GEOCHEMICAL AND STABLE ISOTOPE SOURCE TRACKING OF TERRESTRIAL NUTRIENT POLLUTION TO THE COASTAL WATERS OF WAIALUA BAY, NORTH SHORE, OAHU

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Abstract

Anthropogenic nutrient loading has long been identified as potentially harmful to coastal waters surrounding the Hawaiian Islands, with excess nutrients being delivered by stream runoff as well as by inputs to groundwaters that exit the coast as submarine groundwater discharge (SGD). Identifying, understanding, and quantifying where excess anthropogenic nutrients are introduced to surface and subsurface waters, properly deciphering how they may chemically evolve during transport, and understanding their history and final composition as they are discharged is therefore of vital importance for protecting aquatic resources and the surrounding environments. The Waialua region on the north shore of Oahu is particularly at risk of experiencing harmful effects from nutrient loading due to both its high density of onsite sewage disposal systems (OSDS) and its decades-long history of agricultural nutrient fertilization. We thus used a multi-tracer approach to determine the amount and to differentiate the sources of nutrients entering surface waters, groundwaters and the coastal waters of this region. Nutrient concentrations, $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values, and $\delta^{11}B$ values were used to establish geochemical and hydrological connections between terrestrial nutrient sources and the groundwater, stream, and coastal waters. Geochemical surveys of benthic macroalgae were performed along major beaches in the region to help confirm sources of nutrients, the extent of nutrient loading at each location, and the distance away from shore that nutrient pollution extended. Results indicate that nutrient concentrations in Waialua region streams are elevated relative to other impaired and pristine streams throughout the Hawaiian Islands. All Waialua region streams showed a seasonal shift in the form of nitrogen with a higher proportion of ammonium in the dry season, suggesting a seasonal decrease in the extent of natural excess nutrient remediation processes. Elevated $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values in the region were documented to be associated with the highest OSDS density and indicate significant leaching of wastewater into streams and coastal waters. However, widespread denitrification was found in several beaches and streams, particularly near locations with the highest densities of OSDS. Along the coast, the highest nutrient concentrations were found near the locations with the most OSDS, however the relationship between OSDS density and overall nutrient loading is not simple, as it is clear regions with few OSDS are also experiencing significant nutrient loading from agricultural sources.

Table of Contents

List of Tables

List of Figures

1. Introduction

Input of anthropogenic nutrients to surface waters and groundwater are known to have deleterious effects on coastal environments that can cascade throughout intertwined coastal ecosystems (Bowen et al., 2007; Heisler, 2008; Conley et al., 2009; Fang, 2020). Examples include elevated levels of nitrogen that lead to harmful algal blooms and the eutrophication of surface waters (Hasler et al., 1969; Smith et al., 1999, Li et al., 2014), and linkages exist between increased levels of nitrogen from wastewaters and the promotion of diseases in corals (Redding et al., 2013). Increased nutrient loads of both nitrogen (N) and phosphorus (P) to coastal waters have also been shown to increase macroalgae abundance that have adverse effects on coral physiology by reducing coral calcification, fecundity, and larval development (Fabricius 2005). Increased nutrient loads have been shown to increase coral sensitivity to bioerosion when coupled with low-pH conditions (Decarlo et al., 2015; Prouty et al., 2017).

The Pacific Islands that lack municipal sewage systems are particularly at risk of experiencing the consequences of excess nutrient loading. This creates the possibility that wastewater leachate in addition to freshwater resources such as streams and groundwater aquifers deliver nutrient-derived pollution to coastal environments (UNEP, 2011). To compensate for the lack of sewage systems, many Pacific Islands depend on the use of Onsite Sewage Disposal Systems (OSDS) as a way to treat and dispose of wastewater. There are several types of OSDS, including septic tanks, aerobic units, soil treatment and cesspools. In the Hawaiian Islands, cesspools are the most common, albeit the least efficient at successfully treating wastewater (WRRC and Engineering Solutions, 2008; Whittier and El-Kadi, 2009). Of a total 110,000 OSDS in the Hawaiian Islands, 87,900 are cesspools, and these cesspools are responsible for an estimated 53 million gallons of untreated cesspool effluent discharged into the subsurface daily (HDOH, 2018). On the most populous island of Oahu there are 14,000 OSDS, including 11,700 cesspools responsible for 7.1 million gallons of effluent released per day. Cesspools are designed to release wastewater into the surrounding environment, where microbes theoretically treat the wastewater before it reaches the water table. The distance between a cesspool and underlying water table is critical and is regulated in Hawaii to be at least 1 meter (HDOH, 2016). However, in coastal environments, the water table can vary dramatically, often causing that 1-meter buffer to decrease. Furthermore, failure to regularly maintain cesspools and other OSDS in Pacific Islands have resulted in untreated wastewater reaching the coastal environments (Shuler et al., 2017, Abaya et al., 2018). In practice, nutrients from OSDS may leach directly into the groundwater system and undergo further biological and chemical transformations before being discharged along the coast as submarine groundwater discharge (SGD). In addition to SGD, nutrients from agricultural practices such as fertilizer application can runoff into surface water or percolate into the groundwater, before discharging at the coast.

SGD is often underrepresented as a potentially large medium through which nutrients enter coastal waters. SGD includes any and all flow of water from the seabed to the coastal ocean regardless of composition and is primarily composed both of fresh groundwater and re-circulated seawater (Burnett et al., 2003). While rivers and streams are point source nutrient inputs, nutrient loading by SGD can enter the coastal waters as both point sources through groundwater seeps and as diffuse discharge along an entire coast. In addition, the nutrient concentration and composition of SGD is often different from that of surface waters. SGD is not simply groundwater that is moving through an unreactive medium, but instead travels through and interacts with porous rock with much longer residence times, with chemical and microbial reactions occurring and altering its chemical composition (e.g. Slomp and van Capellan, 2004; Hu, 2006; Burnett et al., 2006; Lee and Kim, 2007).

While SGD has only recently been identified as a medium through which anthropogenic nutrients enter coastal waters, streams and rivers have long been known to transport excess nutrients to coasts. Similar to OSDS near coastal waters, OSDS located adjacent to streams can lead to excess nutrients and harmful pathogens entering surface waters, particularly in gaining reaches of streams were groundwater discharges into streams as baseflow, affecting the stream water quality (Winter et al., 1998). Further, agricultural fertilizers have long been identified as sources of excess nutrients into streams and rivers, and are believed to be the leading cause for impaired stream and river water quality in the United States (EPA, 2002). The application of excess fertilizers above the levels utilized by crops and storage of livestock waste increase the possibility for excess nutrients to runoff into streams, particularly in regions that experience intense rainfall (EPA, 2005; Kato et al., 2009). In the Hawaiian Islands, it has been found that streams located in agricultural watersheds in general have higher nutrient concentrations than streams located in urban or forested watersheds (EPA, 2004), with streams in agricultural watersheds on Oahu having particularly high concentrations in baseflow compared to urban and forested watersheds (Hoover, 2002). Although little studied, coastal watersheds with both a high density of OSDS and large amounts of local and up gradient agricultural production are areas of multiple sources of excess nutrient loading that pose a combined threat to potentially damage coastal ecosystems, with both streams and SGD transporting nutrients to the coastal waters, and therefore require closer examination.

The purpose of this research is to evaluate the roles of nutrient loading from surface waters, groundwater, and SGD to the Waialua Bay region on the north shore of the island of Oahu, Hawaii. This area was chosen for its position at the confluence of both regional stream and groundwater flow, its history of high density of coastal OSDS, and its legacy of heavily fertilized watersheds. There are over 1700 OSDS within the watersheds bordering Waialua Bay, with an OSDS density of 27.0 OSDS/km^2 and 5.7 OSDS/km^2 for the Waialua and Haleiwa neighborhoods, respectively. Of those 1700 OSDS, 1,400 (78%) are cesspools, theoretically modeled to transmit more than 1 million gallons of untreated wastewater to Waialua Bay per day (Whittier and El-Kadi, 2009). In addition, over 50% of the land bordering the two main river systems in the region have been continuously used for agricultural purposes for decades (AECOM 2017), creating the possibility of both legacy and more recent nutrient inputs from fertilizers entering these systems and discharging at the coast. Flanked on three sides by highlands, the Waialua region lies in the middle of the north-central Oahu groundwater body with an estimated discharge of over 4 million gallons of SGD to the coast every day (Shade and Nichols, 1996), presenting a conduit through which large amounts of nutrients can enter the coastal waters. Our goal is therefore to analyze the nutrient conditions and how they vary spatially throughout the region, while also differentiating the sources of anthropogenic nutrients that reach the coast as either wastewater leachate from OSDS or as agricultural runoff. Further, this study aims to determine the relative importance of SGD versus stream nutrient transport to the coast, as well as quantify how nutrients in these different pathways are transformed and/or attenuated as they travel to the coast. This thesis begins by introducing water sampling methods to first identify areas with high levels of nutrients both in streams and along the coast, then discuss the multi-tracer approach developed to delineate sources of nutrients as either wastewater from OSDS or agriculture. We also discuss the transformations of nutrients in aquifers that are apparent as they move towards the coast. Our results describe and delineate the areas of highest concern for excess nutrient loading.

2. Background

2.1 Hydrogeology

The principal area for this study is the watersheds that drain into Waialua Bay on the North Shore of Oahu, Hawaii. The geology of Oahu is dominated by remnants of two highly eroded and overlapping shield volcanoes, represented by the older Waianae Volcanics (3.9-2.5 Mya) in the west and slightly younger Koolau Basalt (2.6-1.8 Mya) in the east (**Figure 2.1**). The Koolau Basalt is entirely basaltic in composition, whereas the Waianae Volcanics were formed during shield and post-shield stages of activity and are therefore more lithologically diverse (Hunt, 1996). The principal study area for this work lies between and includes the basalt flows from each of these volcanoes and empties down gradient towards the ocean to the north (**Figure 2.1**). Nearshore surficial geology is comprised of beach deposits, reef and lagoon deposits, and younger alluvium. In river valleys, the sediments are often made up of older alluvium deposits, formed when basalt in the mountains is weathered and deposited downstream. Nearshore alluvium and beach deposits are grouped together and are generally termed "caprock" throughout Hawaii, owing to their overlying superposition and their often-lower hydraulic conductivity that may impede water from escaping the underlying basalts. On Oahu, caprock deposits are typically made of fine-grained muds and marls, and/or from weathered basalt combined with weathered marine sedimentary rocks. The origin of the caprock can be terrestrial (weathered basalts) or marine (calcareous sedimentary rocks originating from coral reefs, coralline rubble, sands, and lagoonal sands and marls) (Hunt, 1996).

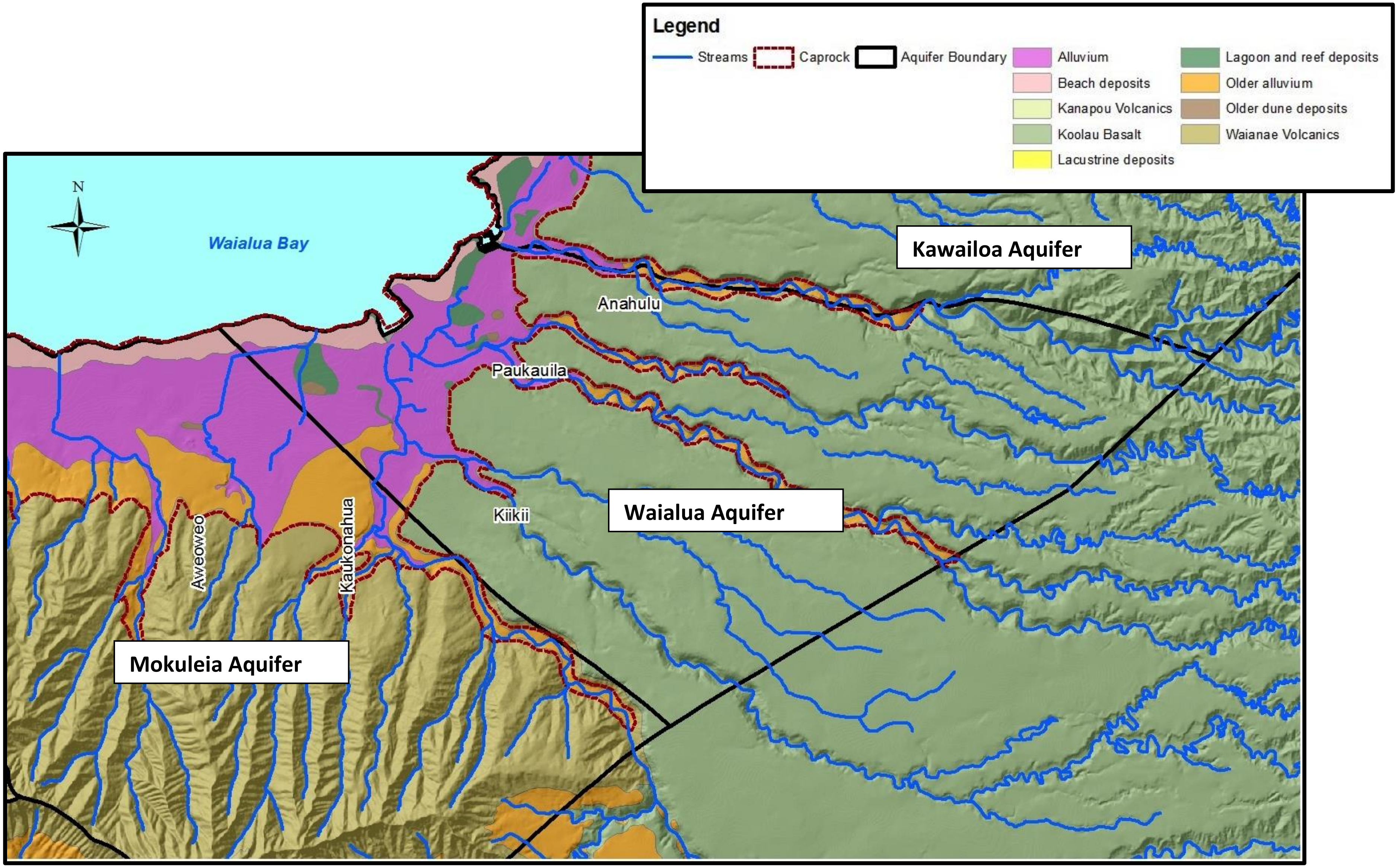

Figure 2.1. Simplified geologic map of the study area showing the major geologic units (Sherrod, 2007).

The aquifers in North-Central Oahu are comprised of a basal, freshwater lens floating on top of salt water. The general aquifer boundaries for Oahu are shown in **Figure 2.2**. Terrestrial waters of most interest to this study are contained in or feed into the North-Central Oahu and Schofield groundwater areas (cf. Dale, 1978). The North-Central Oahu water body is comprised of three separate aquifers, the Waialua aquifer, the Mokuleia aquifer, and the Kawailoa aquifer. These aquifers are mainly comprised of high-permeability basaltic lava flows. However, to the north the basaltic aquifers are mostly overlain by low-permeability caprock, slowing the release of SGD to the coast due to lower hydraulic conductivity. The presence of the caprock confines the three aquifers that make up the North-Central Oahu water body and increases the thickness of the basal lens (Oki, 1998). While unconfined aquifers generally have a hydraulic head of 0.3-0.6 m, the Waialua region and similarly confined aquifers typically have hydraulic heads that are usually around 3-12 m above sea level (Nichols et al., 1996). The two boundaries on either side of the Waialua aquifer are formed by the contact between the Koolau Basalt and Waianae Volcanics on the western boundary, and valley-fill deposits of the ancient Anahulu River on the eastern boundary (Dale, 1978; **Figure 2.1**). Both these boundaries direct flow towards the ocean. The boundary between the North-Central Oahu basal water body and the Schofield high water area to its north is the Schofield groundwater dam (**Figure 2.2**). The composition of this dam is unknown, but according to Miller et al. (1999), it is likely caused by either dikes or buried ridges. Its existence is, however, well known due to the dramatic change in water level above and below the boundary. Below the dam, the water level is around 35 m above sea level, but above the dam the water level jumps to as high as 130 m above sea level (Miller et al., 1999). The boundaries on either side of the Waialua aquifer, combined with groundwater flowing north from the Schofield high-water dam strongly suggest the groundwater flow paths are in the direction of the ocean. As the groundwater flows towards the ocean, nutrients can potentially enter the groundwater system and discharge at the coast.

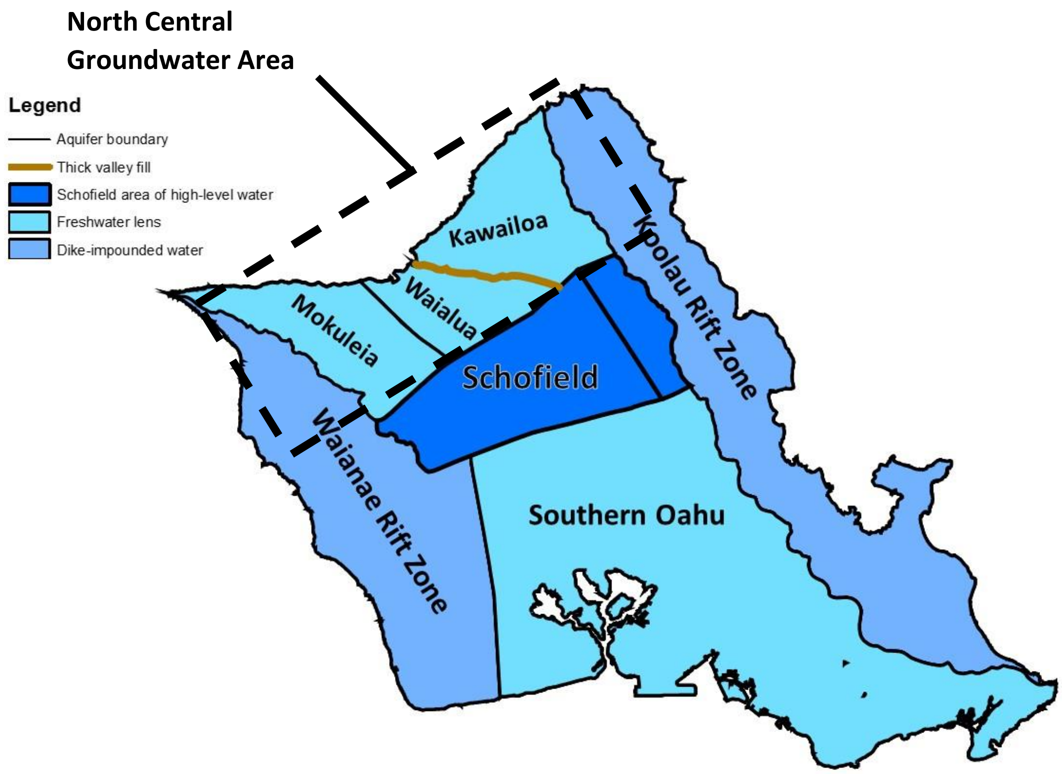

Figure 2.2. Map of major groundwater areas of Oahu as described in Miller et al., 1990. The main study area of this work encompasses the North Central groundwater area, with particular emphasis on the region's main groundwater and surface water drains into the Waialua area. The three types of groundwater are shown: basal freshwater lens, dike-impounded groundwater, and high-level groundwater. The thick Anahulu valley fill border between the Waialua and Kawailoa aquifers is shown in brown. The Kaukonahua valley and Waianae confining bed form the boundary between the Waialua and Mokuleia aquifers.

Our study is comprised mainly of nine watersheds within the Waialua-Haleiwa area on the North Shore of Oahu: the Waialua, Kaukonahua, Paukauila, Loko Ea, Opaeula, Helemano, Kiikii, Poamoho and Anahulu watersheds. (**Table 2.1; Figure 2.3**). The Helemano and Opaeula watersheds both drain into the Paukauila watershed close to the coast, while the Poamoho and Kaukonahua watersheds drain into the Kiikii watershed. All of these watersheds eventually drain into Waialua Bay, which extends from Mokuleia in the east to Haleiwa Beach Park in the west. Other watersheds of interest to this study were the Pahole, Makaleha, Keamanea, Kawailoa, Kawainui, and Kawaiiki watersheds.

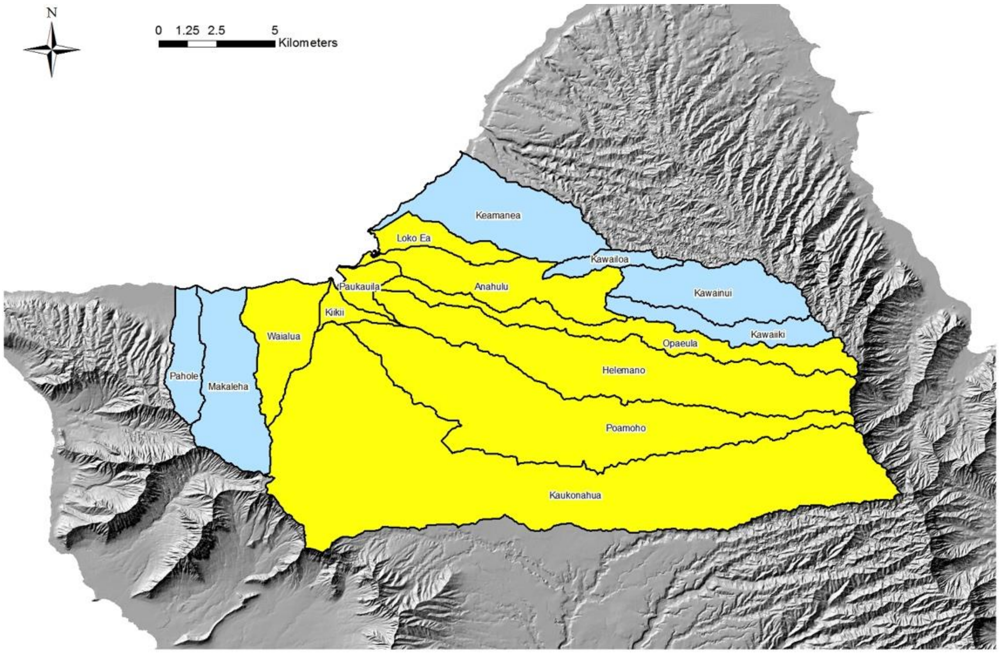

Figure 2.3. Map of watersheds in the study area. The 9 principal watersheds are highlighted in yellow. Other watersheds are areas that either are hydrologically connected to the principal watersheds or contained sampling locations.

Table 2.1. Watersheds in the study area along with their area, perimeter, total OSDS, and OSDS per kilometer. The table is ordered by total area of the watersheds. The 9 principal watersheds are highlighted in yellow.

WATERSHED	AREA (km^2)	PERIMETER (m)	OSDS	OSDS (per km^2)
Kaukonahua	101.81	73.34	241	2.37
Poamoho	47.25	53.71	85	1.80
Helemano	37.85	49.39	15	0.40
Keamanea	19.88	25.60	196	9.86
Makaleha	17.18	22.47	63	3.67
Anahulu	16.21	33.66	140	8.63
Opaeula	15.42	49.04	6	0.39
Kawainui	14.68	21.91	0	0.00
Waialua	12.05	18.29	696	57.74
Kawaiiki	7.83	23.42	0	0.00
Pahole	6.62	14.40	51	7.70
Loko Ea	5.54	15.13	10	1.81
Paukauila	3.50	11.05	293	83.64
Kawailoa	3.35	13.39	0	0.00
Kiikii	2.40	10.40	288	120.23

2.2. Land use

The main sources for excess nutrients that may enter the ocean are wastewater leachate from OSDS near the coast and from agricultural runoff both near the coast and further upslope. Each of these sources are detailed below. **Figure 2.4** is a map showing the distribution of the OSDS, agricultural lands and streams in the study area.

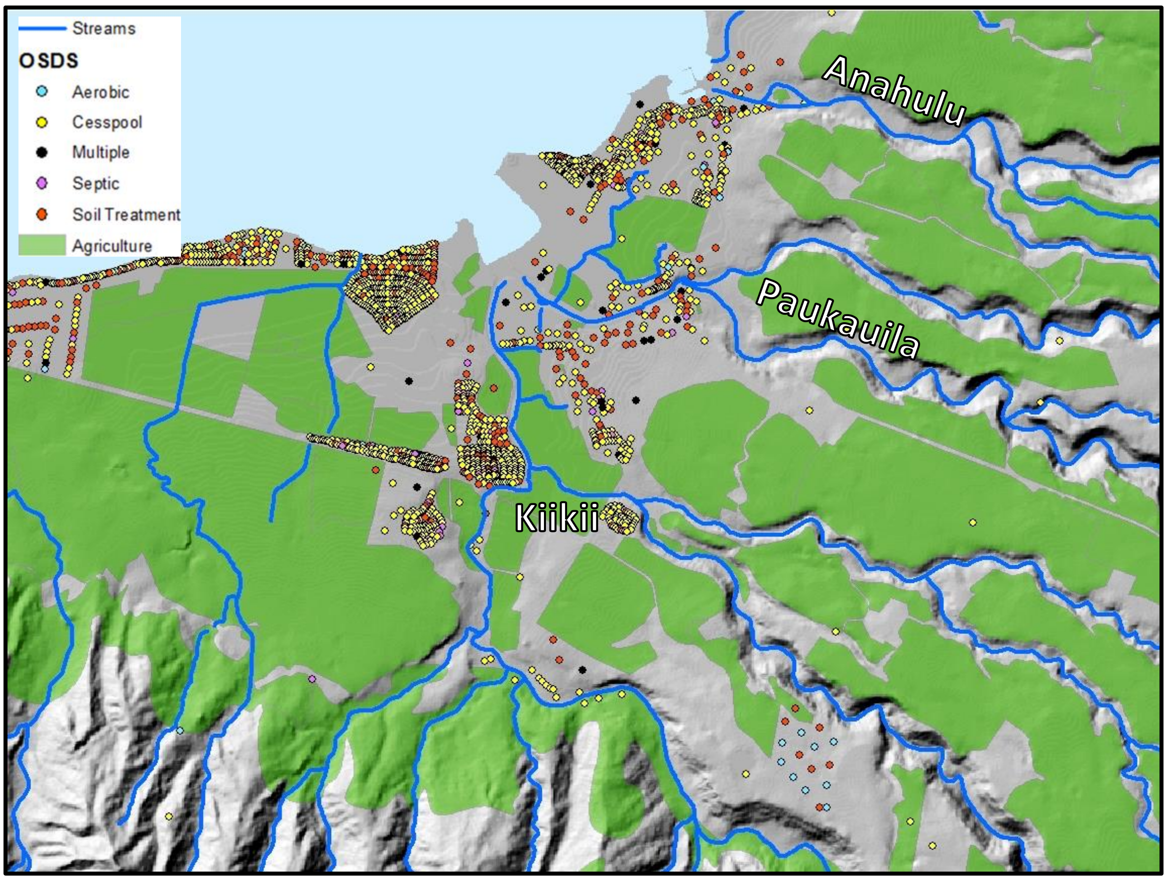

Figure 2.4. Map of Waialua Region showing the sources of anthropogenic nutrients. Each dot represents a single OSDS, and the green shaded regions encompass all types of agriculture and pastureland. The three main stream systems are also labeled.

2.2.1 On site disposal systems

Within the nine principal watersheds of the study area, the Waialua watershed has the highest concentration of OSDS at 696 OSDS, or roughly 33% of the OSDS in all the watersheds. It has the highest density of OSDS out of any of the watersheds at 57.74 OSDS per km^2. Other watersheds of concern are the Kaukonahua and Paukauila, containing over 200 OSDS each. **Table 2.2** lists the breakdown of types of OSDS within the study site, with an estimated typical nitrogen concentration for each waste disposal system (WRRC and Engineering Solutions 2008; Whittier and El-Kadi, 2009). The overwhelming majority of OSDS in the Waialua area are cesspools, which also have the highest typical nitrogen concentration, suggesting this area is the greatest risk of nutrient leaching into the surrounding groundwater. The leachate from OSDS can potentially leak into the surrounding groundwater system, eventually discharging along the coast as tainted SGD. SGD often contains elevated levels of nutrients, as has been found both around the world and throughout the Hawaiian Islands, often in OSDS-dense regions (Johannes, 1980, Johannes and Hearn, 1985; Burnett et al., 2003; Garrison et al., 2003; Paytan et al., 2006; Bowen et al, 2007; Johnson et al., 2008; Street et al., 2008; Kim and Swarzenski, 2010; Kroeger and Charette, 2008; Knee et al., 2010a,b; Moore, 2010; Glenn et al. 2012;Kelly, 2012; Glenn et al. 2013; Kelly et al., 2013; Moosdorf et al., 2015; Rodellas et al., 2015; Amato et al., 2016; Dulai et al., 2016; Wiegner et al., 2016; Bishop et al. 2017).

Table 2.2. Breakdown of different OSDS in the Waialua area and typical nitrogen concentrations (Whittier and El-Kadi, 2009).

OSDS Class	Typical Nitrogen Concentration (mg/L)	Units within Study Area
Class I (Soil Treatment)	1	294
Class II (Septic)	36	47
Class III (Aerobic)	24	33
Class IV (Cesspool)	60.5	1,400
Total		**1,774**

2.2.2 Historic and current agriculture

In addition to wastewater leachate from OSDS, agriculture is another important potential source of excess nutrients to surface waters, groundwaters and the ocean. The land surrounding the Waialua area has long been used to grow various crops, including sugarcane and pineapple. Sugarcane plantations began to develop throughout the Waialua area as far back as 1865, and throughout the 20th century, sugar and pineapple production increased in Waialua. **Figure 2.5** shows the historic agricultural land use for the years 1978-1980, when the majority of land was used for sugarcane production. Widespread production of sugarcane continued in the area until 1994, when the last sugarcane company, Waialua Sugar, ceased production (Hawaii Department of Agriculture, 1999). Pineapple was also grown in the area during this time in the central area of Oahu in watersheds that drain into Waialua Bay.

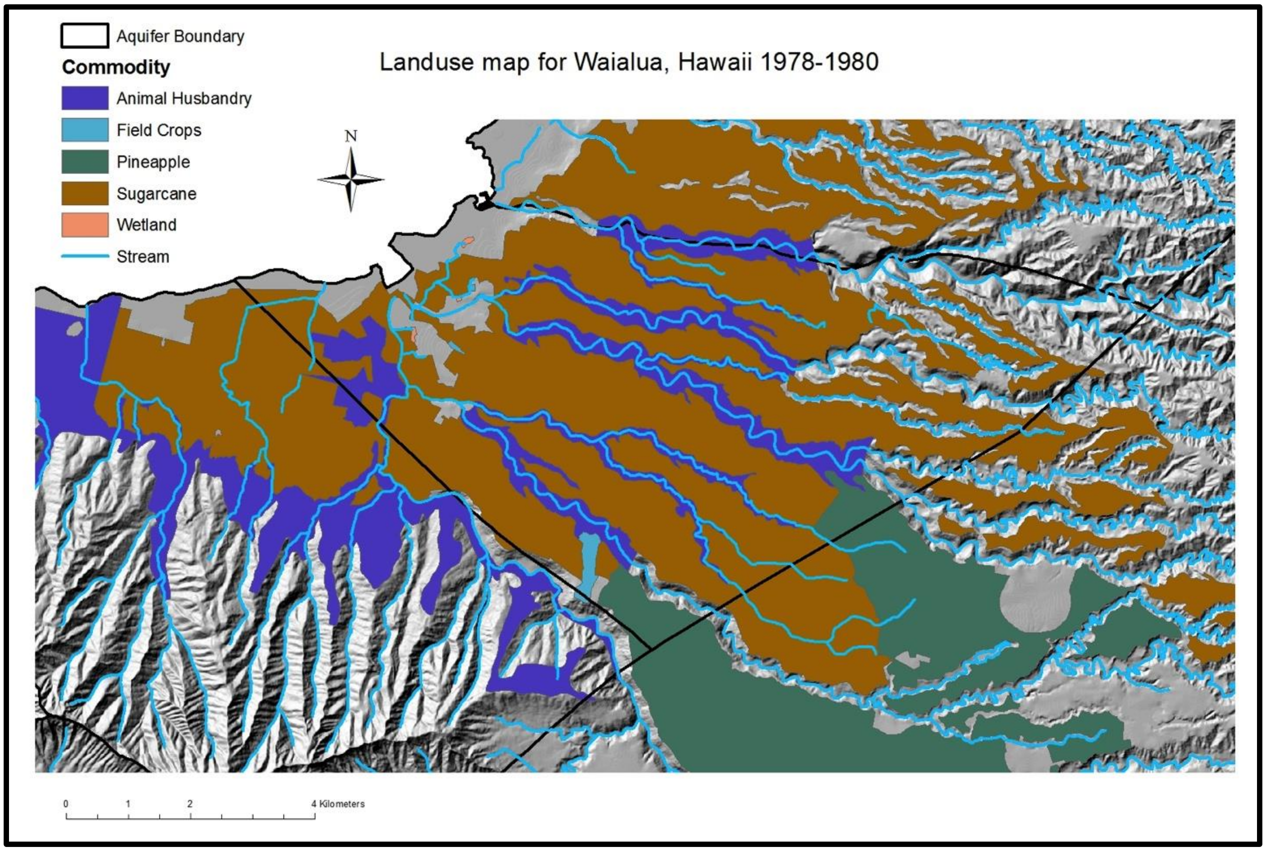

Figure 2.5. Agricultural land use map for areas adjacent to Waialua Bay 1978-1980 (Data from the Hawaii State Office of Planning Statewide GIS Program).

Following the closure of the final sugarcane companies in 1994, pineapple production briefly became the dominant agriculture in the region with Dole Food Company Inc. being the only remaining large corporation growing pineapple. Since 1994, seed production has become the largest agricultural sector on Oahu (HBWS, 2016). **Figure 2.6** shows a map of the land use as of 2015-2016. As shown, there are many different crops grown in the region, however only a few crops make up the majority of the land used for agriculture, including seed production, pastureland, and pineapple. Dole Food Company Inc. is the 2nd largest overall landowner and largest agricultural landowner on the North Shore, with almost 96 km^2, although they lease out much of their land to Biotechnology seed product and development companies such as Monsanto (HBWS, 2016).

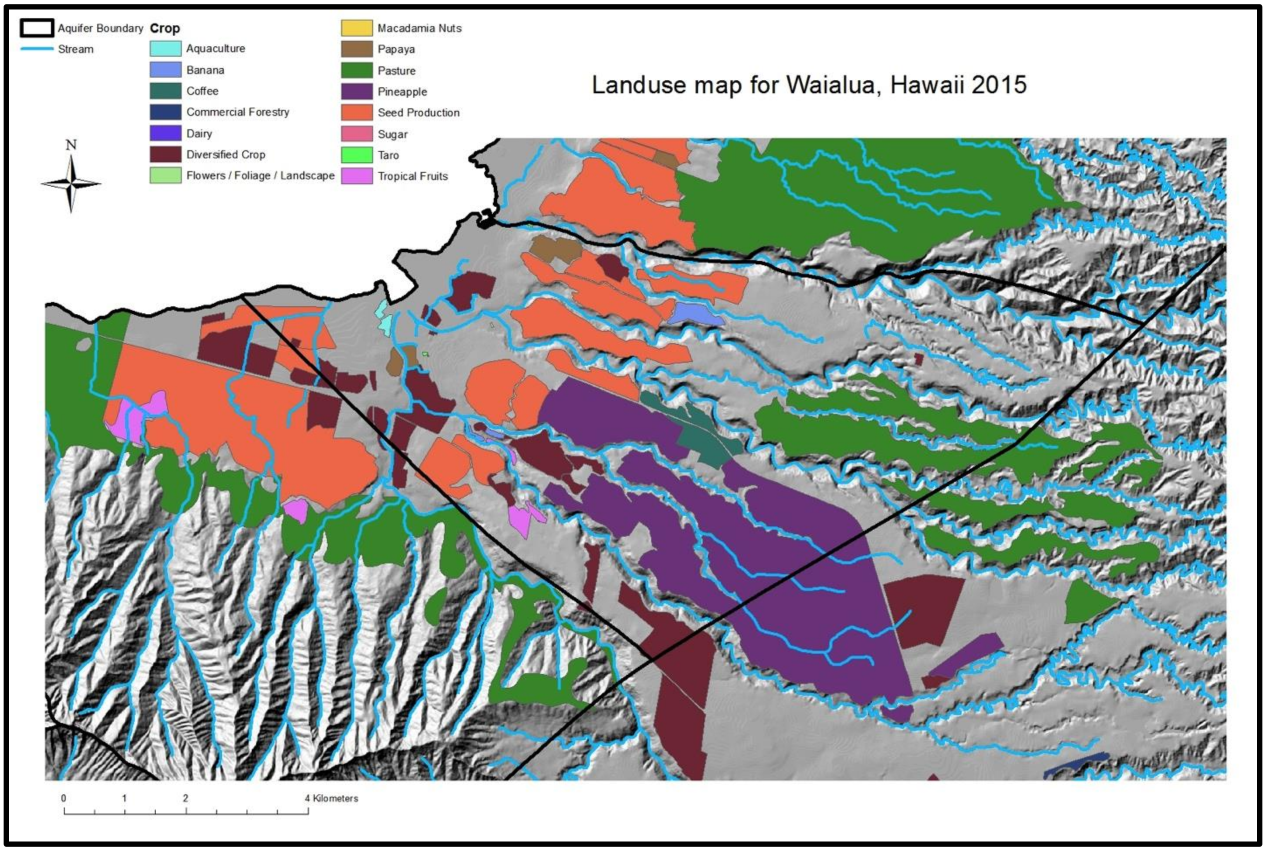

Figure 2.6. Land use map for areas adjacent to Waialua Bay 2015 (Hawaii Department of Agriculture Statewide Agricultural Land Use Baseline 2015).

As Dole Food Company Inc. still owns a large portion of the agricultural land in the region (AECOM, 2017), their fertilization practices are used as an example for this study. Pineapple requires large amounts of fertilizer to grow, and especially high amounts of nitrogen, potassium, and iron, while lower concentrations of phosphorus and calcium are necessary. The fertilizer most widely used in the region is synthetic urea fertilizer ($CO(NH_2)_2$). Since pineapple takes 18 months from planting to harvest, fertilizer is constantly applied to ensure proper growth. General practice for growing pineapple uses around 988 kg/hectare (98.8 g/m^2) of applied urea per year (Bartholomew et al., 2002). This massive amount of nutrient applied to the soil poses the potential of excess nutrients running off into the nearby streams in the study area and eventually reaching the coastal environment. It has been previously estimated that only around 50% of the applied fertilizers is utilized by crops in Hawaii with the excess nutrients potentially entering the groundwater system, and discharge at the coast as SGD (Visher and Mink, 1964). Nitrogen that is not used by plants and is transported beyond the root system can be transported into the groundwater system, generally as nitrate, the more mobile form of nitrogen (Follett, 1995).

2.3 Climate and hydrology

Climate on Oahu is dominated by northeast trade winds and varies seasonally as the strength of the winds change throughout the year, usually being strongest from May through September (Lyons, 1982). Due to the wind direction, most of the precipitation falls as orographic rainfall over the Koolau Range on the eastern coast of Oahu. Resultantly, annual precipitation values are generally lower in areas such as Waialua, which lie to the west in the rain shadow of the Koolau range. Waialua experiences 2 dominant precipitation seasons, with a 5-month dry season from May to September dominated by trade winds, and a 7-month wet season from October to April (Giambelluca and Sanderson, 1993; Norton et al., 2011). During the wet season, average monthly values for precipitation range between 54 mm to around 90 mm, while during the dry season average monthly precipitation values range between 21 to 46 mm (Giambelluca et al., 2013). While trade winds still play a significant role in winter rainfall, increases in precipitation during wet seasons are attributed to mid-latitude cold fronts and Kona storms (Lyon, 1982). These intermittent but intense rainfall events were found to be the most responsible for groundwater recharge on Oahu (Dores, 2018).

Besides nutrients entering the coast through SGD, the rivers and streams in the Waialua area present another conduit through which nutrients could enter the coastal water, especially linked with proximity of agricultural lands to the streams. Groundwater discharge also can play a role in delivering nutrients to these rivers and streams. There are three major perennial stream systems located in the study area: the Kiikii, the Paukauila, and the Anahulu (**Figure 2.4**). All three of these systems are composed of several river branches. The Kiikii system contains the Poamoho stream, the North Kaukonahua, and the South Kaukonahua streams, the Paukauila System contains the Opaeula and Helemano streams, and the Anahulu System contains the Kawaiiki, Kawailoa, and Kawainui streams. Average flow values for the stream systems are: 0.69 m^3/s in the Paukauila system, 0.76 m^3/s in the Anahulu system, and 0.91 m^3/s in the Kiikii system (Hawaii Cooperative Park Service Unit, 1990), although tides affect the stream flow in the lower reaches. Around 57% of the watersheds surrounding the Kiikii and Paukauila river systems are used for some agricultural purpose, which is equal to about 106 km^2 of agriculture. Acceptable standards for nutrients in streams are set by the Hawaii Department of Health in the Hawaii Administrative rules. The acceptable values for rivers and streams vary seasonally, depending on whether it is the wet or dry season. **Table 2.3** lists the accepted standard for nutrients, as well as total suspended solids and turbidity. Most samples collected in this study exceed recommended standards, particularly for nitrate + nitrite (see below). Thus, all streams within the study area are another pathway for nutrients to enter coastal waters.

Table 2.2. Maximum acceptable nutrient levels in streams designated by Hawaii Administrative Rules Chapter 11-54-5.2[b]. Actual values recorded during this study are discussed elsewhere throughout this thesis.

Parameter	Geometric Mean not to exceed the given value		Not to exceed the given value more than 10% of the time		Not to exceed the given value more than 2% of the time	
	Wet Season	Dry Season	Wet Season	Dry Season	Wet Season	Dry Season
Total Nitrogen (µM)	18.0	13.0	37.0	27.0	57.0	43.0
Nitrate+Nitrite (µM)	1.1	0.5	2.9	1.5	4.8	2.7
Total Phosphorus (µM)	1.6	1.0	3.2	1.9	4.8	2.6
TSS (mg/L)	20.0	10.0	50.0	30.0	80.0	55.0
Turbidity (NTU)	5.0	2.0	15.0	5.5	25.0	10.0

2.4 Beaches

The study area is primarily made up of four beaches (**Figure 2.7**). The study site ranges from the Aweoweo beach in the west, to the tip of Haleiwa Beach Park in the northeast. In between these two beaches are Waialua Beach and Haleiwa Alii Beach, which is referred to simply as Alii Beach in the rest of this report. These beaches are important to the North Shore communities for their use in popular ocean recreation activities. Haleiwa beach and Alii beach are especially popular among both locals and tourists because of their ideal location for watersports. Further, Alii beach is a world-famous surfing beach that hosts the World Surf League Hawaiian Pro surf contest each year. North Shore beaches are known for their large waves in the wintertime, often attracting tourists who wish to watch people surf these massive waves. Average maximum wave heights for North Shore beaches in the summer is 0.51 – 0.67 m. During winter average maximum wave heights reach 6.67 m, with daily maximum heights over 10.6+ m (Caldwell, 2005). Despite being popular tourist destinations, most of these beaches are in locations that are at risk of experiencing excess nutrient loading from wastewater because of the high density of OSDS close to the coast. In total, there are 1733 OSDS within 3 kilometers of these beaches' shorelines, and 1170 OSDS within 1 kilometer (**Table 2.3)**.

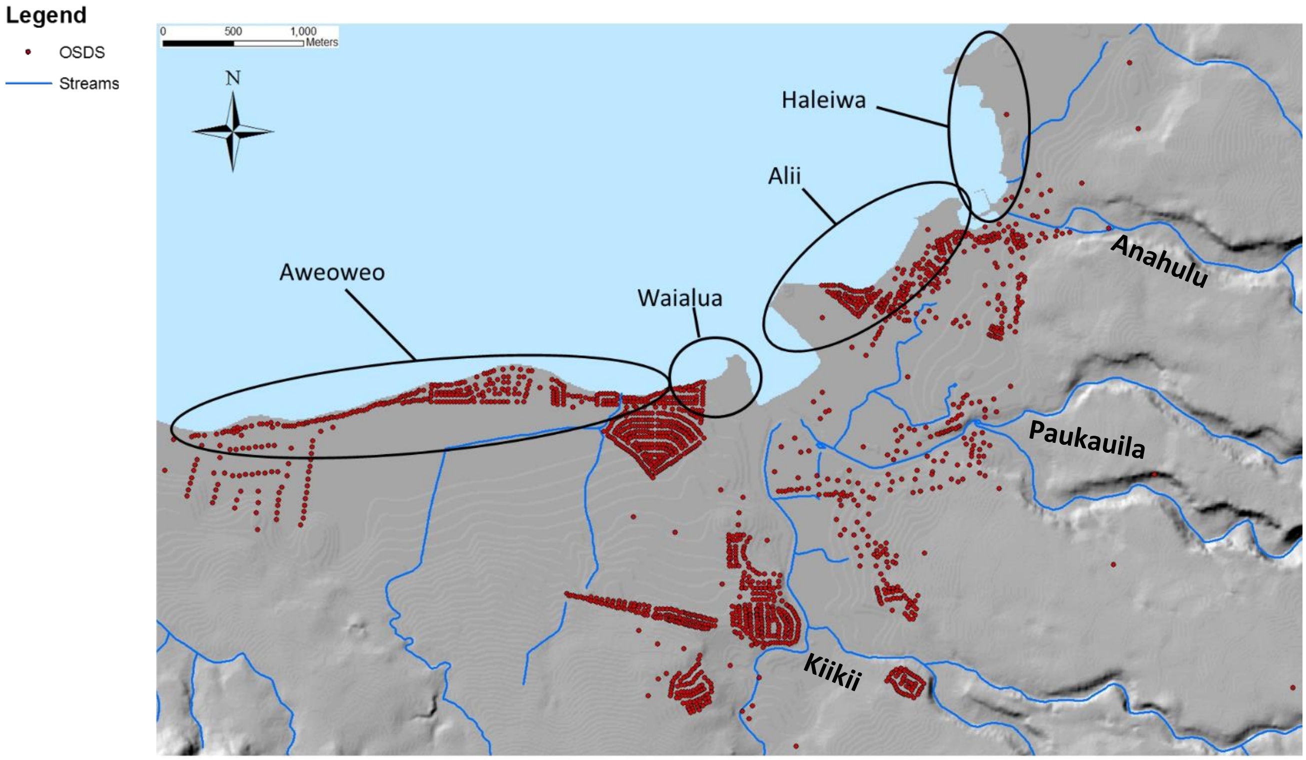

Figure 2.7. Map of the four main beaches in the study area, along with the main streams and OSDS.

Table 2.3. The four main beaches in the study site with their length and total OSDS within 1 kilometer of the coast.

Beach	Length (m)	Total OSDS
Aweoweo	2820	680
Waialua	1460	489
Alii	1810	410
Haleiwa	1360	10

3. Materials and methods

Water samples were collected throughout the nine principal watersheds of our study area and along the three main stream systems. Our sampling strategy was designed to locate areas that are contaminated with excess nutrients, as well as determine sources of anthropogenic contamination, principally from OSDS leachate or surface and groundwater runoff from agriculture. Samples include surface water samples, from streams, estuaries, coastal water, and a fishpond, groundwater samples from privately owned groundwater wells, and shallow pore waters from beach face piezometers. Pore waters along the coast were accessed using Solinst drive point piezometers attached to a 4 ft galvanized steel pipe which was hammered into the sand at various locations along the coast. Water was collected via 2 m-long silicone Masterflex tubing and a Solinst peristaltic pump, filtered through a 0.45 µm capsule filter. To increase the chances of capturing SGD in coastal and pore water samples, coastal pore water samples were collected at low tide when there is the maximum amount of seaward flow of SGD (Maher et al., 2013; Sadat-Noori et al., 2016). Routine water quality parameters were collected at all sampling locations including salinity, pH, total dissolved solids (TDS), specific conductivity (SpC), conductivity (Cond), dissolved oxygen (DO), and temperature using a YSI EXO multi-parameter sonde. In addition to water sampling, algal tissue samples were collected along four beaches in the study area to further delineate nutrient sources in the Waialua region (**Section 3.3**). Three of these four beaches were identified as areas of concern using infrared imagery created for the Waialua Bay project by Mason (2020) (**Figure 3.1**). Endmember nutrient and isotope values came from both measured values and values reported in literature. A full description of the endmembers used in this study can be found in **Tables 5.1** and **5.2**.

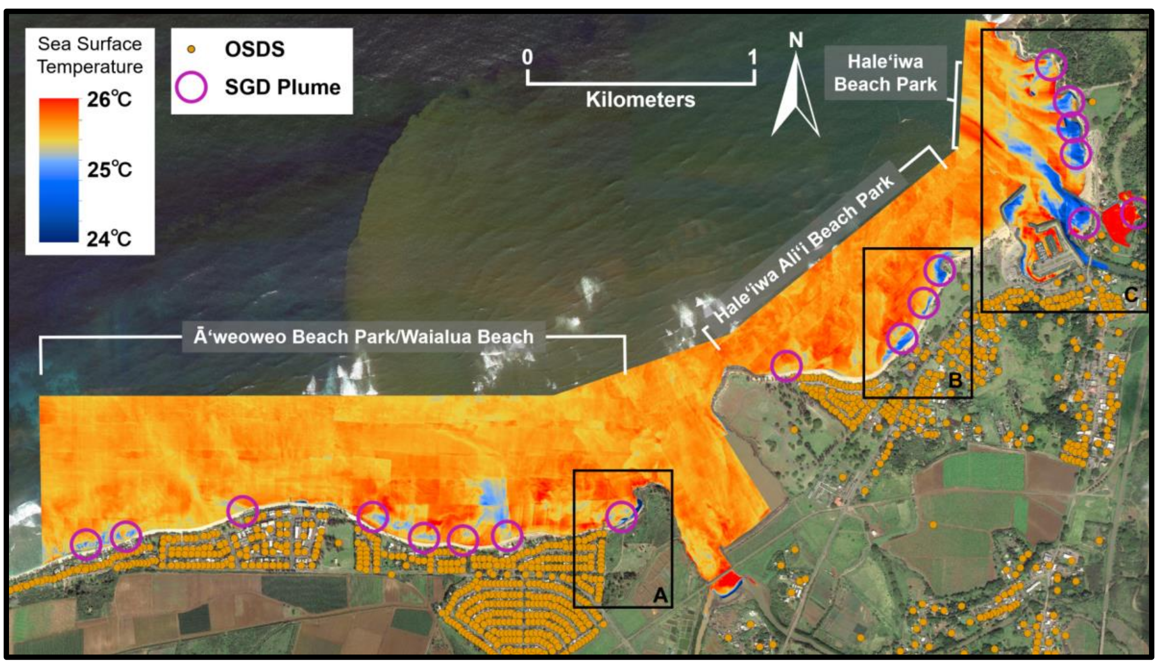

Figure 3.1. Final thermal infrared imagery for the Waialua Region coastline. Temperatures range between 23.8℃ and 33.7℃. The 18 SGD seeps identified are shown in the purple circles. OSDS are also mapped as the orange circles. The vast majority of OSDS are within 500 meters of the coast. Boxes A, B, and C are the three main beaches of concern found in the imagery (photo provided by Jordan Mason).

Reconnaissance and wet season sampling of streams took place during January and February of 2019. During this time, samples from all 3 major stream systems were collected. Dry season stream samples were then collected from August 2019 to September 2019. Beach face piezometer sampling was limited to the summer of 2019 and spring of 2020. The majority of samples were collected from June 2019 to August 2019, with several samples collected in late February 2020. The window of time for beach face piezometer sampling was limited due to the wave action on the North Shore of Oahu. Beach face samples were only possible when waves were <0.33 m in height due to wave run-up reaching the sampling location and contaminating the sample. For similar reasons, the majority of algae sampling was performed in August 2019, with some samples collected in February and March of 2020. Algal sampling was not possible under large wave conditions from both a safety concern and the likelihood that wave impacts and sand scour denuded most of the intertidal shallow subtidal of any moderately sized algae.

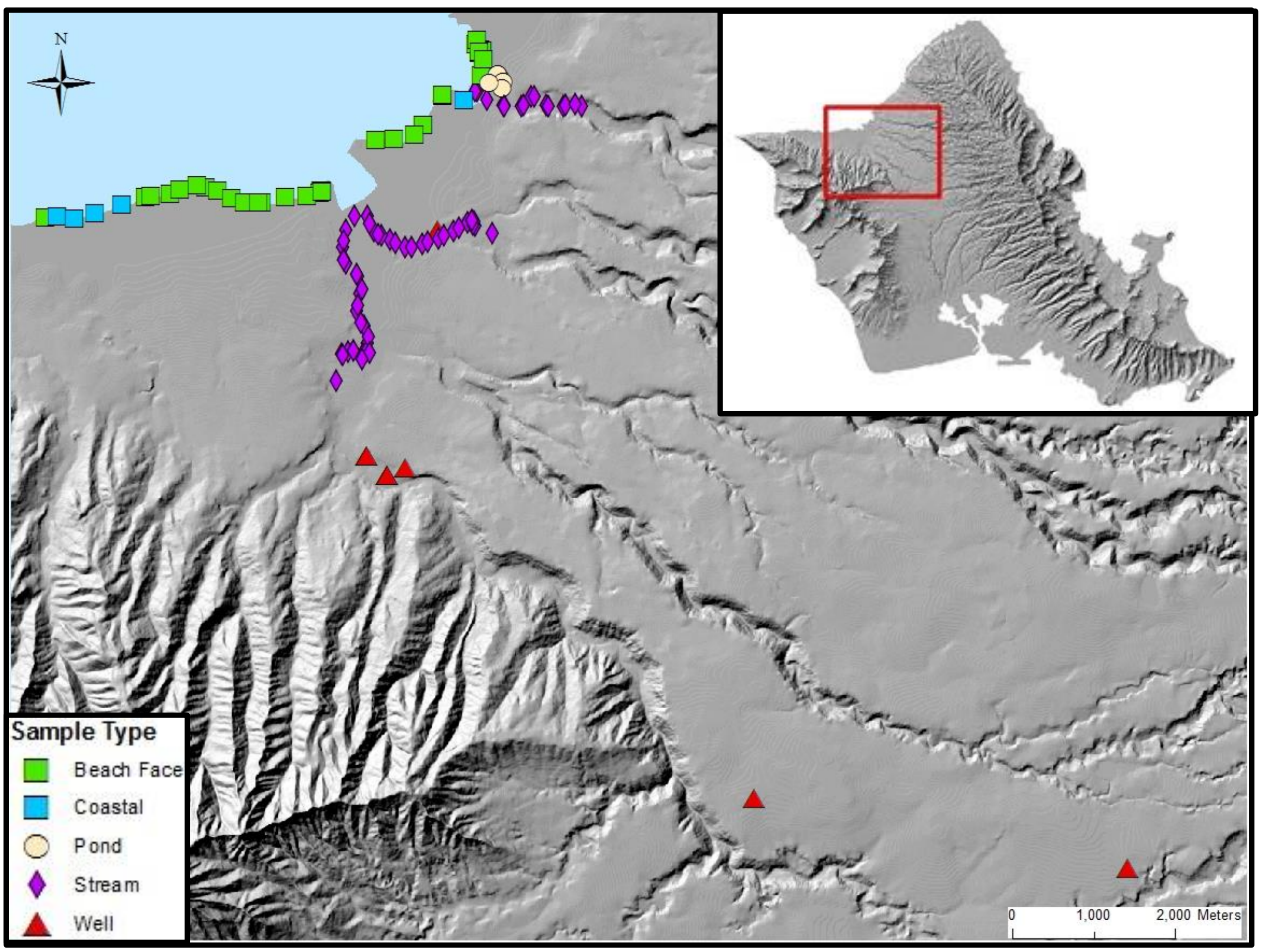

Figure 3.2. Locations of all water samples collected in the study area along with the type of sample.

3.1 Water sampling strategy

Water samples were collected from the three main stream systems and four beaches in the study site (**Figure 3.2**). The Loko Ea watershed, the northeastern most watershed in our study area, has the fewest total OSDS and agricultural land in the region, thus Haleiwa Beach in this watershed was chosen to represent a beach relatively unaffected by OSDS. Overall, there are fewer than 10 OSDS in these regions, compared to the other principal watersheds, which have OSDS ranging from 140 – 696 OSDS. The Anahulu watershed and stream is used to represent a relatively clean stream due to the low number of OSDS that could impact the stream waters. While the Anahulu watershed has 140 OSDS in its boundaries, 134 of those are located within 300 m of the coast, so the upstream reaches should not be impacted by OSDS leachate. Furthermore, the Loko Ea and Anahulu watersheds are hydrogeologically separated from the rest of the study area due to the presence of a hydrogeologic boundary formed due to thick valley-fill deposits of the ancient Anahulu River (Dale, 1978). This reduces the impact of OSDS leachate from neighboring aquifers reaching the groundwater system in the Loko Ea and Anahulu watersheds. Although the Loko Ea and Anahulu watersheds have a relatively small number of OSDS and are therefore expected to be less impacted by OSDS leachate, there are agricultural fields surrounding the upstream reaches so it cannot be described as a 'pristine' control region. However, these watersheds were used to compare with regions with high OSDS density.

3.2 Geochemical source-tracking of water

A multi-tracer approach was used to identify areas experiencing excess nutrient loading and then source-track wastewater and agricultural contamination to identify pathways through which nutrients enter coastal waters (Xue et al. 2009; Minet et al. 2012). Details of the methods used are further explained in individual sections below. In order to identify areas that may be experiencing excess nutrient loading, nutrient concentrations were analyzed for surface water and groundwater samples. Concentrations of total nitrogen (TN), ammonium (NH_4^+), Nitrate + Nitrite (N+N), Total Phosphate (TP), orthophosphate (PO_4^{3-}), and silicate (SiO_2) were measured. To identify the sources of nutrients in water, the nitrogen and oxygen stable isotopic composition of nitrate were used to distinguish between the presence of wastewater leachate or fertilizer in the water body. Because nitrate is not conservative and can be transformed through denitrification (Kendall et al., 1998; Granger and Wankel, 2016) as it moves through the groundwater system, boron concentrations and isotopic composition were also used as an additional tracer to compliment the results of isotopic composition of nitrate and distinguish agricultural sources in streams and SGD. Finally, the combination of dissolved inorganic nitrogen (DIN) and dissolved oxygen (DO) concentrations were used to locate areas with potentially high denitrification. To evaluate the significance of the differences in nitrogen conditions for streams and beaches in the study area, a Kruskal-Wallis one-way analysis of variance was performed. This is the same as a non-parametric ANOVA analysis and does not assume normality for the sample distribution. This test needs one nominal variable (in this case the stream or beach location) and one measurement variable (i.e. TN, N+N, NH_4^+, $\delta^{15}N_{nitrate}$, $\delta^{18}O_{nitrate}$), and can be used to determine if multiple populations of samples are significantly different. In a Kruskal-Wallis test, populations are considered significantly different when there is a P-value of <0.05. This test was performed for all nitrogen parameters we collected.

3.2.1 Nutrient concentrations

Concentrations of total nitrogen (TN), ammonium (NH_4^+), Nitrate + Nitrite (N+N), Total Phosphate (TP), orthophosphate (PO_4^{3-}), and silicate were analyzed in samples from the study area from groundwater wells, streams, coastal water, and shallow pore water from beach face piezometers. While ammonium is reported separately, NO_3^- and NO_2^- were reported together as nitrate + nitrite, while NH_4^+, NO_3^-, and NO_2^-, combine to make up the dissolved inorganic nitrogen (DIN). Samples were collected in HCL-washed (10% v/v) 60 mL HDPE screw top bottles, filtered through a 0.45 µm capsule filter, and frozen until analysis at the SOEST Laboratory For Analytical Biogeochemistry (S-LAB) at the University of Hawaii at Manoa with a Seal Analytical AA3 HR Nutrient Autoanalyzer. Sample precision at 1 standard deviation based on 10 duplicate pairs was as follows: 15.98 µM TN, 0.48 µM TP, 15.66 µM N+N, 0.46 µM PO_4^{3-},134.07 µM SiO_2, and 0.35 µM NH_4^+.

3.2.2 Dual isotopic composition of NO_3^-

A full description of the nitrate nitrogen ($\delta^{15}N_{nitrate}$) and oxygen ($\delta^{18}O_{nitrate}$) isotope values for all endmembers in this study can be found in **section 5.1**. The samples for the stable isotopic composition of N+N were collected in HCl-washed (10% v/v) 60 mL HDPE bottles and frozen until analysis at the UH SOEST Biogeochemical Stable Isotope Facility using the denitrifier method as described in McIlvin and Casciotti (2011). Nitrous oxide gas produced by denitrifying bacteria were analyzed using a Finnigan Mat 252 coupled to a GasBench II. Isotopic abundances were normalized using USGS 32, 34 and 35 as well as NIST 3 reference materials analyzed with each group of 19-20 samples. $\delta^{18}O_{nitrate}$ values are expressed in ‰ versus VSMOW. The accuracy of $\delta^{18}O_{nitrate}$ values was determined by repeated analysis (n = 12) of a laboratory reference sample of analytical grade $NaNO_3$ (GA NO3) of known oxygen isotopic composition (10.57±0.4) and was found to be 10.59±0.43‰. The precision of the $\delta^{18}O_{nitrate}$

measurements based on repeated analysis of GA NO_3 was ±0.26‰ whereas the precision of $\delta^{18}O_{nitrate}$ based on the analysis of 7 duplicate pairs of samples was 0.61‰. $\delta^{15}N_{nitrate}$ is expressed as ‰ against AIR. The accuracy of $\delta^{15}N_{nitrate}$ values was determined by repeated analysis (n = 12) of USGS 34 (-1.80 ± 0.4‰) that was not used to normalize the $\delta^{15}N$ values of samples and was found to be -1.86±0.81‰. The precision of this method based on repeated analysis of USGS 34 was ±0.24‰ whereas the precision of $\delta^{15}N_{nitrate}$ based on the duplicate analyses of samples (n= 7 pairs) was ±0.41‰. One cesspool sample $\delta^{15}N$ value was measured using the ammonia diffusion method adapted from Sigman et al., 1997. The sample was analyzed at the University of Hawaii at Manoa Biogeochemical Stable Isotope Facility using a Costech ECS 4010 Elemental Combustion System interfaced with a ThermoFinnigan Delta XP.

3.2.3 Boron concentrations and isotopic compositions for agricultural differentiation

While the nitrogen and oxygen isotopic composition of nitrate can reflect the sources of the nitrate, it is impossible to discriminate between mixtures of multiple nitrate sources based only on these isotopes. Nitrate is not a conservative compound because it is biologically modified during nitrification, denitrification and anammox (Granger and Wankel, 2016). To predict contamination sources more accurately, a multi-tracer approach is necessary. The concentration of B and $\delta^{11}B$ values will help distinguish the nitrate sources as boron behaves conservatively and is often transported along with nitrate in aquatic systems (Widory et al., 2005; Seiler, 2005. A complete discussion of the boron values for all endmembers can be found in **section 5.1**. Boron samples from 19 locations were collected in 250 mL HDPE screw top bottles and refrigerated until they were sent for analysis at the Stony Brook University Isotope Laboratory on a NU ICP-MS. $\delta^{11}B$ values were reported in ‰ against NIST 951. Sample precision was found to be ±0.68 ppm for B concentrations and ±0.032‰ for $\delta^{11}B$.

3.3 Algal surveys

In August 2019, 57 wild *A. spicifera* samples were collected from the nearshore zones of three beaches of concern, identified through infrared imagery. In February 2020, 10 more *A. spicifera* samples were collected, along with four *Ulva lactuca* samples, to attempt to supplement samples from areas that were not previously sampled. All samples were rinsed in distilled water, holdfast tissues and fouling organisms were removed, blotted dry with a paper towel, and placed on an aluminum foil tray in a drying oven at 60°C for at least one week, until the samples reached a constant mass prior to isotope analysis of tissues. The samples were then ground into a powder, placed in individual glass vials, and stored in a dessicator until analysis at the University of Hawaii at Manoa Biogeochemical Stable Isotope Facility using a Costech ECS 4010 Elemental Combustion System interfaced with a ThermoFinnigan Delta

XP for determinations of tissue $\delta^{15}N$ (‰), $\delta^{13}C$ (‰), %N, and C:N. Sample $\delta^{15}N$ and $\delta^{13}C$ values are reported in ‰ relative to AIR and PDB, respectively.

3.5 Salinity correction

In order to compare nutrient concentrations among samples with varying amounts of seawater dilution, the samples will be normalized to the freshwater endmember as is described in Hunt and Rosa 2009, by using the following equation:

$$C_{source} = \frac{C_{sample} + (C_{sample} - C_{marine}) * (S_{sample} - S_{fresh})}{(S_{marine} - S_{sample})}$$

In this equation, “C” represents the concentration and “S” is the salinity. “Fresh” refers to the freshwater endmember and “marine” is the marine endmember. The freshwater endmember used is a privately owned drinking water well near Wahiawa, Oahu, and the marine endmember is values collected at Station ALOHA.

4. Results

4.1 Geochemical Source-tracking of water

The ranges and averages for all sample parameters are discussed below. Sample locations, sampling times, and values for all samples collected during this study are shown in **Appendix A2**.

4.1.1 Nutrient Concentrations

Nutrient samples (n = 120) were collected from beach face piezometers, privately owned groundwater wells, and the three stream systems (**Figure 3.2**). The wastewater endmember sampled from a nearshore cesspool was found to have the following concentrations: 3296 µM for TN, 182 µM for TP, 164 µM for PO_4^{3-}, 930 for SiO_2, 13 µM for N+N, and 3058 µM for NH_4^+. For the field samples, **Table 4.1** shows the range of nutrient concentrations without saltwater correction. TN and nitrate concentrations vary greatly over the entire study area depending on sample type and location, and range from 3 to 364 µM for TN and 0.2 to 353 µM for nitrate + nitrite (N+N). Average N:P ratio for all samples is 64, but averages vary from 36 for beach samples to 95 for streams. The N:P ratios in the streams and beaches far exceed the Redfield ratio of 16:1 expected for marine phytoplankton (Redfield, 1958), and fit the criteria for a P-limited system of N:P > 22 (Hillebrand and Sommer, 1999). These ratios found are also greater than the expected N:P ratio of terrestrial plants (12 – 13) (Elser et al., 2000; Güsewell, 2004) and soils (4 – 8) (Chen et al., 2016). The ratio for streams was also higher than many rivers found throughout the U.S. and is similar to streams found on coastal plains (Dodds et al. 2016). The N:P ratio in beach face samples is lower than the streams but still greater than the Redfield ratio, despite many samples from beaches having similar salinities to the surrounding ocean water. Furthermore, for most of the samples, the vast majority of the nitrogen is made up of nitrate and nitrite, as opposed to ammonium, however the dry season stream samples showed more ammonium than N+N.

Table 4.1. The range of measured nutrient concentrations and isotope values for all samples collected during this study. The limit of detection is 0.2 μM for ammonium. Values below the limit of detection are reported as <0.2 μM.

Type			TN (μM)	TP (μM)	PO_4^{3-} (μM)	SiO_2 (μM)	N+N (μM)	NH_4^+ (μM)
Stream	*n= 63*	Min	5	0.1	0.1	8	<1	<0.2
		Max	155	7.0	6.5	892	134	29
Beach	*n = 39*	Min	3	0.1	0.0	4	1	<0.2
		Max	118	5.1	4.8	1417	107	2
Well	*n = 9*	Min	45	1.5	1.4	524	36	<0.2
		Max	355	7.1	6.3	1598	334	1
Fishpond	*n = 6*	Min	28	1.5	0.9	846	1	1
		Max	364	6.3	6.2	1414	353	7

To understand better the nutrient conditions in different parts of the study area, the three main stream systems and four beaches were separated and the nutrient concentrations averaged for each. **Table 4.2** shows the average nutrient concentrations for the Paukauila, Kiikii, and Anahulu streams, as well as Haleiwa Beach, Alii Beach, and Aweoweo Beach, all without correction for saltwater dilution

Table 4.2. Average uncorrected nutrient concentrations for all the streams (n = 63), beach face piezometers (n = 39), wells (n = 9), and fishpond (n = 6) samples. Each river was sampled twice, once in the wet season and once in the dry season.

Type	Location	TN (μM)	TP (μM)	PO_4^{3-} (μM)	SiO_2 (μM)	N+N (μM)	NH_4^+ (μM)
Streams	Paukauila Wet Season	54	0.6	0.4	209	44	1
	Paukauila Dry Season	30	0.4	0.4	113	4	13
	Kiikii Wet Season	81	0.6	0.5	294	34	8
	Kiikii Dry Season	39	0.3	0.2	282	13	16
	Anahulu Wet Season	27	0.7	0.6	180	13	1
	Anahulu Dry Season	33	0.5	0.5	202	15	14
	All Streams	44	0.5	0.4	213	20	9
Beaches	Aweoweo Beach	10	0.3	0.2	18	7	<1
	Haleiwa Beach	53	2.2	2.0	504	46	<1
	Alii Beach	20	0.6	0.5	213	17	<1
	Waialua Beach	9	0.4	0.3	25	5	<1
	All Beaches	23	0.9	0.7	189	19	<1
	Wells	174	4.7	4.2	1019	140	<1
	Loko Ea Fishpond	159	4.4	4.2	1277	144	3

Table 4.3 lists the average nutrient concentrations after correction for saltwater dilution (Section 3.5). For uncorrected nutrient values, private water wells had the highest amount of nutrients. Saltwater dilution-corrected ammonium concentrations are not reported as 19 samples fell below the threshold concentration for analysis (0.2 µM) and a further 43 samples had a negative concentration following correction associated with their extremely low measured concentrations. Once corrected, the nutrient values for beach face piezometers and streams all increase, while well sample values do not change (because they are fresh water samples). Highest dilution-corrected TN and N+N concentrations are found at Aweoweo Beach Park. To determine if the stream and beach corrected nutrient concentrations differ significantly, and if there was a significant seasonal difference in nutrient concentrations in a stream, a Kruskal-Wallis one-way analysis of variance (Dressing et al., 2016) was performed for each pair of streams and beaches in the study area (full results in **Table A.8**). Statistically, the concentration of nutrients in streams are significantly lower than the beaches ($P<0.001$ for TN, N+N, and NH_4^+), with all average stream TN values < 100 µM, with the exception of the one anomalously high value for Paukauila stream in the dry season. The Paukauila stream has significant differences for all 3 nitrogen parameters between the wet and dry season ($P=0.04$ for TN, $P=0.03$ for N+N, $P<0.001$ for NH_4^+). Kiikii stream has significantly different concentrations for TN, N+N, and NH_4^+ between the wet and dry season ($P<0.001$ for TN and N+N, $P=0.002$ for NH_4^+), while the Anahulu stream differs significantly between the wet and dry season for NH_4^+ ($P=0.003$), but not for TN ($P=0.2$) or N+N ($P=0.2$). Ammonium concentrations were the only parameter that differed seasonally for all streams and can be seen in **Figure 4.1**. For the streams, the Kiikii and Paukauila streams differed significantly for TN, N+N, and NH_4^+ ($P<0.001$, $P<0.001$, $P=0.01$). The Kiikii and Anahulu streams differed significantly for TN ($P=0.008$) and NH_4^+ ($P=0.01$), but not for N+N ($P=0.08$). The Paukauila and Anahulu streams did not differ significantly for any of the nitrogen parameters.

Table 4.3. Average corrected nutrient concentrations for all beaches, streams, sampled wells, and the fishpond in the study area after applying the unmixing equation for saltwater dilution.

		TN (μM)	TP (μM)	PO_4^{3-} (μM)	SiO_2 (μM)	N+N (μM)
Streams	Paukauila Wet Season	35	0.8	0.6	338	23
	Paukauila Dry Season	78	1.0	1.0	226	8
	Kiikii Wet Season	88	0.6	0.5	319	37
	Kiikii Dry Season	79	0.2	0.4	556	27
	Anahulu Wet Season	44	1.1	0.9	284	24
	Anahulu Dry Season	40	0.6	0.6	257	19
	All Streams	93	0.8	1.0	542	35
Beaches	Aweoweo Beach	330	6.0	9.3	841	320
	Haleiwa Beach	181	7.2	7.8	1575	167
	Alii Beach	181	1.5	5.0	536	226
	Waialua Beach	25	<0.1	2.7	341	100
	All Beaches	174	4.3	6	818	202
	Wells	175	4.7	4.2	1023	141
	Loko Ea Fishpond	178	5.0	4.8	1494	161

While the beach concentrations for TN were all elevated compared to the streams, the concentrations found at Aweoweo Beach are particularly high at 330 μM for TN and 320 μM for N+N. A map of saltwater-corrected N+N concentrations and $\delta^{15}N_{nitrate}$ values for all the sample locations is shown in **Figure 4.1.** NH_4^+ concentrations did not vary significantly between any beaches in the study area. Aweoweo and Alii beaches do not differ significantly for any of the nitrogen parameters measured (P=0.96, P=0.83, P=0.13 for TN, N+N, and NH_4^+, respectively), and neither did Alii and Waialua (P=0.17, P=0.47, P=0.13 for TN, N+N, and NH_4^+, respectively). Haleiwa Beach has significantly different TN concentrations compared to Alii (P=0.02) and Waialua Beach (P=0.02), but only has significantly different N+N concentrations compared to Aweoweo Beach (P=0.03). Aweoweo Beach differed significantly from Waialua Beach for both TN (P=0.008) and N+N (P=0.02). The results vary greatly spatially, but in general highest N+N values measured for the beaches were found at Aweoweo Beach, significantly different than any other beach besides Alii Beach. For the streams, the highest averages for TN and N+N were found in the Kiikii stream system, significantly different from any other stream for any parameter except for N+N in the Anahulu stream. The majority of the samples have N+N concentrations below 1000 μM, however there are some extremely high concentrations including one data point along Alii beach with a concentration of 5190 μM, a concentration nearly 4000 μM higher than any other field sample.

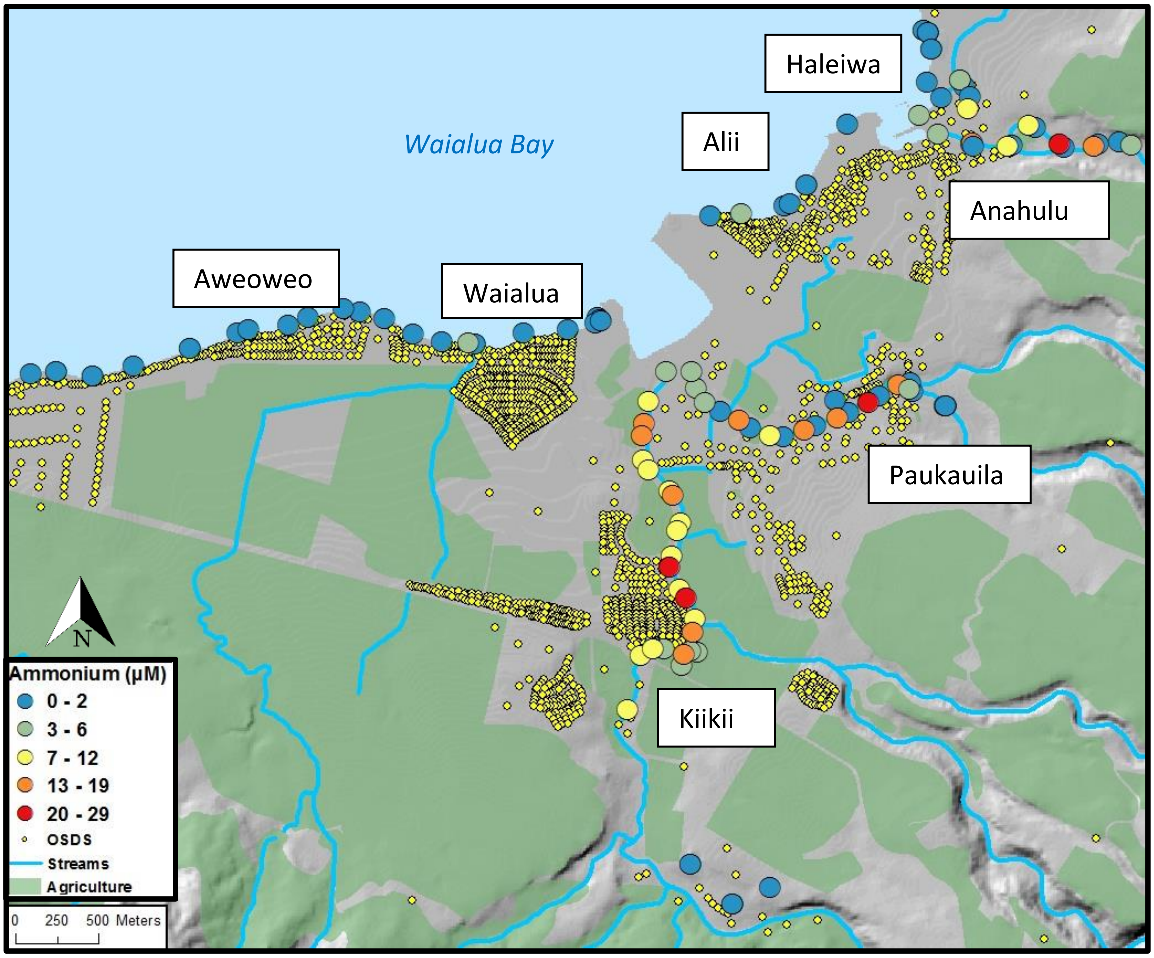

Figure 4.1. Ammonium concentrations for all sample locations in the study area. Location of the 3 major streams and 4 main beach locations are also shown.

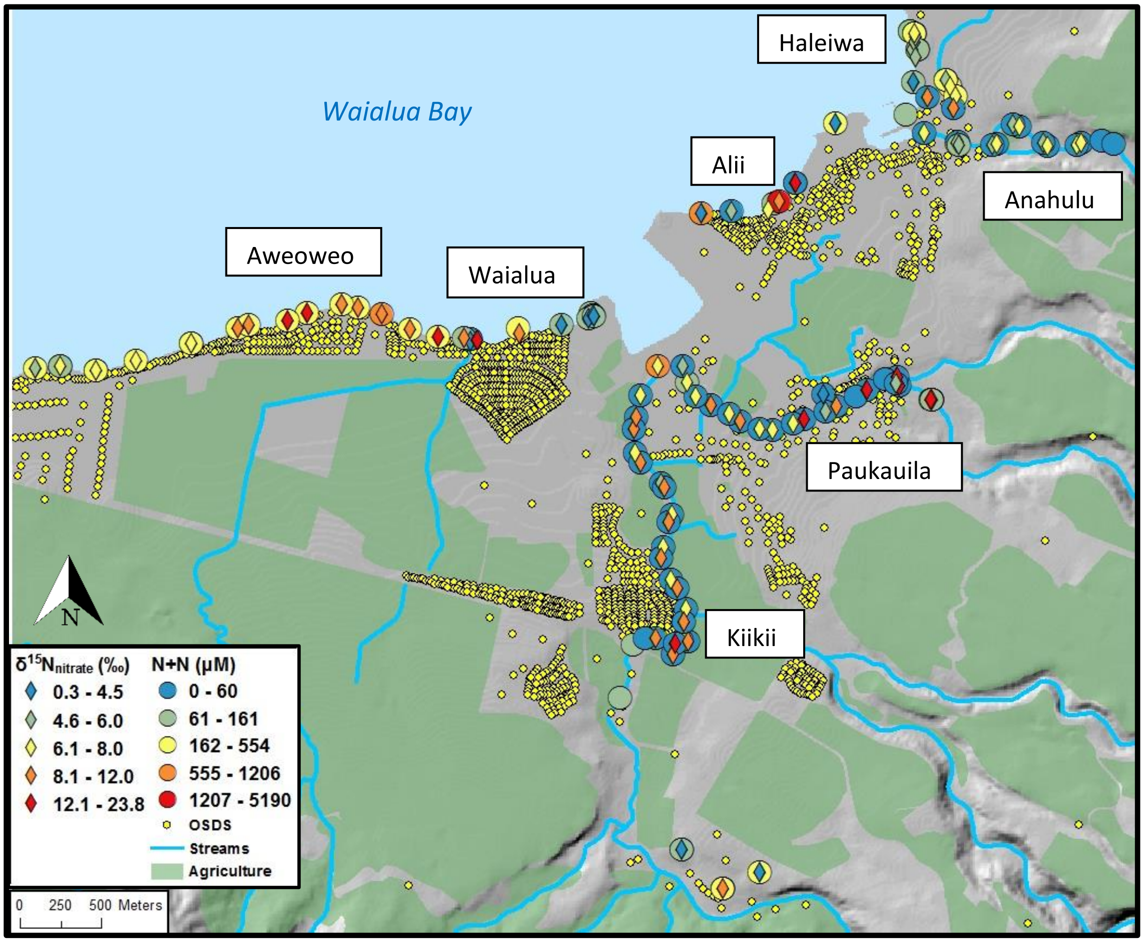

Figure 4.2. Map of $\delta^{15}N_{nitrate}$ values and N+N concentrations corrected for saltwater dilution. N+N concentrations are represented as circles and $\delta^{15}N_{nitrate}$ values are represented as diamonds. Location of the three major streams and four main beach locations are also shown.

4.1.2 Dual isotopic composition of NO_3^-

Table 4.4 lists the average $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values for all streams, beaches, groundwater wells, and fishpond samples collected. **Figure 4.2** illustrates the spatial distribution of all the $\delta^{15}N_{nitrate}$ values and their corrected N+N concentrations for all stream and beach face samples in the study area. **Figure 4.3** lists the relationship between $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values of the samples and type of each sample (beach face piezometer, stream, well, fishpond). Beach face piezometer samples have the largest range of $\delta^{15}N_{nitrate}$ values and include the highest and lowest values measured in this study (0.33 to 23.84‰). The range of $\delta^{15}N_{nitrate}$ values in stream samples are lower (5.2 to 13.5‰).

Table 4.4. Average $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values for the streams, beaches, groundwater wells, and fishpond samples.

Type	Location	Season	$\delta^{15}N$	$\delta^{18}O$
Streams	Anahulu	Wet	6.9	5.1
		Dry	5.6	3.1
		Total	6.2	4.1
	Kiikii	Wet	7.9	6.4
		Dry	8.9	6.4
		Total	8.4	6.4
	Paukauila	Wet	10.8	8.7
		Dry	6.3	3.6
		Total	8.6	6.2
	All Streams		7.7	5.5
Beaches	Aweoweo		13.5	6.4
	Alii		6.7	2.1
	Haliewa		5.3	3.0
	Waialua		4.1	-2.1
	All Beaches		7.4	2.4
	Groundwater wells		5.2	4.7
	Fishpond		5.0	3.5

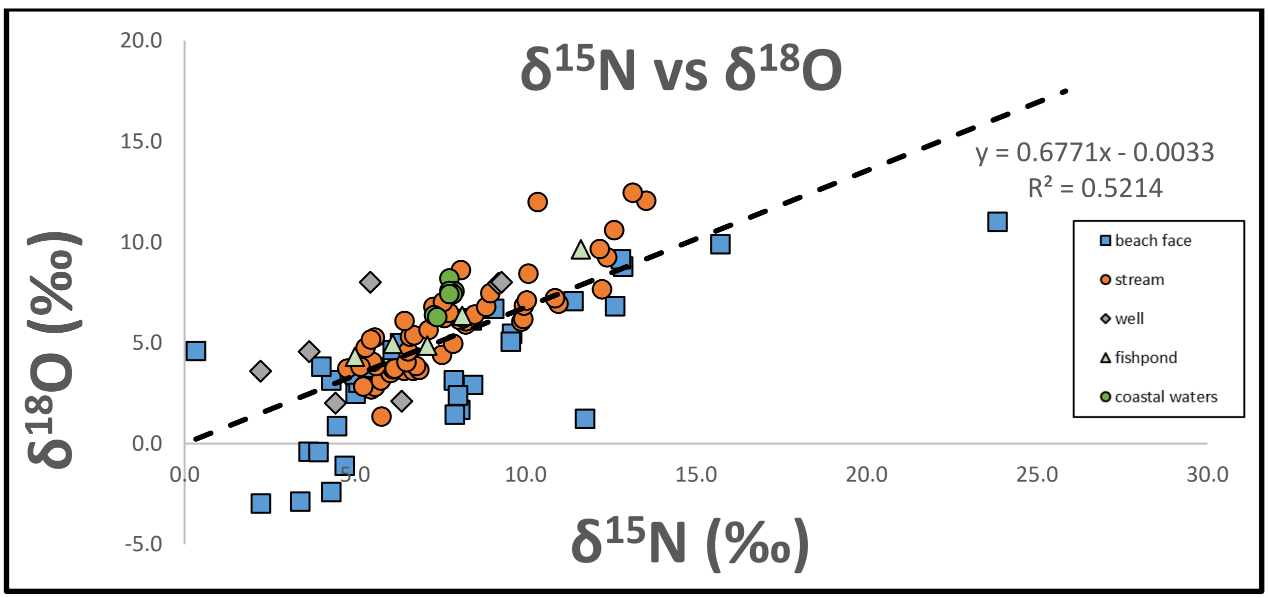

Figure 4.3. **Plot of $\delta^{15}N_{nitrate}$ vs $\delta^{18}O_{nitrate}$. Stream samples are from the Kiikii, Paukauila, and Anahulu stream systems, beach face piezometer samples were collected along the entire coast of the study area, well samples were from privately-owned deep groundwater wells, fishpond samples are from the Loko Ea fishpond, and coastal water samples were collected in the near shore coastal environment. The slope of the least squares regression of 0.67 is consistent with denitrification (Kendall et al. 2007).**

As was done with nutrient concentrations, a Kruskal-Wallis one-way analysis of variance was performed for each pair of streams and beaches in the study area to determine if the differences in $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values were significant. For the streams**,** the Paukauila and Kiikii streams do not differ significantly for either in $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ (P = 0.77 and 0.60, respectively). The Paukauila and Anahulu streams have significantly different in $\delta^{15}N_{nitrate}$ values (P = 0.005), however their $\delta^{18}O_{nitrate}$ values do not differ significantly (P=0.051), while the Kiikii and Anahulu streams significantly differ for both $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ (P < 0.001 for both). For the beaches, the $\delta^{15}N_{nitrate}$ values found at Haleiwa Beach are significantly different than the values at Aweoweo (P < 0.001) and Waialua Beach (P = 0.02), but not Alii Beach (P = 0.53), while the $\delta^{18}O_{nitrate}$ values only significantly differ from those at Waialua Beach. $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ are significantly different between Aweoweo and Waialua (P=0.002, P=0.003), but not between Aweoweo and Alii or between Alii and Waialua Beach

4.1.3 Boron concentrations and isotopes

Boron concentrations from all field samples range from 0.044 ppm to 4.32 ppm, while $\delta^{11}B$ values ranged between 33.5‰ and 69.5‰ (n=21) (all boron results presented in **Table A.6**). The well samples had the lowest B concentrations and the highest $\delta^{11}B$ values, with averages of 0.07ppm and 58.6‰ (n=3), and ranges of 0.04 - 0.08 ppm and 45.4 - 69.5‰, respectively. Streams had an average B concentration of 0.60 ppm and an average $\delta^{11}B$ value of 40.2‰ (n = 6) and ranged between 0.45 - 1.39 ppm and 38.1 - 44.2‰. Beach face piezometers had the highest average B concentration of 2.86 ppm and an average $\delta^{11}B$ values of 38.4‰ (n=11), with a range of 0.53 ppm - 4.32 ppm for B concentrations and 33.5‰ - 39.8‰ for $\delta^{11}B$ values. The majority of beach face sample ^{11}B values fell between 39.0‰ – 40.0‰ (n=8), closely matching reported values for open ocean seawater of 39.2 ± 0.31‰ (Tirez et al., 2010). The one cesspool sample used as the wastewater endmember in this study had a B concentration of 0.123 ppm and $\delta^{11}B$ value of 46.2‰.

4.2 Algal Surveys

$\delta^{15}N$ values from *A. spicifera* tissues varied between 2.3‰ and 13.0‰, whereas all the locations have relatively similar %N values and range between 1.1% and 2.8% (**Figure 4.4,** all algal data are presented in **Table A.5**). A map of $\delta^{15}N$ all benthic macroalgae samples can be seen below in **Figure 4.6**. All samples displayed were *Acanthophora spicifera* (Børgesen, 1910)*,* except for four *Ulva lactuca.* (Linnaeus, 1753) samples collected at Haleiwa Beach. $\delta^{15}N$ values vary greatly throughout the study area (**Figures 4.4 and 4.5**)**.** The majority (80%) of the lowest $\delta^{15}N$ values (5.0‰ or below) were from samples collected at the Waialua Beach and Haleiwa Beach sampling sites. Overall, Waialua had the lowest $\delta^{15}N$ values, ranging from 2.3‰ – 6.3‰, with an average of 5.1‰. Haleiwa Beach has an average $\delta^{15}N$ value of 5.9‰, and Alii Beach has an average $\delta^{15}N$ of 6.5‰. Benthic macroalgal $\delta^{15}N$ increases significantly, however, for samples collected at Aweoweo Beach, where $\delta^{15}N$ ranges from 4.1 ‰ to 13.0 ‰, with an average of 9.9‰, about 3.5‰ higher than the next highest location. To determine if the $\delta^{15}N$ values and %N vary significantly throughout the study area, a Kruskal-Wallis one-way ANOVA test was performed (**Table 4.5**), similar to that used for the nitrogen parameters for the water samples. The $\delta^{15}N$ values for the benthic macroalgae samples at all locations are significantly different than every other location, with Haleiwa and Waialua having the least significant differences. The opposite is true for the %N, as there are none of the beach pairs were significantly different.

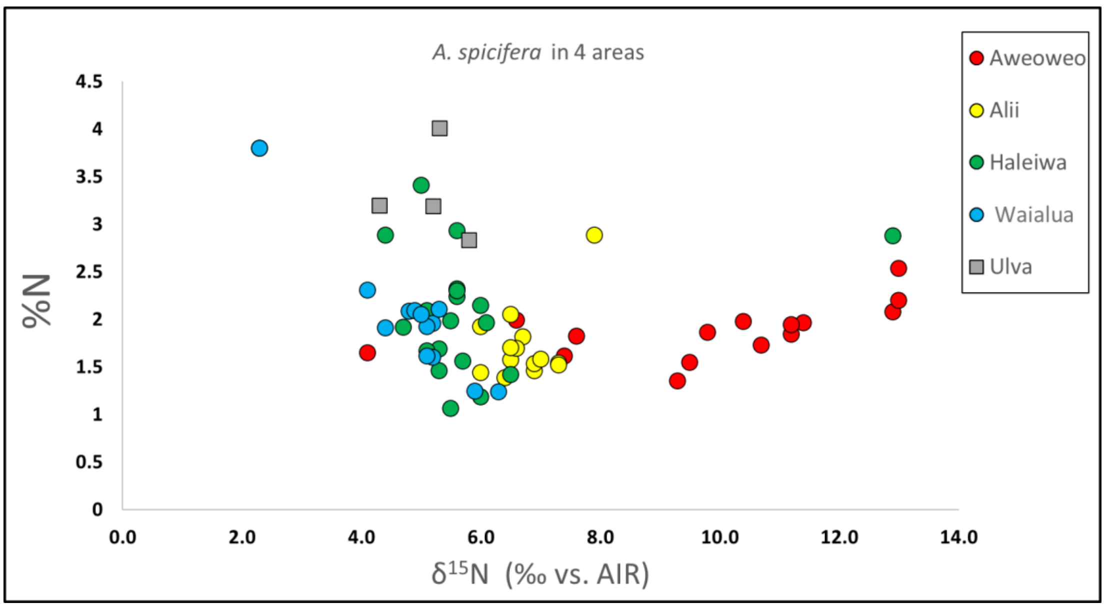

Figure 4.4. $\delta^{15}N$ and %N of all algal samples collected in the study area. All samples were tissues of **Acanthophora spicifera** ***except for four Ulva*** **spp.** ***samples collected at Haleiwa Beach. $\delta^{15}N$ values range from 2.3‰ to 13.0‰, while %N values range from 1.06% to 3.80% for the*** **A.spicifera** ***samples.***

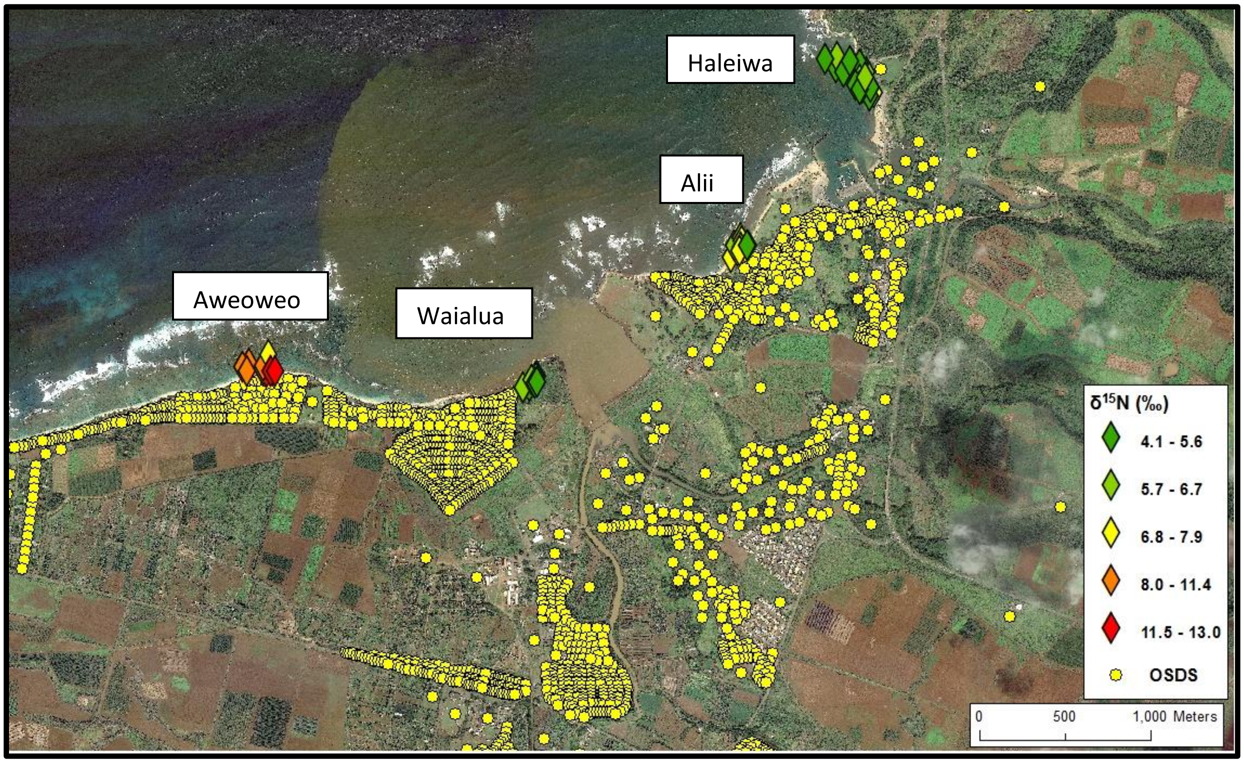

Figure 4.5. Map of all algal samples collected in the study area and their $\delta^{15}N$ values. The lowest $\delta^{15}N$ values were found at Waialua Beach while the highest were found at Aweoweo Beach.

Table 4.5. Kruskal-Wallis H and P values for the one-way ANOVA analysis for in $\delta^{15}N_{nitrate}$ and %N for algae collected for each beach pair in the study area. Population pairs which do not vary significantly for a given parameter are shaded in blue.

Beach pairwise comparisons	Tissue $\delta^{15}N$	Tissue %N
Aweoweo-Alii	H=13.66, P<0.001	H=2.68, P=0.10
Aweoweo-Haleiwa	H=15.13, P<0.001	H=0.78, P=0.38
Aweoweo-Waialua	H=14.69, P<0.001	H=0.06, P=0.81
Haleiwa-Waialua	H=4.47, P=0.03	H=0.73, P=0.39
Haleiwa-Alii	H=12.34, P<0.001	H=1.78, P=0.18
Alii-Waialua	H=13.79, P<0.001	H=1.37, P=0.24

5. Discussion

The high density of OSDS and widespread historical and current agriculture within the watersheds adjacent to Waialua Bay suggest the coastal waters could be susceptible to complex and high levels of anthropogenic nutrient loading. To establish geochemical and hydrological connections between nutrient sources on land with the groundwater, stream, and coastal waters in the Waialua region, we compared nutrient concentrations, $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values, $\delta^{11}B$ values for all waters in the study area to those of the coastal ocean using mass balance. In addition, $\delta^{15}N$ values of algal tissue collected from the coastal waters near four major beaches in the region were measured to help determine sources of nutrients, the extent of nutrient loading in each location, and the distance away from shore nutrient pollution may extend.

As discussed in detail below, our results show that there are high levels of excess nutrients along the entire study area. Two of the three streams show clear evidence for the presence of wastewater leachate, while the third stream is affected by both agriculture and leachate from OSDS. All three streams show higher concentrations of ammonium compared with nitrite + nitrate in the dry season relative to the wet season, suggesting the bioremediation expected to occur in soils is not removing nutrients prior to entering the streams. In general, beach face piezometers samples corrected for saltwater dilution contained higher nutrient concentrations than stream samples. Areas with higher densities of OSDS were found to have nutrients sourced from OSDS wastewater and the highest coastal nutrient concentrations were found at the beach with the most coastal OSDS, however the relationship between OSDS density and the extent of total nutrient input is not simple or linear due to nutrient influx from agriculture. Some areas with very few OSDS also exhibit a high amount of nutrient pollution from agricultural nutrient sources.

5.1 Endmembers

The geochemical composition of endmembers chosen for this study come from both our measured values as well as values reported in literature. When possible, literature values were taken from studies in Hawaii (Abaya et al., 2018) and specifically on Oahu (Hoover and McKenzie, 2009; Richardson et al., 2017; Dores, 2018). **Tables 5.1 and 5.2** compile both the measured and referenced endmembers for all nutrient (TN, TP, PO_4^{3-}, SiO_2, N+N, NH_4^+, $\delta^{15}N_{nitrate}$, $\delta^{18}O_{nitrate}$) and boron parameters ([B], $\delta^{11}B$). Several of our measured values deviate from the known literature values. The reasons and processes responsible for these deviations are discussed below.

Table 5.1. Nutrient and isotopic endmember values for different source water endmembers used in this study

Endmember	Source	Type	$\delta^{15}N_{nitrate}$ (‰)	$\delta^{18}O_{nitrate}$ (‰)	TN (µM)	TP (µM)	PO_4^{3-} (µM)	SiO_2 (µM)	N+N (µM)	NH_4^+ (µM)
Wastewater	*This study*	*Cesspool*	**-0.27**	**1.2**	**3296**	**182**	**164**	**930**	**13**	**3059**
	Dores 2018	*WWTP*	**25.0**	**8.8**	**3643**	**184**	**168**	**755**	**78**	**3149**
	Richardson et al. 2017	*Cesspool*	**12.7 - 13.1**	--	--	--	--	--	--	--
	Abaya et al. 2018	*Cesspool*	**10.45**	--	--	--	**379**	--	**21**	**6367**
Ocean	*Dores 2018*		**4.1**	**5.1**	**5**	**<1**	**<1**	**8**	**0.5**	**1**
	Station ALOHA		--	--	**5.1**	**0.26**	**0.09**	**1.03**	**0.05**	--
	Casciotti et al. 2001 (Deep Ocean)		**5.1**	**0**	--	--	--	--	--	--
Groundwater	*This study*	*Private wells*	**5.2**	**4.7**	**174**	**5**	**4**	**1019**	**140**	**<1**
	Dores 2018	*Municipal wells*	**2.9**	**1.5**	**12**	**2**	**2**	**467**	**9**	**<1**
Agriculture	*Kendall et al. 2007*	*Ammonia fertilizer*	**-5 - +5**	**-5 - +15**	--	--	--	--	--	--
	Bateman and Kelly, 2007	*Ammonia fertilizer*	**-5.9 – +6.6**	**--**	--	--	--	--	--	--
Stream	*Hoover and McKenzie, 2009*		--	--	***9.8***	***0.5***	--	--	***2.2***	***0.3***
	Dores, 2018		**2.3**	**1.4**	**7**	***<1***	***1.1***	***503***	***3***	***1***

Table 5.2. Boron concentration and $\delta^{11}B$ values for different source water endmembers used in this study

Endmember	*Source*	[B] (ppm)	$\delta^{11}B$ (‰)
Wastewater	*This study*	**0.123**	**46.2**
	Dores 2018	**0.178**	**8.6**
	Widory et al. 2005	--	**-4 - 12**
	Briand et al. 2017	**0.083**	**1.9**
Ocean	*Foster et al. 2010*	--	**37.7 - 40.4; 39.5**
	Helvaci 2006	**4.6**	--
	Tirez et al., 2010	**--**	**39.2 ± 0.31**
Groundwater	*This study*	**0.06**	**58.6**
Agriculture	*Tirez et al. 2010*	**0.02 - 0.07**	**0 - 24.6**

5.1.1 Values and processes of nitrogen in endmembers

Stable isotope values have proven useful in distinguishing between different anthropogenic and natural sources of nitrate. Previous studies have used $\delta^{15}N_{nitrate}$, $\delta^{18}O_{nitrate}$, and $\delta^{11}B$ values to distinguish between nutrient sources (e.g., Boyer et al., 2002; Mayer et al., 2002; Widory et al.,2005; Xue et al., 2012; Liu et al., 2013). For these tracers to be effective at distinguishing nutrient sources using isotope mass balance, the isotope values for all endmembers must be different and understood. Agricultural fertilizers, natural soil inputs, and sewage all have distinct isotopic values pertinent to this study, and when determined, can allow for the distinction between nutrient sources.

The wastewater endmembers used in this study to characterize nitrate from OSDS leachate entering surface waters come from both a cesspool sample collected in the study area, and previously published literature. Our measured cesspool $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values of -0.27‰ and 1.22‰ disagree with wastewater endmembers previously reported in Hawaii, including 3 cesspools on the Big Island that had mean $\delta^{15}N_{nitrate}$ values of 10.46‰ (Abaya et al., 2018) and previous work on Oahu, which modeled cesspool $\delta^{15}N_{nitrate}$ to be between 12.7 to 13.1‰ (Richardson et al., 2017) (**Table 5.1**). This discrepancy is because most of the nitrogen in our cesspool sample is in the form of ammonium (3058 µM) with an average measured of $\delta^{15}N$ value of 5.6 ±0.4‰, consistent with $\delta^{15}N$ values for human feces and urine, 3.5 to 7.8‰, depending on the diet of the individual (Kuhnle et al. 2013). The $\delta^{15}N$ value of our cesspool ammonium is also close to literature values for $\delta^{15}N_{ammonium}$ in effluent collected from septic tanks (4.9 to 5.1‰) (Hinckle et el., 2008; Izbicki et al., 2015). As the cesspool is expected to be anoxic with little nitrification occurring, a significant portion of the N+N concentration is in the form of nitrite with very low $\delta^{15}N$ values, as the initial ammonium oxidation is associated with a large, negative isotope effect of -38 - -14‰ (Casciotti and Buchwald, 2012; Casciotti, 2016; Granger and Wankel, 2016). A low rate of nitrite oxidation to nitrate would cause the accumulation of ^{14}N in nitrite and lead to lower $\delta^{15}N_{nitrate}$ values (Casciotti, 2016). Although similar to known $\delta^{15}N$ values for urine, feces, and septic tank effluent, the $\delta^{15}N$ value of 5.6 ‰ is still lower than widely reported values used for wastewater endmembers in Hawaii. In order to reconcile this difference, the processes which affect wastewater leachate both within the direct vicinity of a cesspool and within aquifers further away need to be understood.

Processes occurring in and immediately adjacent to the cesspool, such as ammonia volatilization and denitrification, combined with denitrification and annamox occurring further away from the cesspool, can cause enrichment of ^{15}N. Ammonia volatilization increases $\delta^{15}N$ values due to the accumulation of ^{15}N in the remaining NH_4^+ pool during the volatilization of NH_4^+ to NH_3 gas. This occurs through a multi-step process with isotope fractionation at each step (Hogberg, 1997; Robinson, 2001; Chalk et al., 2019). Equilibrium isotope fractionation between ammonium and ammonia in solution and aqueous and gaseous ammonia, followed by a kinetic isotope fractionation caused by the diffusive loss of gaseous ammonia depleted in ^{15}N, leads to overall isotope fractionation as low as ~25-29‰ (Hogberg, 1997) and as high as 40-60‰ (Robinson, 2001) depending on factors such as pH, temperature, and humidity. Most soils in the study region are slightly acidic (5.8-7.3 pH) to acidic (pH=<5.8), below the optimum range for ammonia volatilization (pH>7) (Hawaii Soil Atlas, Dari et al., 2019). However, when urea fertilizers undergo hydrolysis, ammonium carbonate is produced, raising the pH around the fertilizer granule from pH 4.6 to as high as 9, making it more susceptible to ammonia volatilization in some agricultural fields (Mikkelsen, 2009). Ammonia volatilization would not directly increase the $\delta^{15}N$ value in the nitrate pool, but increase $\delta^{15}N$ value of ammonium from which nitrate is derived. Ammonia volatilization could potentially occur in areas surrounding OSDS, raising the $\delta^{15}N$ value of 5.6‰ found in our cesspool ammonium towards the higher $\delta^{15}N_{nitrate}$ values more often reported, but it is more likely to affect agricultural fields following the application of synthetic urea fertilizers.

Denitrification directly increases $\delta^{15}N_{nitrate}$ values, and can occur immediately in and near the cesspool, or anoxic regions in the groundwater system. During the reduction of nitrate to gaseous N_2, N_2O, and NO_2 in low oxygen conditions, the $\delta^{15}N$ value in the residual nitrate increases exponentially as the nitrate concentrations decrease, with isotope fractionation factors in bacterial culture studies around +30‰ (Delwiche and Styne, 1970; Sigman and Casciotti, 2008) and has resulted in residual nitrate $\delta^{15}N$ values in field studies in Hawaiian soils as high as 180‰ (Houlton et al., 2006). Anammox increases $\delta^{15}N$ values both in residual ammonium and nitrate. Anammox was first identified as a pathway for N loss in wastewater systems (Mulder et al., 1995) and has since been observed in many oxygen-deficient regions and groundwater systems (Kuypers et al., 2005; Shen et al., 2013; Yang et al., 2015; Sonthiphand et al., 2014), and specifically in Hawaiian aquifers (Fackrell et al., 2016). According to a bacterial culture study by Brunner et al. (2013), three different isotope fractionations occur during anammox: an inverse kinetic N isotope fractionation associated with the oxidation of nitrite to nitrate (-31.1 ± 3.9‰), a normal kinetic N isotope fractionation during the reduction of nitrite to N_2 (+16.0 ± 4.5‰), and an equilibrium N isotope effect between nitrate and nitrite (60.5 ± 1.0‰), all of which accumulate ^{15}N values in ammonium or nitrate. Ammonium volatilization, denitrification, and anammox present pathways through which the $\delta^{15}N$ value of nitrogen in our cesspool sample could reach the higher $\delta^{15}N$ values expected in wastewater. It is important to note that the composition of cesspool sample collected by opening the top of the cesspool is very different from the composition of wastewater that leaches out of the cesspool into the groundwater system while undergoing nitrogen transformations. As is apparent by the elevated ammonium concentration in our cesspool sample (3056 µM) compared to relatively little nitrite + nitrate (13 µM), extensive nitrification has not occurred, meaning there has been minimal denitrification that would raise the $\delta^{15}N$ value. The ammonium concentration combined with the low $\delta^{15}N$ value for ammonium in the cesspool (5.6‰) suggest there has not yet been enough ammonia volatilization to raise the $\delta^{15}N$ value to near the endmember values reported elsewhere (**Table 5.1**). Because the above-mentioned processes can affect the $\delta^{15}N$ values, it is also important to determine the form of N in the environment to accurately interpret the data and ascertain the correct nutrient sources. Our data show there are areas in streams where there has not been complete nitrification of ammonium to nitrate, which would lead to differences in $\delta^{15}N_{nitrate}$ values compared to the literature due to the fractionations associated with ammonium oxidation (-38 - -14‰) and nitrite oxidation (0 - 35‰) (Kendall et al., 2007; Granger and Wankel 2016).

The agricultural and marine endmembers for this study come from both literature and previously reported values found on Oahu. The $\delta^{15}N$ value for synthetic ammonium-based fertilizers, including urea, are well documented, with a generally accepted range of $\delta^{15}N$ values between -5 to 5‰, reflecting its source of atmospheric N_2 with little isotope fractionation during the Haber-Bosch process (Widory et al.,2005; Kendall et al., 2007, Bateman and Kelly, 2007). The marine endmember values were taken from a previous study on Oahu (Dores, 2018) and from Station ALOHA, located 100 km north of Oahu (**Table 5.1**). Sigman and Casciotti (2001) reported a $\delta^{15}N_{nitrate}$ value of ~5‰ for mean deep ocean water, with variations in values in ocean water only coming from isotope fractionation during denitrification by bacteria in oxygen-deficient zones or assimilative uptake by phytoplankton at the ocean surface.

5.1.2 Boron concentrations and isotope values in endmembers

Boron concentration and $\delta^{11}B$ values for the various source water endmembers in our study come both from literature and from the cesspool sample collected in our study area (**Table 5.2**). B concentrations and $\delta^{11}B$ values for our marine and agricultural endmembers come from previously reported literature values (39.5‰ for marine; 0 - 24‰ for agriculture). Values for our wastewater endmember comes from a cesspool in the Waialua Region; the $\delta^{11}B$ value measured was 46.2‰ with a B concentration of 0.123 ppm. The $\delta^{11}B$ value does not agree with previous reported wastewater values with ranges around -4 - 12‰, but is similar to the upper range for animal waste of 42‰ (Widory et al., 2005). Anthropogenic input of boron into sewage comes mostly from the use of sodium perborate in many domestic and industrial cleaning detergents, which have low $\delta^{11}B$ values due to the low isotope values of their source borate minerals (-16 to -1.1‰ for natural Na-borate minerals) (Tirez et al., 2010). The study area cesspool sample $\delta^{11}B$ value (46.2‰), combined with its relatively low concentration of boron (0.123 ppm) makes it apparent the cesspool had a high proportion of waste in the form of urea and feces, and lower concentrations of detergents that would lower the $\delta^{11}B$ value and raise the B concentration, which could be due to several scenarios such as the household not having a washing machine or use detergents which do not contain sodium perborate. It is thus apparent that the $\delta^{11}B$ value for our wastewater endmember can be used to identify wastewater that is composed of mainly human waste. Samples with low $\delta^{11}B$ values could still potentially be from wastewater based on values from literature (-4 - 12‰), particularly if the wastewater has a high concentration of detergents. Because the literature values for $\delta^{11}B$ values for wastewater and mineral fertilizers overlap (Widory et al., 2005; Tirez et al., 2010), the $\delta^{11}B$ values must be used with the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values to distinguish between wastewater and fertilizer.

5.2 Processes affecting the concentration and isotopic composition of nitrate

Primary production and denitrification change the concentration and isotopic composition of nitrogen. There is a wide range of reported fractionation factors for nitrate and ammonium assimilation in aquatic environments, ranging from 0 - 20‰ (Fogel and Cifuentes, 1993; Waser et al. 1998; Altabet et al.1999; Granger et al., 2004; Kendall et al., 2007). During nitrate assimilation, the rate-determining step is nitrate reduction within algal cells, causing the accumulation of ^{15}N in nitrate within the cell, with the fractionation effect determined by the rate nitrate efflux out of the cell and into the environment (Umezawa et al., 2002; Granger et al., 2004; Needoba et al., 2004). While the fractionation factor for ^{18}O has not been as widely studied, Granger et al. (2004) found the change of $\delta^{18}O$: $\delta^{15}N$ to be 1:1 during assimilation by marine phytoplankton, consistent with isotope fractionation of nitrogen and oxygen associated with nitrate reductase. Areas in the study site that had slopes for $\delta^{18}O$: $\delta^{15}N$ of around 1 are suspected to have primary production occurring, however a slope of 1 is may also be indicative of denitrification in marine systems.

As discussed in **section 5.1.1**, denitrification and anammox have the potential to greatly affect the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values. Widespread denitrification is apparent throughout our study area when all $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values were plotted (**Figure 4.3**). The slope of the linear regression (0.67) is consistent with the denitrification trend line defined by Kendall et al. (2007), while the slope <1 suggests the effects of anammox in anoxic portions of soils and in aquifers (Granger and Wankel, 2016). By plotting nitrate concentrations and $\delta^{15}N_{nitrate}$ values, regions suspected of experiencing denitrification can be identified (**Figure 5.1**). The red circle highlights samples that have elevated $\delta^{15}N_{nitrate}$ values (>~7‰), while also having relatively low nitrate concentrations (~0-40 µM). These locations are not unique to one type of aquatic environment, as both streams and beaches are locations where denitrification has affected $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values. Keeping in mind the limitations associated with identifying wastewater sources of boron, we chose boron as an additional tracer to compensate for transformations that alter $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values because boron behaves conservatively and is not affected by processes such as denitrification (Widory et al.,2005), however there may be a small isotope fractionation caused by adsorption onto clay minerals (Bassett 1990).

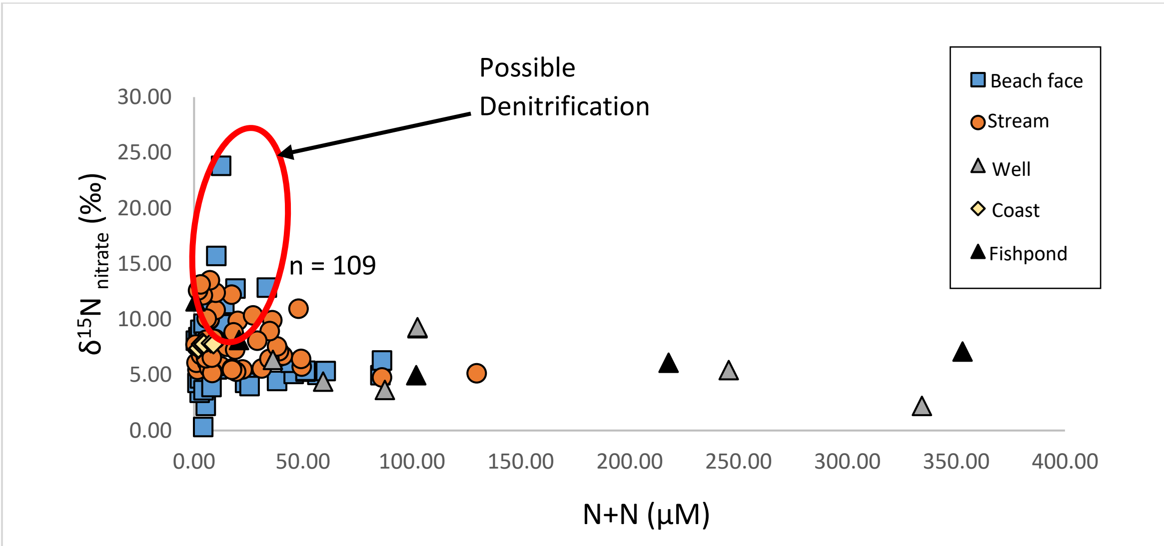

Figure 5.1 N+N⁻ concentrations and $\delta^{15}N_{nitrate}$ values for all samples in the study area. Samples with low N+N⁻ concentrations and elevated $\delta^{15}N_{nitrate}$ values are locations where denitrification may be occurring and are circled in red.

5.3 Nitrogen characteristics of the regional Waialua stream system

Across the three main stream systems in the study area, there are varying trends in nitrogen concentrations and isotopic composition that show differences in nutrient sources and nitrogen transformations. The large aerial extent of agricultural land and lack of OSDS in the upper reaches of the Anahulu river indicate nutrients sources from upland agricultural fertilizers, with increased nutrients near the coast corresponding to increased OSDS density. The high density of OSDS that border the Kiikii and Paukauila streams suggest that the streams are directly influenced by wastewater. Increased N+N concentrations near the coast correspond to clusters of near-shore OSDS in the Paukauila stream and Anahulu River, however the increase in N+N is seasonal in the Paukauila stream and only appears in the wet season, while it is apparent in the wet and dry season for the Anahulu River. All three streams show a seasonal shift in the form of nitrogen, with a greater proportion of ammonium in the dry season due to a lack of nitrification. Several sections along all 3 of the stream systems show evidence of denitrification based on their elevated $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values, likely occurring in the soil between nutrient sources and the streams.

5.3.1 Nutrient sources in the Anahulu River

The Anahulu River is unique in that its nutrients are sourced from agricultural sources, except by the coast where an increase in N+N concentrations suggests input from nearshore OSDS. $\delta^{15}N_{nitrate}$ values do not increase significantly towards the coast, with samples staying relatively consistent throughout the stream, ranging from 6.1 to 7.8‰ and 5.18 and 6.04‰ in the wet and dry season, respectively. Although the $\delta^{15}N_{nitrate}$ values found were above the range for synthetic fertilizers (-5 - +5‰), nitrate could be derived from agricultural sources and their $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values elevated due to denitrification. The slope of $\delta^{18}O_{nitrate}$ vs $\delta^{15}N_{nitrate}$ values is statistically significant ($P<0.05$) and has a value of 0.94, consistent with a system that is undergoing denitrification. The $\delta^{18}O_{nitrate}$ values of samples collected in the upstream reaches (>300 m from coast) are elevated, particularly in the wet season, with three of the four samples having values >5‰. We believe agricultural sources are the main source of nutrients in the reaches of the stream >300 m away from the coast, as there are only eight OSDS upstream of this point, while there is nearly 4.2 km^2 of agricultural land, used mainly for corn seed production by large biotechnology seed production companies. Corn production in tropical islands typically uses around 20 g/m^2 of N-fertilizers, although the amount varies both with the type of corn and location (Brewbaker, 2003). These samples could be indicative of agricultural endmembers for the region which have undergone nitrogen transformations, as it is one of the few locations relatively unaffected by OSDS.

There is apparent shift in nutrient source within 300 m of the coastline as N+N concentrations increase from 4 µM to 49 µM at 280 m from the coast in the wet season and up to 31 µM in the dry season (**Figure 5.2(a)**). This increase in nutrients near the coast corresponds to an increase in OSDS density near the coast, as the reaches >300 m contain eight OSDS, while there are 134 OSDS within 300 m, and no agricultural land within 300 m of the Anahulu River to add nutrients. Although the $\delta^{15}N_{nitrate}$ values do not increase in these near shore locations, it does not immediately rule out the possibility that wastewater is present. The $\delta^{15}N_{nitrate}$ values range between 5.2 and 6.4‰ for the samples within 300 m of the coast, similar to the $\delta^{15}N_{ammonia}$ found in the cesspool endmember (5.6‰). It is possible complete nitrification has occurred, but the additional processes (denitrification, ammonium volatilization) that would raise the wastewater $\delta^{15}N_{nitrate}$ values more towards the expected values have not. Evidence for the lack of denitrification in these samples include low $\delta^{18}O_{nitrate}$ values (< 3.2‰) and the slope of $\delta^{18}O_{nitrate}$ vs $\delta^{15}N_{nitrate}$ values (2.8, r=0.93), higher than what is expected in a region undergoing denitrification. Boron was not effective as an additional tracer in the Anahulu River, as the two boron samples had $\delta^{11}B$ values within the expected range for seawater, while an increase in B concentration towards the coast was likely a result of an increased proportion of seawater as opposed to input from wastewater. In the upstream reaches, nutrients are expected to be sourced from fertilizers which have undergone denitrification based on the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values, the presence of 4.2 km^2 agricultural fields, and a low amount of OSDS (8 total), while reaches close to the coast are likely influenced by OSDS due to a sudden increase in nutrient concentrations corresponding to 134 near shore OSDS.

5.3.2 Seasonal nitrification trends

All streams have a significantly higher proportion of N as NH_4^+ in the dry season (**Table 5.3**). The increased NH_4^+ suggests there is seasonal difference in the rate of nitrification, specifically a slower rate of ammonium oxidation to nitrite, which is controlled by several factors, such as pH, temperature, and oxygen concentration. pH and temperature are not likely the reason for the observed decrease in nitrification rate in the dry season as almost all the samples outside the optimum pH range for nitrification (7 – 8.2) were found during the wet season, and all samples were collected at optimum temperatures (25 – 30 °C) (EPA, 2002; Princic et al., 1998; Watson et al., 1981). Significantly lower DO concentrations during the dry season (P=0.006 for the Anahulu River, P<0.001 for Kiikii and Paukauila streams) inhibit ammonium oxidation to nitrite, increasing the proportion of NH_4^+ in the streams. Low oxygen conditions (<2 mg/L) have been shown to decrease the rate of ammonium oxidation to nitrite (Goreau et al., 1980; Princic et al., 1998). 11 out of the 25 dry season samples had DO concentrations <2 mg/L, and an additional 6 were between 2-3 mg/L. None of the wet season samples had DO concentrations below 6 mg/L. This seasonal shift in nitrification agrees with a previous study by Breuer et al. (2002), which found lower nitrification rates in tropical soils during the dry season, and suggested, along with Riley and Vitousek's (1995) study, that Hawaiian soils have lower nitrification rates compared to other tropical soils due to being derived from younger parent materials. The high concentrations of ammonium in streams suggest the remediation expected to take place between nutrient sources and the streams is not occurring.

Table 5.3. Seasonal ratio of ammonium to nitrite + nitrate for the streams.

Stream	Season	$[NH_4^+]$:[N+N]
Anahulu	Wet	0.08
	Dry	0.91
Paukauila	Wet	0.07
	Dry	3.61
Kiikii	Wet	0.24
	Dry	1.20

5.3.3 Nutrients in the Kiikii and Paukauila streams

The lack of apparent nitrification in the dry season has serious implications for the effectiveness of the natural treatment of wastewater that is supposedly "utilized" by cesspools, particularly in the Kiikii and Paukauila streams, where our isotopic data (**Figure 4.2, Table 4.4**) shows wastewater entering the streams. In the Kiikii stream, the influence of OSDS is apparent in the dry season in the reaches between 1-2 km from the coast, corresponding to a dense cluster of over 260 OSDS bordering the stream (**Figure 5.2(b)**). The highest NH_4^+ (29 µM) concentrations and highest $\delta^{15}N_{nitrate}$ values (12.3‰) are found in this stretch of the Kiikii during the dry season, and had the highest N+N concentrations (48 µM) and $\delta^{15}N_{nitrate}$ values (10.9‰) in the wet season. Further evidence of wastewater input to the Kiikii stream is its $\delta^{11}B$ value of 44.2‰, the most elevated $\delta^{11}B$ value for any stream sample analyzed, and the closest to the $\delta^{11}B$ value of our measured wastewater endmember (46.2‰). While this isotope value could potentially be caused by animal manure in the stream, this is highly unlikely because the adjacent agriculture is almost entirely seed production by biotechnology companies, unlikely to utilize organic fertilizers. There are also 14 OSDS directly adjacent to the stream (within 200 ft of the stream) at this location. These results strongly suggest that nutrients from OSDS are entering these streams throughout the year, as ammonium in the dry season and nitrate in the wet season.

In the Paukauila stream, the reach >500 m from the coast has particularly high NH_4^+ concentrations, between 12 – 27 µM (**Figure 5.2(c)**). Dry season $\delta^{15}N_{nitrate}$ values (5.4 - 6.9‰) are below the typical reported range for wastewater, but the NH_4^+: N+N ratio (3.6) suggests the values will be affected by fractionation associated with incomplete nitrification, as was found with the cesspool sample. The Paukauila $\delta^{15}N_{nitrate}$ values found in the wet season are more representative of complete nitrification followed by partial denitrification, and range from 6.4 – 13.5‰, with 8 of the 10 samples greater than 9‰, indicating the presence of wastewater. One dissolved inorganic carbon (DIC)-total alkalinity (TA)- $\delta^{13}C_{DIC}$ measurement supports the presence of wastewater (A complete description of DIC-TA- $\delta^{13}C_{DIC}$ analysis is in **Appendix A1**). The DIC, TA, and $\delta^{13}C_{DIC}$ values of 5537 µmol/kg, 3903 µmol/kg, and -10.4‰, respectively, closely match the DIC-TA- $\delta^{13}C_{DIC}$ of the wastewater endmember (5602 µmol/kg for DIC, 5666 µmol/kg for TA, and -13.1‰ for $\delta^{13}C_{DIC}$). The DIC value, combined with the $\delta^{15}N_{nitrate}$ value for of 9.6‰, and a high concentration of DIN as NH_4^+ (97%) strongly suggest the presence of untreated wastewater. Both the Kiikii and Paukauila stream have high amounts of OSDS-sourced ammonium leaching into streams in the dry season. Thus, it is apparent that the expected natural bioremediation of wastewater through nitrification and denitrification is limited during the dry season.

Like the Anahulu River, the Paukauila stream shows an increase in N+N concentrations near the coast correspond to a high density of coastal OSDS. Between 1-2 km away from the coast, there is no apparent seasonal change in nutrient sources (**Figure 5.2(c)**), however an increase in N+N in the wet season can be seen within 1 km of the coast. Increased rainfall during the wet season can cause the water table to rise, which would affect some of the 24 coastal OSDS bordering the Paukauila stream, many of which are installed just above the water table (Whittier and El-Kadi, 2009). If the water table rises above the bottom of the cesspool, the effluent can be flushed out of the cesspool and enter the groundwater. The $\delta^{15}N_{nitrate}$ values within 1 km of the coast range from 6.5 – 10.4‰, with the majority of samples above 7.5‰, as would be expected for an area affected by partly denitrified wastewater. Additionally, two agricultural plots which total 0.07 km^2 may introduce nutrients, but we believe this contribution to be minor as the plots are small and unlikely to introduce the large amounts of nutrients found.

5.3.5. Denitrification assessment of the streams

Denitrification affects the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values in sections of all three streams, although to varying degrees and at different times of year. A previous study on Maui by Houlton et al. (2006) found the extent of denitrification in Hawaiian soils was highly dependent on precipitation. Regions of <2750 mm annual rainfall do not undergo complete denitrification and express a denitrification-associated fractionation effect for ^{15}N, while areas with >2750 mm annual rainfall underwent complete or nearly complete denitrification. Average wet season rainfall during this study was only 101 mm (1212 mm annually) so, based on the findings of Houlton, we therefore do not expect complete denitrification and instead expect to see the effects of partial denitrification on the $\delta^{15}N_{nitrate}$ values. For all stream samples, the slope of the $\delta^{15}N_{nitrate}$ vs $\delta^{18}O_{nitrate}$ plot is 0.95 (**Figure 4.3**), consistent with a system with nitrate that has undergone denitrification with the deviation from a slope of 1 coming from the combined effects of denitrification and anammox (Granger and Wankel, 2016). The Paukauila stream and Anahulu stream show more signs that nitrate in the streams has undergone denitrification during the wet season, with both their highest $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values ($\delta^{15}N_{nitrate}$ = 13.5‰, $\delta^{18}O_{nitrate}$ = 12.5 for the Paukauila stream; $\delta^{15}N_{nitrate}$ = 7.9‰, $\delta^{18}O_{nitrate}$ = 6.5‰ for the Anahulu River), and higher average $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values in the wet season (**Table 4.4**). Importantly, while it is apparent there is relatively more denitrification in the streams and surrounding soil in the wet season, we believe this is largely due to the fact there is less nitrification in the dry season. The low oxygen conditions found in soils and in these streams during the dry season are ideal for denitrification, however the low nitrate formation means less overall denitrification, limiting the isotope effect of denitrification for ^{15}N and ^{18}O. The Kiikii stream has similar $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values for both the wet and dry season (**Figure 5.2(b)**). While there is a larger proportion of ammonium in the dry season in the Kiikii, it appears the small amount of nitrate that is produced through nitrification is being denitrified, causing an increase in the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values to compensate for the negative fractionation associated with incomplete nitrification.

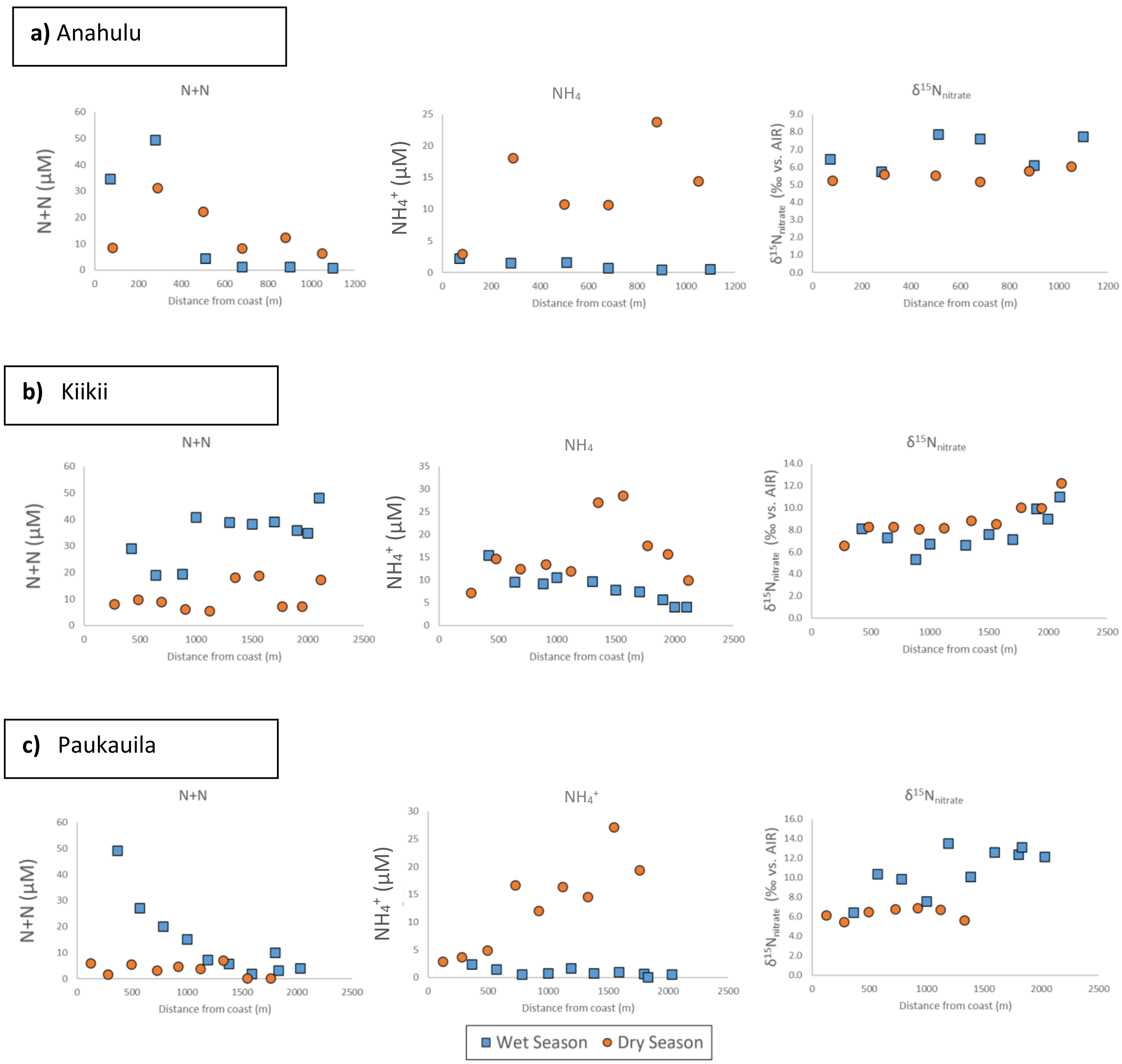

Figure 5.2. N+N concentrations, NH_4^+ concentrations, and $\delta^{15}N$ values for the wet and dry seasons in the a) Anahulu River, b) Kiikii stream, and c) the Paukauila stream. Concentrations are plotted along with the distance away from the coastline for the sampling location.

5.3.5 Comparison to other Hawaiian streams

Table 5.4 illustrates the relative level of nutrient pollution in the study area's streams compared to other streams in Hawaii designated to either be "impaired" or "pristine" (HDOH, 2018). The Waialua streams are similar to other impaired streams found on Oahu, particularly for the TN concentrations (Laws and Ferentinos, 2003), and Kauai (Knee et al., 2008). The dry season (and wet season Kiikii stream) ammonium concentrations of the Waialua streams are greater than any concentration found in all other streams. The dry season Paukauila and Kiikii N+N concentrations are greater than almost all other streams, except for the Kahawai tributary of the Waimanalo stream on Oahu (Knee et al., 2008).

Table 5.4. Comparison of nutrient concentrations Waialua area streams of this study with other "pristine" vs. "impaired" streams in Hawaii.

Stream	Island	Source	Notes	Time	TN	N+N	NH4+
Paukauila	Waialua, Oahu	This study	Impaired Stream	Wet	54	43	1
				Dry	30	4	13
Kiikii	Waialua, Oahu	This study	Impaired Stream	Wet	81	34	8
				Dry	39	13	16
Anahulu	Waialua, Oahu	This study	Impaired Stream	Wet	27	13	1
				Dry	33	15	13
Paukauila (Opaeula Tributary)	Oahu	*Devito 1995*	Historical nutrient values (1995)	Dry	89.2	4.8	<2.7
Anahulu				Dry	53.5	5.6	<2.7
Kawa Stream	Oahu	*HDOH, 2002*	Impaired Stream	Wet	67.0	7.8	2.1
				Dry	65.5	9.5	1.1
Waimanalo Stream (Kahawai Tributary)	Oahu	*Laws and Ferentinos, 2003*	Impaired Stream	Base flow	485.5	114.5	1.7
				Post Rain	337.7	68.9	3.3
Waimanalo Stream (Waimanalo Tributary)	Oahu	*Laws and Ferentinos, 2003*	Impaired Stream	Base flow	47.1	6.1	1.7
				Post Rain	104.9	17.3	2.2
Aihualama	Oahu	*Larned and Santos, 2000*	Conservation land/Pristine	Base flow	--	1.8	0.19
Waiakeakua					--	3.5	0.21
Haiku					--	6.7	0.24
Waianu	Oahu	*Larned and Santos, 2000*	Upstream Agriculture	Base flow	--	7.7	0.15
Kahana Stream Tributary 1	Oahu	*Mayfield 2013*	Conservation/ Pristine		9.9	1.7	1.4
Kahana Stream Tributary 2					7.1	1.3	1.17
Kahana Stream	Oahu	*Hoover, 2009*	Conservation/ Pristine	Base flow	9.8	2.2	0.28
				Storm Runoff	26	7.2	1.2
Hanalei River	Kauai	*Knee et al., 2008*	Impaired Stream	Wet	--	2.2	2.7
				Dry	--	0.9	1.1
Akaka Falls tributary	Big Island	*Michaud and Wiegner, 2011*	Conservation land /Pristine	Feb - July	3.8	0.4	<1
Maili Stream					2.7	1.0	<1
Kamaee Stream					3.6	0.0	<1
Kawainui Stream					3.8	<1	<1
Kaiwiki Stream	Big Island	*Michaud and Wiegner (2011)*	Dominant agriculture	Feb - July	11.9	10.0	<1
Opea Stream					6.4	4.1	<1

5.4 Nutrients and Waialua beaches

5.4.1 Coastal nutrient transport as a component of SGD

Significant nutrient loading from anthropogenic sources is evident in the porewaters of all 4 beaches in the study area, although some differ in the source(s) of nutrients received. Complete nitrification is apparent by the NH_4^+:N+N ratios that ranged between 0.09 and 0.04, indicating that isotope fractionation from incomplete nitrification does not affect these samples. Samples along the coast with nitrogen concentrations and $\delta^{15}N_{nitrate}$ values higher than marine endmembers (**Table 5.1**) indicate the presence of wastewater leachate, while lower $\delta^{15}N_{nitrate}$ values strongly suggest the presence of nutrients sourced from synthetic fertilizers. While the consolidated caprock in the region slows the discharge of groundwater at the coast due to its lower hydraulic conductivity (Gingerich and Oki, 1999), SGD is still readily apparent both in our thermal infrared imagery as well as observations of groundwater seeps at the coast (**Figure 3.1**). All beach face piezometer samples taken at locations where fresh groundwater was observed entering the coast show water with elevated nutrient concentrations.

5.4.2 The effect of OSDS spatial density on the source of nutrients in SGD

In order to determine if a relationship between the density of coastal and nutrients found at beaches could be identified, the spatial distribution of OSDS, DIN concentrations, and $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values were used in a Spearman's rank-order correlation. In total, 30 beach face piezometer samples and 7 coastal water samples were incorporated into a Spearman's rank correlation, which was evaluated at the 95% confidence interval ($P<0.05$, $\rho>0.02$). In this analysis, two different distances were used to determine the relationship between OSDS density and DIN characteristics. First, all OSDS within 200 ft (61 m) of the shoreline was used because the HDOH regulations state there are increased health risks resulting from the placement of any OSDS within 200 ft of a shoreline (HDOH, 2018). As it affects regulation policy, our results indicate that this 200 ft buffer distance established by the HDOH is inadequate, as many high-density areas of OSDS found just farther than 200 ft from the shoreline also impact groundwater quality. Thus, a second rank correlation was performed with a distance of 500 ft (152 m) which allowed high density areas to be represented. For example, several areas that had no OSDS within 200 ft, but nonetheless had the highest densities of OSDS (usually between 20 and 40 OSDS) within 500 ft (152 m). This 500 ft buffer distance to shore matches guidelines set by the Hawaii

Department of Health stating that a cesspool must be within 500 ft to qualify for a maximum $10,000 tax credit to upgrade to a septic system (Act 120, State of Hawaii, 2015).

Computation of a Spearman's rank correlation (**Table 5.5**) shows no identifiable relationship between an increased density of coastal OSDS and increased DIN concentrations in beach face samples. However, there is a significant relationship between the coastal OSDS density and the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values of samples (**Table 5.5**). Although concentrations of nutrients are not necessarily related to the amount of OSDS, the high $\delta^{15}N$ and $\delta^{18}O$ values in OSDS-dense regions strongly suggest the presence of wastewater leachate and that denitrification is occurring. OSDS is not the only nutrient source in the region, and areas with fewer OSDS but similar nitrogen concentrations are influenced by nutrients sourced from agriculture further away from the coast. The fact that all beaches in the study area are experiencing a similar level of nutrient loading in the coastal waters but fed by different nutrients sources is further supported by the %N and $\delta^{15}N$ values of algae samples, discussed further in **section 5.4.3** below. This analysis only considers nutrient concentrations, but it should be noted that wastewater also contains harmful pathogens and bacteria which could be getting into coastal waters that are surrounded by a high density of nearshore OSDS (Lipp et al., 2001; Viau et al., 2011).

Table 5.5. Result of the Spearman's Rank Correlation to determine if there is a significant relationship between OSDS density within 200 ft and 500 ft of the coast and the nitrogen characteristics found at beaches. Parameters that are found not to have a significant relationship with OSDS density are shaded in blue.

Spatial Parameter	TN	N+N	NH_4^+	$\delta^{15}N$	$\delta^{18}O$
OSDS within 200 ft	ρ=0.237, P = 0.157	ρ=0.069, P=0.685	ρ=0.236, P = 0.159	ρ=0.223, P=0.185	ρ=0.417, P=0.010
OSDS within 500 ft	ρ=0.087, P=0.61	ρ=0.121, P=0.474	ρ=0.033, P=0.848	ρ=0.41, P=0.012	ρ=0.388, P=0.017

5.4.3 Nutrient loading into Waialua beaches

Across the beaches, varying trends in nutrient concentrations and isotopic values suggest different and often localized nutrient sources and loading conditions that persist along the Waialua coast. Haleiwa Beach, for example, is relatively unique in its nutrient source, with most nutrients coming from an agricultural source with minor denitrification. This finding was supported by the lower $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values, the $\delta^{15}N_{algae}$, and a $\delta^{11}B$ value. In contrast, Aweoweo and Alii Beach are similar in their nutrient sources, with both showing signs of wastewater contamination and extensive denitrification, while Alii Beach also shows signs of additional nutrient input from agricultural fertilizers. Waialua Beach has the lowest nitrogen and oxygen isotope values with a nutrient source originating from a localized nearshore agricultural plot. Our algae results corroborate the values found in the nitrate and oxygen isotope analyses of nitrate and their associated nutrient sources. The algal data also confirms the findings of **section 5.2.2** all beaches were experiencing nutrient loading regardless of nearshore OSDS density, as the %N for all the beaches were relatively consistent. Despite there not being a relationship between %N and OSDS density, the algae collected suggested excess nutrient loading at all locations, as all 4 beaches had samples %N values greater than 2% reported for high nutrient loading in *Ulva* tissue (Amato et al., 2016). Overall, nutrient sources differ at all locations, but all areas have high nutrient concentrations.

At Haleiwa Beach it is unlikely that OSDS is the dominant source of nutrients because only 1 of the area's 10 OSDS are located within 300 m of most of the beach face samples. Elevated nutrient concentrations measured in beach face piezometer samples at Haleiwa Beach suggest the presence of agriculturally-sourced nutrients, which is supported by the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values of those waters. The average $\delta^{15}N_{nitrate}$ value for Haleiwa (5.3‰) is near the maximum expected $\delta^{15}N$ values of synthetic fertilizer (**Table 5.1**). Denitrification likely raises the $\delta^{15}N_{nitrate}$ values to just above the range for synthetic fertilizer because the $\delta^{15}N_{nitrate}$ vs $\delta^{18}O_{nitrate}$ trend (slope = 0.93) is indicative of a marine system undergoing significant denitrification (~1) (Granger and Wankel, 2016). While the $\delta^{18}O_{nitrate}$ values are not elevated compared to other areas in the region, with the majority of $\delta^{18}O_{nitrate}$ values in beach face samples (n=9) falling between 0-3.5‰, nitrification of ammonium fertilizers is known to lead to $\delta^{18}O_{nitrate}$ values as low as -5‰ (Kendall et al., 2007), which could be raised to the average value of 3.1‰ through denitrification. One $\delta^{11}B$ value collected at Haleiwa suggests an agricultural source of nutrients (34.4‰), which is lower than that expected for seawater (37.7‰-40.4‰) (**Table 5.2**). The lower $\delta^{11}B$ value is likely due to the presence of mineral fertilizers and not wastewater with detergents due to the low $\delta^{15}N_{nitrate}$ values and lack of OSDS (**Table 5.1**). We thus conclude that the majority of nutrients at Haleiwa Beach originate from agricultural sources which have undergone denitrification due to the relatively low $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values and the low density of coastal OSDS.

Aweoweo and Alii beaches show evidence of contamination from wastewater and have regions undergoing denitrification, although, as noted above, samples from Alii also suggest there may be an agricultural source of nutrients in some locations. Alii and Aweoweo beaches have a high number of OSDS within 1 km of the coastline, with 410 OSDS and 680 OSDS for Alii and Aweoweo, respectively, and the highest corrected N+N averages (**Table 4.3**). Porewaters from these two beaches had the highest average $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values of all beaches, with 13.5‰ and 6.7‰ for Aweoweo and Alii, respectively (**Table 4.4**), although the Alii values are not statistically different than Haleiwa Beach due to several samples with low values. Two samples at Alii have low $\delta^{15}N_{nitrate}$ values of 3.6‰ and 2.2‰ and

$\delta^{18}O_{nitrate}$ values of -0.41‰ and -2.99‰, suggesting input from synthetic fertilizers in some areas along the beach. Other samples show the presence of wastewater without evidence of extensive denitrification, as several samples at Aweoweo $\delta^{15}N_{nitrate}$ values between 8-11‰ have low $\delta^{18}O_{nitrate}$ values between 1-3‰. One sample at Alii is greatly impacted by wastewater, indicated by the highest corrected N+N concentration in this study (5190 µM), an elevated $\delta^{15}N_{nitrate}$ value (9.6‰), and a relatively low $\delta^{18}O_{nitrate}$ value of 5.0‰, indicating denitrification alone is not responsible for the high $\delta^{15}N_{nitrate}$. Other samples along the two beaches clearly show certain regions are experiencing denitrification, as 5 samples have $\delta^{15}N_{nitrate}$ values >11‰ and $\delta^{18}O_{nitrate}$ values >7‰, including the sample with highest $\delta^{15}N_{nitrate}$ value of any sample collected (23.5‰). It is likely that the nutrient source for these samples is wastewater from OSDS, but denitrification is partly responsible for the elevated isotope values. One boron sample at Alii beach suggests the presence of OSDS leachate with a $\delta^{11}B$ value of 33.5‰, lower than expected range of seawater (**Table 5.2**). Although similar to the value found at Haleiwa that was determined to be from agriculture (34.4‰), this value is unlikely to come from agriculture due to the high $\delta^{15}N_{nitrate}$ value (12.9‰). While different from our collected boron wastewater endmember (46.2‰), literature values for wastewater containing industrial and domestic detergents are low (-4 - 12‰). The combined used of the of $\delta^{11}B$ and $\delta^{15}N_{nitrate}$ value suggest this sample contains wastewater with domestic detergents. Aweoweo and Alii beaches are influenced by OSDS based on elevated $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values, one low $\delta^{11}B$ value, high nutrient concentrations, and a high density of coastal OSDS.

Waialua Beach, despite having the second highest density of OSDS within 1 km of the coast, does not show signs that OSDS leachate as the primary source of nutrients found. While there are 489 OSDS within 1 km of the coast, most of the samples were collected along a stretch of beach at least 100 m from the nearest OSDS, which may be too far from the sampling locations to have a significant impact (**Figure 4.2**). All Waialua Beach samples were collected through beach face piezometers, several of which displayed weeping beach face leakage of relatively lowered salinity at very low tides. The average salinity-normalized N+N concentration at Waialua Beach was the lowest concentration observed for any beach (100 µM, **Table 4.3**). Waialua Beach also displayed the lowest average $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values, 4.1‰ and -2.1‰, respectively (**Table 4.4**). The $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrates}$ values match published values for synthetic ammonium-based fertilizer (**Table 5.1**). There is a group of aquaculture ponds totaling 0.08 km^2 adjacent to Waialua Beach. Fertilization is an important step in maintaining aquaculture ponds, with synthetic fertilizers commonly used to maintain healthy nutrient levels (Green, 2015). Fertilizer-sourced nutrients from these tracts could enter groundwater system and discharge as

SGD at Waialua Beach. Despite having a high density of OSDS within 1 km of the coast, OSDS do not appear to impact Waialua beach, instead it is mainly impacted by agriculturally sourced nutrients.

The data collected through algal tissue analyses corroborates the results found in the water sampling from beach face piezometers. Previous studies in Hawaii have shown that $\delta^{15}N$ values of opportunistic algae can be used as bioindicators for sewage in coastal waters (e.g. Derse et al., 2007, Dailer et al., 2010, 2012; Amato et al., 2016). Macroalgae reduce nitrate to nitrite intracellularly before assimilation and there is an associated kinetic isotope effect, however past research has shown there is minimal net isotope fractionation during nutrient uptake by macroalgae, associated with the complete use of available nitrate. Therefore, the isotopic composition of algal tissues is expected to be similar to the sources of N (Lapointe et al., 2005, Abaya et al. 2018). For this study, the average (n=16) $\delta^{15}N_{algae}$ value at Haleiwa Beach (5.9‰) is close to the $\delta^{15}N_{nitrate}$ value collected in beach face piezometer samples (5.3‰). This average is skewed by one anomalously high $\delta^{15}N_{algae}$ value of 12.9‰, which is 6.4‰ higher than any other sample collected along this beach. Excluding this high value, the average decreases to 5.5‰, nearly identical to the $\delta^{15}N_{nitrate}$. The algae $\delta^{15}N$ results at Alii (n=9) and Aweoweo Beach (n=11) also match the $\delta^{15}N_{nitrate}$ beach face piezometer values. At Alii Beach the results were 6.5‰ for the $\delta^{15}N_{algae}$ compared to 6.7‰ for the $\delta^{15}N_{nitrate}$, while at Aweoweo the average $\delta^{15}N_{algae}$ value was 9.9‰, the highest of any beach (**Figure 4.6**). The lowest average $\delta^{15}N_{algae}$ values found at Waialua Beach (5.1‰) (**Figure 4.6)**, where the lowest $\delta^{15}N_{nitrate}$ values were also found. For $\delta^{15}N_{algae}$ values, the results at each beach were significantly different than every other beach (**Section 4.2, Table 4.1**)**,** however the differences between Waialua, Haleiwa, and Alii Beach are likely too small to determine different nutrient sources at these beaches from the algal analysis alone. The slightly elevated average of 6.7‰ found at Alii Beach suggests there is a mixture of nutrient sources, most likely from wastewater and agriculture, which agrees with the evidence found with the $\delta^{15}N_{nitrate}$ analysis, while the high $\delta^{15}N$ values of algae found at Aweoweo Beach agree with the $\delta^{15}N_{nitrate}$ analysis and suggests the main source of nutrients is OSDS. The average %N at all beaches did not differ significantly (**Table 4.1**), with only 0.2% separating the lowest and highest averages (**Figure 5.2(b)**). This finding supports the conclusion found in **section 5.3.1**, where the beaches are experiencing relatively similar levels of nitrogen loading regardless of OSDS density near the beach, while the $\delta^{15}N$ values differ significantly throughout the study area, with elevated $\delta^{15}N$ values near the most OSDS-dense areas. When compared to OSDS density, there is a clear decrease in $\delta^{15}N$ values with lower OSDS density, except for at Waialua Beach where it was previously determined the nearshore OSDS did not impact the beach (**Figure 5.2(a)**). There is not a noticeable trend in %N values compared to the OSDS density of the beaches (**Figure 5.2(b)**), while the high %N value measured at Haleiwa Beach suggests there is an additional anthropogenic nutrient source besides OSDS, most likely agriculture.

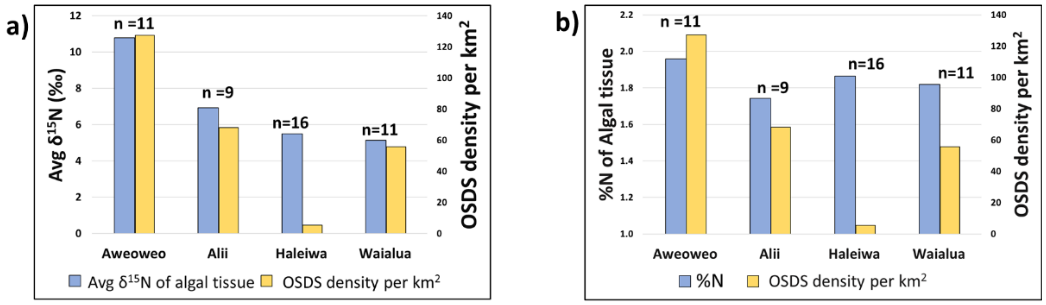

Figure 5.3 Average a) $\delta^{15}N$ and b) %N for all A.spicifera samples collected and the OSDS density found at each sampling location. The $\delta^{15}N$ of algal tissue varies significantly by location, however the %N is relatively consistent throughout the entire study area.

To determine if $\delta^{15}N_{algae}$ varied with distance from the coastline across the four main beaches, we plot (in **Figure 5.3**) the $\delta^{15}N_{algae}$ values for each sample along with the sample distance from the coast. For Alii and Aweoweo Beach, $\delta^{15}N_{algae}$ values decrease with distance offshore, while Haleiwa has relatively constant values, close to background seawater. Samples near the coast at Alii and Aweoweo are elevated relative to background seawater isotope values (~4‰) due to the presence of wastewater increasing the isotope values. Waialua Beach is the only beach where the $\delta^{15}N_{algae}$ values increase with distance from shore. This finding supports the concept that there is a terrestrial nutrient source, such as agriculture, near Waialua Beach that lowers the $\delta^{15}N$ values along the coast, and the sample values increase towards the true background value of $\delta^{15}N$ for seawater away from the coast.

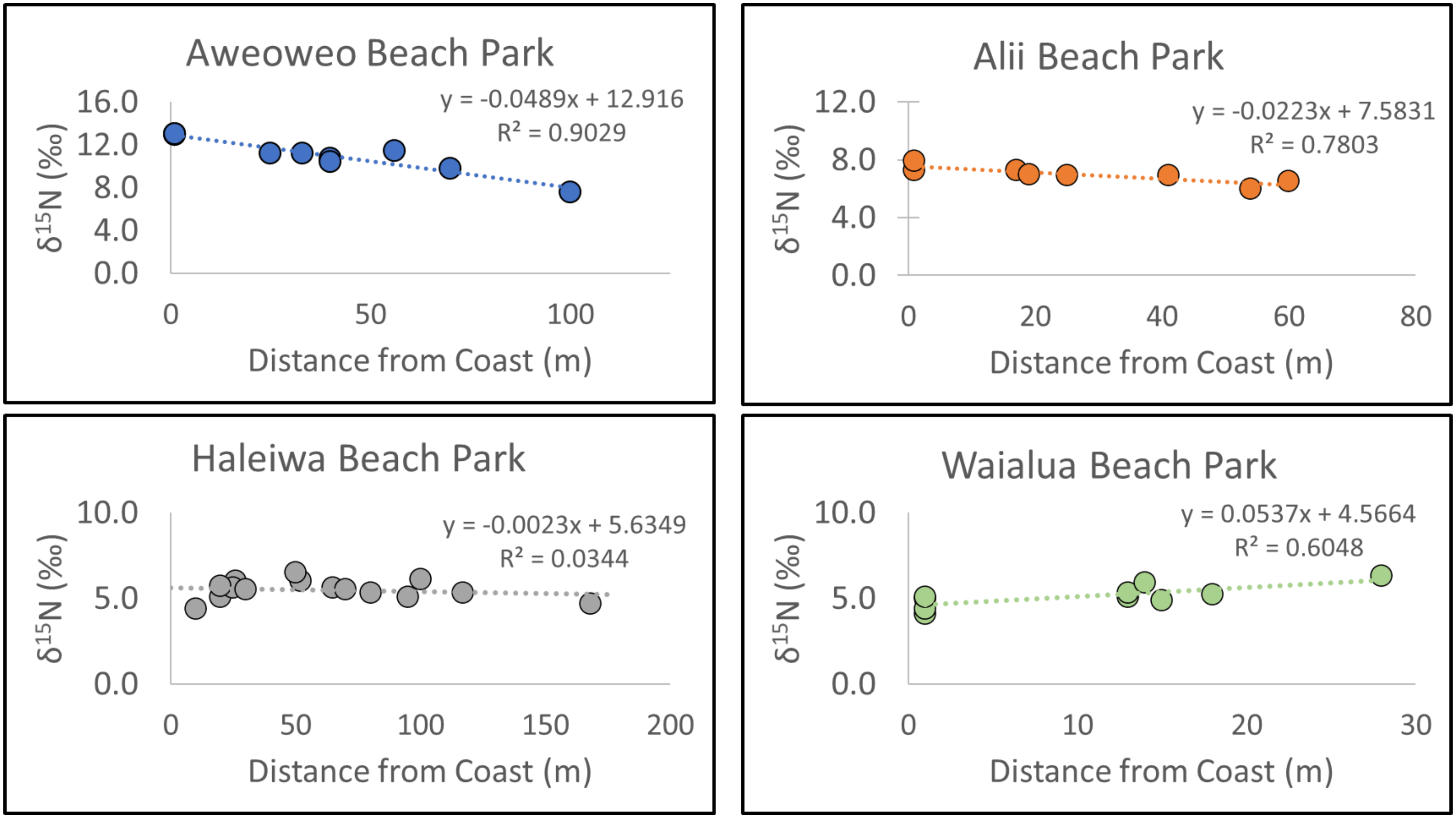

Figure 5.4. $\delta^{15}N$ and distance from coast for all A.spicifera samples collected from the four main beaches in the study area. Aweoweo, Alii, and Haleiwa Beach samples all have a decrease in $\delta^{15}N_{algae}$ as the samples move away from the coast, however Waialua beach shows an increase in $\delta^{15}N_{algae}$ away from the coast

6. Summary and conclusions

A high density of OSDS and long history of agriculture make the Waialua region on the North Shore of Oahu susceptible to excess nutrient loading from anthropogenic sources. Excess nutrients in coastal environments upset natural food chains and often lead to devastating ecological consequences, such as harmful algal blooms and coral diseases. Understanding the locations of excess nutrients and the nutrient sources is vital for determining areas most at risk. In this study, we utilized a multi-tracer approach to identify at risk areas and determine the nutrient sources that most contribute to excess nutrients.

A cesspool wastewater endmember demonstrated the importance of understanding nitrogen transformations when using $\delta^{15}N_{nitrate}$ values as a tracer, as nitrification, denitrification, annamox, and ammonium volatilization can each play an important role in raising wastewater to typically reported endmember $\delta^{15}N_{nitrate}$ values (Hinckle et al., 2008; Richardson et al., 2017; Abaya et al., 2018). The presence of wastewater leachate was identified in reaches of streams through nutrient concentrations $\delta^{15}N_{nitrate}$, $\delta^{18}O_{nitrate}$ values, and $\delta^{11}B$ values and supported by OSDS density and extent of agricultural land. One DIC-TA-$\delta^{13}C_{DIC}$ sample was used to confirm the presence of wastewater in one of the streams. Two of the 3 streams showed strong increases in nutrients towards the coast indicative of near-coast nutrient loading probably from OSDS. All 3 streams showed an increase in ammonium concentrations during the dry season, suggesting the natural expected bioremediation is not occurring in the summer months, which agrees with previous studies in tropical environments that suggest nitrification and denitrification rates are lower in the dry season (Breuer et al., 2002), particularly in Hawaiian soils (Riley and Vitousek, 1995; Houlton et al., 2006). Widespread denitrification was found throughout the study area, with two of the streams showing clear signs of increased denitrification expected to take place in the soils and aquifers during the wet season, most likely a consequence of the decreased dry season nitrification rate. The 3 streams showed elevated nutrient concentrations compared to other impaired and pristine streams throughout the Hawaiian Islands, particularly for ammonium concentrations.

We found nutrients from the OSDS in the region travel through the groundwater system and discharge along the coast through SGD, particularly in regions with a high coastal OSDS density. While the beach with the most coastal OSDS had the highest nutrient concentrations, there was not a statistically identifiable relationship between increased OSDS density and increased nutrient concentrations, as beaches experienced high levels of nutrients regardless of OSDS density due to agricultural sources. There was a significant relationship between the coastal OSDS density and

$\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values, indicating nutrients are leaching into coastal waters in OSDS-dense locations. Algal tissue analyses of $\delta^{15}N$ and percent tissue N were used as secondary tracers for nutrient sources and the results confirmed the source of nutrients to be OSDS at Aweoweo Beach, the region with the highest OSDS density, while also corroborating the $\delta^{15}N_{nitrate}$ analysis along the entire coastline. The algal data supported the theory that all the beaches were receiving a similar amount of nutrients in the coastal waters regardless of OSDS density, as the %N of the algal tissues for every beach was similar. Our results show potentially harmful nutrients sourced from OSDS wastewater and agriculture are present in both the streams and along the coast throughout many regions of the study area.

APPENDICES

Appendix A1. Regional aqueous carbonate geochemistry

Methods

In order to attempt to identify areas with a wastewater component and to quantify the extent of denitrification, samples were analyzed for DIC and TA. CO_2 is produced when organic matter is oxidized, which increases the total DIC in the system (Manahan, 2010). Along with CO_2, carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) all contribute to the total DIC. TA, however, only consists of CO_3^{2-} and HCO_3^-, so the difference between DIC and TA is the excess, dissociated CO_2 produced by organic matter degradation. Systems where denitrification is occurring are expected to produce low concentrations of NO_3^-, low DO and DIC as well as low $\delta^{13}C_{DIC}$ values, high $\delta^{15}N$ values, and high $\delta^{18}O$ values. These expected values are controlled by the organic matter degradation occurring in the system (Kroeger and Charette, 2008, Ding et al., 2014; Fackrell et al., 2016).

Sixteen samples were analyzed for inorganic carbon at the Water Resources Research Center Analytical Chemistry Laboratory at the University of Hawaii at Manoa using a Shimadzu TOC-V Organic Carbon (TOC) analyzer with a Total Nitrogen (TN) detector. Fourteen samples for inorganic carbon isotope analysis were collected in 40 mL borosilicate vials and sealed with a butyl rubber stopper and aluminum crimp-topand preserved with 3 µL $HgCl_2$ solution. Sample $\delta^{13}C_{DIC}$ values were determined at the University of Utah Stable Isotope Ratio Facility for Environmental Research using a ThermoScientific Gas Bench II coupled to a ThermoScientific MAT 253 IRMS via ThermoScientific Conflo Device. Average standard deviation for the 14 samples was 0.1‰. The same 14 samples were analyzed for total alkalinity at the University of California, Davis Analytical Lab through the titration method using 0.025 N H_2SO_4 as described in Standard Methods for the Examination of Water and Wastewater, 20th Edition by Clesceri et al. (1999). Sample precision was found to be ±35.39 µmol/L based on 4 duplicate pairs.

Results

The DIC concentrations in the 16 samples ranged between 88 and 5537 µM. The lowest DIC was from the Kiikii stream and the highest DIC was from the Paukauila stream. Besides one exceptionally high value of 5536 µmol/kg, samples collected from streams had significantly lower DIC values than beach face piezometers (P=0.02), usually falling between 200 and 600 µM. Most of the high values were from beach face piezometer samples, with values usually between 1400 and 2250 µM. One sample from a privately owned drinking water well had a DIC concentration of 3168 µM. TA values range from 300 to 3903 µM, with beach face samples being significantly higher than the streams (P=0.03). The isotopic composition of $\delta^{13}C_{DIC}$ for all samples varied between -14.4 and 0.8‰. The average DIC concentration of all samples collected from beach face piezometers was 1739 µmol/kg, and the average total alkalinity was 2030 µmol/kg (n=7). Average $\delta^{13}C_{DIC}$ for these samples was -1.8‰. For the stream samples collected the averages were 1351 µmol/kg and 1201 µmol/kg for DIC and TA, respectively. The average $\delta^{13}C_{DIC}$ for these same samples was -9.1‰. These averages are skewed by one result however, as one sample collected along the Paukauila stream had DIC, TA, and $\delta^{13}C_{DIC}$ measurements of 5537 µmol/kg, 3903 µmol/kg, and -10.4‰. Without this sample, the average values for streams were 305 µmol/kg for DIC, 525 µmol/kg for TA, and -8.8‰ for $\delta^{13}C_{DIC}$.

Discussion

Average values for DIC and TA for surface marine water endmembers were taken from open ocean data from SOEST Station Aloha (2018) with an average concentration of DIC of 1989 µmol/kg and an average TA concentration of 2301 µmol/kg (n=8). Both these values agree with the historic data found at Station ALOHA, found in Dore et al. (2009). The average $\delta^{13}C_{DIC}$ for Pacific waters is 1.6‰, according to Quay et al. (2003). Groundwater and wastewater endmembers come from Dores (2018) and had average values of 652 µmol/kg for DIC, 350 µmol/kg for TA, and -19.9‰ for $\delta^{13}C_{DIC}$ for groundwater, and 5602 µmol/kg for DIC, 5666 µmol/kg for TA, and -13.1‰ for $\delta^{13}C_{DIC}$ for the wastewater endmembers.

While most of the samples had relatively low DIC-TA values, 2 of the 14 samples collected had values that were elevated to the point where wastewater input was possible. One of these samples comes from a beach face piezometer sample along Haleiwa Beach Park, which had a DIC concentration of 2234 µmol/kg and a $\delta^{13}C_{DIC}$ value of -11.3‰. These values are consistent with the presence of wastewater, however the $\delta^{15}N_{nitrate}$ value for the sample is 4.8‰, making it unlikely for wastewater to be the dominant source of nutrients in the location. The other sample with concentrations greater than 2000 µmol/kg for DIC and TA was the sample collected along the Paukauila stream. The DIC, TA, and $\delta^{13}C_{DIC}$ values of 5537 µmol/kg, 3903 µmol/kg, and -10.4‰ respectively, make this sample a prime candidate for a location with a large component of wastewater based on its similarities to the wastewater endmember. Furthermore, the $\delta^{15}N_{nitrate}$ value for this sample is 9.6‰, within the expected range for raw effluent. The sample is also one of the few samples gathered with the majority of DIN coming in the form of NH_4^+, instead of N+N (only 3% of DIN is in the form of N+N). Nitrification represents a kinetic isotope fractionation, where ^{14}N of ammonium is preferentially utilized leading to an initial lower $\delta^{15}N_{nitrate}$ and increased $\delta^{15}N_{ammonium}$ as nitrification proceeds to completion (Mariotti et al., 1981; Song et al., 2014). As the majority of DIN is in the form of ammonium, extensive nitrification has not yet occurred, suggesting the $\delta^{15}N$ is higher than the measured $\delta^{15}N_{nitrate}$, further supporting the conclusion of a wastewater source. The $\delta^{18}O_{nitrate}$ value for this sample is low at 0.7‰. With the evidence these parameters provide, the sample is very close to a source of nutrients, likely from an OSDS. The high proportion of DIN as NH_4^+ suggests there is very little nitrification occurring between the nutrient source and sampling location. Furthermore, it is unlikely the $\delta^{15}N_{nitrate}$ value is a result of denitrification despite the low concentration of N+N because the $\delta^{18}O_{nitrate}$ value would be elevated, whereas this sample has a low $\delta^{18}O_{nitrate}$ value.

While only the two samples were considered for possible wastewater contamination based on the DIC-TA alone, it does not mean the other samples are not possibly contaminated. Sampling for the beach face piezometer samples occurred during a time of relatively weak tides, causing the water gathered to be higher salinity than desired. This led to many of the samples being diluted with some amount of seawater. Despite not being able to use the reported values for DIC-TA for these samples as a direct indicator for the presence of wastewater, a conservative mixing model was utilized to find expected DIC concentrations and $\delta^{13}C_{DIC}$ values based on the values found in the fresh and marine endmembers, as is described in Bhavya et al. (2018). Comparing the calculated values based on salinity with the measured values at each location would allow us to determine the biogeochemical processes occurring. First, the freshwater fraction, F_{fw}, of each sample was calculated using the following mass balance equation:

$$S_{mix} = S_{fw}F_{fw} + S_{sw}(1-F_{fw}) \quad \textbf{Equation A.1}$$

In this equation, S_{mix} is the salinity measured for each sample, S_{fw} is the salinity of the fresh endmember and S_{sw} is the salinity of the seawater endmember. Once F_{fw} is calculated, the conservative mixing values for [DIC] and $\delta^{13}C_{DIC}$ can be calculated using the following 2 equations:

$$[DIC]_{mix} = [DIC]_{fw}F_{fw} + [DIC]_{sw}(1\text{-}F_{fw}) \qquad \textbf{Equation A.2}$$

$$\delta^{13}C_{mix} = \frac{[DIC]_{fw}\delta^{13}C_{fw}F_{fw} + [DIC]_{sw}\delta^{13}C_{sw}(1\text{-}F_{fw})}{[DIC]_{fw}F_{fw} + [DIC]_{sw}(1\text{-}F_{fw})} \qquad \textbf{Equation A.3}$$

[DIC] represents the DIC concentration, where the subscripts 'sw' and 'fw' denote the seawater and freshwater endmembers, respectively. The subscript 'mix' represents the values for the mixing model between the two endmembers. $\delta^{13}C_{mix}$ is the theoretical of $\delta^{13}C_{DIC}$ if there were no sources or sinks of DIC, and is entirely determined by the salinity and [DIC] of the two endmembers. Once these values are calculated, it allows us to compare the actual values measured to the calculated values for the conservative mixing model. To do so, we calculate $\Delta\delta^{13}C_{DIC}$ and Δ[DIC] to measure the deviations from expected values:

$$\Delta\delta^{13}C_{DIC} = \delta^{13}C_{sample} - \delta^{13}C_{mix} \qquad \textbf{Equation A.4}$$

$$\Delta[DIC] = \frac{[DIC]_{sample} - [DIC]_{mix}}{[DIC]_{mix}} \qquad \textbf{Equation A.5}$$

In general, DIC will decrease if primary production outpaces respiration because of the consumption of DIC during carbon fixation. If DIC is removed during primary production the $\delta^{13}C_{DIC}$ is expected to increase due to the preferential use of the lighter isotope by plants. If [DIC] increases while $\delta^{13}C_{DIC}$ decreases, organic matter degradation is expected to be occurring. For areas with an increase in both [DIC] and $\delta^{13}C_{DIC}$, calcite dissolution is the major process occurring, whereas locations with a decrease of both parameters suggests that calcite precipitation is taking place. **Figures A.1 (a)** and **(b)** show the measured values compared to the mixing line determined from the conservative mixing model, without the use of $\Delta\delta^{13}C_{DIC}$ and Δ[DIC].

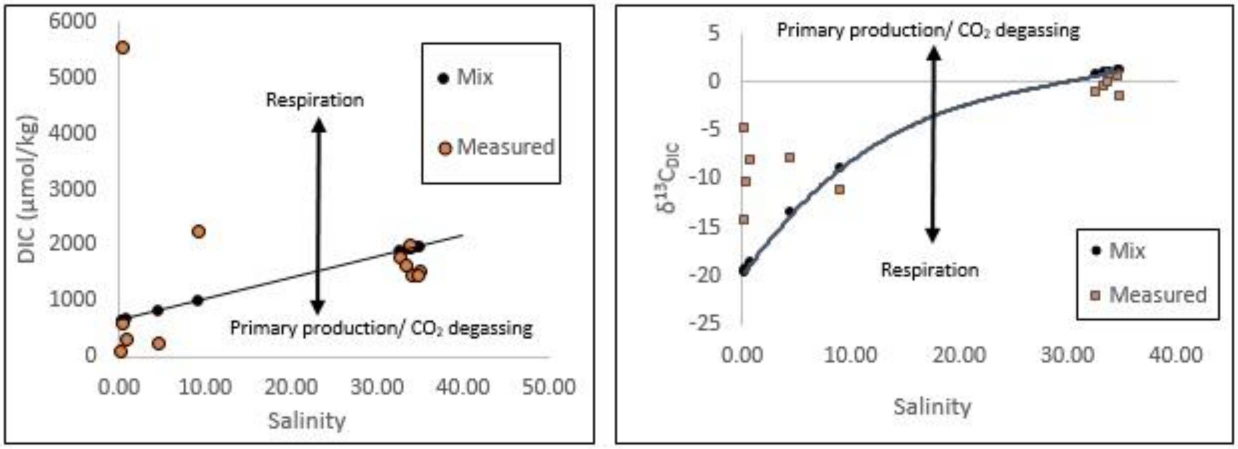

Figure A.1. a) DIC concentrations in the study area against salinity and b) the $\delta^{13}C_{DIC}$ against salinity. Black symbols represent the values from the conservative mixing model while orange symbols are the measured values. The arrows indicate the relative influence of primary production and organic matter degradation on the $\delta^{13}C_{DIC}$ and [DIC].

From the measured DIC and $\delta^{13}C_{DIC}$ compared separately, it is difficult to determine some of the processes occurring at certain locations. In samples with low salinities, deviations from the conservative mixing lines (**Figure A.1 (a)** and **(b)**) suggest that primary production appears to be the main process. Samples from beach face piezometers with high salinities have conflicting results between the two figures, as the DIC concentrations (**Figure A.1 (a)**) appear to show the driving process to be primary productivity, while the $\delta^{13}C_{DIC}$ values (**Figure A.1 (b)**) shows respiration as the main process. As stated above, these are not the two only possible biogeochemical processes occurring, as they both ignore calcite precipitation and dissolution. To better understand the dominant mechanisms that control the local aqueous carbonate geochemistry, the deviations from the conservative mixing model, $\Delta\delta^{13}C_{DIC}$ and Δ[DIC], were compared (**Figure A.2**).

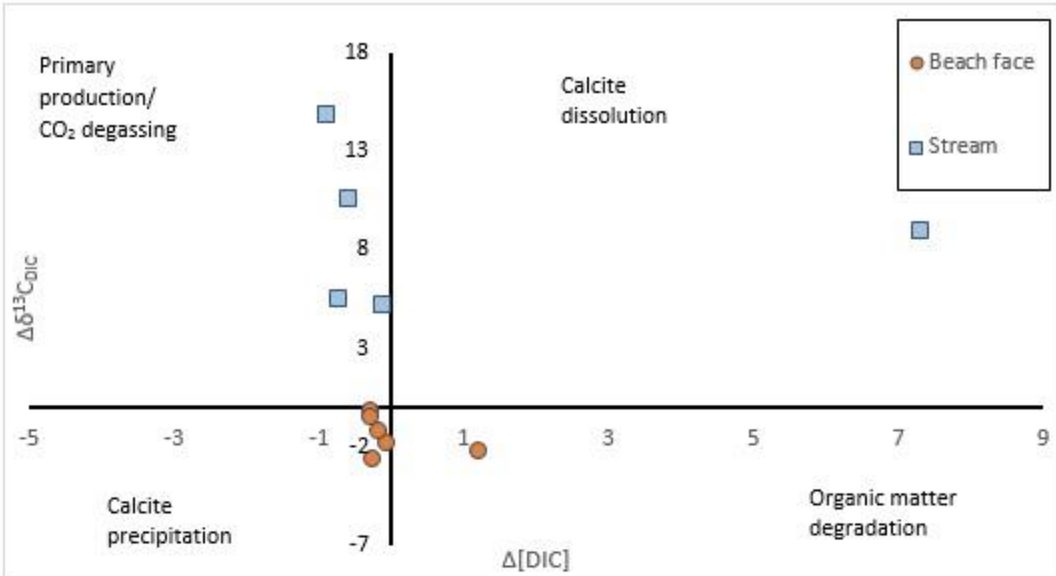

Figure A.2. Deviations in $\delta^{13}C_{DIC}$ ($\Delta\ \delta^{13}C_{DIC}$) versus [DIC] (Δ[DIC]) from the corresponding mixing values to determine the dominant mechanism controlling local aqueous geochemistry throughout the beaches and streams of the study area. The quadrants are labeled with the process that are most likely to cause the deviations found.

The majority of samples collected along stream banks show the dominant process controlling the DIC pool is primary production or CO_2 degassing and the DIC pool of the majority of beach piezometer samples were controlled by calcite precipitation although these data points are so close to the origin they are likely not significant. None of these samples were expected to be contaminated with wastewater based on their DIC-TA concentrations alone. That said, the majority of the beach face piezometer samples and some stream samples have other values that suggest the presence of wastewater, such as elevated N+N concentrations and $\delta^{15}N_{nitrate}$ values. The two samples mentioned earlier, one from Haleiwa Beach Park and the other from the Paukauila stream, which had DIC-TA values in the range expected for wastewater presence, showed different processes controlling the DIC pool. The beach face piezometer sample from Haleiwa Beach Park showed the dominant process controlling the DIC pool was organic matter decomposition. This sample is not considered to have a large component of wastewater due to its relatively low N+N concentration and $\delta^{15}N_{nitrate}$ value that better fit an agricultural nutrient source. The Paukauila stream sample that was believed to contain a significant proportion of wastewater was the only sample that was controlled by calcite dissolution.

Appendix A2. Sampling results

Table A.1. Name, type, date and time, and location for all samples

Name	Type	Date	Time	Easting	Northing
ABB SEEP	Beach Face			590805	2386998
ABP-001	Beach Face	7/3/2019	5:50	590815	2386987
ABP-002	Beach Face	7/3/2019	7:18	590067	2386844
ABP-003	Beach Face	7/5/2019	6:41	588953	2386956
ABP-004	Beach Face	7/5/2019	7:28	587412	2386662
ABP-005	Beach Face	8/28/2019	5:22	590794	2386971
ABP-006	Beach Face	8/28/2019	6:42	590624	2386928
ABP-007	Beach Face	8/28/2019	7:56	590361	2386909
ANA 1A	Stream	Jun-19		592726	2388212
ANA 2	Stream	Jun-19		593996	2388030
ANA 201	Stream	9/6/2019	12:17	591663	2387620
ANA 202	Stream	9/6/2019	12:42	593048	2388044
ANA 203	Stream	9/6/2019	12:55	593256	2388028
ANA 204	Stream	9/6/2019	13:09	593386	2388150
ANA 205	Stream	9/6/2019	13:20	593566	2388039
ANA 206	Stream	9/6/2019	13:34	593775	2388027
ANA001	Stream	2/6/2019	11:27	592844	2388101
ANA002	Stream	2/6/2019	11:45	593040	2388037
ANA003	Stream	2/6/2019	11:56	593283	2388032
ANA004	Stream	2/6/2019	12:15	593423	2388138
ANA005	Stream	2/6/2019	12:30	593597	2388022
ANA006	Stream	2/6/2019	12:40	593799	2388036
ANA007	Stream	2/6/2019	13:15	593925	2388055
AWW001	Beach Face	2/24/2019	10:30	589073	2387000

AWW002	Beach Face	2/24/2019	11:15	589383	2387032
AWW003	Beach Face	2/24/2019	11:45	589527	2386995
AWW004	Beach Face	2/24/2019	12:15	589702	2386901
AWW005	Beach Face	2/24/2019	12:40	589869	2386854
AWW006	Beach Face	2/24/2019	13:12	590072	2386842
Garber Well A	Well	Mar-19	7:00	591363	2383724
Garber Well **B**	Well	Mar-19	7:00	591363	2383724
Gora Well	Well	Mar-19	12:21	592228	2386504
HBP SEEP A	Beach Face	Jun-19		592755	2388720
HBP SEEP B	Beach Face	Jun-19		592755	2388720
HBP-001A	Beach Face	7/1/2019	4:56	592783	2388706
HBP-001B	Beach Face	7/1/2019	4:56	592783	2388706
HBP-002	Beach Face	7/1/2019	6:08	592773	2388407
HBP-003	Beach Face	8/14/2019	5:15	592781	2388707
HBP-004	Beach Face	8/14/2019	6:35	592800	2388605
KAU 1	Stream	Jun-19		590983	2384656
KAU 2	Stream	Jun-19		591060	2384978
KAU 201	Stream	9/7/2019	12:45	591111	2386498
KAU 202	Stream	9/7/2019	12:56	591070	2386296
KAU 203	Stream	9/7/2019	13:06	591111	2386091
KAU 204	Stream	9/7/2019	13:16	591257	2385938
KAU 205	Stream	9/7/2019	13:29	591280	2385726
KAU 206	Stream	9/7/2019	13:40	591234	2385509
KAU 207	Stream	9/7/2019	13:48	591334	2385322
KAU 208	Stream	9/7/2019	14:00	591376	2385114
KAU 209	Stream	9/7/2019	14:10	591318	2384986
KAU 210	Stream	9/7/2019	14:20	591136	2385014
KAU 3	Stream			591361	2385003
KBP-001A	Beach Face	7/2/2019	4:42	592297	2388161
KBP-002A	Beach Face	7/2/2019	5:50	592053	2387796

KBP-002B	Beach Face	7/2/2019	5:50	592053	2387796
KBP-003	Beach Face	7/2/2019	6:40	591476	2387612
KBP-004	Beach Face	8/15/2019	5:06	591923	2387671
KKH001	Stream	1/28/2019	13:18	591081	2386367
KKH002	Stream	1/28/2019	13:40	591075	2386148
KKH003	Stream	1/28/2019	14:45	591236	2385965
KKH004	Stream	1/28/2019	15:00	591303	2385771
KKH005	Stream	1/28/2019	15:17	591246	2385573
KKH006	Stream	1/28/2019	15:33	591291	2385373
KKH007	Stream	1/28/2019	15:48	591384	2385192
KKH008	Stream	1/28/2019	16:02	591402	2384995
KKH009	Stream	1/28/2019	16:17	591202	2385019
KKH010	Stream	1/28/2019	16:37	591310	2384915
LES 1	Pond	12/5/2019	9:50	593000	2388382
LES 2	Pond	12/5/2019	10:08	592973	2388426
LES 2B	Pond	12/5/2019	10:08	592973	2388426
LES 3	Pond	12/5/2019	10:35	593031	2388323
LES 4	Pond	12/5/2019	10:57	593018	2388250
LES 5	Pond	12/5/2019	11:17	592864	2388315
Orion Well	Well			591835	2383586
PAU 201	Stream	9/7/2019	11:03	592605	2386597
PAU 202	Stream	9/7/2019	11:24	592425	2386492
PAU 203	Stream	9/7/2019	11:38	592239	2386400
PAU 204	Stream	9/7/2019	11:47	592040	2386326
PAU 205	Stream	9/7/2019	11:56	591836	2386291
PAU 206	Stream	9/7/2019	12:06	591648	2386384
PAU 207	Stream	9/7/2019	12:15	591446	2386492
PAU 208	Stream	9/7/2019	12:24	591365	2386679
PAU 209	Stream	9/7/2019	12:34	591212	2386680
PAU001	Stream	Jan-19	12:15	591394	2386580

PAU002	Stream	Jan-19	12:30	591537	2386439
PAU003	Stream	Jan-19	12:40	591719	2386340
PAU004	Stream	Jan-19	12:53	591917	2386288
PAU005	Stream	Jan-19	13:03	592108	2386353
PAU006	Stream	Jan-19	13:17	592304	2386433
PAU007	Stream	Jan-19	13:27	592490	2386531
PAU008	Stream	Jan-19	13:39	592691	2386557
PAU009	Stream	Jan-19	13:50	592878	2386470
PAU010	Stream	Jan-19	14:06	592675	2386613
RAD 10A	Beach Face	9/27/2019	10:00	592886	2386469
RAD 12P	Beach Face	9/27/2019	12:00	592886	2386469
RAD 2P	Beach Face	9/27/2019	14:15	592886	2386469
RAD 4P	Beach Face	9/27/2019	16:00	592886	2386469
RAD 8A	Beach Face	9/27/2019	7:50	592886	2386469
RAD 8A-B	Beach Face	9/27/2019	7:50	592886	2386469
Saville Tap	Well	Apr-19	8:35	591612	2383487
Saville Well A	Well	Apr-19	8:30	591612	2383487
Saville Well B	Well	Apr-19	8:30	591612	2383487
See Ba Well	Well	Apr-19	13:08	600708	2378665
Wheeler Well	Well	Apr-19	15:03	596116	2379515
HDIC 1	Beach Face	3/5/2020	15:44	592804	2388611
AN DIC 1	Stream	3/11/2020	17:11	593054	2388026
AL DIC 1	Beach Face	3/5/2020	14:17	592299	2388165
AL DIC 2	Beach Face	3/5/2020	13:03	591956	2387681
AW DIC 1	Beach Face	3/7/2020	17:01	589285	2387054
AW DIC3	Beach Face	3/7/2020	16:17	588646	2386911
OP DIC 1	Stream	3/11/2020	18.37	592669	2386568
KA DIC 1	Beach Face	3/7/2020	17:32	590821	2386984
BD DIC 2	Beach Face	3/7/2020	18:00	590033	2386849
MK 1	Coastal	3/31/2020	10:17	588361	2386818

MK 1B	Coastal	3/31/2020	10:22	588361	2386818
MK 2	Coastal	3/31/2020	11:16	588029	2386710
MK 3	Coastal	3/31/2020	11:42	587561	2386677
MK 3B	Coastal	3/31/2020	11:47	587561	2386677
MK 5	Coastal	3/31/2020	12:48	587779	2386648
MK 5B	Coastal	3/31/2020	12:57	587779	2386648
PAW 1B	Beach Face	2/14/2020	14:37	588714	2386925
DC 2	Coastal	4/10/2020		592563	2388102
DC 3	Stream	4/10/2020		591073	2384966
DC 4	Stream	4/10/2020		591080	2386140
DC 5	Stream	4/10/2020		591505	2386457
DC 6	Stream	4/10/2020		592660	2386621
DC 7	Stream	4/10/2020		592660	2386621
CP1	Cesspool	08/10/20	11:17	592268	2387770

Table A.2. Basic water quality parameters for all samples

Name	Salinity	Temp	Cond	Sp Cond	TDS	pH	ODO%	ODO(mg/L)
ABB SEEP	32.27	24.041	55141.3	49596.3	32238	8.43	70.1	4.67
ABP-001	26.36	25.056	41228.7	41184.5	26770	8.36	62.2	4.42
ABP-002	30.82	27.441	49679.4	47466.8	30853	8.51	68.9	4.59
ABP-003	33.87	27.188	53767.5	51610.5	33547	8.53	102.2	6.71
ABP-004	33.69	28.747	55112.4	51431.5	33430	8.5	83.2	5.33
ABP-005	34.12	25.214	52075.4	51871.2	33719	8.71	82.3	5.58
ABP-006	34.50	25.471	53005.5	52522.4	34131	8.77	94.2	6.34
ABP-007	34.80	25.319	53969.9	52818.3	34327	8.38	100.1	6.74

ANA 1A								
ANA 2	0.22							
ANA 201	12.37	25.915	19243.2	18486.7	13677	7.61	31.1	2.34
ANA 202	9.56	25.743	12922.2	12703.5	6721	7.69	51.5	3.66
ANA 203	6.24	26.701	10178.8	10511.3	7169	7.81	58	4.46
ANA 204	6.06	26.788	11106.6	10676.7	6927	7.9	59	4.53
ANA 205	4.78	26.781	8831.2	8905.1	5594	7.83	62.1	5.16
ANA 206	3.51	26.474	3546.7	3124.3	2586	7.92	86.3	6.89
ANA001	11.82	22.068	15850.4	18576.9	12622	7.53	79.3	6.42
ANA002	18.47	21.822	24957	21539	10539	7.62	76.1	6.13
ANA003	3.43	21.423	5151.2	6133.8	4019	7.48	95.6	8.25
ANA004	1.79	21.15	3005.6	3050	2514	7.42	101.7	8.88
ANA005	1.37	20.637	2018.3	2473.5	1715	7.45	103.2	9.19
ANA006	0.03	20.158	62.3	68.3	45	7.83	106.1	9.61
ANA007	0.03	20.173	57.7	63.5	41	7.67	105.4	9.55
AWW001	33.65	24.017	50263.5	51209.3	33285	8.3	106.4	7.37
AWW002	34.74	25.076	52802.7	52712.1	34269	8.29	105.3	7.12
AWW003	34.74	24.412	52108.2	52701.9	34256	8.31	109.3	7.48
AWW004	33.96	25.046	51712.5	51608.9	33568	8.35	107.6	7.32
AWW005	33.79	24.207	50581.2	51398.1	33416	8.33	108.7	7.51
AWW006	31.64	25.391	48832.4	49471.3	31523	8.31	115.8	7.93
Garber Well A	0.25	23.801	506	517.8	337	6.84	62.1	5.24
Garber Well **B**	0.25	23.801	506	517.8	337	6.84	62.1	5.24
Gora Well	0.31	23.089	609.2	632.6	412	7.8	99.5	8.5
HBP SEEP A	29.47	26.39	46763	45555	29611	8.61	8.31	121.76
HBP SEEP B	29.47	26.39	46763	45555	29611	8.61	8.31	121.76
HBP-001A	4.96	22.48	8446.4	8873.6	5768	8.25	65.5	5.52
HBP-001B	4.96	22.48	8446.4	8873.6	5768	8.25	65.5	5.52
HBP-002	24.47	26.767	39863.8	38562.5	25066	8.65	71.2	4.97
HBP-003	25.39	25.882	38161.2	39751.5	25841	8.4	78.1	5.8

HBP-004	22.41	24.918	35506.6	35562.8	23115	8.48	71.4	5.2
KAU 1	0.01							
KAU 2	0.22							
KAU 201	23.82	29.9	40871.9	37920.6	24565	8.37	64.5	4.29
KAU 202	22.54	29.15	38538.5	36103	23437	8.19	39.2	2.66
KAU 203	18.52	28.056	34967.2	33190.9	19787	8.17	38.9	2.64
KAU 204	16.83	28.378	29222.1	27519.4	17888	8.02	42.1	2.98
KAU 205	19.66	29.139	33191.5	30899.9	20612	7.99	39.2	2.7
KAU 206	22.52	28.81	37835.5	35663	23299	7.96	28.4	1.94
KAU 207	22.06	29.238	35815.1	35343.9	23009	7.82	23.7	1.61
KAU 208	16.41	28.794	26749.6	26878.9	17482	7.74	18.3	1.3
KAU 209	12.24	28.26	21725.4	20453.3	13423	7.8	20.9	1.48
KAU 210	3.50	27.276	6694.1	6410.3	4256	8.03	28.9	2.17
KAU 3	6.49							
KBP-001A	34.38	25.275	52506.6	52232.1	33951	8.6	89.9	6.08
KBP-002A	8.22	24.642	14110.8	14207.9	9235	8.51	52.7	4.19
KBP-002B	8.22	24.642	14110.8	14207.9	9235	8.51	52.7	4.19
KBP-003	34.69	25.9	53577.9	52672.8	34237	8.49	94.4	6.31
KBP-004	34.09	26.091	52948.8	51869.1	33715	8.68	93.3	6.24
KKH001	9.45	21.672	10895.3	13107	10140	7.57	106.7	9.93
KKH002	4.52	21.28	8906	7483	4921	7.48	87.8	7.57
KKH003	3.23	22.32	5335	5479.6	3561	7.54	95.9	8.42
KKH004	3.13	22.234	5729.1	6415.2	4040	7.58	104.1	8.8
KKH005	2.62	22.092	4410	5235.2	2955	7.5	105.4	9.11
KKH006	1.37	21.916	2434	2616.4	1715	7.6	95.2	8.25
KKH007	4.81	21.2	7979.5	8604.2	5593	7.22	106.1	9.17
KKH008	0.23	20.862	447.6	484.9	314	7.48	74.8	6.68
KKH009	0.16	21.024	318	344.1	224	7.61	86.5	7.7
KKH010	0.15	21.14	291.1	313.4	204	7.45	94	8.27
LES 1	2.08	24.252	3870.6	3929.1	2554	9.32	94.9	7.85

LES 2	6.19	22.667	10417.5	10905.5	7089	8.95	74.9	6.17
LES 2B	6.19	22.667	10417.5	10905.5	7089	8.95	74.9	6.17
LES 3	3.08	22.329	5397.1	5687.2	3697	8.93	88.3	7.32
LES 4	5.33	24.252	9369.7	9497.6	6173	8.56	64.6	5.26
LES 5	7.60	25.398	13308.3	13220.5	8593	9.46	115	9.04
Orion Well	0.52	23.514	1023.1	1053.3	685	6.84	68.7	5.82
PAU 201	6.91	26.129	12229	12078.9	7874	7.88	3.2	0.24
PAU 202	7.43	26.126	13540.5	13078.4	8501	7.58	3.9	0.29
PAU 203	7.80	26.462	14193.5	13796.6	8880	7.66	6.3	0.49
PAU 204	8.95	26.566	16567.5	15696	10040	7.69	8.9	0.68
PAU 205	11.91	26.85	23578.1	22725.7	13139	7.61	4.9	0.37
PAU 206	9.12	27.004	16247.3	16085.4	9878	7.71	11.6	0.88
PAU 207	13.58	27.117	22597.6	23016.7	14961	7.8	16.3	1.12
PAU 208	33.30	29.064	54411.5	50657.2	32997	8.5	76.5	4.89
PAU 209	34.67	28.772	56578.9	52790.3	34311	8.58	79.7	5.05
PAU001	13.45	25.432	22209.8	2935.2	14344	7.88	114.3	8.7
PAU002	11.96	23.852	19620.5	20063.6	13049	7.92	134.9	10.64
PAU003	12.32	24.066	20200.2	20589.9	13387	8.29	173.2	13.58
PAU004	12.9	24.172	20771.6	21058.6	13835	8.42	186.8	14.55
PAU005	16.86	24.31	26985	27596.6	17850	8.75	248	18.85
PAU006	17.89	24.188	28044.6	29109.7	18831	8.81	254.4	19.29
PAU007	16.2	23.98	25780.2	26318.4	17205	8.72	276.7	21.25
PAU008	13.45	23.434	22480.7	22729.8	14510	8.53	239.7	18.82
PAU009	12.69	23.715	20669.6	20199	13129	8.55	266.5	20.13
PAU010	14.8	24.096	23835.8	24360.6	15834	8.58	234.9	18.16
RAD 10A	25.77	28.08						
RAD 12P	27.15	29.09						
RAD 2P	24.15	29.83						
RAD 4P	22.14	28.26						
RAD 8A	25.92	25.92						

RAD 8A-B	25.92	25.92						
Saville Tap	0.16	23.977	353.2	360.2	224	6.78	75.7	6.37
Saville Well A	0.16	23.451	335.8	346.3	225	6.57	38.5	3.27
Saville Well B	0.16	23.451	335.8	346.3	225	6.57	38.5	3.27
See Ba Well	0.11	22.826	224.5	234.3	152	7.47	96.4	8.28
Wheeler Well	0.12	22.23	233.6	246.6	160	7.36	88.9	7.73
HDIC 1	9.17	22.27	14864.7	15678.5	10191	9.84	66.8	5.51
AN DIC 1	1.27	24.33	2452.7	2475.1	1609	9.93	98.1	8.15
AL DIC 1	34.90	25.71	53787.5	53175.8	34564	9.82	98.7	6.62
AL DIC 2	30.18	27.3	48694.9	46588.3	30277	10.07	95.6	6.39
AW DIC 1	34.05	24.39	52461.2	53119.3	34528	9.62	96.7	6.62
AW DIC3	34.70	24.67	52391.2	52719.3	3428	9.57	100.4	6.89
OP DIC 1	2.06	22.89	2753.6	3899.2	2534	9.4	92.3	7.82
KA DIC 1	32.66	23.47	48406.9	49953.1	32470	9.41	88.9	6.27
BD DIC 2	33.39	23.95	49833.1	50860.2	33059	9.51	101.7	7.07
MK 1	34.18	24.55	51553.3	51882.1	33767	9.28	113.7	7.79
MK 1B	34.18	24.55	51553.3	51882.1	33767	9.28	113.7	7.79
MK 2	34.64	24.33	51859.3	52515.2	34163	9.3	111.1	7.62
MK 3	34.35	24.93	51927.5	52187	33922	9.38	111.2	7.55
MK 3B	34.35	24.93	51927.5	52187	33922	9.38	111.2	7.55
MK 5	34.43	25.51	51743.7	52283.4	33984	9.37	108.9	7.46
MK 5B	34.43	25.51	51743.7	52283.4	33984	9.37	108.9	7.46
PAW 1B	34.74	26.37	54464.3	53033.2	34472	9.54	99.1	6.54
DC 2	33.8	26.19	52700.6	51549.5	33538	9.46	103.3	6.84
DC 3	0.26	22.38	515.9	543.1	354	10.92	103.4	8.95
DC 4	0.77	24	145.8	147.1	96	10.41	102.8	8.61
DC 5	4.49	25.65	8217.9	8105.1	5268	9.49	101.9	8.02
DC 6	0.37	25.37	766.5	759.4	494	9.87	89.2	7.24
DC 7	0.44	26.871	932.6	899.1	585	9.36	65.3	5.09

Table A.3. Nutrient Concentrations. Nutrients are given in µM.

Name	Type	Salinity	TN	TP	PO_4^{3-}	SiO_2	N+N	NH_4^+
PAU001	Stream	13.45	77.38	2.34	1.52	627.17	49.16	2.45
PAU002	Stream	11.96	32.56	0.88	0.51	338.39	27.16	1.5
PAU003	Stream	12.32	26.44	0.76	0.42	314.19	20.19	0.63
PAU004	Stream	12.9	21.64	0.72	0.34	278.07	15.12	0.84
PAU005	Stream	16.86	17.11	0.35	0.28	109.44	7.3	1.69
PAU006	Stream	17.89	12.64	0.27	0.19	96.33	5.81	0.77
PAU007	Stream	16.2	6.9	0.13	0.08	58.2	1.93	0.99
PAU008	Stream	13.45	19.53	0.35	0.22	116.71	10.04	0.68
PAU009	Stream	12.69	9.85	0.15	0.1	52.72	4.06	0.57
PAU010	Stream	14.8	10.89	0.25	0.18	86.88	3.11	0.08
Orion Well	Well	0.52	354.58	5.96	4.46	1597.89	334.37	0.34
Wheeler Well	Well	0.12	44.81	6.75	5.78	1298.88	36.36	0.04
AWW001	Beach Face	33.65	15.62	0.44	0.37	22.96	12.47	<0.02
AWW002	Beach Face	34.74	8.29	0.45	0.34	38.9	3.72	0.52
AWW003	Beach Face	34.74	12.49	0.41	0.33	4.68	8.55	0.6
AWW004	Beach Face	33.96	16.35	0.4	0.28	9.09	14.02	0.14
AWW005	Beach Face	33.79	23.03	0.45	0.26	15.76	19.04	0.33
AWW006	Beach Face	31.64	7.29	0.47	0.24	26.89	4.46	0.19
ANA001	Stream	11.82	60.872	1.378	1.062	312.737	34.661	2.256
ANA002	Stream	18.47	86.850	2.418	1.965	494.810	49.517	1.486
ANA003	Stream	3.43	13.686	0.328	0.206	115.642	4.417	1.627
ANA004	Stream	1.79	8.140	0.167	0.093	93.585	1.238	0.701
ANA005	Stream	1.37	6.852	0.225	0.159	103.216	1.166	0.473
ANA006	Stream	0.03	6.743	0.377	0.325	79.579	0.761	0.534
ANA007	Stream	0.03	5.737	0.155	0.147	59.428	0.701	0.152
KKH001	Stream	9.45	90.86	0.29	0.26	228.07	29.13	15.47
KKH002	Stream	4.52	44.37	0.35	0.26	213.69	18.99	9.66
KKH003	Stream	3.23	45.32	0.31	0.20	199.67	19.39	9.16
KKH004	Stream	3.13	98.55	0.81	0.64	328.59	40.83	10.56

KKH005	Stream	2.62	91.16	0.49	0.39	258.54	38.94	9.66
KKH006	Stream	1.37	85.53	0.58	0.45	288.11	38.25	7.87
KKH007	Stream	4.81	89.57	0.67	0.55	316.34	39.09	7.45
KKH008	Stream	0.23	83.20	0.86	0.69	376.22	35.98	5.77
KKH009	Stream	0.16	111.13	1.02	0.80	404.40	48.10	4.08
KKH010	Stream	0.15	69.23	0.61	0.50	327.41	34.86	4.15
ANA 1A	Stream		155.27	3.34	2.73	803.22	134.26	3.08
ANA 2	Stream	0.22	60.24	2.03	1.95	498.99	48.98	3.05
KAU 1	Stream	0.01	93.14	1.06	0.93	430.15	82.47	8.88
KAU 2	Stream	0.22	91.15	0.80	0.52	599.11	75.11	11.87
KAU 3	Stream	6.49	145.00	0.71	0.57	515.19	70.25	2.58
ABB SEEP	Beach Face	32.27	18.47	0.81	0.70	26.66	12.23	0.50
HBP SEEP A	Beach Face	29.47	22.66	0.70	0.67	100.13	17.13	0.77
HBP SEEP B	Beach Face	29.47	26.84	0.90	0.84	106.90	16.95	1.08
Garber Well A	Well	0.25	128.44	6.34	5.73	948.54	87.69	0.25
Garber Well B	Well	0.25	129.85	5.99	5.87	958.77	87.88	0.47
Saville Well A	Well	0.16	168.19	1.57	1.36	523.77	102.62	0.11
Saville Well B	Well	0.16	174.86	1.52	1.48	527.41	114.12	0.05
Saville Tap	Well	0.16	218.77	1.51	1.39	662.89	195.11	0.07
See Ba Well	Well	0.11	268.46	7.14	6.26	1381.22	245.6	1.37
Gora Well	Well	0.31	78.22	5.50	5.20	1271.98	59.36	0.58
RAD 2P	Beach Face	24.15	70.43	3.19	3.06	719.44	56.69	0.09
RAD 4P	Beach Face	22.14	70.42	3.52	3.23	769.58	60.59	0.03
RAD 12P	Beach Face	27.15	33.37	2.76	2.53	498.36	23.50	<0.02
RAD 8A	Beach Face	25.92	105.20	2.70	2.68	895.23	85.59	<0.02
RAD 8A-B	Beach Face	25.92	104.94	2.71	2.67	907.25	86.40	<0.02
RAD 10A	Beach Face	25.77	34.41	2.64	2.38	487.80	25.64	<0.02
ABP-001	Beach Face	26.36	4.99	0.36	0.24	52.58	2.82	0.10
ABP-002	Beach Face	30.82	6.61	0.21	0.14	13.19	4.32	0.19
ABP-003	Beach Face	33.87	15.37	0.12	0.10	7.62	10.33	0.42
ABP-004	Beach Face	33.69	12.49	0.12	0.10	17.53	10.61	<0.02
ABP-005	Beach Face	34.12	2.84	0.09	0.07	6.38	2.62	<0.02
ABP-006	Beach Face	34.50	3.26	0.10	0.08	8.34	1.56	0.03

ABP-007	Beach Face	34.80	3.45	0.08	0.03	3.60	0.94	0.08
HBP-001A	Beach Face	4.96	118.06	5.11	4.82	1207.89	107.11	0.35
HBP-001B	Beach Face	4.96	45.84	2.47	1.85	1417.21	44.44	0.21
HBP-002	Beach Face	24.47	41.13	0.47	0.35	46.69	38.16	0.22
HBP-003	Beach Face	25.39	64.84	4.03	3.62	412.07	51.22	1.75
HBP-004	Beach Face	22.41	49.13	1.97	1.63	235.92	45.87	0.02
KBP-001A	Beach Face	34.38	7.71	0.33	0.32	7.32	4.38	0.52
KBP-002A	Beach Face	8.22	39.27	1.27	1.05	515.32	36.47	0.08
KBP-002B	Beach Face	8.22	35.41	1.25	1.03	522.13	33.44	0.09
KBP-003	Beach Face	34.69	10.00	0.18	0.17	4.46	5.51	0.11
KBP-004	Beach Face	34.09	6.62	0.10	0.08	15.34	3.73	0.23
KAU 201	Stream	23.82	32.04	0.37	0.30	132.02	8.17	7.18
KAU 202	Stream	22.54	37.98	0.21	0.21	196.06	9.89	14.75
KAU 203	Stream	18.52	32.17	0.18	0.15	201.00	8.95	12.46
KAU 204	Stream	16.83	28.53	0.20	0.19	295.93	6.16	13.42
KAU 205	Stream	19.66	25.28	0.13	0.12	124.80	5.63	11.94
KAU 206	Stream	22.52	49.34	0.19	0.18	300.18	18.24	27.09
KAU 207	Stream	22.06	54.06	0.15	0.14	241.97	18.70	28.60
KAU 208	Stream	16.41	30.29	0.17	0.15	248.56	7.21	17.56
KAU 209	Stream	12.24	42.33	0.44	0.42	407.99	17.29	15.66
KAU 210	Stream	3.50	54.42	0.54	0.46	674.98	31.64	9.93
PAU 201	Stream	6.91	28.52	0.27	0.23	86.73	0.22	19.39
PAU 202	Stream	7.43	46.50	0.39	0.30	153.02	0.21	27.15
PAU 203	Stream	7.80	36.24	0.45	0.36	133.93	7.09	14.55
PAU 204	Stream	8.95	29.95	0.32	0.25	111.72	3.83	16.39
PAU 205	Stream	11.91	28.01	0.52	0.49	147.81	4.79	12.03
PAU 206	Stream	9.12	34.62	0.68	0.53	141.91	3.28	16.67
PAU 207	Stream	13.58	24.10	0.48	0.44	101.82	5.54	4.91
PAU 208	Stream	33.30	20.75	0.45	0.29	30.20	1.62	3.74
PAU 209	Stream	34.67	21.45	0.32	0.26	106.62	6.08	2.96
ANA 201	Stream	12.37	13.54	0.26	0.25	72.77	8.60	2.98
ANA 202	Stream	9.56	62.99	0.85	0.85	470.50	31.12	18.11
ANA 203	Stream	6.24	35.73	0.92	0.89	236.58	22.29	10.80

ANA 204	Stream	6.06	22.42	0.41	0.38	119.81	8.31	10.69
ANA 205	Stream	4.78	37.78	0.46	0.41	172.69	12.31	23.78
ANA 206	Stream	3.51	24.96	0.29	0.28	141.24	6.33	14.49
LES 1	Pond	2.08	363.75	6.29	6.17	1343.81	353.02	1.40
LES 2	Pond	6.19	112.11	3.79	3.62	845.83	102.10	3.02
LES 2B	Pond	6.19	179.32	5.79	5.57	1414.34	167.45	2.44
LES 3	Pond	3.08	229.53	5.66	5.43	1342.23	218.05	0.83
LES 4	Pond	5.33	28.45	3.46	3.36	1304.12	0.67	7.12
LES 5	Pond	7.60	39.03	1.45	0.91	1413.71	20.78	1.36
HDIC 1	Stream	9.17	96.33	2.67	2.31	983.51	86.43	0.59
AN DIC 1	Stream	1.27	143.55	3.55	3.08	892.45	129.89	1.24
AL DIC 2	Beach Face	34.90	19.13	0.70	0.50	87.91	12.82	0.38
AW DIC 1	Beach Face	34.05	9.70	0.37	0.20	5.63	5.08	0.21
AW DIC3	Beach Face	34.74	6.78	0.23	0.13	5.04	2.93	0.30
OP DIC 1	Stream	2.06	36.31	0.59	0.41	197.73	17.44	4.55
KA DIC 1	Beach Face	32.66	12.06	0.55	0.49	29.23	8.04	0.39
BD DIC 2	Beach Face	33.39	12.50	0.43	0.07	15.81	4.38	1.97
MK 1	Coastal	34.18	13.30	0.27	0.12	14.18	8.89	0.24
MK 1B	Coastal	34.18	12.45	0.25	0.12	12.48	7.75	0.72
MK 2	Coastal	34.64	9.58	0.35	0.15	6.78	3.24	0.41
MK 3	Coastal	34.35	8.09	0.34	0.15	5.36	1.99	0.31
MK 3B	Coastal	34.35	9.69	0.41	0.21	4.80	1.96	1.45
MK 5	Coastal	34.43	10.88	0.39	0.22	11.11	4.50	0.78
MK 5B	Coastal	34.43	10.68	0.27	0.16	10.38	3.97	1.26
PAW 1B	Beach Face	34.74	8.62	0.30	0.14	4.51	2.13	0.88
DC 2	Beach Face	33.8	7.37	0.47	0.29	21.16	1.09	0.65
DC 3	Stream	0.26	6.26	0.24	0.11	7.50	1.93	0.05
DC 4	Stream	0.77	11.60	0.32	0.24	101.19	7.06	0.33
DC 5	Stream	4.49	5.28	<0.08	0.06	29.43	2.34	1.00
DC 6	Stream	0.37	20.75	0.31	0.27	271.75	14.46	1.65
DC 7	Stream	0.44	54.43	6.99	6.52	607.83	1.61	20.69
CP1	Cesspool	0.5	3296	182	164	930	13	3059

Table A.4. Nitrate Stable Isotopic composition

SAMPLE	$\delta^{15}N_{nitrate}$	$\delta^{18}O_{nitrate}$
ABP001	**4.70**	**-1.10**
ABP002	**0.33**	**4.59**
ABP003	**15.71**	**9.89**
ABP004	**5.51**	**3.63**
ABP004 DUP	**5.55**	**3.76**
ABP005	**3.39**	**-2.88**
ABP006	**4.30**	**-2.40**
ABP007	**8.09**	**1.67**
ANA 201	**5.24**	**2.83**
ANA 202	**5.58**	**2.82**
ANA 203	**5.51**	**4.04**
ANA 204	**5.18**	**3.86**
ANA 205	**5.78**	**1.34**
ANA 206	**6.04**	**3.50**
ANA001	**6.45**	**6.08**
ANA002	**5.76**	**3.13**
ANA003	**7.88**	**4.96**
ANA004	**7.62**	**6.23**
ANA005	**6.12**	**3.68**
ANA006	**7.75**	**6.49**
AWW001	**23.84**	**11.01**
AWW002	**11.75**	**1.22**
AWW003	**8.46**	**2.90**
AWW004	**11.41**	**7.06**
AWW005	**12.79**	**9.15**
AWW006	**12.63**	**6.81**
Garber Well	**3.66**	**4.56**
Gora Well	**4.42**	**2.01**
HBP001	**6.10**	**4.64**
HBP002	**4.47**	**0.86**
HBP003	**5.38**	**3.47**
HBP003 DUP	**5.30**	**3.25**
HBP004	**5.10**	**3.01**
KAU 201	**6.56**	**4.57**
KAU 202	**8.24**	**5.91**
KAU 203	**8.25**	**6.07**

KAU 204	**8.06**	**6.14**
KAU 205	**8.18**	**6.22**
KAU 206	**8.84**	**6.77**
KAU 207	**8.50**	**6.41**
KAU 208	**10.03**	**7.09**
KAU 208 DUP	**9.95**	**6.85**
KAU 209	**12.25**	**7.66**
KBP001A	**3.64**	**-0.41**
KBP002B	**12.86**	**8.78**
KBP003	**2.24**	**-2.99**
KBP004	**7.90**	**3.13**
KKH001	**8.10**	**8.61**
KKH002	**7.29**	**6.78**
KKH003	**5.31**	**4.75**
KKH004	**6.73**	**5.36**
KKH005	**6.61**	**5.30**
KKH006	**7.58**	**7.02**
KKH007	**7.16**	**5.64**
KKH008	**9.93**	**6.18**
KKH009	**10.97**	**6.94**
KKH010	**8.97**	**7.46**
LES 1	**7.12**	**4.87**
LES 2	**4.99**	**4.31**
LES 3	**6.10**	**4.94**
LES 4	**11.62**	**9.64**
LES 5	**8.14**	**6.33**
Orion Well	**2.23**	**3.59**
PAU 203	**5.61**	**3.85**
PAU 204	**6.71**	**3.61**
PAU 205	**6.88**	**3.66**
PAU 206	**6.79**	**3.84**
PAU 207	**6.51**	**4.03**
PAU 208	**5.47**	**2.68**
PAU 209	**6.16**	**3.72**
PAU001	**6.45**	**3.60**
PAU002	**10.36**	**11.99**
PAU003	**9.88**	**6.05**
PAU004	**7.55**	**4.39**
PAU005	**13.54**	**12.04**
PAU006	**10.08**	**8.43**
PAU007	**12.60**	**10.60**

PAU008	**12.40**	**9.24**
PAU008 DUP	**10.86**	**7.21**
PAU009	**12.17**	**9.65**
PAU010	**13.15**	**12.45**
RAD 10A	**4.02**	**3.81**
RAD 12P	**4.30**	**3.14**
RAD 2P	**5.02**	**2.47**
RAD 4P	**5.35**	**3.18**
RAD 8A	**4.99**	**3.44**
RAD 8A-B	**6.32**	**4.99**
Rob Well	**6.37**	**2.10**
Saville Well	**9.21**	**7.95**
Saville Well DUP	**9.29**	**8.00**
See Ba Well	**5.45**	**8.00**
MK 3B	**7.32**	**6.36**
MK 3	**7.41**	**6.27**
MK 2	**7.76**	**8.20**
MK 5B	**7.91**	**7.56**
MK 5	**7.76**	**7.57**
MK 1B	**7.87**	**7.42**
MK 1	**7.77**	**7.42**
AW DIC3	**9.08**	**6.68**
BD DIC 2	**9.61**	**5.45**
AW DIC 1 DUP	**7.92**	**1.43**
AW DIC 1	**8.02**	**2.39**
KA DIC 1	**3.92**	**-0.43**
AL DIC 2	**9.57**	**5.04**
OP DIC 1	**5.58**	**5.26**
OP DIC 1 DUP	**5.46**	**5.17**
HDIC 1	**4.78**	**3.72**
AN DIC 1	**5.16**	**3.81**
DC 2	**7.89**	**8.57**
DC 7	**9.61**	**0.67**
DC 3	**12.15**	**7.40**
DC 5	**10.45**	**7.28**
DC 4	**11.74**	**7.25**
DC 6	**6.00**	**5.63**
DC 6 DUP	**6.04**	**5.47**

Table A.5. Values for all analyzed algae samples

Sample ID	***Species***	***Easting***	***Northing***	***Weight (mg)***	***µg N***	***δ¹⁵N (‰ vs. AIR)***	***µg C***	***δ¹³C (‰ vs. VPDB)***	***%N***
A2	*A.spicifera*	589219	2387046	*3.2650*	*67.7*	*12.9*	*627.0*	*-15.2*	2.07
A21	*A.spicifera*	589118	2387099	*3.2886*	*61.2*	*9.8*	*580.0*	*-16.8*	1.86
AW2	*A.spicifera*	588721	2386934	*3.3104*	*54.4*	*4.1*	*786.3*	*-14.4*	1.64
AW1	*A.spicifera*	588716	2386932	*3.2231*	*64.0*	*6.6*	*892.5*	*-14.4*	1.99
A22	*A.spicifera*	589078	2387077	*3.3026*	*64.8*	*11.4*	*589.9*	*-16.2*	1.96
A24	*A.spicifera*	589191	2387074	*2.9469*	*54.2*	*11.2*	*538.5*	*-15.7*	1.84
A26	*A.spicifera*	589206	2387086	*3.3281*	*57.4*	*10.7*	*610.3*	*-15.9*	1.72
A262	*A.spicifera*	589206	2387086	*3.2419*	*52.2*	*7.4*	*596.2*	*-15.5*	1.61
A28	*A.spicifera*	589197	2387084	*3.3840*	*66.9*	*10.4*	*642.3*	*-17.2*	1.98
A29	*A.spicifera*	589232	2387148	*3.2680*	*59.5*	*7.6*	*624.3*	*-15.8*	1.82
A3	*A.spicifera*	589244	2387049	*3.2919*	*83.3*	*13.0*	*757.2*	*-16.1*	2.53
A35	*A.spicifera*	589107	2387053	*3.1346*	*60.9*	*11.2*	*626.1*	*-15.1*	1.94
A37?	*A.spicifera*			*3.4796*	*47.0*	*9.3*	*576.8*	*-14.6*	1.35
A4	*A.spicifera*	589269	2387052	*3.2170*	*70.6*	*13.0*	*675.3*	*-14.3*	2.19
A?	*A.spicifera*			*3.2159*	*49.6*	*9.5*	*533.9*	*-16.7*	1.54
B1	*A.spicifera*	592786	2388682	*3.1705*	*48.8*	*7.3*	*555.9*	*-14.4*	1.54
B11	*A.spicifera*	535204	8424905	*3.4064*	*61.8*	*6.7*	*675.6*	*-13.1*	1.81
B12	*A.spicifera*	535202	8424883	*3.4646*	*66.5*	*6.0*	*884.3*	*-14.7*	1.92
B13	*A.spicifera*	535076	8424815	*3.4173*	*53.6*	*6.5*	*761.5*	*-13.0*	1.57
B15	*A.spicifera*	535152	8424828	*3.2331*	*54.6*	*6.6*	*621.9*	*-14.2*	1.69
B18	*A.spicifera*			*3.4176*	*47.3*	*6.4*	*532.4*	*-14.5*	1.38
AL1	*A.spicifera*	592184	2388055	*3.3531*	*127.3*	*2.3*	*1044.2*	*-14.3*	3.80
AL2	*U.lactuca*	592184	2388055	*2.6978*	*86.2*	*4.3*	*775.7*	*-12.8*	3.20

B19	*A.spicifera*	591946	2387721	*3.1849*	*48.4*	*7.3*	*603.7*	*-13.5*	1.52
B2	*A.spicifera*	591983	2387759	*3.1533*	*45.9*	*6.9*	*585.9*	*-15.1*	1.46
B3	*A.spicifera*	591964	2387789	*3.2314*	*54.8*	*6.5*	*634.0*	*-13.1*	1.70
B4	*A.spicifera*	592002	2387832	*3.4037*	*48.9*	*6.0*	*607.5*	*-15.2*	1.44
B5	*A.spicifera*	592008	2387812	*3.3932*	*52.0*	*6.9*	*636.5*	*-14.5*	1.53
B6	*A.spicifera*	592004	2387779	*3.4238*	*70.2*	*6.5*	*779.1*	*-14.3*	2.05
B7	*A.spicifera*	591994	2387760	*3.2937*	*52.0*	*7.0*	*632.4*	*-13.6*	1.58
B8	*A.spicifera*	592044	2387792	*3.3662*	*96.9*	*7.9*	*760.7*	*-14.6*	2.88
H1	*A.spicifera*	592759	2388664	*3.3901*	*70.7*	*5.1*	*682.7*	*-14.3*	2.09
H10	*A.spicifera*	592738	2388805	*3.1148*	*66.8*	*6.0*	*585.1*	*-14.5*	2.14
H11	*A.spicifera*	592700	2388850	*3.1930*	*71.3*	*5.6*	*666.4*	*-13.8*	2.23
H12	*A.spicifera*	592717	2388710	*3.1397*	*37.1*	*6.0*	*544.7*	*-14.5*	1.18
HB1	*U.lactuca*	592793	2388620	*2.5757*	*82.2*	*5.2*	*765.9*	*-13.2*	3.19
HB2	*U.lactuca*	592780	2388710	*2.4689*	*99.0*	*5.3*	*873.4*	*-10.9*	4.01
HB3	*U.lactuca*	592783	2388683	*2.2553*	*63.9*	*5.8*	*759.2*	*-12.6*	2.83
HB4	*A.spicifera*	592793	2388620	*2.6951*	*91.8*	*5.0*	*826.6*	*-13.3*	3.41
HB5	*A.spicifera*	592783	2388683	*2.6618*	*78.0*	*5.6*	*796.0*	*-13.0*	2.93
H13	*A.spicifera*	592703	2388765	*3.3522*	*47.4*	*6.5*	*599.0*	*-16.0*	1.41
H18	*A.spicifera*	592765	2388716	*3.2492*	*93.6*	*4.4*	*745.7*	*-16.0*	2.88
H19	*A.spicifera*	592698	2388719	*3.0243*	*70.1*	*5.6*	*734.6*	*-15.0*	2.32
H2	*A.spicifera*	623435	2371052	*3.4160*	*78.4*	*5.6*	*646.1*	*-14.5*	2.30
H20	*A.spicifera*	592563	2388833	*3.4019*	*57.4*	*5.3*	*672.9*	*-13.1*	1.69
H3	*A.spicifera*	592568	2388898	*3.4349*	*67.3*	*6.1*	*676.5*	*-13.6*	1.96
H4	*A.spicifera*	592605	2388805	*3.2822*	*54.6*	*5.1*	*738.3*	*-14.0*	1.66
H5	*A.spicifera*	592679	2388729	*3.3826*	*49.3*	*5.3*	*623.9*	*-15.3*	1.46
H6	*A.spicifera*	592500	2388883	*3.2430*	*62.0*	*4.7*	*653.9*	*-13.5*	1.91
H7	*A.spicifera*	592699	2388702	*3.1537*	*33.5*	*5.5*	*464.9*	*-15.6*	1.06
H7	*A.spicifera*	592699	2388702	*3.1741*	*91.3*	*12.9*	*746.0*	*-15.8*	2.88
H8	*A.spicifera*	592642	2388872	*3.2923*	*65.2*	*5.5*	*746.5*	*-14.0*	1.98
H9	*A.spicifera*	592736	2388777	*3.3331*	*52.0*	*5.7*	*554.8*	*-12.6*	1.56

P1	*A.spicifera*			*3.2619*	*68.0*	*4.8*	*807.4*	*-14.5*	2.08
P10	*A.spicifera*	590776	2386995	*3.3573*	*65.6*	*5.2*	*766.9*	*-13.7*	1.95
P14	*A.spicifera*	590802	2387021	*3.4569*	*55.2*	*5.2*	*702.2*	*-14.2*	1.60
P15	*A.spicifera*	590806	2387021	*3.2246*	*67.3*	*4.9*	*734.8*	*-14.6*	2.09
P16	*A.spicifera*	590766	2386961	*3.0823*	*71.0*	*4.1*	*688.0*	*-14.4*	2.30
P2	*A.spicifera*	590803	2387014	*3.2837*	*63.0*	*5.1*	*811.7*	*-14.3*	1.92
P3	*A.spicifera*	590725	2386953	*3.4302*	*72.2*	*5.3*	*788.2*	*-14.2*	2.10
P4	*A.spicifera*	590725	2386955	*3.4675*	*43.0*	*5.9*	*661.0*	*-15.4*	1.24
P6	*A.spicifera*	590775	2387004	*3.2749*	*40.5*	*6.3*	*667.1*	*-14.9*	1.24
P7	*A.spicifera*	590797	2386980	*3.4326*	*70.2*	*5.0*	*780.9*	*-13.7*	2.05
P8	*A.spicifera*	590809	2386990	*3.2454*	*61.8*	*4.4*	*742.5*	*-13.0*	1.90
P9	*A.spicifera*	592041	2387791	*3.2797*	*52.9*	*5.1*	*693.8*	*-15.1*	1.61
AL1	*A.spicifera*	592184	2388055	*3.3531*	*127.3*	*2.3*	*1044.2*	*-14.3*	3.80
AL2	*U.lactuca*	592184	2388055	*2.6978*	*86.2*	*4.3*	*775.7*	*-12.8*	3.20

Table A.6. Boron Analyses

Sample	$\delta^{11}B$ (‰)	B Concentration (ppm)
ANA-001	40.4	0.66
ANA-003	38.6	0.14
KKH-004	38.1	0.24
KKH-008	44.2	0.045
PAU-002	39.8	1.39
PAU-008	39.8	1.09
RAD-8A	34.4	0.87
Gora Well	61.0	0.080
PAW01	39.0	1.90
PAW02	38.9	2.86
Rob Well	69.5	0.051
Seeba Well	45.4	0.044
ABP-004	39.3	2.96
ABP-005	39.5	3.47
AWW-001	39.7	4.32
AWW-004	39.4	3.43
AWW-006	39.3	2.28
HBP-004	39.5	3.06
KBP-002B	33.5	0.53
KBP-003	39.8	2.85
CPI	46.2	0.123

Table A.7. Aqueous Carbonate Geochemistry

Sample Name	Type	Easting	Northing	Salinity	DIC (umol/kg)	TA (mmol/kg)	13C (VPDB)
ALDIC2	Beach Face	591956	2387681	34.90	1534.17	2502.25	-1.552566225
ALDIC3	Beach Face	591527	2387621		2070.83	2001.8	0.843761775
AWDIC1	Beach Face	289285	2387054	34.05	1450.83	2101.89	0.7386642
AWDIC3	Beach Face	588646	2386911	34.74	1449.17	2201.98	0.601030275
KADIC1	Beach Face	590821	2386989	32.66	1795.83	2302.07	-1.185886725
BDDIC2	Beach Face	590033	2386849	33.39	1635.00	700.63	-0.43316085
HDIC1	Beach Face	592804	2388611	9.17	2234.17	2402.16	-11.28584115
DC2	Coast	592563	2388102	33.8	2014.17	2402.16	-0.160475
DC3	Stream	591073	2384966	0.26	82.58	600.54	-4.760495
DC4	Stream	591080	2386140	0.77	299.58	300.27	-8.1349797
DC5	Stream	591505	2386457	4.49	238.83	400.36	-8.04150225
DC6	Stream	592660	2386621	0.37	599.08	800.72	-14.30165093
DC7	Stream	592660	2386621	0.44	5536.67	3903.51	-10.3743069
ANDIC1	Stream	593054	2388026		1110.00	1000.9	
OPDIC1	Stream	592669	2386568		839.17		
SBW	Well	600708	2378665		3167.50		

Table A.8. Results from Kruskal-Wallis One-way ANOVA test. Results that are shaded in blue are not considered significant.

Streams	TN	N+N	NH_4^+	$\delta^{15}N_{nitrate}$	$\delta^{18}O_{nitrate}$
Paukauila-Kiikii	H=19.89, P<0.001	H=15.84, P<0.001	H=6.20, P=0.01	H=0.09, P=0.77	H=0.28, P=0.60
Kiikii-Anahulu	H=6.96, P=0.008	H=2.95, P=0.08	H=6.37, P=0.01	H=12.82, P<0.001	H=12.27, P<0.001
Paukauila-Anahulu	H=0.716, P=0.72	H=1.69, P=0.19	H=0.02, P=0.9	H=8.05, P=0.005	H=3.79, P=0.051

Beaches	TN	N+N	NH_4^+	$\delta^{15}N_{nitrate}$	$\delta^{18}O_{nitrate}$
Haleiwa-Alii	H=4.95, P=0.02	H=0.017,P=0.90	H=0.93, P=0.37	H=0.40, P=0.53	H=0.10, P=0.75
Haleiwa-Aweoweo	H=3.39,P=0.065	H=5.04, P=0.025	H=0.39, P=0.53	H=16.93, P<0.001	H=1.74, P=0.19
Haleiwa-Waialua	H=5.35, P=0.021	H=1.83, P=0.176	H=0.73, P=0.39	H=5.30, P=0.02	H=8.47, P=0.004
Aweoweo-Waialua	H=7.08, P=0.008	H=5.38, P=0.02	H=1.75, P=0.19	H=8.84, P=0.002	H=9.00, P=0.003
Alii-Waialua	H=1.84, P=0.175	H=0.535, P=0.465	H=2.34, P=0.13	H =0.54, P=0.462	H=2.16, P=0.142
Aweoweo-Alii	H=0.0032,P=0.955	H=0.044, P=0.833	H=2.34, P=0.13	H=0.168, P=0.20	H=1.19, P=0.28

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