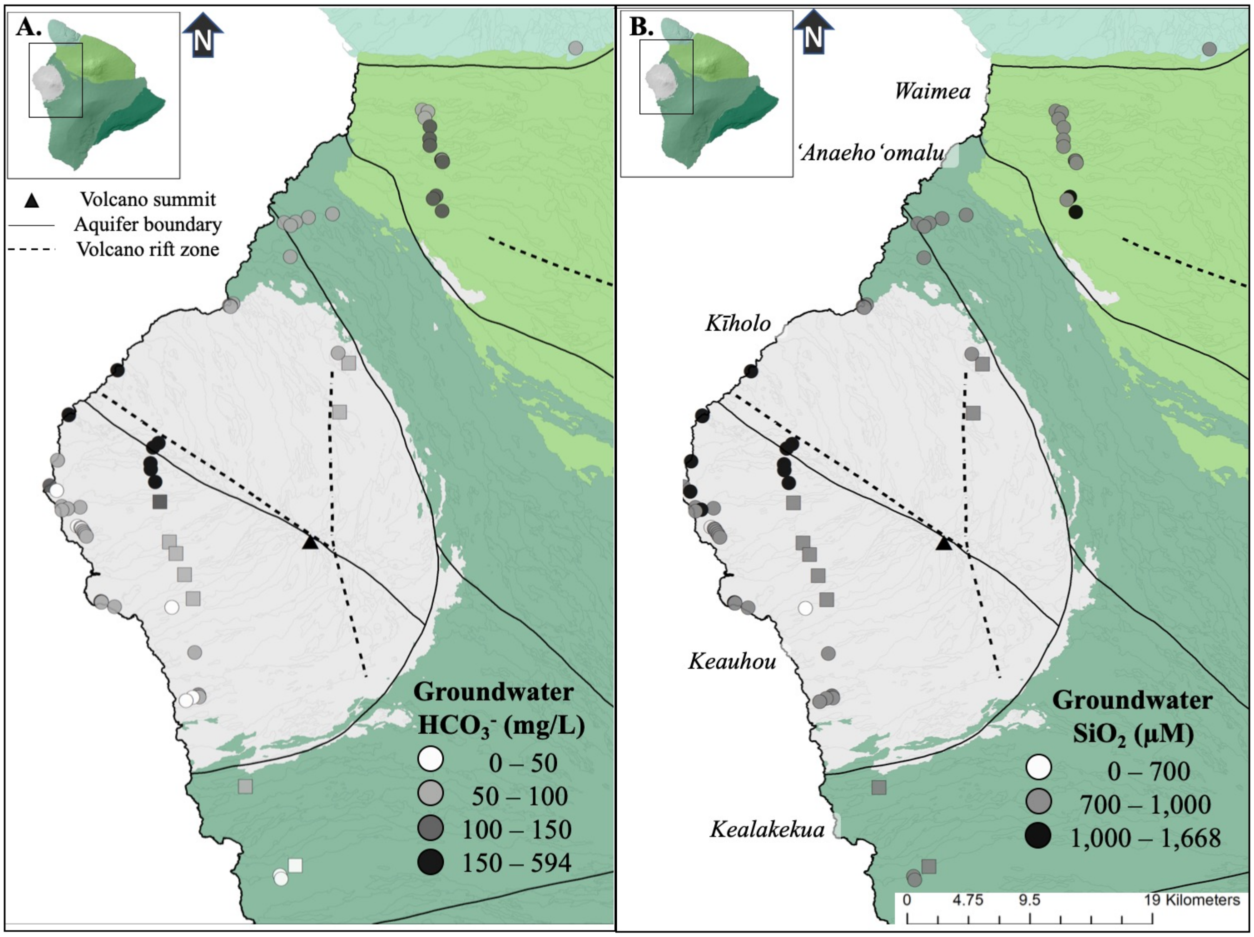

Figure 4.6. Salinity-corrected bicarbonate (HCO_3^-) concentrations (mg/L) and silica (SiO_2) concentrations (µM). A.: Dissolved salinity-corrected bicarbonate concentration values range from 0 mg/L to 594 mg/L. Dissolved bicarbonate is higher along the Hualālai rift zone and in the Waimea aquifer. **B.**: Dissolved salinity-corrected silica concentration values range from 0 µM to 1,668 µM. Dissolved silica is higher along the Hualālai rift zone and in the Waimea aquifer.

Magnesium (Mg^{2+}, Figure 4.7A) and sodium + potassium (Na^{+} + K^{+}, Figure 4.7B) are common ions found in basaltic rocks (e.g. Macdonald et al., 1983; Drever, 1997). Tachera et al. (in prep) described these dissolved concentrations using Hydrochemical Facies and Piper diagrams, which demonstrated higher abundances of magnesium in rift zone samples but higher abundances of sodium + potassium in the remainder of the study region (Figure 3.3 and 3.4). Note that although higher abundances of sodium are located along the coast, this does not reflect seawater intrusion because these are salinity-corrected samples. The elevated sodium concentrations may be attributed to leakage from on-site sewage disposals in the heavily urbanized region of Kailua-Kona, as sodium salts are frequently used in household products such as laundry detergents (Patterson et al., 1997).

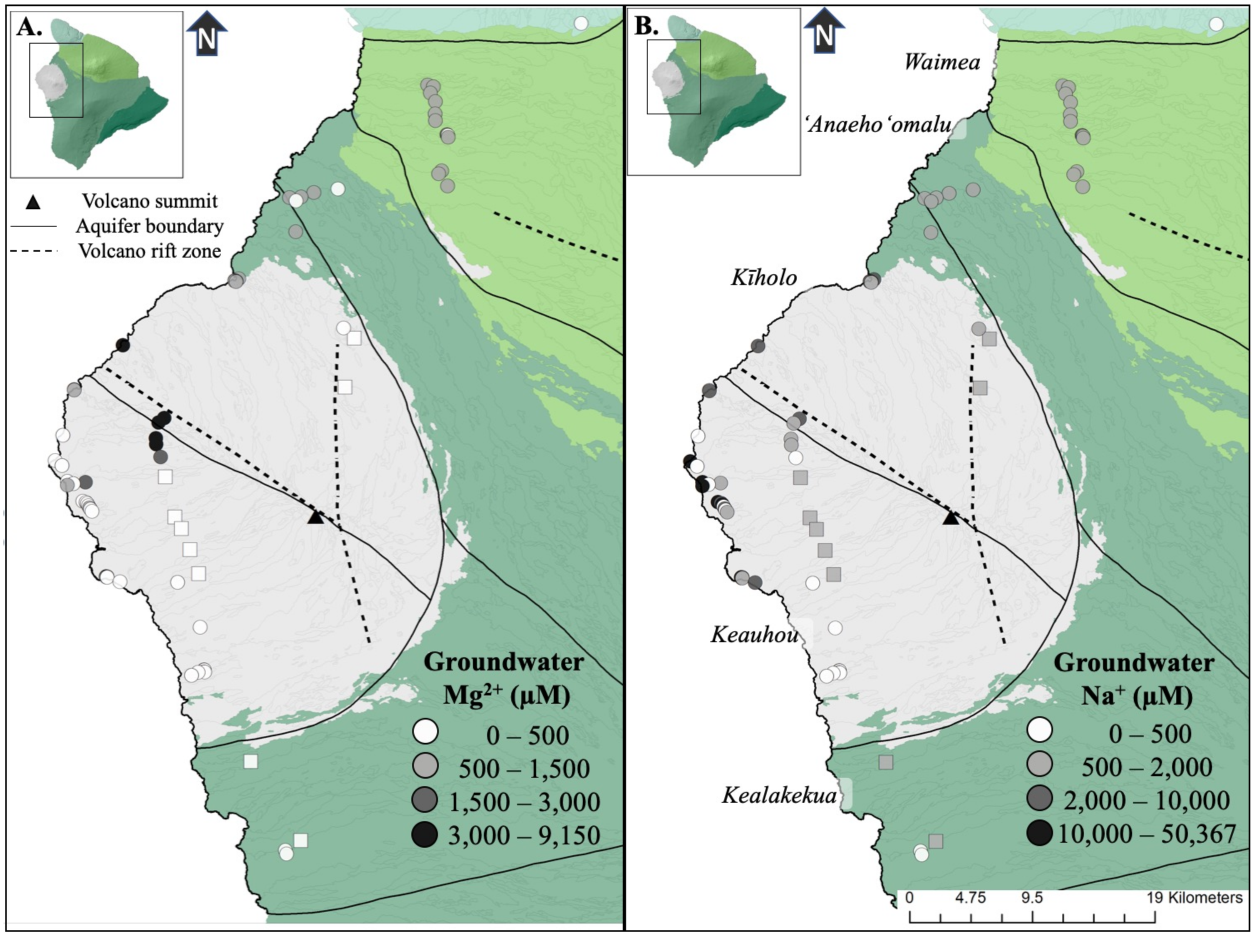

Figure 4.7. Salinity-corrected magnesium (Mg^{2+}) and sodium (Na^{+}) concentrations (µM). **A.**: Dissolved salinity-corrected magnesium concentration values range from 0 µM to 9,150 µM. Dissolved magnesium is observed in higher abundances along the Hualālai rift zone. **B.**: Dissolved salinity-corrected sodium concentration values range from 0 µM to 50,367 µM. Dissolved sodium is observed in higher abundances along the coast.

Dissolved salinity-corrected nitrate + nitrite (NO_3^- + NO_2^-) concentrations show a different spatial pattern, however, namely no distinct variations with the above defined geologic features but rather with anthropogenic effects, as those are observed in higher abundances along coastal sites, in both groundwater wells and coastal ponds (Figure 4.8). Excessive inputs of nitrate + nitrite and other nutrients to coastal ecosystems are of concern because they can be detrimental to ecosystem health (e.g., Amato et al., 2020). The majority of high concentration sites observed in this study are downgradient of increased development with multiple on-site sewage disposal systems (OSDS), specifically in the Keauhou aquifer (Whittier and El-Kadi, 2014). Other high concentrations of dissolved nitrate + nitrite are observed downgradient of the Kealakehe Wastewater Treatment Plant (Figure 4.8). Similar to dissolved sodium concentrations, these higher abundances of nitrate + nitrite are likely due to anthropogenic inputs, typically wastewater leakages from OSDS, which accumulate along groundwater flow paths (Okuhata et al., 2021).

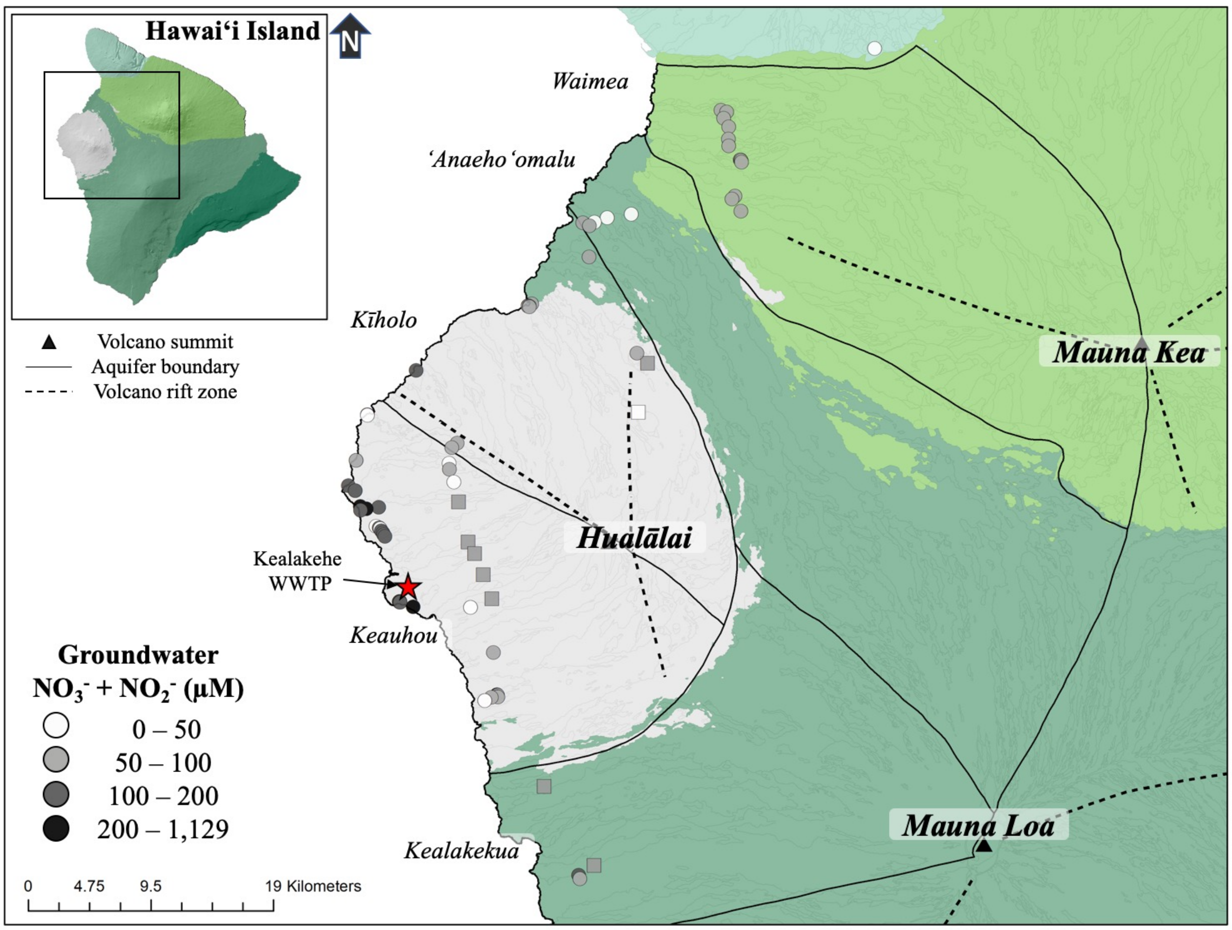

Figure 4.8. Salinity-corrected nitrate + nitrite (NO_3^- + NO_2^-) concentrations (µM). Red star depicts the location of the Kealakehe Wastewater Treatment Plant (WWTP). Dissolved salinity-corrected nitrate + nitrite concentration values range from 0 µM to 1,129 µM. Dissolved nitrate + nitrite is observed in higher abundances along the coast.

4.3.3 Implications for water resource management

As with previous work, the results from this study indicate that the hydrogeology of West Hawaiʻi is complex. A few conclusions have implications for sustainable yield and management strategies. In the northern section of the study region, the isotopic compositions of the groundwater suggest that recharge from the slopes of Kohala and Mauna Kea volcanoes travel to the coastal regions and mix in the Waimea, ʻAnaehoʻomalu, and Kīholo aquifers (Figure 4.9). In this scenario, groundwater passes through three different managed aquifer systems (Waimea, ʻAnaehoʻomalu, Kīholo). However, in the calculation of sustainable yield these aquifers are treated independently.

The complexities of the interconnectivity of the basal and high-level aquifers adds additional error to sustainable yield calculations. In the Kīholo and Keauhou aquifers, stable isotopic compositions of water suggest that isolated groundwater flow paths are likely to connect the high-level and basal aquifers as demonstrated by the isotopically-depleted compositions of both mauka and makai groundwater samples (Figure 4.9). However, using chlorofluorocarbons, previous research estimated the apparent ages of young waters and demonstrated that basal wells located south of the Hualālai rift zone in the Keauhou aquifer are dominated by young recharge (≥ 40%), whereas inland high-level wells contain < 16% young recharge (Kelly and Glenn, 2015). Geophysical research by Attias et al. (2020), however, suggests that vertically-segregated groundwater bodies of ash and soil layers impede percolation of recharge. Therefore, the depth to which a well is drilled determines the freshwater layer encountered and thus the cumulative elevation of recharge. The nuances of how this layered structure affects the observed geochemical evidence presented in this paper are not obvious. Most wells sampled here were from shallow parts of the aquifer and only a few penetrated below any suspected confining layers. Wells that could sample water from confined, deeper structures are scarce and as a result we do not have information on water sources and flow paths for those groundwater samples.

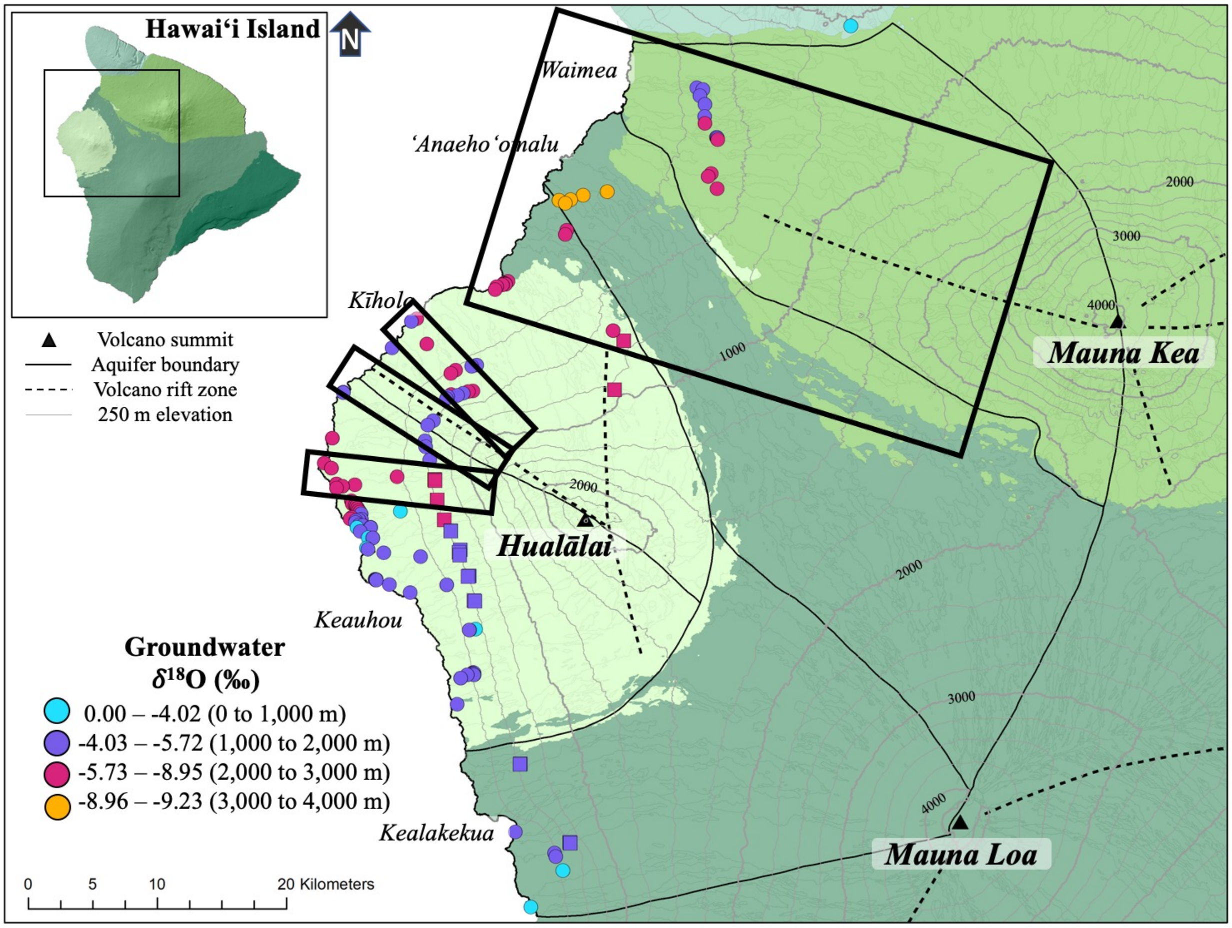

Figure 4.9. Groundwater isotopic composition interpretations for resource management. Samples are colored based on corresponding isotopic elevation ranges, delineated by recharge elevations calculated by Tachera et al. (2021): blue = 0 ‰ to -4.02 ‰ (0-1,000 m); purple = -4.03 ‰ to -5.72 ‰ (1,000-2,000 m); magenta = -5.73 ‰ to -8.95 ‰ (2,000-3,000 m); orange = -8.96 ‰ to -12.71 ‰ (3,000-4,250 m). Black boxes demonstrate groundwater management interpretations of groundwater mixing and isolated mauka-to-makai flow.

4.4 Conclusions and future work

This research collected water samples from 96 sites in West Hawaiʻi between May 2017 and March 2019, analyzed for stable isotopic compositions and dissolved ions, and aimed to identify the source and movement of groundwater within aquifers. This study demonstrates that stable isotopes of water are helpful in identifying (1) the source of groundwater being on the flanks of Mauna Kea, Mauna Loa, or Hualālai through calculations of recharge elevations; (2) zones of groundwater mixing in the Waimea, ʻAnaehoʻomalu, and Kīholo aquifers; and (3) movement of isolated water bodies from mauka to makai in the Kīholo and Keauhou aquifers.

Additionally, the results of this study are consistent with previous work indicating the complex hydrogeology of West Hawaiʻi's aquifers. Dissolved ions, such as bicarbonate, silica, and magnesium, are elevated along the Hualālai rift zone, likely indicating a thermal source allowing for increased leaching of ions into the groundwater system. Increased dissolved nitrate also indicates input likely from agricultural use of fertilizers and wastewater leakage from onsite sewage disposal systems. The increased concentrations of dissolved ions, specifically nitrate + nitrite, has the potential for significant impacts to the coastal ecosystems.

The results of this research have direct implications for groundwater management in West Hawaiʻi. The stable isotopic compositions and dissolved ion concentrations in the study region demonstrate areas in which groundwaters cross over aquifer boundaries established for management purposes, as well as regions in which lateral flow is impeded by, or enhanced by, subsurface geologic structures *within* management areas. Sustainable yield is currently estimated as a function of aquifer head level, recharge, and discharge, all of which depend on established aquifer boundaries. Revised estimates of sustainable yield and/or revised aquifer management unit boundaries should utilize groundwater geochemistry and other data-driven investigations to inform management strategies. Appropriate identification of groundwater aquifer boundaries, along with acknowledging and accounting for the interconnectivity of aquifers, is a critical step in mitigating anthropogenic pollution and planning for increased demands on groundwater pumping.

Chapter 5. REFRAMING FUNDING STRATEGIES TO BUILD RECIPROCITY

Published as: Tachera, D. (2021), Reframing funding strategies to build reciprocity, Eos, 102, https://doi.org/10.1029/2021EO210546. Published on 13 October 2021.

5.1 Introduction

University education and academic systems in the United States are permeated by a legacy of colonization of Indigenous peoples. The Morrill Land-Grant Acts, enacted in 1862 and 1890, resulted in the dispossession and sale of more than 10 million acres of Indigenous lands, providing financial security to universities across the country in the name of educating students and promoting economic development (McCoy et al., 2021). This colonization constitutes attacks on people and land and has been accomplished through purposeful misrepresentations of Indigenous cosmologies (Watts, 2013).

Western knowledge and science have long benefited from colonization of Indigenous peoples through the continued exploitation of their lands and knowledge (Tuhiwai Smith, 2012; Nyblade and McDonald, 2021). In today's Western scientific establishment, this exploitation extends to the devaluing of work done by Indigenous community members who assist academic researchers. Together with other extractive behaviors, this devaluation erodes trust among Indigenous peoples toward the Western scientific traditions.

To improve relationships and engagement with Indigenous communities, scientists must recognize the limitations and failings of our current academic and research systems and work toward improvement (Cartier, 2019). The science community is making significant progress through grass-roots efforts. Now it is time for academic, federal, and industry leadership to demonstrate their commitment to advancing justice, equity, diversity, and inclusion in the geosciences (Ali et al., 2021; Morris, 2021).

This manaʻo (opinion) is the product of my observations and experiences as a kanaka Ph.D. student in the geosciences. It follows in the footsteps of many past and ongoing conversations by and with mentors and colleagues (e.g., Trask, 1992). I call for changes in research funding systems so they value equitable relationships with communities; acknowledge, in the grant process, the kuleana (responsibility) and timelines required to build relationships and pursue research and broader impacts in Indigenous communities; and enforce accountability from the highest levels within academics to encourage best practices as common practices in research (e.g. Kūlana Noiʻi Working Group, 2021).

5.2 Who bears the burden of broader impacts

Building relationships with Indigenous communities where research is conducted requires substantial labor. This labor is typically unpaid and often falls to early career researchers, and especially to faculty and graduate students from these communities (Kimmerer, 2013; Kearns, 2021). As a kanaka (Native Hawaiian) graduate student at the University of Hawaiʻi at Mānoa, I am often asked and expected to volunteer in the relationship-building process with the local Native Hawaiian community. This process involves developing professional and personal connections with community members over months to years. And because I am a member of this community, my behavior and reputation hold many personal consequences that I—and my ʻohana (family) —cannot walk away from. Despite these expectations, Indigenous scientists are often told by academic, federal, and industry leaders that this work is not valued as rigorous research—that it's "not a good use of my time" in the academic setting compared with producing publications and giving conference presentations. This added and undervalued labor creates hurdles for Indigenous scholars to succeed.

Community members are often also asked to provide expertise, time, and energy on behalf of scientists (Gewin, 2021). These individuals sometimes go without pay or even recognition of their contributions and are otherwise left out of the research process because they are not seen as members of the research team. Academic researchers that do not recognize intellectual property rights and acknowledge contributions and efforts from Indigenous communities fail to honor the ethical guideline of free, prior, and informed consent, which "works to ensure that knowledge holders within Indigenous communities retain informed decision-making authority regarding their participation in the research process" (David-Chavez and Gavin, 2018).

Broader impacts statements and plans are now required for many research proposals. Researchers often submit plans that, though they may sound ethical and broadly beneficial, cover a wide range of engagement activities that may not be feasible given funding and research timelines. Do such broader impacts actually consider community practices and meet the needs of community members? And do funding agencies hold grantees accountable for following through with the plans? Without explicit metrics gauging outcomes of broader impacts, it is impossible to evaluate their effectiveness, let alone how Western researchers are fulfilling responsibilities of reciprocity (Nadkarni and Stasch, 2013). Meanwhile, is anyone holding the funders themselves accountable for ensuring that engagement efforts are respectful?

There have been repeated calls for federal organizations like the National Science Foundation (NSF) and NASA to hold themselves and the researchers they support accountable for the impacts their work has on local communities and environments (e.g. Kahanamoku et al., 2020; Morris, 2021). One way to create this accountability is by changing how our academic and funding systems are structured so they better value relationship building and broader impacts to communities by ensuring that funding timelines realistically reflect the needs of the relationship building process and provide support for Indigenous communities who provide unpaid labor to the scientific community. Without this accountability, the same mistreatments will continue to occur, and scientists will build animosity and mistrust, rather than the equitable relationships that are necessary for effective and ethical work with communities.

5.3 Enacting accountability in community engagement

Although there are funding programs that promote community-based research and relationship building, such as NSF's Established Program to Stimulate Competitive Research (EPSCoR) and Geoscience Opportunities for Leadership in Diversity - Expanding the Network (GOLD-EN), this work is not valued across all funding systems and academia. Until it is, ethical research practices will not be given full merit in hiring, tenure, and promotion processes. In some cases, proposing community-focused work can even be detrimental to researchers, because it may not be seen as impactful research in the scientific community (Gewin, 2021).

Relationship building is an increasingly important aspect of research for all scientists, but it is inherently a kuleana for Indigenous scholars: There is no way for us to *not* do it. When academic hiring and promotion processes do not value relational work, Indigenous scholars and communities are thus undervalued for their contributions.

Currently, there are few incentives for researchers to take time to build relationships before writing grant proposals, or to continue relationships beyond a grant's expiration date. However, if relationship building were valued in academia—and incentivized by funding agencies—researchers would in turn be prompted to also value equitable relationships and collaborations with the communities in which they work. How, then, do we start to bring about this change?

All too often, when researchers do work within communities, community members are exploited for their knowledge, not credited for their contributions, and not given authority over the research process (David-Chavez and Gavin, 2018). Community leaders and organizations are seen as volunteer outside collaborators who can be called upon when needed—and thus are often kept in the dark about research plans, methodologies, and final outcomes or products.

Although it takes time to build trust with communities, it is scientists' kuleana to ensure that we follow proper protocols of engagement. The United Nations Declaration of the Rights of Indigenous Peoples outlines the bare minimum of expectations for how we should be engaging (United Nations, 2008). Among other points, these protocols guarantee Indigenous peoples the right to free and informed consent. In some cases, discussions between researchers and communities may lead to the outcome that no research is consented to and therefore none can be conducted—an outcome that researchers must respect and value as part of rebuilding trust.

In the relationship-building process, honoring Indigenous Knowledge systems and cultural practices is paramount (Kahanamoku et al., 2020). To promote respectful and reciprocal engagement with local communities, targeted funding in grants for relationship building should be provided to both the communities and researchers. This funding would provide resources and time to support mutually beneficial and respectful interactions that focus not only on producing meaningful research, but also on the needs and concerns of community leaders, including questions of data sovereignty, ownership, and access as well as co-authorship or co-review of project outcomes.

5.4 Encouraging best practices in community-driven research

The development of the Thirty Meter Telescope (TMT) on the sacred land of Mauna Kea is one example of how the geosciences have perpetuated extractive behaviors in Hawaiʻi and elsewhere (e.g. Hofschneider, 2019). Despite misconceptions, protests by Native Hawaiians opposed to the TMT are not rooted in anti-science perspectives (although they do reflect erosion of trust in the Western scientific establishment); rather they are motivated because extractive practices are detrimental to the health and cultural prosperity of Native Hawaiians.

The historic "lack of transparency and egregious mismanagement of Mauna Kea," as Alegado (2019) describes it, highlights important aspects missing from science collaborations, especially respect for Indigenous peoples' cultural integrity and the process of building relationships (Montgomery and Blanchard, 2021). The TMT protests mark a significant moment in our history, when kānaka are standing up and saying enough is enough, that scientists must understand the history of how scientific advancements have impacted communities around the world, and that they must learn from earlier mistakes to change their approaches (Kagawa-Viviani, 2019; Montgomery and Blanchard, 2021).

There are resources that can help develop relationship-building and -sustaining skills, as I have learned over the past few years. The Kūlana Noiʻi outlines best practices and guiding questions regarding respect, reciprocity, self-awareness and capacity, communication, maintaining a long-term focus, community engagement and co-review, knowledge ownership and access, and accountability (Kūlana Noiʻi Working Group, 2021). Kanaka ʻŌiwi Methodologies: Moʻolelo and Metaphor, includes a collection of methodology-focused essays from kānaka scholars in varying disciplines (Oliveira and Wright, 2015). The authors describe how they use these methodologies to guide and inform their research process and to gain a deeper understanding of language and culture, allowing for positive social changes.

Some organizations, such as the Rising Voices Center for Indigenous and Earth Sciences at the National Center for Atmospheric Research (NCAR), hold space for the coming together of Western and Indigenous scientists. Among other contributions, the Rising Voices Center has identified that recognizing Indigenous community needs in research, including data sovereignty, co-authorship, and accountability, has been an important step forward in developing scientific collaborations. At the Indigenous Geography website, researchers can find resources about collaborative research methodologies from around the world, which can help to start the relationship-building process with Indigenous communities.

5.5 Raising our standards

As a kanaka scholar, I am required to follow proper protocols and procedures in my academic research: Take time to talk with community members, meet frequently to share back results, and conduct my work in a pono (moral) way. As a researcher, I am held to the highest standards of quality and ethics when reporting my research: sharing quality assurance and quality control information, calculating analytical errors in data sets, and detailing my research methodologies. Why are similarly high standards not applied when communicating and collaborating with Indigenous communities? It is not only our kuleana as scientists to hold ourselves accountable, but it is also incumbent upon funding agencies to hold themselves and the scientists they support to the highest standards when engaging Indigenous communities.

As we move down the path of knowledge together, empowering Indigenous knowledges, peoples, and cultures to remain sovereign is essential. Updating funding systems is just one step the scientific community can take to value equitable relationships with communities and the processes needed to build those relationships. This change will allow for more accountability across all levels of academia, and will result in science that is mutually beneficial to, and respectful of, everyone involved.

Chapter 6. CONCLUSIONS

6.1 Summary

This dissertation focused on the source, flow, and interconnectivity of groundwaters in West Hawaiʻi through geochemical investigations. Chapter 2 collected precipitation at 20 sites from Central to West Hawaiʻi between August 2017 and November 2019, analyzed for stable isotopic compositions and bulk ion deposition concentrations. The samples were compared to previous studies conducted on Hawaiʻi Island with the goal of better characterizing the source of groundwater in the study region. The local meteoric water line (LMWL) established during this study is similar to the global meteoric water line and local meteoric water lines for East Hawaiʻi and East Maui, however differing from the LMWL previously established for West Hawaiʻi by Fackrell et al. (2020). A combined volume-weighted average for replicated sites produced averages that better characterize groundwater isotopic compositions for the study region, demonstrating that long-term studies (> 2 years) are needed to better understand the variations observed in meteoric waters.

Chapter 2 also provided insight into extreme events in Hawaiʻi that can impact the dissolved chemical composition of rainfall. Below the inversion layer, increased concentrations of sulfate and chloride were observed during periods of low rainfall (less than 250 mm) and the 2018 Kīlauea lower east rift zone eruption. Results from this study support previous research that observed a correlation between increased aerosols and decreased rainfall downwind of the volcano. In addition, observed sulfate concentrations increased during the Kīlauea eruption, demonstrating the dynamic impacts of volcanism in Hawaiʻi on precipitation chemistry.

Chapter 3 presented a new, flow-path specific method to calculate salinity corrections, and applied this method to 43 groundwater sites sampled in West Hawaiʻi between May 2017 to March 2019. The new method utilized precipitation and ocean water end-member values derived from within the probable flow path to each groundwater sample, utilizing precipitation end-member observations from Chapter 2. This method provided better results than previously-published methods of calculating the correction. Chapter 3 also demonstrated that charge balance error cannot always be used as a sole indicator of dataset quality because alkalinity analyses can introduce significant error. Two potential problems result from alkalinity analyses: (1) the time between sample collection and sample analysis, and (2) random errors.

Appropriate salinity corrections are crucial to groundwater management because these corrections are a necessary step in the characterization of groundwater aquifer chemistry. Seawater intrusion is a natural process that affects groundwater salinity in coastal environments. In Hawaiʻi, and elsewhere around the world, salinity corrections are required to separate out the ocean water fraction from the freshwater fraction in a sample, and in turn understand the degree of seawater inundation and/or anthropogenic contamination. Especially in settings such as West Hawaiʻi where the hydrogeology is very complex, it is crucial to use proper end-members for these corrections. This study demonstrates that utilizing end-members from within flow paths allows for better characterization of groundwater systems that can be temporally and spatially heterogeneous.

Chapter 4 analyzed stable isotopic composition and dissolved ion concentrations from 96 sites in West Hawaiʻi to identify the source and movement of groundwater within aquifers. The results from this study identified recharge elevations from Hualālai, Mauna Kea, and Mauna Loa. Additionally, results from this study demonstrate the complex heterogeneity of the subsurface geology through interconnectivity in the Waimea, ʻAnaehoʻomalu, and Kīholo aquifers but lack of interconnectivity across lines parallel to mauka to makai flow in the Kīholo and Keauhou aquifers. Elevated dissolved ion concentrations along the Hualālai rift zone, such as bicarbonate, silica and magnesium, likely indicate a thermal source. Elevated concentrations of sodium and nitrate to the coastal aquifers likely indicate agricultural fertilizer and wastewater leakage from onsite sewage disposal systems.

For the entirety of this dissertation research, engagement and communication with the West Hawaiʻi community has been incredibly important. Respect and reciprocity are necessary for the long-term investment in building successful community relationships. It is also important to conduct research in collaboration with Indigenous communities, giving credit and authorship to local Indigenous knowledge. This research was only possible through the support of the local resource managers, ranchers, and homeowners who generously allowed this project to access their lands and waters, while also sharing their time and knowledge of their places and families.

Ultimately, the results of this dissertation have implications for groundwater management in West Hawaiʻi, to ensure the quantity and quality of water available to the community and surrounding ecosystems.

6.2 Future work

Long-term precipitation data, collected on frequent sampling intervals, are crucial to developing local meteoric water lines. Multi-decadal sampling, although challenging, will be crucial to determining the variability of stable isotopes in precipitation across time. Wide spatial distributions of studies are also crucial to understand the complex interactions of weather and climate patterns that will be impacted by future climate change. Continued collection of bulk deposition, particularly in the current quiet period of Kīlauea Volcano, would aid in understanding the importance and impacts of volcanic emissions on rainfall rates and compositions. Analyses of the effects of sea salt aerosol deposition on ecological processes and water quality are also needed.

Building off of the research from this dissertation, additional investigation is needed into the widely-used assumption that the isotopic composition of present-day rainfall is representative of the climatic conditions during groundwater recharge, which can occur hundreds to thousands of years before present is needed. In groundwater research, the stable isotopic compositions are treated as conservative, meaning that they remain constant once they enter the groundwater system after falling as rain. Results from this dissertation demonstrate that the isotopic composition of rainfall can vary based on climate variability, and combined with groundwater age dates from ongoing research, additional investigation is needed into the widely used assumption that stable isotopic compositions of water from present day are representative of groundwater recharged from hundreds to thousands of years ago.

Extensive groundwater studies for the entirety of Hawaiʻi Island, combining geochemical and geophysical techniques, will be crucial for developing a better understanding of the complex heterogeneity of subsurface structures. Ultimately, future work should also focus on community needs related to water resources. Future groundwater management scenarios, as well as revisiting current strategies, should utilize groundwater geochemistry and other data-driven investigations to inform management strategies. Appropriate identification of groundwater aquifers, and the interconnectivity of aquifers, is a critical step in preparation for anthropogenic pollution and increased utilization of groundwater pumping.

APPENDIX A. Chapter 2 Supplementary Materials

Table A.1. Individual samples from precipitation collectors.

Individual sampling for 20 precipitation collectors from the West Hawai‘i region. Samples are organized by sampling trip, and within each trip from lowest to highest elevation site. Replicated sites from the Fackrell et al. (2020) study are denoted with an asterisk, sites within 2 kilometers and approximately 100 meters elevation denoted with two asterisks. [1]Sampling trip: 2 (11/12/17 - 11/15/17), 3 (3/13/18 - 3/22/18), 4 (6/10/18 - 6/15/18), 5 (8/8/18 - 8/16/18), 6 (8/28/18, after Hurricane Lane), 7 (11/7/18 - 11/20/18), 8 (3/14/19 - 3/25/19), 9 (8/12/19 - 8/17/19), 10 (11/12/19 - 11/20/19). Data available for download (Tachera, 2020).

Site	Latitude	Longitude	Elevation (m)	Trip[1]	pH	Precipitation (mm)	Fl (µM)	Cl (µM)	Br (µM)	SO_4^{2-} (µM)	Na (µM)	NH_4 (µM)	K (µM)	Mg (µM)	Ca (µM)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
*Keāhole	19.72	-156.05	5	2		22	--	--	--	--	--	--	--	--	--	-3.6	-17.1
Kalaoa	19.71	-155.97	540	2		103		85		125	109			16	17	-3.9	-16.7
Pu‘u Wa‘awa‘a	19.77	-155.84	780	2		185	1	85	1	186	98			15	96	-5.4	-35.4
*Keāhole	19.72	-156.05	5	3		123	1	533		250	470		26	58	142	-3.5	-17.3
Kalaoa	19.71	-155.97	540	3		99		330	3	343	544	29	26	25	60	-4.4	-22.2
Pu‘u Wa‘awa‘a	19.77	-155.84	780	3		155	1	164	1	281	291		15	25	107	-5.3	-32.7
*Hōlualoa	19.64	-155.88	1380	3		65		68		125	104	7	5	12		-6.7	-42.9
*Keāhole	19.72	-156.05	5	4		27	3	553	1	346	579		23	91	309	-2.8	-22.1
**Pālamanui	19.73	-156.01	140	4	6.6	37	1	443		209	835		20	66	17	-3.4	-19.3
Kalaoa	19.71	-155.97	540	4	3.9	173	2	138	1	184	226	64	36	16	65	-3.7	-18.6
**Kaloko	19.69	-155.96	660	4	4.3	35	14	231	3	683	283		61	41	62	-1.7	-0.2

Hu‘ehu‘e	19.74	-155.96	730	4	4.2	95	3	51		140	57		15	8	10	-4	-21.1
Pu‘u Wa‘awa‘a	19.77	-155.84	780	4	4.6	148	6	220	1	371	374		18	45	92	-3.7	-19.2
*Hōlualoa	19.64	-155.88	1380	4	3.4	100	2	1221	1	296	1179	7	26	111	12	-6.4	-39.4
Ka‘ohe	19.79	-155.63	1620	4	9.3	338	2	93		134	144	7	240	136	150	-11.1	-83.6
Pu‘u Lā‘au	19.83	-155.59	2270	4	8.0	195		11		34	17		8	8	17	-9.9	-70.6
Humu‘ula	19.60	-155.47	2430	4	5.0	730	2	8		75	17		3	8	57	-5.8	-43
Hale Pōhaku	19.76	-155.45	2840	4	4.4	212	2	17		47	35		5	4	20	-9.7	-66.5
Mauna Loa	19.53	-155.57	3400	4	5.2	189	1	8		50	17		3	8	12	-13.3	-96.5
*Kīholo	19.85	-155.92	3	5		3	14	940	3	1011	780	1	377	188	301	-1.2	-2
*Keāhole	19.72	-156.05	5	5		11	23	1028	3	1105	976	36	118	173	530	-1.3	-3.1
Ka‘ūpūlehu	19.82	-155.98	17	5		4	46	1068	2	2055	1045	4	66	218	676	0.4	6.3
**Pālamanui	19.73	-156.01	140	5	6.2	27	8	177	1	444	227	18	20	24	67	-1.8	-4
Kalaoa	19.71	-155.97	540	5		67	12	350	4	581	531	37	16	45	115	-2.7	-8.6
**Kaloko	19.69	-155.96	660	5		167	11	295	3	688	417		58	48	86	-1.8	-3.5
Hu‘ehu‘e	19.74	-155.96	730	5		29	6	218	3	428	430	20	20	21	40	-2.9	-11.1
Pu‘u Wa‘awa‘a	19.77	-155.84	780	5		35	21	275	2	1205	451		43	59	205	-0.8	1
*Hōlualoa	19.64	-155.88	1380	5		33	5	166	2	490	268	10	22	20	75	-4	-18.7
Ka‘ohe	19.79	-155.63	1620	5		32	26	379	3	4590	470	1	353	316	1061	-3.2	-17.1
Pu‘u Lā‘au	19.83	-155.59	2270	5		6	11	167	1	527	187	1	124	35	85	-3.8	-21.2
Humu‘ula	19.60	-155.47	2430	5		89	21	115	5	1016	196	1	6	26	508	-2	-16.3

Hale Pōhaku	19.76	-155.45	2840	5		11	14	51	1	293	100		33	7	15	-7.2	-47.5
Mauna Loa	19.53	-155.57	3400	5		10	22	79	3	336	142	1	11	10	20	-6.3	-36.1
Mauna Kea	19.82	-155.47	4200	5		9	2	36		99	51		10	6		-9.2	-61.7
*Keāhole	19.72	-156.05	5	6		19	5	226	2	114	284	3	9	35	151	-9.5	-70.7
Ka‘ūpūlehu	19.82	-155.98	17	6		22	11	289	1	371	315		16	67	209	-9.4	-70.4
**Pālamanui	19.73	-156.01	140	6		12	8	138		198	170		22	17	220	-8.8	-65.6
Kalaoa	19.71	-155.97	540	6		52	4	110	1	109	146		25	21	92	-5.7	-35.7
**Kaloko	19.69	-155.96	660	6		86	4	51	1	44	87		5	10	41	-5.8	-39.2
Pu‘u Wa‘awa‘a	19.77	-155.84	780	6		111	5	28		41	70		4	8	57	-7	-46.3
Humu‘ula	19.60	-155.47	2430	6		183	3	17		32	54		2	5	29	-11.1	-79.6
Hale Pōhaku	19.76	-155.45	2840	6		445	4	10		14	46		1	4	18	-12.8	-89.2
Mauna Loa	19.53	-155.57	3400	6		291	5	17		19	75	2	5	4	13	-12.1	-86.9
*Kīholo	19.85	-155.92	3	7		69	2	122		81	84		26	41	161	-4.1	-22.7
*Keāhole	19.72	-156.05	5	7		59	1	131		32	106		3	17	109	-3	-12.9
Ka‘ūpūlehu	19.82	-155.98	17	7		62	5	371		197	283	1	14	77	280	-2.6	-9.4
**Pālamanui	19.73	-156.01	140	7		44	2	126		34	90		16	14	149	-2.9	-11
Kealakekua	19.47	-155.89	430	7		206	1	54		32	45		3	11	43	-3.2	-12
Kalaoa	19.71	-155.97	540	7		62	1	46		16	56		3	16	60	-2.8	-7.6
**Kaloko	19.69	-155.96	660	7		469	1	58		32	56		5	12	21	-2.9	-9.1
Hu‘ehu‘e	19.74	-155.96	730	7		225	1	51			40	1	3	9	44	-4.3	-21.1

Pu‘u Wa‘awa‘a	19.77	-155.84	780	7		234	1	35		10	30	1	5	9	48	-3.7	-14.4
*Hōlualoa	19.64	-155.88	1380	7		103	1	38		21	25		6	9	67	-5.7	-32.5
Ka‘ohe	19.79	-155.63	1620	7		504	5	96		745	68	1	70	73	273	-5.4	-32.5
Pu‘u Lā‘au	19.83	-155.59	2270	7		202	1	18		32	15		8	5	23	-7.4	-48
Humu‘ula	19.60	-155.47	2430	7		229	1	6		34	6		1	2	62	-5.9	-35.5
Hale Pōhaku	19.76	-155.45	2840	7		163	1	4		6	3			2	40	-7.1	-42.6
Mauna Loa	19.53	-155.57	3400	7		150	1	6		18	6		1	4	8	-8.5	-55
Mauna Kea	19.82	-155.47	4200	7		358		5		7	5		1	9	9	-13.7	-97.8
*Kīholo	19.85	-155.92	3	8	5.7	42	1	268		46	217	5	22	65	175	-5.7	-34.2
*Keāhole	19.72	-156.05	5	8	6.2	30	1	1769	2	248	1457	1	36	213	585	-5.5	-32.8
Keahuolū	19.65	-156.00	12	8	5.2	18	1	339		71	300		9	36	85	-5.5	-33
Ka‘ūpūlehu	19.82	-155.98	17	8	6.5	25	7	1588	2	544	1370	6	63	224	525	-5.2	-33
**Pālamanui	19.73	-156.01	140	8	6.3	28	2	339		76	278	1	14	65	199	-5.4	-32.9
Waikoloa	19.93	-155.79	250	8	5.8	37	1	293		60	244		26	37	59	-6.3	-39.8
Kealakekua	19.47	-155.89	430	8	6.3	73	1	200		61	161	5	10	19	93	-4.3	-20.8
Kalaoa	19.71	-155.97	540	8	5.8	93	1	186		44	157	7	8	20	22	-4.5	-22
**Kaloko	19.69	-155.96	660	8	7.7	242	2	347		100	309	4	60	63	114	-3.2	-11.8
Hu‘ehu‘e	19.74	-155.96	730	8	10.4	193	15	3515	5	1693	3493	3	208	1428	720	-5.1	-26.8
Pu‘u Wa‘awa‘a	19.77	-155.84	780	8	5.9	76	1	99	2	10	87		4	15	118	-5.6	-31.1
*Hōlualoa	19.64	-155.88	1380	8	6.1	65	1	118		69	91	5	6	21	128	-6.1	-31.8

Ka‘ohe	19.79	-155.63	1620	8	6.2	200	3	161		119	117	8	62	39	231	-6.5	-38.9
Pu‘u Lā‘au	19.83	-155.59	2270	8	5.0	62		34		24	30		25	5	21	-8.5	-55.1
Humu‘ula	19.60	-155.47	2430	8	6.5	130	2	23		45	17		2	5	216	-7.2	-46.9
Hale Pōhaku	19.76	-155.45	2840	8	6.5	169		51		28	96		5	11	82	-9.9	-64.5
Mauna Loa	19.53	-155.57	3400	8	5.9	99		406		81	387		10	56	13	-10.8	-80.4
Mauna Kea	19.82	-155.47	4200	8	6.4	60	1	310		56	261		25	39	17	-10.6	-73.6
*Kīholo	19.85	-155.92	3	9		57	1	152		17	96		66	54	108	-2.2	-6.1
*Keāhole	19.72	-156.05	5	9		109	1	248		38	207		8	38	136	-2.2	-4.5
Keahuolū	19.65	-156.00	12	9		128	5	162		49	141	1	60	54	525	-2	-2.6
Ka‘ūpūlehu	19.82	-155.98	17	9		34	5	749		215	678		29	134	172	-0.1	1
**Pālamanui	19.73	-156.01	140	9		78	5	153		170	329		41	79	97	-2.9	-10.3
Waikoloa	19.93	-155.79	250	9		245	3	145		61	128		61	23	78	-2.1	-5.1
Kealakekua	19.47	-155.89	430	9		444	1	136		46	116		16	14	31	-2	-2.3
Kalaoa	19.71	-155.97	540	9		477	1	99		31	89	1	5	16	35	-2.6	-5.2
**Kaloko	19.69	-155.96	660	9		1201	1	72		24	70		8	9	16	-2.7	-5.6
Hu‘ehu‘e	19.74	-155.96	730	9		286		89		9	73	2	32	14	23	-2.9	-7.5
Pu‘u Wa‘awa‘a	19.77	-155.84	780	9		217		40		9	35		3	8	36	-4	-17.5
*Hōlualoa	19.64	-155.88	1380	9		189	1	36		10	30	1	6	6	32	-3.2	-9.4
Ka‘ohe	19.79	-155.63	1620	9		247	2	103		78	67		168	31	119	-3.9	-15.8
Humu‘ula	19.60	-155.47	2430	9		187	1	11		9	14	1	1	5	100	-6.6	-40.5

Mauna Loa	19.53	-155.57	3400	9		201	1	8		5	5	1		1	5	-8	-51.2
*Kīholo	19.85	-155.92	3	10		19	--	--	--	--	--	--	--	--	--	-1.8	-6.3
*Keāhole	19.72	-156.05	5	10		37	--	--	--	--	--	--	--	--	--	-1.8	-3
Keahuolū	19.65	-156.00	12	10		76	--	--	--	--	--	--	--	--	--	-2.3	-5.2
Ka‘ūpūlehu	19.82	-155.98	17	10		368	--	--	--	--	--	--	--	--	--	-2.6	-10.8
**Pālamanui	19.73	-156.01	140	10		60	--	--	--	--	--	--	--	--	--	-2.5	-7.9
Waikoloa	19.93	-155.79	250	10		133	--	--	--	--	--	--	--	--	--	-2.2	-4.2
Kealakekua	19.47	-155.89	430	10		572	--	--	--	--	--	--	--	--	--	-2.3	-4.7
Kahalu‘u	19.58	-155.93	520	10		612	--	--	--	--	--	--	--	--	--	-2.1	-3.6
Kalaoa	19.71	-155.97	540	10		371	--	--	--	--	--	--	--	--	--	-3.1	-10.8
**Kaloko	19.69	-155.96	660	10		590	--	--	--	--	--	--	--	--	--	-3.1	-9.5
Hu‘ehu‘e	19.74	-155.96	730	10		148	--	--	--	--	--	--	--	--	--	-3.2	-11.3
Pu‘u Wa‘awa‘a	19.77	-155.84	780	10		136	--	--	--	--	--	--	--	--	--	-3	-9.1
*Hōlualoa	19.64	-155.88	1380	10		25	--	--	--	--	--	--	--	--	--	-4.1	-17.8
Ka‘ohe	19.79	-155.63	1620	10		89	--	--	--	--	--	--	--	--	--	-4.8	-25.8
Humu‘ula	19.60	-155.47	2430	10		102	--	--	--	--	--	--	--	--	--	-6	-34.4
Pu‘u o Uo	19.50	-155.69	2615	10		747	--	--	--	--	--	--	--	--	--	-6.4	-36.8
Mauna Loa	19.53	-155.57	3400	10		94	--	--	--	--	--	--	--	--	--	-9.2	-59.7

APPENDIX B. Chapter 3 Supplementary Materials

Table B.1. Raw, individual in-situ and stable isotope of water data.

Raw (un-corrected) data for 43 groundwater and 3 ocean water sites during the study period of May 2017 to March 2019, organized by site from North (Waimea aquifer) to South (Kealakekua aquifer), followed by chronological sampling trip order. Sampling trip: 1 (05/2017), 2 (08/2017) 3 (11/2017), 4 (03/2018), 5 (08/2018), 6 (11/2018), 7 (03/2019). pH, temperature (°C), specific conductivity (µS/cm), and dissolved oxygen (% and mg/L) are collected in the field. Stable isotopes of water $\delta^{18}O$ and $\delta^{2}H$ are reported in per mil (‰). Relative standard deviations are reported for the geochemical parameters.

Sample Name	Trip	pH	Temperature (°C)	Specific Conductance (µS/cm)	Salinity	Dissolved Oxygen (%)	Dissolved Oxygen (mg/L)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
Relative Standard Deviation								**0.78**	**0.46**
Parker Ranch Deepwell	3	7.85	22.8	123.4	0.048	91	7.84	-3.6	-12.1
Parker Ranch Deepwell	4	7.85	23	153.4	0.06	88.8	7.34	-3.4	-11.7
Parker Ranch Deepwell	5	6.98	24	169	0.07	99.2	8.31	-3.5	-11.9
Lalamilo C Deepwell	3	8.04	26.1	470.1	0.205	102.8	8.38	-5.5	-28.9
Lalamilo C Deepwell	4	7.84	26.3	475.7	0.21	70.9	5.62	-5.4	-28.8
Lalamilo C Deepwell	5	7.59	26.2	679	0.31	91.2	7.36	-5.4	-28.6
Lalamilo C Deepwell	6	7.87	26.1	660.00	0.31	105.40	8.63	-5.4	-28.8
Lalamilo A Deepwell	3	8.06	26.1	452.7	0.197	73.5	5.7	-5.2	-28.4
Lalamilo A Deepwell	4	7.89	26.1	460	0.2	82.3	6.43	-5.5	-29
Lalamilo A Deepwell	6	7.9	26.5	486.00	0.23	89.20	7.8	-5.4	-28.7
Lalamilo B Deepwell	3	8.08	26.3	431	0.187	79.3	6.08	-5.6	-29.8
Lalamilo B Deepwell	4	7.9	26.1	480.2	0.21	78.8	6.16	-5.6	-29.9
Lalamilo B Deepwell	5	7.36	26.2	556	0.25	77.3	6.23	-5.6	-30.3

Lalamilo B Deepwell	6	7.83	26.2	523.00	0.25	110.60	8.7	-5.5	-29.9
Lalamilo B Deepwell	7	7.79	26.2	496	0.23	100.9	8.16	-5.6	-29.8
Parker #2 Deepwell	3	8.04	26.8	756	0.344	58.3	4.58	-5.7	-30.7
Parker #2 Deepwell	4	7.9	26.6	517	0.23	85.3	6.53	-5.7	-30.9
Parker #2 Deepwell	5	7.88	26.7	739	0.34	90.4	7.19	-5.7	-31
Parker #2 Deepwell	6	7.89	26.7	658.00	0.33	117.10	9.23	-5.6	-30.6
Parker #2 Deepwell	7	7.77	26.7	703	0.34	107.6	8.75	-5.7	-31.2
Parker #3 Deepwell	4	7.79	26.2	363.3	0.16	83.7	6.62	-5.8	-31.1
Parker #3 Deepwell	5	7.8	26.7	439.6	0.19	96	7.58	-5.7	-31.1
Parker #3 Deepwell	6	7.87	26.7	430.70	0.21	106.80	8.69	-5.6	-30.6
Parker #3 Deepwell	7	7.83	26.6	435.7	0.21	97.6	7.74	-5.6	-30.6
Parker #4 Deepwell	3	8.06	27.2	738	0.335	69.2	5.32	-6.1	-32.5
Parker #4 Deepwell	4	7.92	26.9	532	0.23	75.1	5.79	-5.8	-31.9
Parker #4 Deepwell	5	7.85	27.1	770	0.35	84.8	6.74	-5.3	-30.6
Parker #4 Deepwell	6	7.91	27.2	734.00	0.36	116.10	8.44	-5.8	-32.3
Parker #4 Deepwell	7	7.69	27	765	0.38	98.5	7.83	-5.8	-31.9
Waikoloa 1	6	7.98	26.7	328.10	0.16	109.10	8.77	-5.5	-29.9
DW-7	3	8.14	26.5	287.6	0.120	66.5	5.19	-5.7	-31.6
DW-7	4	7.99	26.2	287.7	0.12	80.5	6.28	-5.8	-31.4
DW-7	7	7.9	27	340.1	0.16	103.6	8.31	-5.7	-31.4
Parker 5	3	8.19	26.5	303.8	0.128	75.3	5.87	-5.7	-30.9
Waikoloa 1	4	8.05	26.3	296.4	0.12	83.3	6.45	-5.8	-31.2
Parker 4	3	8.15	26.7	301.3	0.127	67.1	5.23	-5.8	-31.6
Parker 4	4	7.97	26.6	299.1	0.13	84.6	6.58	-5.8	-31.7
Parker 4	5	8.19	26.6	356.7	0.15	87.6	6.82	-5.8	-31.5

Parker 4	6	7.91	26.7	352.40	0.17	107.80	8.62	-5.8	-31.6
Parker 4	7	7.81	26.7	350.1	0.17	97.3	7.85	-5.8	-31.6
Waikoloa 3	3	7.87	27.3	528	0.233	71.5	5.5	-6.9	-42.1
Waikoloa 3	5	8.1	28.2	510	0.22	72.4	5.58	-6.8	-41.5
Waikoloa 3	7	7.87	28.3	512	0.24	123.5	9.5	-6.9	-42.2
Waikoloa 2	3	8.04	27.9	621	0.278	60.7	4.73	-7.1	-43.5
Waikoloa 2	4	7.92	28.6	660	0.3	78.5	5.82	-7.1	-43.4
Waikoloa 2	6	7.93	28.6	781.00	0.38	118.20	9.15	-7.1	-43.3
Waikoloa DW-6	3	8.1	28.3	707	0.320	64.7	4.89	-7.6	-48.6
Waikoloa DW-6	4	7.97	28.5	717	0.32	72.4	5.38	-7.7	-48.2
Waikoloa DW-6	5	8.11	28.4	726	0.33	77.2	5.79	-6.9	-46.2
Waikoloa DW-6	6	7.93	28.5	839.00	0.41	136.50	10.72	-7.6	-48.2
Waikoloa DW-6	7	7.89	28.6	845	0.41	108.2	8.26	-7.6	-48
Resort Irr 2	4	7.94	24.7	2522	1.28	90.5	7.38	-8.9	-61
Waikoloa Irr 3	3	8.14	24.1	2184	1.091	79.1	6.46	-9.1	-62.2
Waikoloa Irr 3	4	8	23.9	2140	1.07	92.1	7.43	-8.9	-60.9
Waikoloa Irr 3	5	8.01	24.1	2166	1.08	96.5	7.69	-8.8	-60.9
Waikoloa Irr 3	6	8.03	24.1	2,507.00	1.29	120.00	9.78	-8.9	-61.1
Waikoloa Irr 3	7	8.06	24.1	2489	1.28	104.4	8.7	-9	-61.4
Resort 1	4	7.95	23.7	2692	1.37	87.3	7.12	-8.9	-61
Resort 1	5	8.11	23.9	2710	1.38	93.9	7.73	-8.7	-60.5
Resort 1	6	8.04	23.9	3,139.00	1.64	120.90	10.1	-8.8	-60.8
Resort 1	7	8.04	24	3131	1.63	99.4	8.28	-8.9	-60.9
Nursery	4	7.84	23.5	3459	1.8	85.6	7.01	-8.6	-58.2
Nursery	5	7.66	23.5	3527	1.84	91.4	7.6	-8.7	-59.3

Nursery	6	7.97	23.5	4,062.00	2.15	120.40	9.54	-8.6	-59.2
Nursery	7	8.02	23.6	4095	2.17	106.7	8.96	-8.6	-59.2
Fifty-One FT STP	3	7.94	24.6	3417	1.776	72.2	5.93	-8.7	-59.6
Fifty-One FT STP	4	7.81	23.7	3424	1.78	80.9	6.55	-8.7	-58.8
West Hawaii Landfill	5	8.02	22.4	3603	1.88	102.2	8.78	-7.9	-53.1
West Hawaii Landfill	6	7.96	22.4	4,161.00	2.21	122.70	10.35	-7.9	-53.1
West Hawaii Landfill	7	8.13	22.5	4216	2.24	105.7	9.02	-7.7	-52.6
Makani Golf Course	6	8.22	23	567.00	0.27	108.30	9.35	-8.1	-53.7
Makani Golf Course	7	7.8	22.7	545	0.27	113.3	9.7	-8.2	-53.8
Puu Lani	2	8.31	23.7	387.5	0.17	83.5	7.14		
Puu Lani	4	8.08	23.4	394.6	0.17	83.6	7.15	-7.9	-51.3
Puu Lani	5							-7.9	-51.2
Puu Lani	6	8.21	23	447.20	0.22	108.60	9.23	-7.8	-51
Puu Lani	7	8.07	23.7	460.1	0.22	104.8	8.79	-7.9	-51.1
Puu Waawaa	2	8.31	24.6	272.8	0.11	80.8	6.9		
Puu Waawaa	4	8.14	22.9	256.4	0.11	85.1	7.22	-8.1	-52.7
Puu Waawaa	5							-7.9	-52
Puu Waawaa	6	8.16	24.1	303.80	0.14	96.60	8.19	-7.5	-51.2
Puu Waawaa	7	7.82	23.2	288.1	0.14	104.2	8.9	-8.1	-52.6
Huehue Ranch 5	3	7.14	23.9	1803	0.886	50.3	4.33	-5	-25
Huehue Ranch 5	5	7.11	23.7	1530	0.74	67.3	5.67	-4.7	-23.8
Huehue Ranch 5	7	6.94	23.6	1991	1.01	68	5.62	-5.1	-25.8
Huehue Ranch 3	3	7.24	20.6	1536	0.744	37	3.89	-4.9	-24.2
Huehue Ranch 3	4	7.06	20.1	1484	0.72	33.9	3.04	-4.9	-24.1
Huehue Ranch 3	7	7.08	20.3	1970	1.01	63.2	5.42	-4.8	-23.7

Huehue Ranch 4	5	6.75	23.5	1422	0.68	68.1	5.73	-5.2	-28
Huehue Ranch 4	6	6.63	23.7	1,664.00	0.84	56.60	4.76	-5.2	-27.7
Huehue Ranch 4	7	6.55	24.2	1112	0.6	58.7	4.96	-5.4	-28.6
Huehue Ranch 2	3	6.98	21.9	1335	0.639	52.5	4.5	-4.8	-24.6
Huehue Ranch 2	4	6.71	21.4	1332	0.64	60.6	5.37	-5	-25.2
Huehue Ranch 2	6	6.94	22.1	1,616.00	0.81	80.50	7.03	-4.8	-24.8
Kau (Makalei) Deepwell	5	7.45	24.2	1152	0.54	89.1	7.19	-5	-25.7
Kau (Makalei) Deepwell	6	7.16	24.4	1,626.00	0.82	111.10	9.2	-5.1	-25.9
Kalaoa Deepwell	1	7.77	21.09	479		87	7.59	-6.6	-40.1
Kalaoa Deepwell	3	8.03	23.6	289.2	0.121	60	4.99	-6.7	-40.2
Kalaoa Deepwell	4	7.92	23.2	274.2	0.11	82.4	6.91	-6.7	-40.4
Kalaoa Deepwell	5	7.79	23.3	276.4	0.12	82	7.01	-6.7	-40.2
Kalaoa Deepwell	6	7.76	23.3	318.80	0.15	127.40	10.29	-6.5	-39.8
Kalaoa Deepwell	7	7.69	23.3	319	0.15	94.2	8.02	-6.6	-40.1
Palani Ranch Deepwell	3	8.08	22	231.3	0.095	81.7	7.22	-6.9	-42.4
Palani Ranch Deepwell	4	7.87	22	224.9	0.09	98.2	8.3	-7	-43.4
Honokohau Deepwell	1	8.02	21.9	216.5		82.7	7.23	-6.9	-42.3
Honokohau Deepwell	7	7.63	21.9	251.3	0.12	104.4	9.17	-6.9	-42.3
Queen Liliuokalani Trust (Keahuolu) Deepwell	1	8.14	21.2	159.1		93	8.29	-5.5	-30.1
Queen Liliuokalani Trust (Keahuolu) Deepwell	4	8.02	21	159.8	0.06	99.5	8.4	-5.5	-29.6
Queen Liliuokalani Trust (Keahuolu) Deepwell	5	7.93	20.9	159.2	0.06	99.3	8.61	-5.5	-29.8
Queen Liliuokalani Trust (Keahuolu) Deepwell	6	7.87	20.9	183.70	0.09	119.10	10.29	-5.4	-29.5
Queen Liliuokalani Trust (Keahuolu) Deepwell	7	7.78	20.9	178	0.09	103.4	9.23	-5.4	-29.5
Keopu Deepwell	4	8	21	153.2	0.06	82.8	7.33	-5.1	-26.2

Keopu Deepwell	5	7.95	21.3	157.7	0.06	101	8.75	-5.2	-27.1
Keopu Deepwell	6	7.81	21.3	133.30	0.05	106.80	9.65	-5.1	-26.9
Keopu Deepwell	7	7.89	21.4	184.3	0.09	95	8.42	-5.2	-27.4
Holualoa Deepwell	1	8.03	20.6	924		99.8	9.13	-4.1	-19
Holualoa Deepwell	3	7.88	20.8	923	0.428	81.5	7.42	-4.1	-18.9
Holualoa Deepwell	4	7.86	20.5	931	0.43	96.8	8.48	-4.1	-19
Holualoa Deepwell	5	7.69	20.6	895	0.41	101.5	8.75	-4.2	-18.8
Holualoa Deepwell	6	7.84	20.4	1,032.00	0.51	120.00	10.71	-3.8	-18
Holualoa Deepwell	7	7.77	20.5	1075	0.53	123.2	10.87	-4.1	-18.7
Kahaluu A Deepwell	3	7.95	20.8	724	0.328	79.5	6.95	-5.2	-28.5
Kahaluu A Deepwell	4	7.89	20.4	503.9	0.22	105.7	9.2	-5.3	-28.2
Kahaluu C Deepwell	3	8.12	20.3	345.3	0.147	75.2	6.97	-5.3	-28.5
Kahaluu C Deepwell	4	7.81	20.3	346.5	0.15	89.2	7.95	-5.3	-28.4
Kahaluu C Deepwell	5	7.81	20.2	313.7	0.13	100.1	8.95	-5.3	-28.4
Kahaluu C Deepwell	6	7.85	20.2	334.50	0.16	110.30	9.98	-5.3	-28.4
Kahaluu C Deepwell	7	7.89	24.9	199	0.09	100.1	8.48	-5.2	-27.9
Kahaluu B Deepwell	3	7.95	20.5	980	0.456	93.7	8.33	-5.3	-28.4
Kahaluu B Deepwell	4	7.97	20.4	943	0.44	107.4	9.56	-5.3	-28.2
Kahaluu B Deepwell	5	7.57	20.2	937	0.43	113.9	10.21		
Kahaluu B Deepwell	6	7.85	20.2	1,082.00	0.53	142.80	12.32	-5.3	-28.4
Kahaluu B Deepwell	7	8.05	20.3	1152	0.57	148.4	13.11	-5.2	-28.1
Kahaluu D Deepwell	3	7.52	20.1	940	0.436	77	6.79	-5.3	-28.3
Kahaluu D Deepwell	4	8.25	20.2	1226	0.58	102.1	9	-5.2	-27.9
Kahaluu D Deepwell	5	7.2	20.2	925	0.43	98.5	8.54	-5.2	-28
Kahaluu Shaft	3	7.79	20.4	1149	0.543	83.1	7.71	-5.2	-27.4

Kahaluu Shaft	4	7.82	20.4	1291	0.62	88.7	7.83	-5.2	-27.4
Kahaluu Shaft	5	6.98	20.2	1499	0.72	91.3	8.13	-5.1	-27
Kahaluu Shaft	6	7.84	20.3	1,699.00	0.86	104.00	9.22	-5.1	-27.3
Kahaluu Shaft	7	7.97	20.3	1510	0.76	104.8	9.42	-5.1	-27.2
Halekii Deepwell	3	8.04	21.5	138.5	0.054	68.4	6.37	-5.9	-32.4
Halekii Deepwell	4	7.8	21.3	133.1	0.05	104.5	8.5	-5.9	-32.6
Halekii Deepwell	5	7.22	21.4	134.3	0.05	105.8	9.12	-5.8	-32.5
Halekii Deepwell	6	7.83	21.3	154.40	0.07	137.60	12.2	-5.9	-32.6
Halekii Deepwell	7	7.82	21.4	154.1	0.07	103	9.03	-5.9	-33
Keei D Deepwell	3	8.25	19.3	137.2	0.054	97.7	8.78	-5.4	-28.1
Keei D Deepwell	4	8.02	18.9	117.5	0.05	134.6	12.09	-5.4	-27.9
Keei D Deepwell	5	6.55	18.7	118.7	0.05	115.2	10.4	-5	-26.6
Keei D Deepwell	6	7.79	18.7	138.50	0.07	150.40	13.72	-5.3	-27.8
Keei D Deepwell	7	7.71	18.7	132.7	0.06	106.5	9.95	-5.3	-28
Keei A Deepwell	3	7.91	19.6	1528	0.740	76.2	6.66	-4.5	-21.5
Keei A Deepwell	4	7.68	20.2	1501	0.73	116	10.38	-4.5	-21.4
Keei A Deepwell	5	7.33	19.8	2119	1.06	94.7	8.56	-4.5	-21.7
Keei A Deepwell	6	7.41	19.6	1,946.00	0.99	100.40	10.03	-4.5	-21.4
Keei A Deepwell	7	7.85	19.6	1638	0.83	115.1	10.49	-4.4	-21.1
Keei B Deepwell	3	7.73	19.1	1183	0.560	79.1	7.12	-4.6	-22.7
Keei B Deepwell	5	7.12	19.2	1094	0.51	110.1	10.1		
Ocean End Member 21m	3							0.3	2.4
Ocean End Member 21m	6	8.05	27.7	61,240.00	41.1	120.50	7.58	0.4	2.8
Ocean End Member 21m	7	7.91	24.8	60613	40.7	102.8	6.76	0.3	2.6
Ocean End Member 674m	3							0.1	0.0

Ocean End Member 674m	6	7.5	6.3	61,591.00	40.6	18.80	1.78	0	-0.5
Ocean End Member 674m	7	7.54	6	61614	40.59	36.1	3.37	0	0
Ocean End Member 900m	3							0.0	-0.2
Ocean End Member 900m	6	7.29	4.94		34.62		2.45	-0.1	-0.5
Ocean End Member 900m	7	7.55	5.2	60858	35.76	58.7	5.55	0.1	0.2

Table B.2. Raw, individual dissolved ion data.

Raw (un-corrected) data for 43 groundwater and 3 ocean water sites during the study period of May 2017 to March 2019, organized by site from North (Waimea aquifer) to South (Kealakekua aquifer), followed by chronological sampling trip order. Sampling trip: 1 (05/2017), 2 (08/2017) 3 (11/2017), 4 (03/2018), 5 (08/2018), 6 (11/2018), 7 (03/2019). Fluoride (F^-), chloride (Cl^-), bromide (Br^-), sulfate (SO_4^{2-}), lithium (Li^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}) are reported as raw values in mg/L. Relative standard deviations are reported for the geochemical parameters.

Sample Name	Trip	Fluoride (mg/L)	Chloride (mg/L)	Bromide (mg/L)	Sulfate (mg/L)	Lithium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Magnesium (mg/L)	Calcium (mg/L)
Relative Standard Deviation		**4.94%**	**4.55%**	**4.70%**	**4.58%**	**1.86**	**2.68**	**2.44**	**3.38**	**5.9**
Parker Ranch Deepwell	3	0.09	8	0	3.3	0	12	3	7.5	10.7
Parker Ranch Deepwell	4	0.11	8	0	3	0	12	2	7.7	11.4
Parker Ranch Deepwell	5	0.07	7.3	0	3.1	0	11.3	2.7	7.1	10.9
Lalamilo C Deepwell	3	0.24	79	0.3	22.1	0	59	6	16.6	12.5
Lalamilo C Deepwell	4	0.38	82	0.4	23	0	57	6	18.4	14.9
Lalamilo C Deepwell	5	0.24	109.2	0.47	26.4	0	70.8	6.5	21.6	15.8
Lalamilo C Deepwell	6	0.24	110.2	0.46	27.4	0	70.8	6.44	21.23	15.26
Lalamilo A Deepwell	3	0.25	73	0.2	21.3	0	55	6	16.4	12.3
Lalamilo A Deepwell	4	0.35	76	0.4	22	0	54	5	18.4	14.8
Lalamilo A Deepwell	6	0.26	68.8	0.28	20.8	0	48.2	5.23	18.81	14.46
Lalamilo B Deepwell	3	0.26	66	0.2	21	0	51	5	16.2	12.7
Lalamilo B Deepwell	4	0.29	82	0.3	23	0	57	5	19	15.7
Lalamilo B Deepwell	5	0.25	80.7	0.34	23.2	0	56.2	5.7	20	15.5
Lalamilo B Deepwell	6	0.24	76.9	0.29	22.8	0	53.3	5.45	19.34	14.86
Lalamilo B Deepwell	7	0.23	69.3	0.27	21.63	0.002	54.5	5.68	19.23	14.53

Parker #2 Deepwell	3	0.35	112	0.6	27.7	0	75	6	22.2	16.8
Parker #2 Deepwell	4	0.39	94	0.4	26	0	65	6	21.5	17
Parker #2 Deepwell	5	0.27	118.9	0.58	29.6	0	76.8	6.4	23.5	16.4
Parker #2 Deepwell	6	0.28	117.9	0.5	30.2	0	76.4	6.31	22.95	15.88
Parker #2 Deepwell	7	0.23	110.5	0.42	27.67	0.002	77.2	6.38	24.31	16.7
Parker #3 Deepwell	4	0.4	48	0.2	19	0	42	5	16.3	13.7
Parker #3 Deepwell	5	0.25	48.5	0.22	19.2	0	41.9	4.8	15.7	11.8
Parker #3 Deepwell	6	0.27	50.9	0.25	20.4	0	42.6	4.84	16.31	12.48
Parker #3 Deepwell	7	0.24	50.2	0.26	19.44	0.002	45.5	5.13	17.93	13.58
Parker #4 Deepwell	3	0.32	147	0.4	33.3	0	97	7	25.1	18.8
Parker #4 Deepwell	4	0.48	97	0	26	0	70	6	20.8	16
Parker #4 Deepwell	5	0.26	124.4	0.55	30.9	0	83.2	6.7	23	15.9
Parker #4 Deepwell	6	0.28	122.6	0.5	31.6	0	82.4	6.67	22.47	15.29
Parker #4 Deepwell	7	0.25	147.3	0.5	33.37	0.003	99	7.53	26.25	17.19
Waikoloa 1	6	0.26	26.7	0.14	15.8	0	31.1	4.01	13.9	10.33
DW-7	3	0.33	26	0.1	16.4	0	33	4	12.7	9.5
DW-7	4	0.42	27	0	16	0	31	4	14.6	11.7
DW-7	7	0.24	26.4	0.11	16.55	0.002	33.6	4.37	14.55	10.4
Parker 5	3	0.33	28	0.1	16.6	0	34	4	12.9	9.9
Waikoloa 1	4	0.37	29	0	17	0	33	4	14.9	11.9
Parker 4	3	0.3	30	0.1	17.4	0	36	4	13.1	9.7
Parker 4	4	0.55	28	0	17	0	33	4	15.1	12
Parker 4	5	0.26	30.9	0.16	17.5	0	34.8	4.3	14.5	13.6
Parker 4	6	0.27	31.5	0.15	17.9	0	34.3	4.2	14.93	10.89
Parker 4	7	0.25	29.2	0.11	17.47	0.002	36.6	4.48	14.48	10.22

Waikoloa 3	3	0.4	68	0.3	30.6	0	66	6	18.7	13.4
Waikoloa 3	5	0.33	72.5	0.33	31.6	0	63.5	6.1	19.6	12.7
Waikoloa 3	7	0.33	54.5	0.22	28.77	0.004	61.4	6.02	19.06	12.12
Waikoloa 2	3	0.33	109	0.4	37	0	87	7	22.3	13.8
Waikoloa 2	4	0.46	116	0.3	38	0	87	7	27.1	17.9
Waikoloa 2	6	0.36	127.9	0.53	39.8	0	90	7.45	28.53	16.56
Waikoloa DW-6	3	0.35	127	0.4	40.4	0.01	100	8	23.4	14.6
Waikoloa DW-6	4	0.8	128	0.5	41	0	97	8	27.2	17.9
Waikoloa DW-6	5	0.35	128.2	0.59	41.6	0	97.4	8.2	25.6	15.1
Waikoloa DW-6	6	0.37	132.1	0.61	41.5	0	96.8	8.05	27.46	15.38
Waikoloa DW-6	7	0.32	129.1	0.44	40.21	0.004	102.8	8.46	27.5	15.68
Resort Irr 2	4	0.52	679	2.5	132	0.01	398	18	64.6	28.6
Waikoloa Irr 3	3	0.56	565	2.1	114.3	0.01	345	16	49.2	22.6
Waikoloa Irr 3	4	0.75	565	2.1	117	0.01	335	15	56.7	25.1
Waikoloa Irr 3	5	0.64	577.3	2.19	120.3	0.01	340.5	15.9	59.7	21.6
Waikoloa Irr 3	6	0.69	568.4	2.33	114.6	0.01	340.6	15.51	65.09	19.18
Waikoloa Irr 3	7	0.59	574.8	2.08	116.86	0.005	364.1	16.42	59.14	20.87
Resort 1	4	0.42	737	3	137	0.01	433	19	66	28.5
Resort 1	5	0.66	761.5	2.98	140.9	0.01	444.5	19.8	77.3	24.1
Resort 1	6	0.69	724.9	2.62	136.3	0.01	438.5	19.12	74.22	21.08
Resort 1	7	0.6	724.3	2.56	133.6	0.01	464.4	20.1	72.1	23.6
Nursery	4	0.84	1221	4.5	212	0.01	704	30	102.5	43.3
Nursery	5	0.64	1015.5	4.71	179.1	0.01	582.4	25	93.6	29.2
Nursery	6	0.58	986	4.1	171.6	0.01	585.4	24.78	96.42	25.37
Nursery	7	0.64	986.8	3.49	168.8	0.01	617.3	25.7	97.7	28

Fifty-One FT STP	3	0.64	974	2.8	170.2	0.01	583	25	79.1	34.3
Fifty-One FT STP	4	0.86	1210	4.4	211	0.01	698	30	101.4	42.3
West Hawaii Landfill	5	0.83	1042.6	3.96	187	0.01	595.7	27.2	97.5	30.1
West Hawaii Landfill	6	0.8	989.3	3.89	176.3	0.01	582.9	26.17	98.51	25.54
West Hawaii Landfill	7	0.79	991.1	3.9	173.7	0.01	630.4	27.9	102.3	30.2
Makani Golf Course	6	0.67	68.2	0.37	63.4	0.01	63.9	4.16	14.73	21.42
Makani Golf Course	7	0.63	63	0.23	58.32	0.006	67.8	4.33	14.26	19.84
Puu Lani	2	0.77	39	0.1	48.9	0.01	64	4	5.1	9.2
Puu Lani	4	0.89	40	0	48	0.01	53	4	11.1	19.1
Puu Lani	5	0.8	41.4	0.18	48.8	0.01	53.6	3.7	10.4	17
Puu Lani	6	0.85	42.4	0.19	50.1	0.01	53.5	3.67	10.53	17.39
Puu Lani	7	0.81	41	0.2	48.67	0.006	57.1	3.86	11.73	18.95
Puu Waawaa	2	0.61	21	0	25.4	0.01	40	3	4.7	7.1
Puu Waawaa	4	0.73	21	0.1	25	0.01	34	3	7.8	12
Puu Waawaa	5	0.64	21.6	0.11	26	0.01	34.4	2.8	7.5	11
Puu Waawaa	6	0.67	21.8	0.12	27.5	0.01	34.5	2.84	8.6	13.13
Puu Waawaa	7	0.63	20.9	0.09	25.09	0.006	35.9	2.92	7.9	11.41
Huehue Ranch 5	3	1.54	139	0.4	314.4	0.05	183	10	138.4	48.3
Huehue Ranch 5	5	1.88	84.5	0.37	293.3	0.05	165.4	7.7	124.8	38.7
Huehue Ranch 5	7	1.46	73	0	337.3	0.03	130.3	9.4	179.9	53.1
Huehue Ranch 3	3	1.36	171	0	240.2	0.02	98	9	148.6	42.3
Huehue Ranch 3	4	2.23	165	0.4	242	0.02	94	8	152.8	44.8
Huehue Ranch 3	7	1.36	203.4	0.89	246.2	0.02	107.7	10.1	169.8	43.8
Huehue Ranch 4	5	0.71	161.4	0.79	104.3	0.02	115.6	12.9	125.5	44.8
Huehue Ranch 4	6	0.75	163.4	0.48	103.9	0.02	112.9	12.43	121.05	41.84

Huehue Ranch 4	7	0.4	86	0.36	61.96	0.008	72.5	8	73.72	25.78
Huehue Ranch 2	3	0.65	177	0	61.9	0.01	107	11	92.6	43.4
Huehue Ranch 2	4	0.87	200	1.1	69	0.01	114	11	100	47.4
Huehue Ranch 2	6	0.72	233.8	0.96	73.8	0.01	122.8	12.09	107.94	45.98
Kau (Makalei) Deepwell	5	0.74	206.1	1.07	59.7	0.01	115.4	12.9	72.8	40.5
Kau (Makalei) Deepwell	6	0.77	271.5	0.79	69.6	0.01	144	13.93	79.26	44.29
Kalaoa Deepwell	1	0.37	9.2	0	27.6	0	31	5.3	10.5	9.3
Kalaoa Deepwell	3	0.5	10	0	28.3	0	32	5	11	11.9
Kalaoa Deepwell	4	0.57	10	0	28	0	31	5	11.6	12.8
Kalaoa Deepwell	5	0.4	9.8	0.06	29	0	31.5	5.3	11.2	12
Kalaoa Deepwell	6	0.43	9.8	0	31.1	0	31.4	5.24	12.67	13.86
Kalaoa Deepwell	7	0.39	9.3	0.03	28.76	0.001	33	5.54	12.21	12.75
Palani Ranch Deepwell	3	0.43	8	0	22.3	0	27	4	8.4	11
Palani Ranch Deepwell	4	0.55	9	0	22	0	26	4	8.8	11.9
Honokohau Deepwell	1	0.39	7.8	0	19.7	0	25	4.1	7.2	8.6
Honokohau Deepwell	7	0.39	7.8	0	20.34	0.001	26.4	4.23	8.31	11.6
Queen Liliuokalani Trust (Keahuolu) Deepwell	1	0.23	6.5	0	9.9	0	16	3.3	5.3	7.8
Queen Liliuokalani Trust (Keahuolu) Deepwell	4	0.4	7	0	10	0	16	3	6	10.7
Queen Liliuokalani Trust (Keahuolu) Deepwell	5	0.24	6.4	0	10.5	0	16.7	3.3	6	10.1
Queen Liliuokalani Trust (Keahuolu) Deepwell	6	0.24	6.5	0.04	10.6	0	16.8	3.26	5.91	10.13
Queen Liliuokalani Trust (Keahuolu) Deepwell	7	0.22	6	0	10.05	0.001	17.4	3.43	6.51	11.11
Keopu Deepwell	4	0.23	6	0	9	0	15	3	6.3	10.7
Keopu Deepwell	5	0.22	6	0.05	9.9	0	15.9	3.5	6	9.9
Keopu Deepwell	6	0.23	6.6	0.03	10.6	0	16.3	3.56	6.1	9.84
Keopu Deepwell	7	0.21	6.2	0	10.04	0.001	17.1	3.75	6.65	10.75

Holualoa Deepwell	1	0.17	236	0.72	36.6	0	133	8	19	15.8
Holualoa Deepwell	3	0.11	221	0.9	36.5	0	131	8	22.5	25.3
Holualoa Deepwell	4	0.24	224	0.7	38	0	129	7	23.9	26.7
Holualoa Deepwell	5	0.18	224	1.03	35.4	0	126.3	7.7	26.6	28.8
Holualoa Deepwell	6	0.15	227.2	0.74	35.8	0	124.8	7.6	26.99	27.19
Holualoa Deepwell	7	0.14	218.2	0.64	36.39	0	132.1	7.6	24.19	23.23
Kahaluu A Deepwell	3	0.18	166	0.4	30.8	0	98	5	17.3	25
Kahaluu A Deepwell	4	0.38	110	0.4	24	0	66	4	11.8	17.9
Kahaluu C Deepwell	3	0.19	58	0	16.4	0	38	3	9.7	17.8
Kahaluu C Deepwell	4	0.32	65	0.2	18	0	43	3	8.3	13.3
Kahaluu C Deepwell	5	0.24	56.4	0.24	17.3	0	39.7	3.1	7.7	12.1
Kahaluu C Deepwell	6	0.23	54	0.24	16.6	0	36	3.05	8.52	14.22
Kahaluu C Deepwell	7	0.21	10.3	0	10.44	0.001	19.7	3.69	6.91	11.24
Kahaluu B Deepwell	3	0.23	247	0.9	42.1	0	144	6	21.2	26
Kahaluu B Deepwell	4	0.37	276	0.9	47	0	156	6	23.9	27.1
Kahaluu B Deepwell	5									
Kahaluu B Deepwell	6	0.25	243.9	1.07	40.2	0	134	5.5	23.89	26.29
Kahaluu B Deepwell	7	0.2	256.6	0.81	43.78	0.002	152.3	5.92	24.2	26.2
Kahaluu D Deepwell	3	0.19	242	0.9	41.8	0	144	6	20.6	23.3
Kahaluu D Deepwell	4	0.12	271	1.1	46	0	156	6	27.1	31.5
Kahaluu D Deepwell	5	0.24	238.6	1.16	40.4	0	136.4	5.8	23.8	25.1
Kahaluu Shaft	3	0.13	292	0.6	47.5	0	161	7	29.4	38.4
Kahaluu Shaft	4	0.4	398	1.4	62	0	212	8	36.2	40.1
Kahaluu Shaft	5	0.2	395	1.5	61.4	0	209.1	8.6	39.9	44.8
Kahaluu Shaft	6	0.21	389	1.59	61.8	0	206.8	8.48	37.52	40.39

Kahaluu Shaft	7	0.19	321.2	1.11	51.72	0.002	182.4	7.88	30.45	32.52
Halekii Deepwell	3	0.25	4	0	14.4	0	17	2	3.4	8.2
Halekii Deepwell	4	0.36	5	0	15	0	16	2	3.7	9.1
Halekii Deepwell	5	0.25	4.2	0.03	15	0	16.8	2.1	3.7	8.8
Halekii Deepwell	6	0.26	6.2	0	15.8	0	17.6	2.14	3.69	8.46
Halekii Deepwell	7	0.24	4.6	0	14.47	0.001	17.8	2.19	3.72	8.61
Keei D Deepwell	3	0.24	4	0	10.4	0	13	2	3.6	8
Keei D Deepwell	4	0.39	4	0	11	0	13	2	3.8	8.5
Keei D Deepwell	5	0.23	4.1	0	10.5	0	12.9	1.7	3.6	7.8
Keei D Deepwell	6	0.23	4.7	0	11.1	0	13.3	1.73	3.84	8.19
Keei D Deepwell	7	0.22	3.8	0	10.32	0.001	13.6	1.79	4.19	8.9
Keei A Deepwell	3	0.14	398	1.6	63.1	0	233	9	37.8	24.1
Keei A Deepwell	4	0.19	401	1	66	0	226	9	41.7	26
Keei A Deepwell	5	0.22	505.9	2	78.2	0	281	10.9	54.2	29.4
Keei A Deepwell	6	0.22	429.6	1.54	68.1	0	240	9.41	43.09	19.78
Keei A Deepwell	7	0.21	368.6	1.29	60.23	0.003	219.1	8.67	35.94	19.33
Keei B Deepwell	3	0.13	245	1.5	39.3	0	147	6	23.8	16.5
Keei B Deepwell	5									
Ocean End Member 21m	3	0	19,484.00	70	2751.7	0.17	11,081	389	1557.1	493.6
Ocean End Member 21m	6	0	19,208.40	75.63	2736	0.14	11117.9	377.51	1597.97	314.96
Ocean End Member 21m	7	0	19,722.00	77.58	2749.6	0.13	11570	386.8	1617.8	294.8
Ocean End Member 674m	3	0	19444	75.7	2769.6	0.18	11,035	387	1507.9	443.4
Ocean End Member 674m	6	0	19981.3	75.96	2832.7	0.13	10955.4	375.14	1582.19	319.14
Ocean End Member 674m	7	0	19747	61.76	2747.5	0.12	11569.8	387.2	1623.8	298.4
Ocean End Member 900m	3	0	20055	64.6	2865.3	0.19	11,385	398	1552.9	453.5

Ocean End Member 900m	6	0	20326.9	71.25	2885.2	0.12	11116.4	381.5	1495.72	278.64
Ocean End Member 900m	7	0	19917.7	81.78	2759	0.12	11678.9	391.1	1641.4	300.7

Table B.3. Raw, individual nutrient data.

Raw (un-corrected) data for 43 groundwater and 3 ocean water sites during the study period of May 2017 to March 2019, organized by site from North (Waimea aquifer) to South (Kealakekua aquifer), followed by chronological sampling trip order. Sampling trip: 1 (05/2017), 2 (08/2017) 3 (11/2017), 4 (03/2018), 5 (08/2018), 6 (11/2018), 7 (03/2019). Silica (SiO_2), phosphate (PO_4^{3-}), nitrate + nitrite ($NO_3^- + NO_2^-$), ammonia + ammonium ($NH_3 + NH_4^+$), total phosphorus (TP), and total nitrogen (TN) are reported as raw values in µg/L. Alkalinity is reported in mg/L. Relative standard deviations are reported for the geochemical parameters.

Sample Name	Trip	Si (µg/L)	PO4 (µg/L)	NO3 & NO2 (µg/L)	NH3 & NH4 (µg/L)	TP (µg/L)	TN (µg/L)	Alkalinity (mg/L)
Relative Standard Deviation		**1.61**	**5.04**	**12.55**	**12.19**			
Parker Ranch Deepwell	3	23,221.00	104.4	284	2.5	336.4	1,262.40	64
Parker Ranch Deepwell	4	23,973.60	111.8	295.4	6.5	124.6	1,094.70	65
Parker Ranch Deepwell	5	24,600.40	87.1	175.3	7.7	81.9	728.4	61
Lalamilo C Deepwell	3	26,768.00	100	1,276.90	1.9	111.6	1,885.20	83
Lalamilo C Deepwell	4	26,695.20	100	1,223.10	4.8	74.3	1,193.50	80
Lalamilo C Deepwell	5	26,956.40	83.4	1,237.30	3.2	82.7	1,632.60	80
Lalamilo C Deepwell	6	26,172.00	73.1	1,257.60	-0.4	72	1,970.40	80
Lalamilo A Deepwell	3	26,051.00	99.2	1,255.90	2.1	100.8	2,026.40	84
Lalamilo A Deepwell	4	27,474.80	87.2	1,266.20	4.4	87.2	1,262.80	82
Lalamilo A Deepwell	6	25,909.00	66.2	1,276.50	2.4	90.8	1,935.60	80
Lalamilo B Deepwell	3	26,410.00	95.8	1,287.10	2.7	98.8	1,882.80	82
Lalamilo B Deepwell	4	26,856.00	91.3	1,288.10	4.3	37.8	959.2	82
Lalamilo B Deepwell	5	26,955.60	81.1	1,242.90	-4.4	93.7	1,717.60	80
Lalamilo B Deepwell	6	26,195.00	73.6	1,343.80	-0.3	73.6	1,975.20	81
Lalamilo B Deepwell	7	28,079.60	82.5	1,388.20	1.3	90.1	3,652.00	85

Parker #2 Deepwell	3	26,943.00	97.5	1,280.50	2.3	86	1,952.00	84
Parker #2 Deepwell	4	27,508.80	96.8	1,269.50	6.8	78.8	1,282.60	84
Parker #2 Deepwell	5	27,302.80	80.4	1,240.80	5.6	74.5	1,657.20	84
Parker #2 Deepwell	6	26,325.00	71.1	1,308.70	0.9	62.8	1,915.20	84
Parker #2 Deepwell	7	28,246.40	81.9	1,318.30	1.5	98.8	3,504.80	88
Parker #3 Deepwell	4	27,100.80	85	1,272.10	4.4	88.4	1,612.50	84
Parker #3 Deepwell	5	27,203.60	89.8	1,265.70	1.2	79.8	1,647.00	82
Parker #3 Deepwell	6	26,830.00	80	1,358.20	0.1	73.6	2,176.80	82
Parker #3 Deepwell	7	28,698.80	86.2	1,402.50	1.6	100.2	3,746.00	88
Parker #4 Deepwell	3	26,541.00	86.7	1,331.00	2.6	138.8	2,152.00	86
Parker #4 Deepwell	4	26,774.40	87.1	1,295.60	5.3	82.9	1,311.10	84
Parker #4 Deepwell	5	27,525.60	80.6	1,309.90	5.4	76.5	1,757.00	84
Parker #4 Deepwell	6	26,572.00	71.8	1,335.50	1.4	69.6	1,851.60	82
Parker #4 Deepwell	7	28,476.80	80.4	1,365.30	1.7	89.2	3,550.40	89
Waikoloa 1	6	26,817.00	71.2	1,290.00	2	70.8	1,841.60	84
DW-7	3	27,156.00	86	1,268.60	2.4	82.8	1,868.80	84
DW-7	4	26,194.00	90.6	1,222.00	4.5	92.9	1,618.90	83
DW-7	7	28,670.00	77.5	1,467.60	0.9	97.3	3,556.00	87
Parker 5	3	24,601.00	80.9	1,293.50	2.9	75.6	1,911.20	82
Waikoloa 1	4	27,014.00	88.5	1,273.50	4.1	96.7	1,544.00	85
Parker 4	3	26,547.00	89.1	1,365.90	3.4	90	2,034.00	84
Parker 4	4	27,686.40	97.1	1,375.60	4.1	82.5	1,401.70	86
Parker 4	5	31,313.20	79.7	1,427.10	0.2	71.7	1,767.10	82
Parker 4	6	26,713.00	71.4	1,383.20	2.3	73.6	2,119.60	84
Parker 4	7	28,572.40	75.6	1,364.10	1.7	80.6	3,432.40	86

Waikoloa 3	3	26,892.00	87	1,330.50	2.8	85.6	2,027.60	103
Waikoloa 3	5	28,637.60	75.1	1,321.60	0.7	69.8	1,765.90	101
Waikoloa 3	7	30,190.00	81.4	1,498.30	0.9	87.4	3,562.80	106
Waikoloa 2	3	26,715.00	86.2	1,241.20	3.5	82	1,890.00	104
Waikoloa 2	4	27,802.80	87	1,223.20	5.5	96.7	1,500.40	103
Waikoloa 2	6	27,787.00	68.6	1,303.50	2.1	58	1,843.60	102
Waikoloa DW-6	3	28,370.00	76.9	1,079.60	2.7	82	1,730.80	112
Waikoloa DW-6	4	26,864.00	79.7	973.9	4.6	101.5	1,625.00	111
Waikoloa DW-6	5	29,508.00	70.7	1,067.10	-0.4	64.4	1,514.00	108
Waikoloa DW-6	6	27,598.00	62.8	1,139.60	10.3	58	1,621.60	110
Waikoloa DW-6	7	29,825.20	71.4	1,149.40	1.3	72.6	3,298.00	114
Resort Irr 2	4	23,566.00	58	517	15.9	75.1	1,068.80	64
Waikoloa Irr 3	3	23,367.00	68.6	614.9	2.8	107.2	1,356.40	68
Waikoloa Irr 3	4	24,050.40	66.2	598.4	4.2	115	1,230.60	66
Waikoloa Irr 3	5	27,136.80	61.6	636.5	2.2	52.4	1,246.60	64
Waikoloa Irr 3	6	23,637.00	52.1	663.7	3.4	42.4	1,210.40	66
Waikoloa Irr 3	7	25,484.80	57.8	691.9	-1.6	62.8	2,731.20	70
Resort 1	4	23,912.00	71.7	616.7	6.8	67.8	962.5	66
Resort 1	5	25,005.60	57.8	620	-1.1	56.1	1,397.10	64
Resort 1	6	23,447.00	56	683.4	1.3	46	1,276.00	66
Resort 1	7	25,437.20	60.3	695.1	-0.5	76.4	2,968.40	70
Nursery	4	23,956.40	89.7	698	4.4	38.9	980.8	70
Nursery	5	24,768.40	66.7	744.6	2.9	68.5	1,360.40	68
Nursery	6	23,303.00	72.5	823.6	0.6	72.8	1,445.60	66
Nursery	7	24,882.00	86.5	746.1	0.8	95.6	3,174.00	68

Fifty-One FT STP	3	22,393.00	86.9	684	2.4	89.2	1,467.20	69
Fifty-One FT STP	4	23,453.60	82	664	5.5	266.5	1,224.50	68
West Hawaii Landfill	5	22,882.80	74.8	873	-3.8	68.9	1,314.20	79
West Hawaii Landfill	6	22,249.00	69.1	964.6	1.6	69.2	1,700.80	70
West Hawaii Landfill	7	23,842.00	73.6	980.4	1.4	81.9	3,269.60	74
Makani Golf Course	6	19,947.00	46.8	904.6	-7.4	37.2	1,544.40	76
Makani Golf Course	7	21,303.20	46.9	874.4	2	67.1	2,848.80	78
Puu Lani	2							
Puu Lani	4	20,255.20	69.2	1,217.30	4.1	43.9	1,035.10	80
Puu Lani	5	20,621.20	69.5	1,159.80	3.7	63.1	1,585.40	76
Puu Lani	6	19,891.00	69.7	1,231.30	-9.1	60.4	1,915.60	78
Puu Lani	7	21,230.40	66.2	1,294.30	1.4	80.7	3,371.60	85
Puu Waawaa	2							
Puu Waawaa	4	21,197.60	48.4	490.8	16.4	73.9	786.2	69
Puu Waawaa	5	21,330.00	33.1	476.1	2.1	33.2	983.3	67
Puu Waawaa	6	20,674.00	34.7	571.2	3.1	34.8	1,159.60	68
Puu Waawaa	7	22,156.00	28.2	536	1.9	151.8	2,754.40	72
Huehue Ranch 5	3	28,729.00	226	1,038.40	2.7	229.6	1,670.00	486
Huehue Ranch 5	5	32,289.60	177.5	1,084.70	2.1	158.6	1,651.60	448
Huehue Ranch 5	7	33,447.20	227.8	1,252.70	0.7	227.2	3,700.40	576
Huehue Ranch 3	3	27,427.00	357.2	923	3.4	305.2	1,402.40	365
Huehue Ranch 3	4	30,126.00	360.4	933.2	4.2	249.8	1,177.90	360
Huehue Ranch 3	7	31,316.80	334.8	1,016.10	1.1	277.5	2,869.20	381
Huehue Ranch 4	5	43,990.00	339.3	581.3	-0.3	283.7	1,163.50	454
Huehue Ranch 4	6	39,379.00	329.3	722.9	-6.7	280	1,415.20	454

Huehue Ranch 4	7	44,090.80	309.1	647.3	1	264.4	2,846.00	484
Huehue Ranch 2	3	32,108.00	306.6	766.5	2.9	277.6	1,315.60	360
Huehue Ranch 2	4	30,520.00	278.3	722.1	4.4	317.1	1,425.60	358
Huehue Ranch 2	6	33,521.00	270.8	865.8	-4.8	254.4	1,436.00	346
Kau (Makalei) Deepwell	5	35,015.20	225	577	0.7	197.4	1,090.30	246
Kau (Makalei) Deepwell	6	32,715.00	196	678.7	4.4	203.2	1,164.00	244
Kalaoa Deepwell	1							
Kalaoa Deepwell	3	24,440.00	140	955.2	2	129.6	1,628.00	95
Kalaoa Deepwell	4	24,197.60	134.4	5,728.80	17	128	4,616.50	90
Kalaoa Deepwell	5	24,879.60	125	961.7	3.9	116.8	1,464.30	90
Kalaoa Deepwell	6	24,032.00	104.4	842.3	4.9	117.6	1,603.60	93
Kalaoa Deepwell	7	25,601.60	125.2	984	0.7	126.7	3,110.00	98
Palani Ranch Deepwell	3	22,940.00	138.6	998.1	2.5	154	1,545.60	78
Palani Ranch Deepwell	4	21,896.00	136.1	981.6	6.8	125.7	1,313.10	74
Honokohau Deepwell	1							
Honokohau Deepwell	7	23,803.60	120.6	1,123.50	0.7	125.8	3,205.60	76
Queen Liliuokalani Trust (Keahuolu) Deepwell	1							
Queen Liliuokalani Trust (Keahuolu) Deepwell	4	19,722.40	125.3	1,177.00	6.1	126.5	1,594.60	56
Queen Liliuokalani Trust (Keahuolu) Deepwell	5	21,672.40	125.2	1,214.40	5.6	118.1	1,638.10	56
Queen Liliuokalani Trust (Keahuolu) Deepwell	6	21,183.00	115.7	1,263.30	-0.6	116.4	1,829.60	56
Queen Liliuokalani Trust (Keahuolu) Deepwell	7	22,074.00	120.2	1,207.20	4	123.4	3,245.60	58
Keopu Deepwell	4	20,357.60	129.1	1,030.40	6.1	125.9	1,351.00	56
Keopu Deepwell	5	21,710.00	118.2	1,064.10	3	115.1	1,513.20	54
Keopu Deepwell	6	21,088.00	118.2	1,134.20	-1.4	115.2	1,599.20	62
Keopu Deepwell	7	22,296.40	120.8	1,189.20	1.4	131.2	3,258.80	58

Holualoa Deepwell	1							
Holualoa Deepwell	3	19,815.00	130.8	1,044.70	2.2	129.6	1,488.80	54
Holualoa Deepwell	4	19,518.00	127.4	1,088.00	4.8	120	1,424.70	54
Holualoa Deepwell	5	20,752.80	118.4	1,112.00	5.1	104.4	1,505.50	52
Holualoa Deepwell	6	20,028.00	102.5	1,474.40	27.2	102.8	2,208.80	53
Holualoa Deepwell	7	21,184.40	115.9	1,179.30	1.1	120	3,336.80	57
Kahaluu A Deepwell	3	21,625.00	154.6	1,156.60	2.8	154	1,953.20	43
Kahaluu A Deepwell	4	20,308.40	147.2	8,281.60	54.2	132	5,810.30	42
Kahaluu C Deepwell	3	21,743.00	151.9	1,199.40	2.3	156	1,633.60	42
Kahaluu C Deepwell	4	21,361.60	151.8	1,231.50	2.6	134.4	1,543.60	42
Kahaluu C Deepwell	5	22,158.80	139.7	1,167.90	5.7	134.1	1,524.10	40
Kahaluu C Deepwell	6	21,420.00	135.3	1,293.20	1.7	124.4	1,856.00	42
Kahaluu C Deepwell	7	22,327.60	122	1,219.30	1.2	130.2	3,204.00	63
Kahaluu B Deepwell	3	20,863.00	158	1,145.20	4.2	148	2,034.80	43
Kahaluu B Deepwell	4	20,802.40	145.4	1,144.90	3.4	133.8	1,396.00	42
Kahaluu B Deepwell	5							
Kahaluu B Deepwell	6	21,212.00	135.7	1,209.20	-1.1	135.2	2,004.00	41
Kahaluu B Deepwell	7	22,396.00	138.7	1,246.20	2	133.2	3,289.20	44
Kahaluu D Deepwell	3	21,426.00	142	1,144.70	2.9	143.6	1,659.60	42
Kahaluu D Deepwell	4	20,505.60	155.6	1,141.30	4.7	146.2	1,593.30	42
Kahaluu D Deepwell	5	23,130.80	148.9	1,202.00	-1	133.2	1,612.00	41
Kahaluu Shaft	3	21,663.00	148	1,230.70	2.8	126.8	1,862.40	42
Kahaluu Shaft	4	20,996.00	144.6	1,221.50	5.3	140.7	1,558.00	42
Kahaluu Shaft	5	21,666.80	129.6	1,227.40	6.5	125.5	1,662.60	42
Kahaluu Shaft	6	21,364.00	126.9	1,278.40	-0.3	116.4	1,918.00	42

Kahaluu Shaft	7	22,374.80	132.7	1,369.10	1.5	133.2	3,443.20	44
Halekii Deepwell	3	22,176.00	146.9	1,018.10	2.1	158.8	1,660.80	42
Halekii Deepwell	4	18,312.00	127.6	933.8	3.8	130.9	1,297.40	40
Halekii Deepwell	5	22,475.60	138.5	1,035.20	-1.8	126.5	1,478.10	39
Halekii Deepwell	6	21,590.00	111	1,024.10	7.2	127.2	1,634.80	42
Halekii Deepwell	7	23,361.20	129.7	1,010.80	0.2	130.8	3,190.40	42
Keei D Deepwell	3	21,455.00	157	704.4	2.1	156	1,340.80	40
Keei D Deepwell	4	20,102.40	146.7	696.2	2.7	133.8	994	38
Keei D Deepwell	5	21,507.60	142.8	749.5	-0.3	135.9	1,231.40	37
Keei D Deepwell	6	20,857.00	135.6	725.7	4.6	129.6	1,280.40	38
Keei D Deepwell	7	22,222.00	140	773.7	0.1	156.3	2,788.00	39
Keei A Deepwell	3	21,854.00	137.8	1,690.70	2.6	156	2,429.60	37
Keei A Deepwell	4	21,985.20	126.2	1,761.00	3.5	125.3	1,966.50	38
Keei A Deepwell	5	22,096.00	120.1	1,598.90	-0.8	117.8	1,981.60	36
Keei A Deepwell	6	21,594.00	118	1,773.90	1.8	109.6	2,395.20	36
Keei A Deepwell	7	23,635.60	124.6	2,141.20	1	127.6	3,810.80	38
Keei B Deepwell	3	21,954.00	154.4	1,093.10	1.8	126	1,768.40	38
Keei B Deepwell	5	22,198.00	139.1	1,169.60	-0.1	132.7	1,645.00	37
Ocean End Member 21m	3							
Ocean End Member 21m	6	23	1.6	0.8	3.3	11.2	78	114
Ocean End Member 21m	7	82	69.8	14.7	-0.8	101.2	28	120
Ocean End Member 674m	3							
Ocean End Member 674m	6	2,218.00	84	544	6.8	86	572	116
Ocean End Member 674m	7	2,627.90	120.1	612.2	9.9	104.9	614	124
Ocean End Member 900m	3							

Ocean End Member 900m	6	2,818.00	86	568	0.5	90	580	120
Ocean End Member 900m	7	3,183.80	120.6	642.6	-5.5	128.6	647	126

Table B.4. Raw, individual trace metal data.

Raw (un-corrected) data for 43 groundwater and 3 ocean water sites during the study period of May 2017 to March 2019, organized by site from North (Waimea aquifer) to South (Kealakekua aquifer), followed by chronological sampling trip order. Sampling trip: 1 (05/2017), 2 (08/2017) 3 (11/2017), 4 (03/2018), 5 (08/2018), 6 (11/2018), 7 (03/2019). Arsenic (As), boron (B), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), rhenium (Re), antimony (Sb), selenium (Se), strontium (Sr), uranium (U), vanadium (V), and zinc (Zn) are reported in raw values in parts per million (ppm). Relative standard deviations are reported for the geochemical parameters.

Sample Name	Trip	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	Re (ppm)	Sb (ppm)	Se (ppm)	Sr (ppm)	U (ppm)	V (ppm)	Zn (ppm)
Relative Standard Deviation		**2.91%**	**3.42**	**3.19**	**3.32%**	**2.34%**	**2.74%**	**2.42%**	**3.01%**	**3.37%**	**3.16%**	**2.35%**	**3.00%**	**4.12%**	**2.33%**	**2.73%**	**2.41%**	**3.41%**	**5.12%**	**3.44%**	**2.44%**
Parker Ranch Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.108	0.000	0.007	0.000
Parker Ranch Deepwell	4	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.100	0.000	0.000	0.021
Parker Ranch Deepwell	5	0.000	0.000	0.012	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.098		0.015	0.058
Lalamilo C Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.074	0.000	0.046	0.000
Lalamilo C Deepwell	4	0.000	0.000	0.007	0.000	0.000	0.000	0.004		0.000	0.000	0.004	0.000	0.015	0.000	0.000	0.000	0.074	0.000	0.053	0.009
Lalamilo C Deepwell	5	0.005	0.000	0.012	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.081		0.048	0.002
Lalamilo C Deepwell	6	0.000	0.030	0.005	0.000	0.000	0.000	0.004	0.000	0.000	0.001	0.004	0.000	0.003	0.005	0.000	0.000	0.084	0.000	0.051	0.003
Lalamilo A Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.070	0.000	0.046	0.000
Lalamilo A Deepwell	4	0.000	0.000	0.006	0.000	0.000	0.000	0.004	0.002	0.006	0.000	0.004	0.000	0.014	0.000	0.000	0.000	0.071	0.000	0.050	0.012
Lalamilo A Deepwell	6	0.000	0.029	0.005	0.000	0.000	0.000	0.003	0.002	0.006	0.001	0.004	0.000	0.002	0.004	0.000	0.000	0.064	0.000	0.046	0.071
Lalamilo B Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.071	0.000	0.046	0.000
Lalamilo B Deepwell	4	0.000	0.000	0.006	0.000	0.000	0.000	0.004		0.000	0.000	0.004	0.000	0.014	0.000	0.000	0.000	0.078	0.000	0.053	0.003
Lalamilo B Deepwell	5	0.005	0.000	0.011	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.070		0.049	0.002
Lalamilo B Deepwell	6	0.000	0.032	0.004	0.000	0.000	0.000	0.004	0.003	0.000	0.000	0.004	0.000	0.003	0.003	0.000	0.000	0.069	0.044	0.051	0.002
Lalamilo B Deepwell	7	0.002	0.026	0.003	0.000	0.000	0.000	0.004	0.002	0.002	0.000	0.004	0.000	0.004		0.000	0.000	0.066	0.000	0.051	0.002

Parker #2 Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.090	0.000	0.050	0.000
Parker #2 Deepwell	4	0.000	0.035	0.008	0.000	0.000	0.000	0.004		0.006	0.000	0.004	0.000	0.015	0.000	0.000	0.000	0.078	0.000	0.055	0.013
Parker #2 Deepwell	5	0.005	0.037	0.012	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.087		0.054	0.002
Parker #2 Deepwell	6	0.000	0.044	0.006	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.005	0.000	0.003	0.005	0.000	0.000	0.087	0.000	0.055	0.004
Parker #2 Deepwell	7	0.001	0.037	0.005	0.000	0.000	0.000	0.004	0.002	0.000	0.000	0.004	0.000	0.000		0.000	0.000	0.084	0.000	0.053	0.005
Parker #3 Deepwell	4	0.000	0.000	0.005	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.005	0.000	0.015	0.000	0.000	0.000	0.056	0.000	0.054	0.002
Parker #3 Deepwell	5	0.005	0.000	0.012	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.053		0.053	0.000
Parker #3 Deepwell	6	0.000	0.030	0.004	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.005	0.000	0.003	0.003	0.000	0.000	0.055	0.045	0.054	0.001
Parker #3 Deepwell	7	0.002	0.027	0.003	0.000	0.000	0.000	0.004	0.002	0.000	0.000	0.004	0.000	0.005		0.000	0.000	0.055	0.040	0.053	0.005
Parker #4 Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.107	0.000	0.051	0.000
Parker #4 Deepwell	4	0.000	0.000	0.007	0.000	0.000	0.000	0.004		0.017	0.000	0.004	0.000	0.015	0.000	0.000	0.000	0.077	0.000	0.057	0.017
Parker #4 Deepwell	5	0.005	0.044	0.014	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.084		0.053	0.000
Parker #4 Deepwell	6	0.000	0.044	0.006	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.005	0.000	0.003	0.004	0.000	0.004	0.085	0.000	0.058	0.002
Parker #4 Deepwell	7	0.002	0.043	0.006	0.000	0.000	0.000	0.004	0.001	0.002	0.000	0.004	0.000	0.011		0.000	0.000	0.096	0.000	0.054	0.004
Waikoloa 1	6	0.000	0.029	0.005	0.000	0.000	0.000	0.004	0.000	0.005	0.001	0.005	0.000	0.003	0.003	0.000	0.000	0.042	0.000	0.055	0.012
DW-7	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.040	0.000	0.040	0.000
DW-7	4	0.000	0.000	0.006	0.000	0.000	0.000	0.004		0.000	0.000	0.004	0.000	0.015	0.000	0.000	0.000	0.044	0.000	0.053	0.004
DW-7	7	0.001	0.024	0.004	0.000	0.000	0.000	0.004	0.002	0.000	0.000	0.004	0.000	0.004		0.000	0.000	0.045	0.000	0.052	0.002
Parker 5	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.048	0.000	0.055	0.000
Waikoloa 1	4	0.000	0.000	0.005	0.000	0.000	0.000	0.004		0.000	0.000	0.004	0.000	0.015	0.000	0.000	0.000	0.045	0.000	0.053	0.005
Parker 4	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.051	0.000	0.048	0.000
Parker 4	4	0.000	0.000	0.005	0.000	0.000	0.000	0.004		0.000	0.000	0.005	0.002	0.014	0.000	0.000	0.000	0.046	0.000	0.053	0.007
Parker 4	5	0.004	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.006	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.054		0.052	0.000
Parker 4	6	0.000	0.030	0.004	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.005	0.000	0.003	0.004	0.000	0.000	0.046	0.000	0.053	0.002
Parker 4	7	0.002	0.026	0.002	0.000	0.000	0.000	0.004	0.002	0.000	0.000	0.004	0.000	0.004		0.000	0.000	0.046	0.000	0.054	0.007

Waikoloa 3	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.066	0.000	0.056	0.000
Waikoloa 3	5	0.004	0.047	0.004	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.065		0.064	0.003
Waikoloa 3	7		0.041	0.004	0.000	0.000	0.000	0.004	0.003	0.002	0.000	0.007	0.000	0.002		0.000	0.004	0.056	0.000	0.065	0.003
Waikoloa 2	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.080	0.000	0.058	0.000
Waikoloa 2	4	0.000	0.042	0.008	0.000	0.000	0.000	0.004		0.000	0.000	0.008	0.000	0.015	0.000	0.000	0.000	0.089	0.000	0.063	0.007
Waikoloa 2	6	0.000	0.052	0.008	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.008	0.000	0.003	0.003	0.000	0.000	0.093	0.000	0.065	0.002
Waikoloa DW-6	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.094	0.000	0.053	0.000
Waikoloa DW-6	4	0.000	0.047	0.009	0.000	0.000	0.000	0.004		0.006	0.000	0.010	0.000	0.015	0.000	0.000	0.000	0.090	0.000	0.060	0.006
Waikoloa DW-6	5	0.005	0.047	0.008	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.088		0.061	0.000
Waikoloa DW-6	6	0.000	0.055	0.009	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.010	0.000	0.003	0.004	0.000	0.003	0.090	0.000	0.062	0.002
Waikoloa DW-6	7	0.000	0.056	0.007	0.000	0.000	0.000	0.004	0.002	0.002	0.000	0.009	0.000	0.004		0.000	0.000	0.090	0.000	0.059	0.004
Resort Irr 2	4	0.000	0.244	0.015	0.000	0.000	0.000	0.005		0.000	0.000	0.010	0.000	0.020	0.000	0.000	0.000	0.406	0.000	0.166	0.010
Waikoloa Irr 3	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.211	0.000	0.094	0.000
Waikoloa Irr 3	4	0.006	0.138	0.007	0.000	0.000	0.000	0.003		0.078	0.000	0.007	0.000	0.013	0.000	0.000	0.000	0.245	0.000	0.117	0.008
Waikoloa Irr 3	5	0.007	0.135	0.005	0.000	0.000	0.000	0.003	0.000	0.007	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.225		0.107	0.000
Waikoloa Irr 3	6	0.000	0.151	0.005	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.007	0.000	0.002	0.005	0.000	0.004	0.248	0.042	0.120	0.002
Waikoloa Irr 3	7	0.002	0.129	0.003	0.000	0.000	0.000	0.003	0.003	0.002	0.000	0.006	0.000	0.003		0.000	0.000	0.221	0.000	0.105	0.002
Resort 1	4	0.000	0.169	0.008	0.000	0.000	0.000	0.004		0.000	0.000	0.007	0.000	0.015	0.000	0.000	0.000	0.290	0.000	0.114	0.006
Resort 1	5	0.011	0.182	0.000	0.000	0.000	0.000	0.005	0.000	0.145	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.288	0.000	0.111	0.931
Resort 1	6	0.000	0.196	0.005	0.000	0.000	0.000	0.003	0.000	0.006	0.000	0.007	0.000	0.002	0.006	0.000	0.003	0.306	0.000	0.125	0.003
Resort 1	7	0.003	0.162	0.003	0.000	0.000	0.000	0.003	0.002	0.002	0.000	0.006	0.000	0.005		0.000	0.000	0.264	0.000	0.105	0.003
Nursery	4	0.000	0.213	0.010	0.000	0.000	0.000	0.003	0.004	0.000	0.000	0.007	0.000	0.012	0.000	0.000	0.000	0.377	0.000	0.104	0.006
Nursery	5	0.000	0.230	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.372	0.000	0.103	0.001
Nursery	6	0.000	0.268	0.007	0.000	0.000	0.000	0.003	0.003	0.008	0.000	0.007	0.000	0.003	0.006	0.000	0.000	0.427	0.000	0.125	0.004
Nursery	7	0.003	0.214	0.004	0.000	0.000	0.000	0.003	0.003	0.000	0.000	0.006	0.000	0.003		0.000	0.000	0.354	0.000	0.103	0.003

Fifty-One FT STP	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.383	0.000	0.108	0.000
Fifty-One FT STP	4	0.000	0.205	0.011	0.000	0.000	0.000	0.003	0.004	0.000	0.000	0.006	0.000	0.013	0.000	0.000	0.000	0.362	0.000	0.111	0.011
West Hawaii Landfill	5	0.000	0.228	0.000	0.000	0.000	0.000	0.003	0.000	0.013	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.364	0.000	0.133	0.025
West Hawaii Landfill	6	0.000	0.265	0.009	0.000	0.000	0.000	0.004	0.001	0.008	0.001	0.006	0.000	0.003	0.008	0.000	0.005	0.402	0.000	0.152	0.015
West Hawaii Landfill	7	0.004	0.215	0.006	0.000	0.000	0.000	0.004	0.002	0.003	0.000	0.004	0.000	0.000		0.000	0.000	0.343	0.000	0.129	0.003
Makani Golf Course	6	0.000	0.041	0.002	0.000	0.000	0.000	0.003	0.000	0.000	0.001	0.005	0.000	0.002	0.004	0.000	0.000	0.058	0.000	0.138	0.028
Makani Golf Course	7	0.000	0.038	0.000	0.000	0.000	0.000	0.003	0.002	0.002	0.000	0.005	0.000	0.002		0.000	0.000	0.056	0.000	0.134	0.016
Puu Lani	2	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.031	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.049	0.000	0.145	0.000
Puu Lani	4	0.000	0.040	0.000	0.000	0.000	0.000	0.004	0.000	0.008	0.000	0.005	0.002	0.010	0.000	0.000	0.000	0.050	0.000	0.142	0.002
Puu Lani	5	0.004	0.038	0.008	0.000	0.000	0.000	0.003		0.006	0.000	0.005	0.004	0.000	0.000	0.000	0.000	0.045		0.131	0.000
Puu Lani	6	0.000	0.047	0.003	0.000	0.000	0.000	0.003	0.002	0.009	0.001	0.005	0.008	0.002	0.005	0.000	0.000	0.046	0.000	0.133	0.003
Puu Lani	7	0.002	0.039	0.000	0.000	0.000	0.000	0.003	0.002	0.002	0.000	0.005	0.000	0.000		0.000	0.000	0.046	0.000	0.135	0.003
Puu Waawaa	2	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.033	0.000	0.125	0.049
Puu Waawaa	4	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.007	0.000	0.004	0.002	0.011	0.000	0.000	0.000	0.030	0.000	0.113	0.056
Puu Waawaa	5	0.005	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.029		0.110	0.018
Puu Waawaa	6	0.000	0.025	0.003	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.004	0.000	0.002	0.003	0.000	0.000	0.030	0.000	0.113	0.014
Puu Waawaa	7	0.002	0.024	0.000	0.000	0.000	0.000	0.002	0.003	0.003	0.003	0.004	0.002	0.000		0.000	0.003	0.030	0.000	0.112	0.039
Huehue Ranch 5	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.074	0.000	0.071	0.000
Huehue Ranch 5	5	0.003	0.117	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.002	0.007	0.004	0.000	0.000	0.000	0.004	0.047		0.075	0.095
Huehue Ranch 5	7		0.079	0.000	0.000	0.000	0.000	0.000	0.003	0.007	0.005	0.006	0.002	0.004		0.000	0.004	0.062	0.000	0.085	0.078
Huehue Ranch 3	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.070	0.000	0.075	0.000
Huehue Ranch 3	4	0.000	0.054	0.005	0.000	0.000	0.000	0.000		0.000	0.000	0.007	0.002	0.015	0.000	0.000	0.000	0.065	0.000	0.076	0.005
Huehue Ranch 3	7	0.000	0.058	0.002	0.000	0.000	0.000	0.000	0.003	0.003	0.000	0.006	0.000	0.003		0.000	0.000	0.071	0.000	0.073	0.005
Huehue Ranch 4	5	0.003	0.067	0.004	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.004	0.002	0.000	0.000	0.000	0.000	0.100		0.072	0.062
Huehue Ranch 4	6	0.000	0.076	0.006	0.000	0.001	0.000	0.001	0.004	0.006	0.000	0.005	0.002	0.005	0.010	0.000	0.008	0.109	0.000	0.082	0.048

Huehue Ranch 4	7	0.000	0.067	0.004	0.000	0.000	0.000	0.000	0.005	0.003	0.000	0.004	0.002	0.008		0.000	0.004	0.101	0.000	0.075	0.050
Huehue Ranch 2	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.109	0.000	0.087	0.000
Huehue Ranch 2	4	0.000	0.042	0.011	0.000	0.000	0.000	0.001	0.003	0.000	0.000	0.003	0.002	0.018	0.000	0.000	0.000	0.111	0.000	0.095	0.012
Huehue Ranch 2	6	0.000	0.060	0.011	0.000	0.000	0.000	0.001	0.003	0.000	0.000	0.004	0.002	0.003	0.009	0.001	0.003	0.123	0.000	0.097	0.008
Kau (Makalei) Deepwell	5	0.004	0.062	0.012	0.000	0.000	0.000	0.001	0.004	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.086		0.098	0.095
Kau (Makalei) Deepwell	6	0.000	0.074	0.015	0.000	0.000	0.000	0.002	0.005	0.005	0.000	0.006	0.001	0.005	0.008	0.000	0.000	0.113	0.056	0.105	0.060
Kalaoa Deepwell	1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Kalaoa Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.029	0.000	0.081	0.000
Kalaoa Deepwell	4	0.000	0.000	0.004	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.004	0.000	0.013	0.000	0.000	0.000	0.027	0.000	0.089	0.005
Kalaoa Deepwell	5	0.005	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.025		0.088	0.003
Kalaoa Deepwell	6	0.000	0.028	0.003	0.000	0.000	0.000	0.003	0.001	0.000	0.000	0.004	0.000	0.002	0.003	0.000	0.000	0.026	0.000	0.088	0.004
Kalaoa Deepwell	7	0.000	0.024	0.000	0.000	0.000	0.000	0.003	0.002	0.000	0.000	0.004	0.000	0.003		0.000	0.000	0.026	0.000	0.088	0.003
Palani Ranch Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.027	0.000	0.073	0.000
Palani Ranch Deepwell	4	0.000	0.000	0.006	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.003	0.000	0.012	0.000	0.000	0.000	0.024	0.000	0.074	0.012
Honokohau Deepwell	1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Honokohau Deepwell	7	0.000	0.021	0.004	0.000	0.000	0.000	0.002	0.003	0.002	0.000	0.003	0.000	0.000		0.000	0.000	0.025	0.000	0.076	0.007
Queen Liliuokalani Trust (Keahuolu) Deepwell	1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Queen Liliuokalani Trust (Keahuolu) Deepwell	4	0.006	0.000	0.006	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.011	0.000	0.000	0.000	0.026	0.000	0.056	0.003
Queen Liliuokalani Trust (Keahuolu) Deepwell	5	0.003	0.000	0.004	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.024		0.056	0.000
Queen Liliuokalani Trust (Keahuolu) Deepwell	6	0.000	0.016	0.004	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.002	0.004	0.000	0.000	0.024	0.000	0.056	0.002
Queen Liliuokalani Trust (Keahuolu) Deepwell	7	0.000	0.014	0.002	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.001	0.000	0.000		0.000	0.003	0.024	0.000	0.058	0.004
Keopu Deepwell	4	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.004	0.000	0.000	0.000	0.022	0.000	0.053	0.015

Keopu Deepwell	5	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.006	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.024		0.056	0.008
Keopu Deepwell	6	0.000	0.015	0.004	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.002	0.004	0.000	0.000	0.023	0.000	0.056	0.008
Keopu Deepwell	7	0.001	0.016	0.002	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.002	0.000	0.002		0.000	0.003	0.024	0.000	0.057	0.007
Holualoa Deepwell	1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Holualoa Deepwell	3	0.000	0.000	0.012	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.149	0.000	0.037	0.000
Holualoa Deepwell	4	0.000	0.046	0.013	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.012	0.000	0.000	0.000	0.138	0.000	0.039	0.011
Holualoa Deepwell	5	0.003	0.054	0.009	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.127		0.040	0.012
Holualoa Deepwell	6	0.000	0.050	0.011	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.003	0.005	0.000	0.000	0.133	0.000	0.042	0.009
Holualoa Deepwell	7	0.002	0.047	0.010	0.000	0.000	0.000	0.002	0.002	0.002	0.000	0.000	0.000	0.003		0.000	0.000	0.133	0.000	0.038	0.008
Kahaluu A Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.127	0.000	0.043	0.000
Kahaluu A Deepwell	4	0.002	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.071	0.000	0.046	0.035
Kahaluu C Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.053	0.000	0.044	0.000
Kahaluu C Deepwell	4	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.004	0.000	0.000	0.000	0.048	0.000	0.046	0.007
Kahaluu C Deepwell	5	0.004	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.044		0.049	0.006
Kahaluu C Deepwell	6	0.000	0.022	0.004	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.002	0.003	0.000	0.000	0.044	0.000	0.049	0.007
Kahaluu C Deepwell	7	0.001	0.015	0.003	0.000	0.000	0.000	0.003	0.004	0.003	0.000	0.002	0.000	0.000		0.000	0.000	0.031	0.000	0.056	0.007
Kahaluu B Deepwell	3	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.173	0.000	0.041	0.000
Kahaluu B Deepwell	4	0.000	0.047	0.008	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.004	0.000	0.000	0.000	0.160	0.000	0.044	0.006
Kahaluu B Deepwell	5																				
Kahaluu B Deepwell	6	0.000	0.047	0.011	0.000	0.000	0.000	0.002	0.000	0.005	0.000	0.001	0.000	0.003	0.005	0.000	0.000	0.158	0.000	0.049	0.005
Kahaluu B Deepwell	7	0.002	0.040	0.010	0.000	0.000	0.000	0.002	0.002	0.003	0.000	0.001	0.000	0.004		0.000	0.000	0.159	0.000	0.045	0.004
Kahaluu D Deepwell	3	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.156	0.000	0.043	0.000
Kahaluu D Deepwell	4	0.002	0.039	0.010	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.003	0.000	0.000	0.000	0.153	0.000	0.051	0.004
Kahaluu D Deepwell	5	0.006	0.043	0.009	0.000	0.000	0.000	0.002	0.000	0.006	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.135		0.047	0.000
Kahaluu Shaft	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.193	0.000	0.033	0.000

Kahaluu Shaft	4	0.000	0.061	0.010	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.004	0.000	0.000	0.000	0.218	0.000	0.039	0.002
Kahaluu Shaft	5	0.000	0.057	0.013	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.246	0.000	0.037	0.001
Kahaluu Shaft	6	0.000	0.066	0.015	0.000	0.000	0.000	0.002	0.000	0.005	0.000	0.002	0.000	0.010	0.007	0.000	0.000	0.250	0.000	0.045	0.001
Kahaluu Shaft	7	0.001	0.045	0.010	0.000	0.000	0.000	0.002	0.001	0.000	0.000	0.001	0.000	0.000		0.000	0.000	0.190	0.000	0.041	0.001
Halekii Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.018	0.000	0.053	0.000
Halekii Deepwell	4	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.012	0.000	0.000	0.000	0.018	0.000	0.054	0.010
Halekii Deepwell	5	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.017		0.057	0.011
Halekii Deepwell	6	0.000	0.015	0.002	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.003	0.003	0.000	0.000	0.018	0.000	0.054	0.008
Halekii Deepwell	7	0.002	0.015	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.000	0.002	0.000	0.004		0.000	0.000	0.018	0.000	0.056	0.008
Keei D Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.019	0.000	0.052	0.000
Keei D Deepwell	4	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.004	0.000	0.000	0.000	0.016	0.000	0.051	0.009
Keei D Deepwell	5	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.017		0.049	0.003
Keei D Deepwell	6	0.000	0.015	0.003	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.003	0.003	0.000	0.000	0.016	0.000	0.053	0.005
Keei D Deepwell	7	0.000	0.011	0.000	0.000	0.000	0.000	0.002	0.003	0.002	0.000	0.001	0.000	0.008		0.000	0.000	0.017	0.000	0.055	0.004
Keei A Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.211	0.000	0.045	0.128
Keei A Deepwell	4	0.000	0.087	0.000	0.000	0.000	0.000	0.001	0.000	0.026	0.000	0.001	0.000	0.011	0.000	0.000	0.000	0.190	0.000	0.046	0.093
Keei A Deepwell	5	0.005	0.108	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.217		0.041	0.100
Keei A Deepwell	6	0.000	0.094	0.004	0.000	0.000	0.000	0.001	0.001	0.008	0.001	0.001	0.000	0.003	0.005	0.000	0.000	0.205	0.000	0.049	0.084
Keei A Deepwell	7	0.000	0.076	0.002	0.000	0.000	0.000	0.001	0.002	0.004	0.000	0.000	0.000	0.003		0.000	0.000	0.168	0.000	0.044	0.062
Keei B Deepwell	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.059	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.125	0.000	0.043	0.161
Keei B Deepwell	5																				
Ocean End Member 21m	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	6.307	0.000	0.015	0.000
Ocean End Member 21m	6	0.000	3.996	0.000	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.164	0.000	0.000	6.830	0.000	0.000	0.066
Ocean End Member 21m	7	0.000	4.638	0.000	0.000	0.000	0.008	0.000	0.020	0.000	0.000	0.000	0.000			0.000	0.000	7.673	0.000	0.000	0.019
Ocean End Member 674m	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	5.501	0.000	0.044	0.000

Ocean End Member 674m	6	0.104	4.072	0.000	0.000	0.000	0.000	0.000	0.136	0.000	0.000	0.000	0.000	0.000	0.140	0.000	0.000	6.942	0.000	0.000	0.040
Ocean End Member 674m	7	0.000	4.830	0.000	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000			0.000	0.000	8.038	0.000	0.000	0.008
Ocean End Member 900m	3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	5.224	0.000	0.022	0.000
Ocean End Member 900m	6	0.000	4.252	0.000	0.000	0.000	0.012	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.152	0.000	0.000	7.356	0.000	0.000	0.018
Ocean End Member 900m	7	0.038	4.938	0.000	0.000	0.000	0.010	0.000	0.046	0.055	0.000	0.000	0.000			0.000	0.000	8.255	0.000	0.000	0.000

APPENDIX C. Chapter 4 Supplementary Materials

Table C.1. Salinity-corrected, averaged in-situ and stable isotope of water data.

Salinity-corrected data for 96 groundwater (production, monitoring, irrigation wells; anchialine ponds; submarine groundwater discharge springs) and 3 ocean water sites during the study period of May 2017 to March 2019, organized by site from North (Waimea aquifer) to South (Kealakekua aquifer). The reported salinity-corrections follow the methods of section 3.4.2.2., and report the corrected values using the 21 m depth ocean water end member. pH, temperature (°C), specific conductivity (µS/cm), and dissolved oxygen (% and mg/L) are collected in the field. Stable isotopes of water $\delta^{18}O$ and $\delta^{2}H$ are reported in per mil (‰). Relative standard deviations for the geochemical parameters are reported in Appendix B.

Well Name	pH	Temperature (°C)	Specific Conductivity (µS/cm)	Salinity	Dissolved Oxygen (%)	Dissolved Oxygen (mg/L)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	Ocean Water Fraction
Parker Ranch Deepwell	7.85	23	153.4	0.06	91	7.84	-3.50	-11.90	0.00
Lalamilo C Deepwell	7.855	26.15	567.85	0.26	97	8.38	-5.43	-28.95	0.00
Lalamilo A Deepwell	7.9	26.1	460	0.2	82.3	5.7	-5.42	-28.81	0.00
Lalamilo B Deepwell	7.83	26.2	496	0.23	79.3	6.08	-5.62	-30.03	0.00
Parker #2 Deepwell	7.89	26.7	2	0.34	90.4	4.58	-5.73	-31.09	0.01
Parker #3 Deepwell	7.815	26.65	433.2	0.2	96.8	6.62	-5.66	-30.93	0.00
Parker #4 Deepwell	7.91	27.1	738	0.35	84.8	5.32	-5.84	-32.12	0.01
Waikoloa 1	8.015	26.5	312.25	0.14	96.2	6.45	-5.66	-30.59	0.00
DW-7	7.99	26.5	287.7	0.12	80.5	5.19	-5.71	-31.44	0.00
Parker 5	8.19	26.5	303.8	0.128	75.3	5.87	-5.71	-30.94	0.00
Parker 4	7.97	26.7	350.1	0.15	87.6	5.23	-5.81	-31.65	0.00
Waikoloa 3	7.87	28.2	512	0.233	72.4	5.5	-6.92	-42.24	0.00

Waikoloa 2	7.93	28.6	660	0.3	78.5	4.73	-7.14	-43.66	0.01
Waikoloa DW-6	7.97	28.5	726	0.33	77.2	4.89	-7.65	-48.52	0.01
Resort Irr 2	7.94	24.7	2522	1.28	90.5	7.38	-9.23	-63.28	0.03
Waikoloa Irr 3	8.03	24.1	2184	1.091	96.5	6.46	-9.17	-62.99	0.03
Resort 1	8.04	23.9	2920.5	1.505	96.65	7.12	-9.20	-63.30	0.04
Nursery	7.905	23.5	3794.5	1.995	99.05	7.01	-9.08	-62.53	0.05
Fifty-One FT STP	7.875	24.15	3420.5	1.778	76.55	5.93	-9.23	-62.85	0.06
West Hawaii Landfill	8.02	22.4	4161	2.21	105.7	8.78	-8.34	-56.07	0.05
Back spring	7.68	20.8	5211	2.815	104.05	9.8	-7.51	-49.16	0.07
Mouth ocean	7.915	24.2	29469.5	18.275	119.65	8.65	-7.49	-49.42	0.47
Inside mouth channel	7.67	22.4	8341.5	4.655	102.9	9.4	-7.52	-48.52	0.10
Big Bridge	7.515	21.85	6840	3.77	92.7	8.65	-7.37	-48.40	0.09
Kitchen corner inlet	7.43	21.6	7512.5	4.18	93.35	8.58	-7.30	-47.82	0.08
Makani Golf Course	8.01	22.85	556	0.27	110.8	9.35	-8.18	-53.93	0.00
Puu Lani	8.145	23.55	420.9	0.195	94.2	7.14	-7.92	-51.25	0.00
Kekaha Kai - Kua Bay	8.04	24.7	14615	8.49	121.8	6.23	-5.29	-28.07	0.19
Kekaha Kai - Kaelehuluhulu	7.73	25.7	25651	15.63	98.3	7.13	-4.99	-27.82	0.40
Kekaha Kai - Small Pool	7.5	29.3	21222	12.52	106.4	7.62	-5.20	-28.21	0.31
Puu Waawaa	8.15	23.65	280.45	0.125	90.85	6.9	-8.01	-52.35	0.00
Huehue Ranch 5	7.11	23.7	1803	0.886	67.3	4.33	-5.02	-25.08	0.00
Huehue Ranch 3	7.08	20.3	1536	0.744	37	3.89	-4.94	-24.30	0.01

NELHA Well #12B	8.01	23.09	16724	9.99	92.2	6.88	-5.71	-32.08	0.28
NELHA Well #12A	7.84	22.13	34761	22.14	36.6	2.65	-6.69	-40.47	0.64
NELHA Well #12	7.8	21.795	41867	27.51	24.35	0	-7.18	-46.00	0.79
Huehue Ranch 4	6.63	23.7	1422	0.68	58.7	5.73	-5.24	-28.21	0.01
Huehue Ranch 2	6.94	21.9	1335	0.64	60.6	4.5	-4.85	-25.04	0.01
Kau (Makalei) Deepwell	7.305	24.3	1389	0.68	100.1	7.19	-5.11	-26.11	0.01
NELHA A1	7.99	24.05	24473	14.99	106.3	9.27	-6.18	-35.59	0.41
NELHA Well #3B	7.93	23.7	46441	8.43	0	5.88	-5.87	-33.91	0.22
NELHA Well #3A	7.96	23.54	13983	8.22	0	6.35	-5.95	-34.36	0.23
NELHA Well #3	7.77	20.9	41362	26.14	0	2.94	-7.36	-45.06	0.76
Kalaoa Deepwell	7.78	23.3	304	0.121	84.7	7.59	-6.65	-40.16	0.00
NELHA A2	7.775	23.04	19629.5	11.775	113.2	5.33	-5.99	-35.08	0.31
NELHA Well #1	7.76	20.8	18815	11.33	91.65	4.83	-6.24	-36.87	0.32
NELHA Well #9B	7.76	19.21	23788	15.06	116.1	5.99	-6.23	-36.02	0.43
NELHA Well #9A	7.71	17.56	32393	20.36	127.4	6.09	-6.81	-40.53	0.59
NELHA Well #9	7.76	16.47	36316	22.95	129.3	6.48	-7.08	-42.92	0.67
NELHA A3	7.785	21.6	23994	14.69	111.1	5.6	-5.85	-33.19	0.38
Kohanaiki #1	7.93	19.9	16252	9.68	79.5	6.7	-6.52	-38.74	0.28
Kohanaiki #2	7.835	21.05	15408	9.135	99.7	10.18	-5.77	-32.41	0.27
Kohanaiki #3	7.95	20.7	14961	8.85	98.2	8.43	-6.56	-39.28	0.27
Kohanaiki #4	7.87	20.7	14385	8.25	104.4	8.71	-6.30	-37.37	0.23

Kohanaiki #5	7.92	19.8	14591	8.61	91.6	6.95	-6.18	-37.81	0.21
Kohanaiki #6	7.745	19.5	14772.5	8.315	114.25	9.3	-6.46	-38.82	0.27
Kohanaiki #7	7.815	21	15522	8.45	100.55	10.23	-5.64	-31.43	0.24
Kohanaiki A2	7.46	24.1	21682	11.54	126	13.44	-5.35	-30.37	0.34
Kohanaiki A30	7.72	25.2	20880	12.72	101.4	7.2	-5.62	-32.02	0.33
Kohanaiki A43	8.055	23.85	21527	13.15	101.35	7.6	-6.39	-38.03	0.37
Kohanaiki A5	8.05	24.6	20664	12.58	116	8.99	-6.17	-36.56	0.37
Kohanaiki A69	7.59	25.1	23339	14.23	92.5	9.14	-5.16	-31.19	0.41
Kohanaiki A172	8.23	28.2	22907	13.62	119.2	18.05	-5.24	-31.62	0.39
Kohanaiki A121	7.98	26.75	22360	11.255	123.1	11.68	-0.23	-1.97	0.43
Kohanaiki A139	8.21	27.35	27118	16.905	162.7	14.35	-6.07	-36.41	0.48
Kohanaiki A48	7.74	24.5	18130	7.74	64	4.98	-4.13	-20.90	0.19
Kohanaiki A46	7.11	22.85	16091	9.585	66.8	6.68	-4.50	-24.28	0.25
Kohanaiki A77	7.85	22.9	22503	13.8	113.1	8.65	-6.12	-36.23	0.39
Kohanaiki A120	8.2	24.2	24153	14.9	158.9	12.16	-6.03	-35.88	0.43
Palani Ranch Deepwell	7.975	22	228.1	0.0925	89.95	7.22	-6.95	-42.91	0.00
Honokohau Deepwell	7.825	21.9	233.9	0.12	93.55	7.23	-6.90	-42.30	0.00
Queen Liliuokalani Trust (Keahuolu) Deepwell	7.93	20.9	159.8	0.075	99.5	8.29	-5.50	-29.60	0.00
Keopu Deepwell	7.92	21.3	155.45	0.06	98	7.33	-5.15	-27.00	0.00
QLT A1	7	25.65	22926	13.955	64.1	3.53	-4.31	-20.92	0.38
QLT A32	6.885	24.4	23102	14.2	24.15	1.82	-4.39	-23.05	0.46

QLT A4S	7.055	25.6	26155	16.05	57.25	1.43	-4.29	-21.80	0.41
QLT A36	7.09	27.15	24843.5	15.37	42	2.7	-4.19	-20.97	0.39
QLT A30	7.7	25.4	19166	11.59	86.6	6.61	-4.12	-20.27	0.37
QLT A5	7.765	26.9	30472.5	19.02	68.85	4.32	-4.43	-22.99	0.51
QLT A8	7.225	25.1	24359	14.92	81.5	5.4	-4.36	-21.87	0.41
QLT Maka Eo	7.64	21.45	22039.5	13.395	109.95	6.51	-4.30	-20.91	0.39
Keopu 2	8.375	21.8	440	0.205	85	7.52	-5.10	-26.65	0.00
Keopu 1	10.77	21.3	1980	0.98	17.6	1.53	-5.07	-26.39	0.03
Holualoa Deepwell	7.85	20.55	927.5	0.43	100.65	9.13	-4.15	-19.09	0.01
Kahaluu A Deepwell	7.92	20.6	613.95	0.274	92.6	6.95	-5.29	-28.56	0.01
Kahaluu C Deepwell	7.85	20.3	334.5	0.147	100.1	6.97	-5.31	-28.48	0.00
Kahaluu B Deepwell	7.95	20.3	980	0.456	113.9	8.33	-5.37	-28.69	0.01
Kahaluu D Deepwell	7.52	20.2	940	0.436	98.5	6.79	-5.27	-28.37	0.01
Kahaluu Shaft	7.82	20.3	1499	0.72	91.3	7.71	-5.21	-27.90	0.02
Kahaluu DW1 (96m)	8.49	21.7	3110	1.6	16.7	1.45	-5.31	-28.00	0.25
Kahaluu DW1 (115m)	8.27	22.3	38350	24.64	21.6	1.55	-5.39	-28.96	0.65
Kahaluu DW	8.8	23.9	4560	2.43	0	0	-5.25	-28.06	0.04
Halekii Deepwell	7.82	21.4	138.5	0.054	104.5	6.37	-5.90	-32.60	0.00
Keei D Deepwell	7.79	18.7	132.7	0.054	115.2	8.78	-5.30	-27.90	0.00
Keei A Deepwell	7.68	19.6	1638	0.83	100.4	6.66	-4.60	-21.90	0.02
Keei B Deepwell	7.425	19.15	1138.5	0.535	94.6	7.12	-4.66	-23.02	0.01

Ocean End Member 21m	7.98	26.25	60926.5	40.9	111.65	0	0	0	0
Ocean End Member 674m	7.52	6.15	61602.5	40.595	27.45	0	0	0	0
Ocean End Member 900m	7.42	5.07	60858	35.19	58.7	0	0	0	0

Table C.2. Salinity-corrected, averaged dissolved ion data.

Salinity-corrected data for 96 groundwater (production, monitoring, irrigation wells; anchialine ponds; submarine groundwater discharge springs) and 3 ocean water sites during the study period of May 2017 to March 2019, organized by site from North (Waimea aquifer) to South (Kealakekua aquifer). The reported salinity-corrections follow the methods of section 3.4.2.2., and report the corrected values using the 21 m depth ocean water end member. Fluoride (F^-), chloride (Cl^-), bromide (Br^-), sulfate (SO_4^{2-}), lithium (Li^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}) are reported as averaged, salinity-corrected values in µM. Relative standard deviations for the geochemical parameters are reported in Appendix B.

Well Name	Fluoride (µM)	Chloride (µM)	Sulfate (µM)	Lithium (µM)	Sodium (µM)	Potassium (µM)	Magnesium (µM)	Calcium (µM)
Parker Ranch Deepwell	4.74	225.67	70.55		374.54	66.06	288.61	269.65
Lalamilo C Deepwell	12.69	2696.76	360.36		503.36	112.12	501.99	340.17
Lalamilo A Deepwell	13.74	2059.24	353.35		589.97	98.10	519.52	333.39
Lalamilo B Deepwell	13.21	2169.25	383.16		514.74	101.78	540.69	341.90
Parker #2 Deepwell	14.82	3159.38	382.16		597.44	106.16	576.47	374.45
Parker #3 Deepwell	13.72	1392.10	395.38		667.58	102.07	512.49	306.78
Parker #4 Deepwell	14.83	3509.17	449.89		585.72	109.93	536.80	352.08
Waikoloa 1	16.60	785.61	398.52		754.81	89.45	506.09	267.28
DW-7	17.39	744.71	404.88		832.16	90.06	517.13	249.99
Parker 5	17.39	789.84	404.11		836.02	89.25	443.79	236.87
Parker 4	14.23	846.26	422.51		821.23	93.37	503.00	260.82
Waikoloa 3	17.43	1918.19	683.14		1223.79	122.81	576.37	292.75
Waikoloa 2	19.06	3272.21	704.41		1056.31	123.81	747.54	370.86
Waikoloa DW-6	18.54	3616.36	744.96		1207.40	144.68	710.71	336.52

Resort Irr 2	28.35	19153.74	1194.77	0.77	621.43	122.74	399.66	457.85
Waikoloa Irr 3	34.69	16033.85	1202.97	0.88	874.42	124.56	550.42	321.27
Resort 1	34.44	20619.18	1111.14	0.72	1248.77	134.46	584.45	314.25
Nursery	35.50	28241.18	1145.72	0.43	1524.77	150.56	668.13	328.86
Fifty-One FT STP	41.81	30803.95	1231.49	0.33	946.98	160.67	49.93	547.99
West Hawaii Landfill	44.35	27957.69	1222.91	0.44	1527.90	205.69	766.34	372.37
Back spring	51.56	36320.17	771.38	0.12	2143.47	166.66	687.01	382.23
Mouth ocean	112.19	257007.05	2303.51	1.23	2016.57	0.00	639.91	0.00
Inside mouth channel	55.28	57801.13	883.95	0.85	3562.96	173.35	957.56	414.61
Big Bridge	50.75	48095.91	887.80	0.44	2284.10	151.69	787.02	408.03
Kitchen corner inlet	55.99	43375.18	1032.61	0.62	1699.23	140.50	724.89	392.33
Makani Golf Course	34.32	1850.49	1633.06	1.09	1343.82	77.63	390.32	491.52
Puu Lani	42.72	1156.56	1362.63	1.41	1420.13	80.18	309.57	419.84
Kekaha Kai - Kua Bay	69.27	107562.76	8595.37	5.86	9060.25	449.22	9150.26	277.67
Kekaha Kai - Kaelehuluhulu		217689.70	1182.64	0.00	0.00	259.36	2290.32	1279.14
Kekaha Kai - Small Pool	47.97	170186.18	1422.02	0.00	5762.50	311.20	1406.07	742.23
Puu Waawaa	33.72	592.38	718.84	1.42	1084.10	66.20	264.39	278.15
Huehue Ranch 5	81.30	2383.64	9584.72	7.17	5802.72	212.22	5518.87	1185.71
Huehue Ranch 3	72.12	4823.70	6968.51	2.75	709.31	158.56	5845.98	1042.71
NELHA Well #12B	53.73	156699.58	0.00		2507.93	137.20	0.00	97.58
NELHA Well #12A		353201.69	1084.84	0.00	0.00	0.00	4.01	0.00

NELHA Well #12		432045.13	3911.49	0.00	0.00	140.83	0.00	0.00
Huehue Ranch 4	37.63	4552.89	2670.34	2.76	1601.81	251.73	4560.40	996.86
Huehue Ranch 2	38.24	5641.75	1405.71	1.27	685.29	195.53	3564.11	1087.34
Kau (Makalei) Deepwell	40.18	6736.25	1098.46	1.24	402.09	238.42	2441.72	983.26
NELHA A1		223102.96	879.37	0.00	49236.47	89.72	0.00	565.03
NELHA Well #3B		122313.12	392.64	0.00	0.00	0.00	131.35	548.90
NELHA Well #3A	33.56	127418.90	155.74	0.00	3129.08	48.31	0.00	350.11
NELHA Well #3		420507.76	4815.22	0.00	0.00	0.00	0.00	0.00
Kalaoa Deepwell	21.85	276.45	873.14		1272.79	132.86	456.15	307.28
NELHA A2	56.35	169844.85	0.00	0.00	17833.77	21.51	276.83	244.04
NELHA Well #1		175909.73	1391.65	0.00	785.50	11.71	2159.98	780.72
NELHA Well #9B		238118.48	1524.14	0.00	6066.50	0.00	1882.97	943.51
NELHA Well #9A		325444.29	975.05	0.00	0.00	0.00	0.00	0.00
NELHA Well #9	132.76	371001.41	1472.67	2.45	0.00	0.00	0.00	223.31
NELHA A3		210409.03	640.90	0.00	14845.55	0.00	1430.37	0.00
Kohanaiki #1	53.48	154894.22	0.00	0.00	25189.21	39.42	0.00	0.00
Kohanaiki #2	28.30	151057.83	24.88	0.00	9485.76	0.00	0.00	568.57
Kohanaiki #3	98.29	149478.14	0.00		23988.52	32.33	0.00	0.00
Kohanaiki #4	31.32	124851.90	576.28	0.00	0.00	0.00	0.00	316.10
Kohanaiki #5	35.45	117275.04	131.01	0.03	5696.57	185.04	724.48	307.51
Kohanaiki #6	17.60	147066.29	203.50	0.00	150.36	0.00	0.00	356.01

Kohanaiki #7	36.45	133067.70	337.99	0.00	1570.15	42.99	323.80	372.85
Kohanaiki A2	53.83	189675.60	0.00	0.00	19399.82	0.00	0.00	572.10
Kohanaiki A30	44.97	183074.75	0.00	0.00	10091.35	86.90	0.00	100.09
Kohanaiki A43	23.90	204795.49	431.42	0.00	13148.55	0.00	0.00	1036.54
Kohanaiki A5	54.85	201664.32	0.00		34036.48	0.00	0.00	0.00
Kohanaiki A69	30.97	222849.08	829.95	0.00	0.00	0.00	0.00	0.00
Kohanaiki A172	58.33	212496.47	1862.41	0.00	0.00	0.00	0.00	520.84
Kohanaiki A121	44.37	236812.41	320.05		50367.97	0.00	0.00	0.00
Kohanaiki A139	85.38	265105.78	863.63	0.00	22320.20	0.00	0.00	1669.40
Kohanaiki A48	31.08	103012.69	3.30	0.67	0.00	154.32	0.00	338.71
Kohanaiki A46	17.55	137729.20	342.65	0.00	0.00	56.38	2358.33	1497.55
Kohanaiki A77		215684.06	35.19	0.00	0.00	0.00	3934.27	2942.53
Kohanaiki A120		236925.25	1774.35		0.00	0.00	3132.91	3099.57
Palani Ranch Deepwell	25.80	239.77	679.78		1089.65	101.03	345.29	284.70
Honokohau Deepwell	20.53	220.03	616.39		1072.19	105.60	312.87	251.29
Queen Liliuokalani Trust (Keahuolu) Deepwell	12.63	183.36	311.09		712.91	84.13	245.03	252.54
Keopu Deepwell	11.84	172.07	310.35		696.72	90.21	254.61	256.94
QLT A1	23.40	209806.77	0.00	0.00	135.66	97.39	0.00	163.72
QLT A32	44.04	250850.49	0.00	0.30	23730.85	0.00	0.00	157.26
QLT A4S	30.88	226504.94	0.00	0.00	3512.78	132.56	0.00	112.22
QLT A36		212870.24	0.00	0.00	4224.44	171.00	647.31	301.31

QLT A30	46.50	201354.02	0.00	0.00	36581.24	16.41	0.00	0.00
QLT A5	29.76	282382.23	0.00	0.00	2694.00	79.20	0.00	0.00
QLT A8	51.69	225156.56	0.00	0.00	768.64	43.21	0.00	111.04
QLT Maka Eo	25.96	215424.54	0.00	0.00	2240.85	0.00	0.00	0.00
Keopu 2	14.74	169.25	282.37		673.42	74.98	259.37	298.91
Keopu 1	16.84	17179.13	8.67		0.00	160.47	0.00	2952.77
Holualoa Deepwell	8.52	6318.76	191.47		315.93	87.34	265.95	568.20
Kahaluu A Deepwell	14.84	3892.81	287.86		362.49	49.83	163.77	486.32
Kahaluu C Deepwell	12.14	1590.97	309.19		473.62	53.99	181.45	313.44
Kahaluu B Deepwell	12.79	7102.96	272.93		416.80	29.40	165.05	563.85
Kahaluu D Deepwell	10.12	6826.52	280.48		480.18	35.45	194.50	538.65
Kahaluu Shaft	10.74	10973.20	245.92		0.00	11.74	210.19	864.02
Kahaluu DW1 (96m)	21.10	138504.94	0.00	0.00	0.00	0.00	0.00	1808.38
Kahaluu DW1 (115m)		356417.49	0.00	0.00	0.00	0.00	3170.82	7542.24
Kahaluu DW	7.16	24583.92	0.00		0.00	0.00	21.48	879.29
Halekii Deepwell	13.16	129.76	461.24		701.88	52.95	147.13	214.24
Keei D Deepwell	12.11	112.83	323.49		542.75	45.32	153.26	203.99
Keei A Deepwell	11.28	11311.71	319.91		300.10	29.47	385.65	450.58
Keei B Deepwell	6.93	6911.14	169.52		431.43	31.76	169.95	318.65
Ocean End Member 21m		549619.1819	0	0	0	0	0	0
Ocean End Member 674m		557038.0818	0	0	0	0	0	0

Ocean End Member 900m		565726.3752	0	0	0	0	0	0

Table C.3. Salinity-corrected, averaged nutrient data.

Salinity-corrected data for 96 groundwater (production, monitoring, irrigation wells; anchialine ponds; submarine groundwater discharge springs) and 3 ocean water sites during the study period of May 2017 to March 2019, organized by site from North (Waimea aquifer) to South (Kealakekua aquifer). The reported salinity-corrections follow the methods of section 3.4.2.2., and report the corrected values using the 21 m depth ocean water end member. Silica (SiO_2), phosphate (PO_4^{3-}), nitrate + nitrite ($NO_3^- + NO_2^-$), ammonia + ammonium ($NH_3 + NH_4^+$), total phosphorus (TP), and total nitrogen (TN) are reported as salinity-corrected values in µM. Alkalinity and bicarbonate (HCO_3^-) are reported in mg/L. Relative standard deviations are reported for the geochemical parameters.

Well Name	Silica (µM)	Phosphate (µM)	NO3 + NO2 (µM)	NH3 + NH4 (µM)	Total Phosphorus (µM)	Total Nitrogen (µM)	Alkalinity (mg/L)	Bicarbonate (mg/L)
Parker Ranch Deepwell	853.87	3.37	20.28	0.46	4.02	78.18	63.98	78.06
Lalamilo C Deepwell	956.39	2.97	89.49	0.18	2.54	126.16	79.82	97.38
Lalamilo A Deepwell	930.96	2.82	90.73	0.17	2.94	138.68	81.87	99.88
Lalamilo B Deepwell	959.92	2.67	92.31	0.09	2.91	134.92	81.87	99.88
Parker #2 Deepwell	977.66	2.65	91.93	0.16	2.55	137.49	83.81	102.25
Parker #3 Deepwell	969.13	2.77	94.12	0.10	2.72	136.82	82.92	101.16
Parker #4 Deepwell	959.35	2.61	95.62	0.19	2.68	133.00	83.79	102.23
Waikoloa 1	959.63	2.58	91.63	0.22	2.71	121.01	84.46	103.04
DW-7	968.13	2.78	90.68	0.17	3.00	133.58	83.96	102.43
Parker 5	877.11	2.61	92.47	0.21	2.44	136.62	81.95	99.98
Parker 4	987.22	2.58	98.35	0.16	2.60	145.42	83.95	102.42
Waikoloa 3	1022.93	2.63	95.29	0.06	2.77	145.21	102.96	125.61
Waikoloa 2	995.00	2.79	89.11	0.25	2.65	132.35	102.92	125.56
Waikoloa DW-6	1016.52	2.31	77.56	0.19	2.35	116.72	110.96	135.37

Resort Irr 2	869.06	1.90	38.21	1.17	2.45	78.90	62.10	75.77
Waikoloa Irr 3	881.75	2.01	46.78	0.20	2.03	91.53	64.48	78.67
Resort 1	904.48	1.94	48.30	0.03	2.01	98.96	64.03	78.11
Nursery	914.06	2.64	56.05	0.13	2.31	105.35	65.36	79.74
Fifty-One FT STP	864.30	2.82	50.93	0.29	5.97	101.53	65.64	80.08
West Hawaii Landfill	858.08	2.44	72.50	0.10	2.26	127.69	71.71	87.49
Back spring	824.89	2.36	71.90		2.32	171.41	69.36	84.62
Mouth ocean	849.75	2.82	65.42	1.05	3.72	273.45	76.62	93.48
Inside mouth channel	817.72	2.45	68.08	1.13	2.45	177.20	76.22	92.99
Big Bridge	807.55	2.38	70.05	0.27	2.30	177.45	73.17	89.27
Kitchen corner inlet	866.54	2.66	75.56	0.42	2.29	173.83	76.84	93.74
Makani Golf Course	736.70	1.51	63.70		1.68	157.31	76.87	93.79
Puu Lani	729.10	2.24	87.57	0.18	1.99	125.20	78.93	96.29
Kekaha Kai - Kua Bay	1111.12	2.25	142.07	0.56	2.00	182.52	465.87	568.37
Kekaha Kai - Kaelehuluhulu	1185.97	5.43	55.07	2.72	4.76	143.62	141.80	173.00
Kekaha Kai - Small Pool	1114.74	4.87	35.40	3.54	3.99	148.46	132.91	162.15
Puu Waawaa	757.78	1.09	36.68	0.19	1.75	76.56	68.46	83.52
Huehue Ranch 5	1153.06	7.31	77.66	0.15	7.35	119.56	487.08	594.24
Huehue Ranch 3	1080.61	11.61	67.11	0.24	9.01	100.84	366.84	447.54
NELHA Well #12B	1055.67	5.22	81.16	0.21	4.44	145.58	89.04	108.62
NELHA Well #12A	1553.15	6.90	83.93	0.33	4.76	229.69	63.86	77.90

NELHA Well #12	1668.91	9.77	81.53	0.26	5.22	334.96	51.58	62.93
Huehue Ranch 4	1577.13	10.70	46.53		9.09	101.71	456.33	556.72
Huehue Ranch 2	1153.43	9.05	55.21	0.21	9.03	102.65	360.15	439.39
Kau (Makalei) Deepwell	1219.01	6.86	45.31	0.18	6.52	81.31	246.40	300.61
NELHA A1	902.77	5.94	185.77	1.04	5.29	309.69	101.86	124.27
NELHA Well #3B	899.48	4.09	133.25	0.15	3.46	189.72	75.86	92.55
NELHA Well #3A	902.21	4.16	139.04	0.17	3.40	183.96	75.36	91.94
NELHA Well #3	1631.95	5.03	115.78	0.73	4.60	365.17	38.28	46.70
Kalaoa Deepwell	870.39	4.04	68.67	0.28	4.09	116.25	93.00	113.45
NELHA A2	870.73	4.59	225.31	0.12	4.18	273.73	70.71	86.26
NELHA Well #1	943.26	4.31	122.90	0.05	3.74	186.93	71.43	87.14
NELHA Well #9B	955.71	4.69	179.35	0.17	3.95	257.46	72.91	88.95
NELHA Well #9A	1033.45	6.28	179.84	0.21	5.22	320.99	75.34	91.91
NELHA Well #9	1138.19	8.00	217.35	0.33	5.26	386.86	70.86	86.45
NELHA A3	921.95	4.52	177.69	0.57	4.23	254.95	68.41	83.46
Kohanaiki #1								
Kohanaiki #2	794.62	4.84	104.42	0.54	4.08	140.20	61.86	75.47
Kohanaiki #3								
Kohanaiki #4	828.11	4.00	106.40	0.33	3.55	153.83	69.79	85.15
Kohanaiki #5	872.54	3.94	122.30	0.91	3.59	226.23	74.43	90.81
Kohanaiki #6	850.49	3.98	112.28	0.12	3.64	194.19	71.96	87.79

Kohanaiki #7	884.53	4.72	104.95	0.19	4.05	175.06	62.93	76.77
Kohanaiki A2	765.95	2.55	113.92	7.64	2.17	185.76	66.63	81.29
Kohanaiki A30	760.54	2.39	80.01	5.92	2.17	168.21	74.28	90.63
Kohanaiki A43	788.66	2.89	90.69	3.93	2.33	143.10	70.80	86.37
Kohanaiki A5								
Kohanaiki A69	734.34	1.28	44.26	7.75	1.27	145.20	61.52	75.05
Kohanaiki A172	724.32	0.64	50.35	4.38	0.76	146.95	68.93	84.09
Kohanaiki A121	808.87	2.37	86.46	5.51	3.14	216.57	44.99	54.89
Kohanaiki A139	823.65	0.54	13.81	8.92	0.47	133.96	72.59	88.56
Kohanaiki A48	603.41	1.91	73.64	2.26	2.17	154.79	49.34	60.20
Kohanaiki A46	628.51	2.81	79.46	3.56	4.76	151.05	56.31	68.70
Kohanaiki A77	807.66	1.45	89.58	8.29	1.06	163.24	74.22	90.55
Kohanaiki A120	803.51	1.32	1129.13	4.40	0.94	1372.46	69.56	84.87
Palani Ranch Deepwell	798.32	4.43	70.68	0.33	4.52	102.06	75.99	92.71
Honokohau Deepwell	847.64	3.89	80.22	0.05	4.06	228.88	76.00	92.72
Queen Liliuokalani Trust (Keahuolu) Deepwell	762.98	3.96	86.44	0.34	3.90	123.79	56.00	68.32
Keopu Deepwell	761.94	3.86	78.47	0.16	3.89	111.10	57.00	69.54
QLT A1	783.84	24.82	173.85	6.85	19.83	445.77	55.57	67.79
QLT A32	1062.40	37.43	134.45	9.18	26.44	230.08	45.29	55.25
QLT A4S	778.77	20.47	113.75	10.16	17.20	246.48	48.99	59.77
QLT A36	856.43	20.69	177.10	5.49	17.77	365.66	56.64	69.10

QLT A30								
QLT A5	795.41	12.44	37.77	7.60	11.73	182.40	49.16	59.98
QLT A8	838.31	19.53	154.90	8.40	14.97	339.03	44.19	53.92
QLT Maka Eo	819.06	4.63	261.92	0.80	3.54	350.54	49.60	60.51
Keopu 2	723.68	4.45	71.31	0.29	12.16	86.59	50.01	61.01
Keopu 1	41.15	0.29	0.69	59.87	8.44	78.32	36.52	44.55
Holualoa Deepwell	721.07	3.85	80.27	0.35	3.90	108.64	53.30	65.02
Kahaluu A Deepwell	751.52	4.90	339.16	2.05	4.64	278.95	42.00	51.24
Kahaluu C Deepwell	776.08	4.52	87.26	0.16	4.34	116.90	41.82	51.02
Kahaluu B Deepwell	758.50	4.63	85.10	0.19	4.37	145.94	41.56	50.70
Kahaluu D Deepwell	772.12	4.85	82.71	0.21	4.67	116.43	41.09	50.13
Kahaluu Shaft	786.66	4.35	89.60	0.20	4.14	135.53	40.51	49.42
Kahaluu DW1 (96m)	179.80	1.42	4.71	17.61	17.48	131.28	22.12	26.99
Kahaluu DW1 (115m)	727.31	2.34	15.71	17.70	32.67	258.72	17.48	21.32
Kahaluu DW								
Halekii Deepwell	789.66	4.19	72.69	0.15	4.22	116.72	41.99	51.23
Keei D Deepwell	763.97	4.61	51.81	0.15	4.39	91.42	38.00	46.36
Keei A Deepwell	799.03	4.08	128.32	0.13	4.09	174.47	35.34	43.11
Keei B Deepwell	795.84	4.78	81.77	0.06	4.21	123.32	36.51	44.54
Ocean End Member 21m	0	0	0	0	0	0	0	0
Ocean End Member 674m	0	0	0	0	0	0	0	0

Ocean End Member 900m	0	0	0	0	0	0	0	0

Table C.4. Salinity-corrected, averaged trace metal data.

Salinity-corrected data for 96 groundwater (production, monitoring, irrigation wells; anchialine ponds; submarine groundwater discharge springs) sites and 3 ocean water sites during the study period of May 2017 to March 2019, organized by site from North (Waimea aquifer) to South (Kealakekua aquifer). The reported salinity-corrections follow the methods of section 3.4.2.2., and report the corrected values using the 21 m depth ocean water end member. Arsenic (As), boron (B), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), rhenium (Re), antimony (Sb), selenium (Se), strontium (Sr), uranium (U), vanadium (V), and zinc (Zn) are reported in salinity-corrected values in nM. Relative standard deviations for the geochemical parameters are reported in Appendix B.

Well Name	As (nM)	B (nM)	Ba (nM)	Be (nM)	Cd (nM)	Co (nM)	Cr (nM)	Cu (nM)	Fe (nM)	Mn (nM)	Mo (nM)	Ni (nM)	Pb (nM)	Re (nM)	Sb (nM)	Se (nM)	Sr (nM)	U (nM)	V (nM)	Zn (nM)
Parker Ranch Deepwell																	1112.1		137.5	315.9
Lalamilo C Deepwell			42.8				69.6				40.3		7.0				513.3		978.7	33.2
Lalamilo A Deepwell			32.9				66.6	25.3	106.0		43.9		8.7				516.9		907.6	177.8
Lalamilo B Deepwell			31.4				71.4	11.8			44.5		13.1				496.2		996.5	35.0
Parker #2 Deepwell		1334.9	44.7				79.3				44.0						555.0		1069.3	56.1
Parker #3 Deepwell	14.7	347.7	35.0				80.0				46.8		19.1				436.7	169.7	1051.8	23.5
Parker #4 Deepwell		1648.2	44.0				78.4				44.6		15.1				485.3		1061.5	32.8
Waikoloa 1		843.8	38.6		0.9		81.8		47.5	8.2	46.2		43.0	6.7			396.9		1066.3	129.4
DW-7			26.2				74.1	16.5			43.3		16.9				406.4		1020.7	36.4
Parker 5																	444.6		1081.1	
Parker 4			16.8				77.0				48.5		15.9				416.1		1037.3	24.1
Waikoloa 3	24.8	2594.5	25.6				64.6				76.3						494.3		1251.2	40.5
Waikoloa 2		1824.3	54.9				78.3				88.6		15.5				574.9		1237.8	26.8
Waikoloa DW-6		2057.9	56.4				71.6				97.0		13.1				535.9		1180.6	30.5

Resort Irr 2		10109.6	115.4				95.6				111.7		102.0				2013.5		3369.1	144.2
Waikoloa Irr 3	32.3	1885.9	39.7				57.4		38.7		71.9		11.9				325.0		2169.6	16.7
Resort 1	17.7	2570.3	29.1				68.9		73.5		70.9		17.3				408.4		2291.7	56.8
Nursery		1741.9	44.1				64.9	51.0			74.7		15.0				308.6		2143.5	39.4
Fifty-One FT STP		0.0	40.9				30.6	36.7			30.9		33.2				0.0		2280.6	71.3
West Hawaii Landfill		2521.6	46.8				79.0	18.2	149.0		65.9			0.0			220.4		2752.7	228.0
Back spring	19.6	3553.8	44.8		2.9	7.3	67.9	21.9	17.3	11.7	49.6		9.3	31.0			555.3		3089.9	12.5
Mouth ocean	244.4	13357.4				31.9	72.2	66.5	12988.5	170.9	97.9			395.0			1722.8		2085.9	304.7
Inside mouth channel	51.4	6617.5	43.9	49.6	3.0	7.6	65.5	15.8			57.6		13.5	12.0			1317.6		3119.5	20.2
Big Bridge	54.8	5159.3	55.8	158.0	9.3	26.0	82.2	100.0		27.9	71.4	14.9	19.0	0.0	14.4		888.6		3171.7	55.5
Kitchen corner inlet	42.0	4351.0	44.3			16.6	64.7	25.6			56.6		14.1	20.7			854.0		3049.8	99.2
Makani Golf Course		2454.7	8.8				63.7	15.8	21.6	4.6	51.5		10.2	22.3			404.9		2677.5	338.6
Puu Lani		2942.4	6.6				59.7	11.8	138.1		53.3	25.6					376.7		2652.5	30.1
Kekaha Kai - Kua Bay	397.7	21656.8	67.8				71.6	97.7			64.7			0			0.0	1134.5	1738.5	82.6
Kekaha Kai - Kaelehuluhulu		23668.8	252.8			84.2					86.2			18.6			6486.2		2385.6	0.0
Kekaha Kai - Small Pool		9046.6				73.6					90.5			13.1			4224.1		2063.3	26.8
Puu Waawaa							46.2				38.6						275.3		2211.0	596.0
Huehue Ranch 5	19.4	6240.2						41.0		31.0	59.6	30.8				47.0	480.8		1470.7	1191.8
Huehue Ranch 3		2301.4	13.2					23.8			67.7		14.1				227.0		1483.2	71.1
NELHA Well #12B		0.0	28.5				53.8										0.0		2226.0	0.0
NELHA Well #12A		0.0															0.0			

NELHA Well #12		38547.6															4422.4			
Huehue Ranch 4		3704.1	31.5				7.7	55.5	50.5		46.2	29.2	25.8	23.2		54.8	622.4		1477.8	771.1
Huehue Ranch 2		628.9	77.1				19.4	47.6			35.8	30.9	15.6				582.2		1881.5	124.0
Kau (Makalei) Deepwell	24.3	2325.8	99.7		1.8		30.6	68.4	47.1		64.2	4.3	11.5	16.9			294.1	237.0	2014.6	1196.0
NELHA A1		0.0	183.8			85.7					87.7			0			0.0		2328.6	0.0
NELHA Well #3B		12401.4				27.3											2753.2		1829.0	0.0
NELHA Well #3A		0.0															278.9		1604.2	
NELHA Well #3		29756.4															3465.5			
Kalaoa Deepwell							50.0				41.2		4.8				280.0		1719.6	49.3
NELHA A2		3786.6	52.7			73.6								28.6			1062.3		1855.3	0.0
NELHA Well #1		9544.5				37.4											5229.6		1414.1	28.2
NELHA Well #9B		16104.3															2648.3		1848.8	
NELHA Well #9A		3863.2															4459.4			
NELHA Well #9		8018.0															3091.6			
NELHA A3	324.3	7229.3	74.3					369.6						0			2653.4		1507.0	20.5
Kohanaiki #1			57.8														0.0		1437.1	
Kohanaiki #2			25.1														0.0		757.6	
Kohanaiki #3			51.0														0.0		1590.2	
Kohanaiki #4																	2076.8		1416.7	
Kohanaiki #5																	2065.0		1401.9	
Kohanaiki #6		0.0															0.0		1695.8	

Kohanaiki #7		0.0						420.3									971.7		1863.7	0.0
Kohanaiki A2		9044.5	72.2														2539.9		1219.5	0.0
Kohanaiki A30		0.0															0.0		1209.3	
Kohanaiki A43	1020.7	0.0	395.0														0.0		730.3	67.5
Kohanaiki A5			77.0														0.0		1230.5	
Kohanaiki A69		0.0	257.1														0.0		943.9	0.0
Kohanaiki A172		7623.4	124.6														6930.0			
Kohanaiki A121			101.0														0.0		861.9	
Kohanaiki A139	1443.3	0.0	715.7						2323.6								0.0		642.5	87.4
Kohanaiki A48		20642.8									38.5			169.5			0.0	3829.5	1473.0	37.5
Kohanaiki A46		32591.7	335.1							60.7				0.0			3822.5		776.8	223.0
Kohanaiki A77		13299.1															7711.9			400.0
Kohanaiki A120																				
Palani Ranch Deepwell			22.212				20.7				17.5		27.8				279.5		1444.6	92.1
Honokohau Deepwell		950.3	14.9				17.3	21.2	16.1		16.9						133.0		744.1	51.6
Queen Liliuokalani Trust (Keahuolu) Deepwell			26.2				41.4				17.7						275.2		1099.3	31.3
Keopu Deepwell		672.6	8.7				45.7				16.7		10.6				268.2		1101.6	118.5
QLT A1		2277.2	36.5			41.1		114.5									0.0		682.3	0.0
QLT A32		0.0	45.5										904.7				0.0			
QLT A4S		9557.7	39.0					160.5									268.7		1234.9	0.0
QLT A36	239.5	0.0	127.7					333.7		59.4		55.6					0.0		1439.5	0.0

QLT A30			68.9														0.0		811.3	
QLT A5	363.6	0.0	59.1			52.3		339.7									0.0		1540.9	43.1
QLT A8		4005.9	132.5										198.2				0.0		1283.0	0.0
QLT Maka Eo		0.0	35.3			41.8											0.0		1498.9	0.0
Keopu 2		789.6	15.7		0.9		26.9		93.1	177.4	15.4	11.9	11.3	7.0			317.0	90.3	905.1	774.2
Keopu 1		0.0	84.9						218.0		24.7	40.4					1383.4			30.3
Holualoa Deepwell		192.4	77.7				33.1						6.83				659.8		768.2	129.0
Kahaluu A Deepwell	15.5						19.4						7.53				614.2		875.4	268.3
Kahaluu C Deepwell							38.6				13.1						314.4		955.0	99.0
Kahaluu B Deepwell		0	74.8				36.0		24.5		9.0		14.91				861.3		882.9	60.3
Kahaluu D Deepwell	31.1	0	75.9				33.1				12.7						822.9		931.1	
Kahaluu Shaft		0	73.5				37.3				12.8						985.7		775.8	12.2
Kahaluu DW1 (96m)																				
Kahaluu DW1 (115m)																				
Kahaluu DW		0	92.2				10.1	54.3		121.8	20.4	21.4		29.6			2874.6		102.7	54.7
Halekii Deepwell							28.9				18.2		13.5				197.7		1069.3	119.3
Keei D Deepwell							26.9				11.5		12.5				185.8		1020.8	55.8
Keei A Deepwell		565.1					23.6		138.9		11.7		13.8				767.3		901.7	1452.3
Keei B Deepwell									1073.3								470.5		854.6	2483.5
Ocean End Member 21m		0												0			0.0			0.0
Ocean End Member 674m		0												0			0.0			0.0

Ocean End Member 900m		0				0								0			0			

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