

IMPACT OF FLUX, RESIDENCE TIME AND NUTRIENT LOAD OF SUBMARINE
GROUNDWATER DISCHARGE ON COASTAL PHYTOPLANKTON GROWTH IN
COASTAL WATERS OF HAWAI'I

THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAI'I IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

GEOLOGY AND GEOPHYSICS

DECEMBER 2011

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Acknowledgements

This project has been a great undertaking and would not have been possible without many contributors. I would like to begin with thanking my advisor, Dr. Craig Glenn, for giving me the opportunity to come to Hawaii and research submarine groundwater discharge and its importance as a contributor of nutrients to the coastal ocean. I have learned many things from Dr. Glenn, which will impact my future as a scientist. I would like to thank Dr. Henrieta Dulaiova for serving not only as a committee member but as a secondary advisor. As a woman in science, Dr. Dulaiova has constantly inspired me with both her knowledge and integrity. In addition, I would like to thank Dr. Brian Popp for serving on my committee and always making time to answer any question I have had. My three committee members have helped me throughout my research by offering guidance and support. They have dedicated their knowledge, experience, and skills to this project in order to facilitate the completion of my project.

My research would not have been possible without the aid of many contributing members. I would especially like to thank my fellow SGD team members Jacque Kelly, Christine Waters, and Joe Fackrell for their support and advice. My graduate experience would not have been as amusing without the antics of my fellow SGD team. In addition, I would like to recognize Kim Mayfield, Joe Kennedy, and Dave Morse for their help with both field and laboratory endeavors. This research project would not have been successful without their assistance. I would like to thank the members of the Graduate Department and the Geology and Geophysics Department who listened to my problems; I do not know where I would be without their answers and aid. Also, I would like to thank

the Honolulu Board of Water Supply as well as the County of Hawaii Department of Water Supply for allowing us to sample upland wells, which were crucial to this investigation.

This thesis was funded by the NSF Hawai'i EPSCoR Program through National Science Foundation under award number EPS-0903833 as well as by a grant/cooperative agreement from the National Oceanic and Atmospheric Administration, Project R/HE-2, which is sponsored by the University of Hawaii Sea Grant College Program, SOEST, under Institutional Grant No. #NA09OAR4170060 from NOAA Office of Sea Grant, Department of Commerce. The views expressed herein are solely the responsibility of the author and do not necessarily represent the official views of NSF, NOAA, or any of NOAA's subagencies. In addition, I would like to thank the Geological Society of America for awarding me the Harold T. Sterns Fellowship for the 2010 award period.

Lastly, I would like to thank my family, friends, and past mentors for their constant support. These individuals have continually believed in me as well as instilled a foundation of integrity. They have spent untold hours offering aid in the form of advice or a much needed drink. Without their support I would not be here today.

Abstract

Submarine groundwater discharge (SGD) is an important land-to-ocean pathway for biogeochemically significant nutrients, such as nitrate, silicate and phosphate. Introduction of new bioavailable nutrients from SGD into coastal waters can alter a coastal system's nutrient balance, and may result in increases in phytoplankton or macroalgae growth that in turn can cause other ecological shifts in biological species' composition (Valiela et al., 1990).

In order to attempt a first investigation of the possible relative impact(s) of the amount, flux, and residence times of SGD and SGD-derived nutrients on coastal phytoplankton in the oligotrophic coastal waters off Hawaii, detailed studies were completed to compare the flux and residence times of SGD and SGD-derived nutrients on biological processes at three sites on the leeward-side of the Koolau Mountains along the southern shore of Oahu (the Ala Wai Canal, Black Point, and Wailupe Beach) and at one site on the leeward-side of Hualalai, on the western side of the Big Island of Hawaii (Honokohau Harbor, Hawaii). At each site, radon and short-lived radium isotopes were used to calculate the flux of SGD and SGD-derived constituents into the coastal areas and their residence times. The rate of uptake of ^{13}C by photoautotrophs was determined using *in situ* incubation experiments with addition of ^{13}C -labeled bicarbonate at most sites and was used as a relative indicator of photosynthetic activity and its response to potential input of SGD-derived nutrients

At study sites along the southern shore of Oahu, nutrient fluxes for a shoreline length of 1.18 km was 281 PO_4^{3-} , 113,015 Si(OH)_4 , and 10,505 NO_3^- mol/d, respectively. Nutrient fluxes for Honokohau Harbor, estimated to have a 375-m wide seepage face, were 194 PO_4^{3-} , 31,998 Si(OH)_4 , and 3,123 NO_3^- mol/d respectively. Photosynthetic carbon production rates were significantly higher for the Ala Wai Canal (1.39 $\mu\text{gC/L/h}$) than for Honokohau Harbor (0.10 $\mu\text{gC/L/h}$). Using these carbon uptake rates and assuming a Redfield C:N:P ratio of 106:16:1, nitrogen and phosphorus uptake rates for both the Ala Wai Canal and Honokohau Harbor were less than 2% of the nutrients delivered by SGD. Variation in the N:P ratios observed in the groundwater and coastal waters could imply nutrient limitation. We found for the restricted estuarine-like embayments of the Ala Wai canal (water mass residence time 10-13 days) and Honokohau Harbor (water mass residence time 0.5 -6 days), that primary productivity is not controlled by the availability of nutrients (nutrient supply > phytoplankton demand in both settings), but is nonetheless directly linked to each water mass' residence time. As nutrients are in excess of demand in both settings, we conclude that it is the physical longevity and residence time of the phytoplankton itself that ultimately controls each basin's ultimate level of sustained primary productivity.

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Chapter 1: Introduction

Submarine groundwater discharge (SGD) is defined as the discharge of fluids of any composition expelled along the land-sea interface (Burnett et al., 2003), and in most instances this means that SGD is a mixture of fresh water and recirculated seawater (Figure 1). On a regional scale, the input of SGD may be quite voluminous. Previous estimates (based on radium isotope inventories) estimated that the total flux of SGD (recirculated seawater + freshwater) to the Atlantic Ocean was 80% -160% of river flux (Moore et al., 2008). In addition, SGD is also an important land-to-ocean pathway for the transfer and recycling of biogeochemically significant compounds, including nutrients such as nitrate and phosphate (e.g. Moore, 1999, 2000, 2002, 2010; Miller and Ullman 2004; Slomp and Van Cappellen, 2004; Burnett et al. 2007) and as a pathway for non-point source pollution (Buddemeier, 1996). Introduction of bioavailable nutrients from SGD may cause increases in phytoplankton and macroalgae growth in coastal environments (Valiela et al., 1990). Indeed, phytoplankton algal blooms have been associated with nutrients transferred by groundwater (Larouche et al., 1997; Lee et al., 2007; Lee et al., 2010).

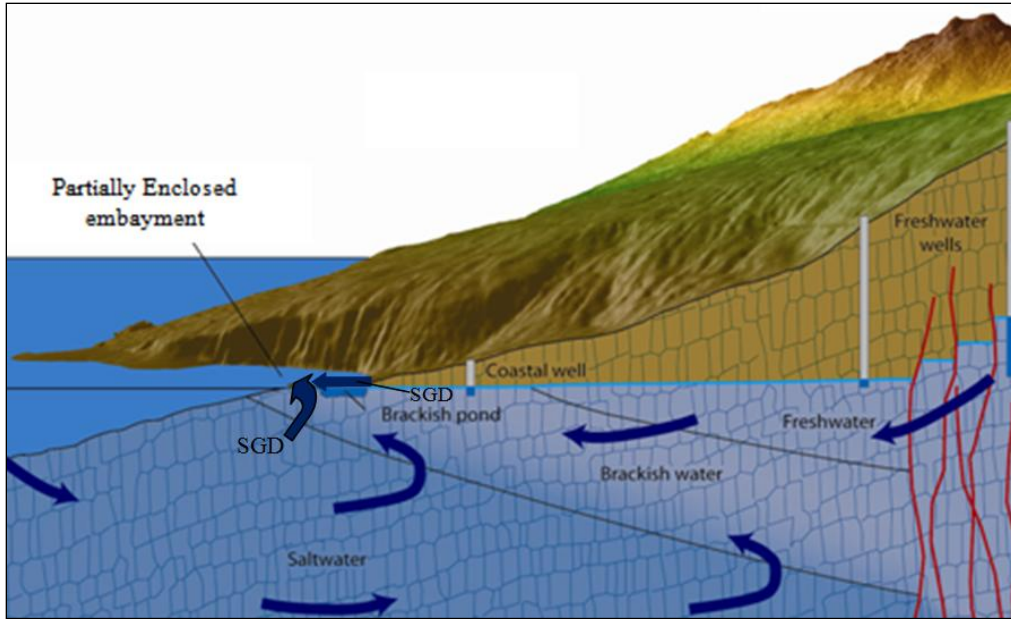


Figure 1: Schematic cross section of West Hawaii groundwater system (reproduced from Johnson, 2008, with permission). Arrows represent water movement. Fresh groundwater moving from the land is expelled along the coast. Intruding seawater is mixed and recirculated with seaward flowing fresh groundwaters within the brackish “subterranean estuary,” and eventually discharges back into the coastal zone. Vertical height and thickness of lava flows are greatly exaggerated.

The flux of SGD into coastal environments can be measured in different ways (see Burnett et al., 2006 for a review). However, the inherent temporal and spatial variability of SGD has often made it difficult to precisely locate, as well as quantitatively assess SGD; therefore, each measurement technique suffers from its own set of limitations and errors. Historically, large-scale water balances have been utilized to estimate fluxes of SGD to coastal environments, but these measurements only quantify the flux of freshwater, which underestimates the flux of SGD (e.g. Kay et al., 1977). Seepage meters (e.g. Lee, 1977) and piezometers (e.g. Freeze and Cherry, 1979) have been used in past studies to directly measure the groundwater flux at discrete sample sites, but both of these methods may only represent fluxes through a small area, which

requires assumptions to be made about the distribution of SGD in order to scale local data to larger, regional coastal environments. As a consequence, methods that allow the assessment of SGD over intermediate sized areas, such as geochemical tracers, have gained widespread acceptance as an additional, indirect method for estimating volumes of SGD. The isotopes of radon (Rn) and radium (Ra), in particular, have been frequently employed as SGD tracers (Moore 1996; Moore, 2000; Burnett and Dulaiova, 2003; Moore and Krest, 2004; Charette & Sholkovitz, 2005; Dulaiova, 2006; Peterson et al., 2007, 2009). Groundwater discharge (fresh waters with salinities less than 5, brackish waters with a salinity range of 5-32, and salty waters with salinities greater than 32) and diffusion from benthic sediments supply coastal waters with Rn (an inert gas), while atmospheric evasion, mixing with surface waters, and radioactive decay removes Rn from coastal environments (Charette et al., 2008). Ra is introduced to coastal environment by brackish to salty groundwater discharge, desorption from river-born particles, and diffusion from sediments. Coastal mixing and radioactive decay are the major processes that remove Ra from this environment. Consequently, Rn and Ra are enriched in groundwater and depleted in marine surface waters and this concentration gradient makes Rn and Ra applicable tracers of SGD.

Due to high rainfall, topographic relief, and permeability of bedrock, tropical volcanic islands, such as the Hawaiian Islands, usually have higher fluxes of SGD than continental environments (Zektser, 2000). In Hawaii, geohydrological budgets indicate that large volumes of freshwater exit the islands as either stream flow or SGD (McGowan, 2004). In addition, previous studies indicate the SGD in Hawaii is nutrient

rich and contributes a substantial amount of nutrients to the coastal environment (Dollar and Atkinson, 1992; Garrison et al., 2003; Derse et al., 2007; Knee et al., 2008; Johnson et al., 2008; Street et al., 2008; Knee 2010). SGD-derived nutrients have been associated with areas where macroalgal blooms occur (Parsons et al., 2008; Smith et al., 2005; Dailer et al., 2010). Dollar and Atkinson (1992) used chlorophyll-a concentrations and assumed Redfield stoichiometry to estimate that nutrient uptake by marine microalgae was less than 2% of the SGD-derived nutrient flux at study sites along the Kona Coast of the Big Island of Hawaii; however, potential linkages between phytoplankton and SGD have not been singularly investigated in Hawaii, which the present study addressed. The goal of this study was to examine the impact of SGD and groundwater-derived nutrients on phytoplankton growth and nutrient uptake. Four governing questions were established in order to accomplish this goal: 1) what are the fluxes of SGD and SGD-derived nutrients to Hawaii's coastal environments, 2) are these fluxes variable between coastal settings, 3) do SGD-derived nutrients impact phytoplankton inorganic carbon uptake in surface waters, and 4) how does the residence time of SGD-derived nutrients impact the nutrient budget of coastal areas? These questions were addressed by assessing the photosynthetic production in coastal waters, SGD derived nutrient budgets, and residence time of SGD-derived nutrients within two leeward and relatively dry rain shadow areas within the Hawaiian Islands, which have been estimated to have large SGD fluxes (Johnson et al., 2008; Kelly personal communication). The sites studied include (1) Wailupe Beach (21.27944°N and 157.76306°W), Black Point (21.25921°N and 157.7904°W), and the Ala Wai Canal (21.28722°N and 157.83112°W) along the southern shore of Oahu (Figure 2),

and (2) within Honokohau Harbor (Figure 3) on the Big Island of Hawaii (19.66925°N and 156.02108°W).

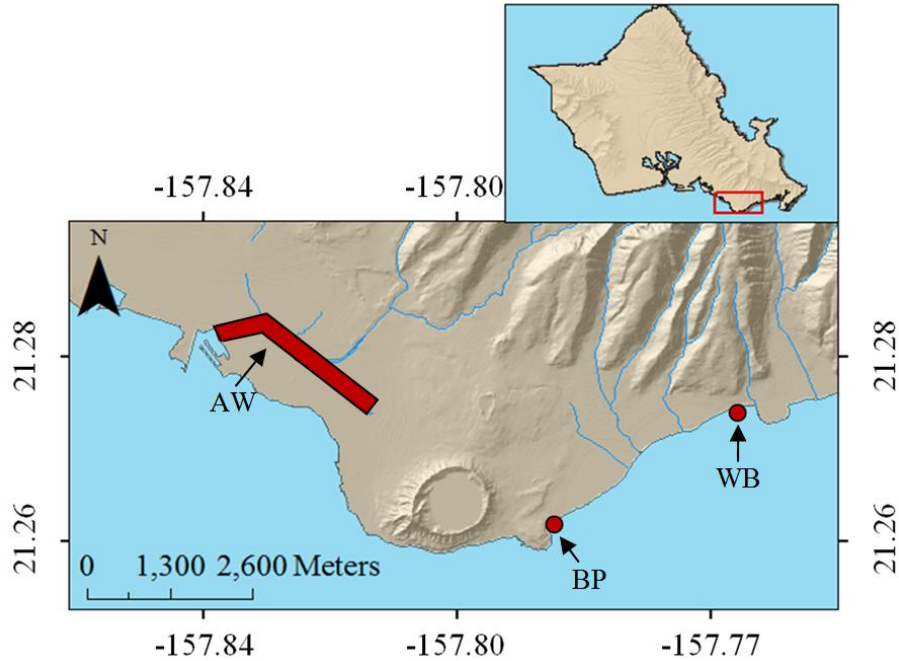


Figure 2: Map of the southern shore of Oahu with study sites. The Ala Wai Canal (AW) is represented by a solid red polygon while Black Point (BP) and Wailupe Beach (WB) are represented by solid red dots.

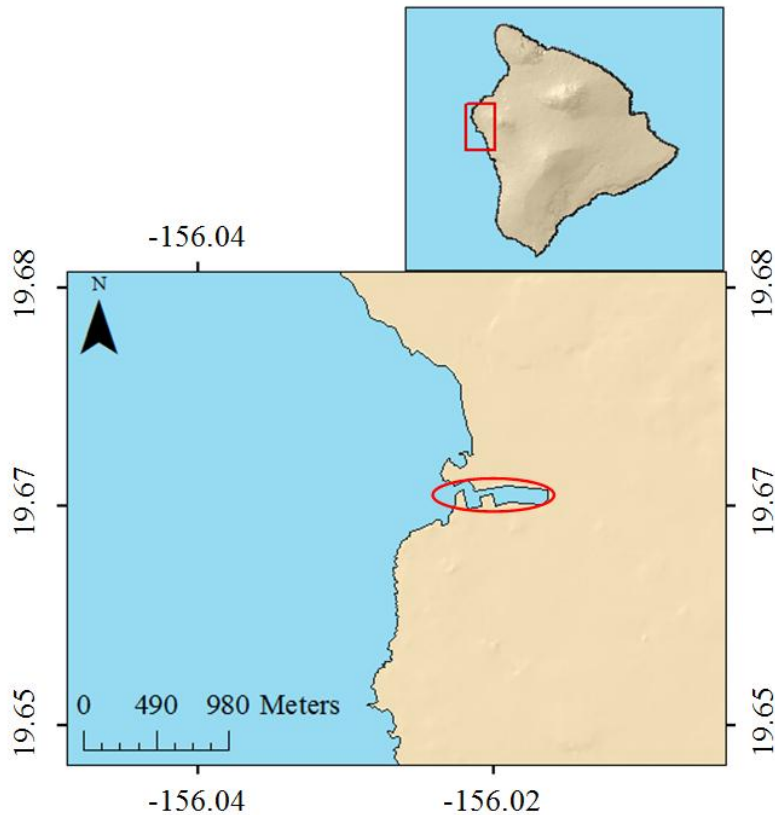


Figure 3: Map of the Kona Coast of Hawaii with study site (Honokohau Harbor) indicated by red oval.

A major tenet of this study is that the rate of microalgal photosynthetic carbon fixation within the coastal systems of Hawaii depends not only on the direct rates of SGD-borne nutrient supply, but also on degree of coastal mixing and water mass residence time. All other factors being relatively equal (e.g. sunlight, temperature, physical conditions, water column remineralization, etc.), it is expected that the higher the nutrient input and/or residence time of these nutrients within the coastal water body, the higher its photosynthetic production rates. This may be due to the sustained length of time that phytoplankton may assimilate a given amount of newly introduced nutrients, as well as the length of time that a given standing stock of microalgae may be able to double

within the same spatial area (Ketchum, 1954). In cases where SGD flow rates are sufficiently intense, the flow of the SGD itself may reduce the residence time of a given water body, particularly those which are narrowly confined, such as in harbors or coastal inlets. It is assumed that the relationship between SGD-derived nutrients and phytoplankton carbon uptake will be a trade-off between nutrient supply and the time the nutrients are available to the phytoplankton (Ketchum, 1954).

Study area

The groundwater systems of the Hawaiian Islands consist of basal and high level (confined and unconfined) aquifers; the basal aquifers exist as Ghyben-Herzberg lenses (Mink 1980, Oki 1999). The Ghyben-Herzberg lens is defined as a freshwater lens floating on seawater with a brackish transition between the two water bodies (Mink 1980). This lens occurs due to density differences between the freshwater, which is more buoyant than seawater. Geohydrological budgets indicate SGD provides large fluxes of freshwater to the coastal environments in Hawaii (Shade 1995; Shade and Nichols, 1996). These budgets have estimated that ~3,100,000 and 141,000,000 m³/d SGD is expelled along the coastal zones of Oahu (Shade and Nichols, 1996), and Honokohau Harbor (Shade 1995), respectively.

Oahu is the most densely populated of all the Hawaiian Islands. In 2009, the U.S. Census estimated its population to be 907,574 people (U.S. Census Bureau). Due to the large population, Oahu has the highest demand for freshwater. Its groundwater system is divided into two major aquifer systems: the Waianae and Koolau aquifers; the Koolau

aquifer supports demand along the southern shore of Oahu. Groundwater discharged along the southern coast of Oahu occurs as diffuse seepage and spring flow (Hunt, 1996; Shade and Nichols, 1996). Submarine groundwater discharge likely occurs as diffuse seepage through interstratified alluvium classified as a “caprock” which acts as a semi-confining layer (Langenheim and Clague, 1987). Coastal springs however manifest as nearshore groundwater vents of larger diameter with significant volumetric discharge. Hydrological budgets have estimated that the flux of SGD into the coastal zone along the south shore of Oahu is $\sim 17,900 \text{ m}^3/\text{d}$. Past studies along Wailupe Beach, Oahu have estimated the SGD fluxes to be $0.75 \text{ m}^3/\text{m}^2/\text{d}$ via seepage meters (McGowan, et al., 2004). With the exception of the Ala Wai Canal, which is capped by a warm lid of stream water, aerial thermal infrared spectrophotometry displays pronounced cool SGD plumes existing along much of the length of the south shore of Oahu from Wailupe to Black Point (Kelly, personal communication). With the exception of McGowan (2004) and Kennedy (2011), previous in situ SGD flux rates have not been reported for the southern shore of Oahu.

The Island of Hawaii is the youngest of the Hawaiian Islands. Along the Kona Coast on the western shore of the island of Hawaii, groundwater is the principle water source (Mink et al., 1993). Honokohau Harbor (Figure 3) was constructed in 1970 by removing rocks along $\sim 40,469 \text{ m}^2$ of shoreline (Bienfang, 1983). The harbor was constructed by two phases of construction; the last phase (ending in 1978) expanded the harbor’s area, increasing the harbor’s water residence time from 12 days to 27 days (Bienfang, 1983). Aerial thermal infrared spectrophotometry shows extensive buoyant

cool water surface water plumes of SGD exit the mouth and coastlines adjacent to Honokohau Harbor (Johnson et al., 2008). Johnson et al. (2008) used TIR surveys in conjunction with nutrient analysis of discrete samples to further map and characterize the Honokohau Harbor SGD plume as a seaward flowing layer of cooler and nutrient rich water, extending to depths < 2 m below the surface. Low salinity and low temperature characteristics of the SGD plume were recorded from the northeastern margin of the harbor (defined as the back of the harbor) to 400 meters outside of the harbor's mouth. As the brackish water surface plume flows seaward, it mixes with and entrains warm seawater below and around it (Bienfang 1980; Johnson et al., 2008). Past studies have used multiple methods to quantify the flux of SGD to the harbor (Bienfang, 1980; Peterson et al., 2009). As based on floating drogue deployments and other methods, previous estimates quantified the SGD flux within the Honokohau Harbor to be between $5600 \text{ m}^3/\text{d}$ and $7600 \text{ m}^3/\text{d}$ (Bienfang, 1980). Peterson et al. (2009) calculated a Rn budget using a non-steady-state mass balance box model (Peterson et al., 2009) in order to derive the flux of SGD to the harbor. An average concentration of 170 Bq/m^3 ($10,200 \text{ dpm/m}^3$) was observed for the harbor, which resulted in a total SGD flux of $12,000 \text{ m}^3/\text{d}$ (Peterson et al., 2009).

Chapter 2: Methods

Vertical profiles of salinity and temperature

SGD from the Hawaiian Islands is usually less saline and several degrees Celsius colder than seawater along the coast. Since this temperature gradient persists year-around, SGD is easily identifiable as a freshwater plume floating on top of denser and saline seawater. To characterize groundwater plumes, vertical and horizontal profiles of temperature and salinity through the water column were measured at each study site. A YSI multiparameter probe (YSI-6920) with an accuracy of ± 0.1 salinity and $\pm 0.15^{\circ}\text{C}$ temperature was deployed from a small coastal vessel at several locations along transects at each site that extended from the beach face to open ocean conditions (defined as salinities ≤ 34 , see Appendix A). These transects extended ~ 4000 m in the Ala Wai Canal and ~ 1030 m in Honokohau Harbor. Temperature and salinity profiles were collected within the Ala Wai Canal and Honokohau Harbor on 23 July 2010 and 24 September 2010, respectively. Within the Ala Wai Canal (Figure 11; Table 14) twelve profiles were measured at 0.25 m depth intervals from the surface to maximum depths (up to 2.5 m). Fourteen profiles were taken within Honokohau Harbor (Figure 12; Table 15); the transect of the profiles originated at the (back of the harbor) and extended until open ocean conditions with respect to salinity were measured; the measurements on this transect were taken at intervals that captured salinity changes of no more than 2 units until the bottom of the harbor was reached. Temperature and salinity profiling was not completed for either Black Point or Wailupe Beach.

Regional nutrient sampling

Water samples for nutrient analyses were collected from freshwater upland wells, nearshore groundwater vents, and surface coastal waters. Coastal water nutrient samples were collected along the southern shore of Oahu (Figures 4-6) between April 2010 and July 2010 and within Honokohau Harbor (Figures 7-10) between June 2010 and September 2010 for major inorganic macronutrient concentrations, including Si(OH)_4 , NO_3^- , NO_2^- , NH_4^+ , and PO_4^{3-} , total nitrogen (TN), and total phosphorus (TP). Water samples were collected in acid clean, triple rinsed, high-density polyethylene bottles. A volume of 125 mL from each sample was split into a 250 mL acid clean, triple rinsed, high-density polyethylene bottle for TN and TP analyses, while a volume of 55 mL of sample water was syringe-filtered using 0.45 micrometer pore size acetate filters for specific nutrient analyses. Samples were immediately frozen and stored at -20°C . Samples were shipped frozen to the Marine Chemistry Laboratory at the University of Washington School of Oceanography for spectrophotometric segmented flow nutrient analysis using Technicon Model AAII auto analyzer (UNESCO, 1994) with detection limits for TP, TN, Si(OH)_4 , NO_3^- , NO_2^- , NH_4^+ , and PO_4^{3-} of 0.03, 0.34, 0.02, 0.21, 0.15, 0.01, and 0.05 μM , respectively. Errors of the reported concentrations (Table 1-6) for TP, TN, Si(OH)_4 , NO_3^- , NO_2^- , NH_4^+ , and PO_4^{3-} were $\pm 0.49\%$, 4.0%, 3.4%, 1.1%, 0.72%, 0.59%, and 1.14%, respectively.

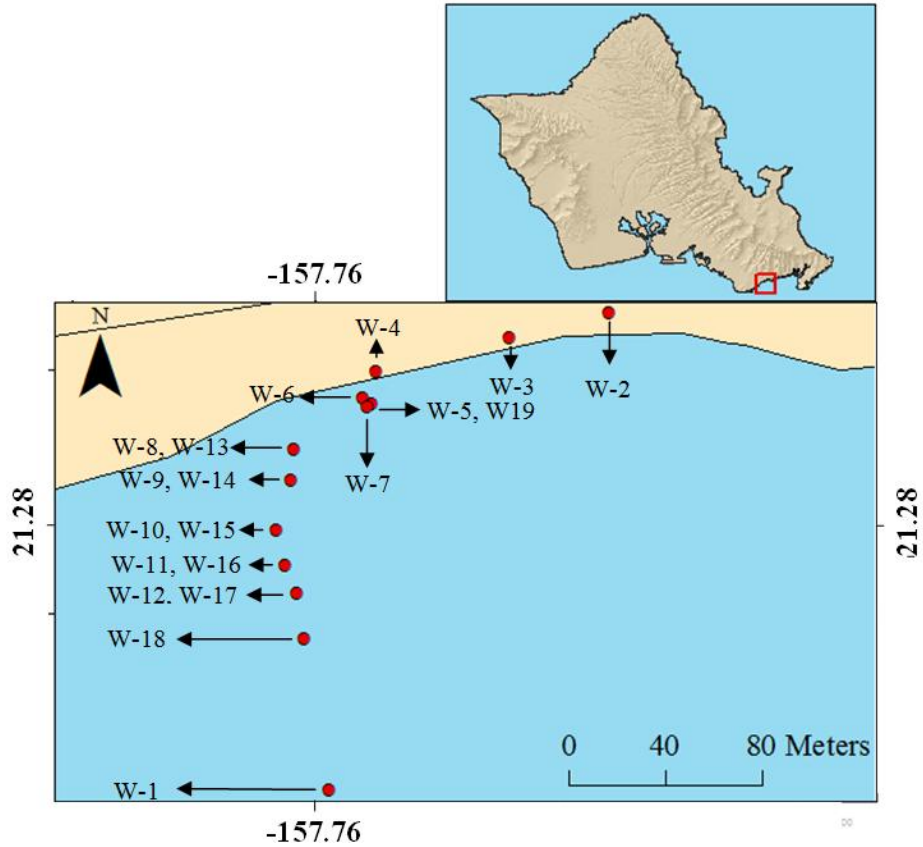


Figure 4: Map of Wailupe Beach with April and May 2010 nutrient and Ra sample sites indicated by solid red dots. Labels indicate sample names. The Rn platform was located at station W-10 during April 2010 and W-15 during May 2010. Beach samples were collected at sample sites W2-W4. Nearshore groundwater vents were located at stations W-6,W-7, W-8, and W19 which are in vicinity to nearshore groundwater vents identified by McGowan, 2004.

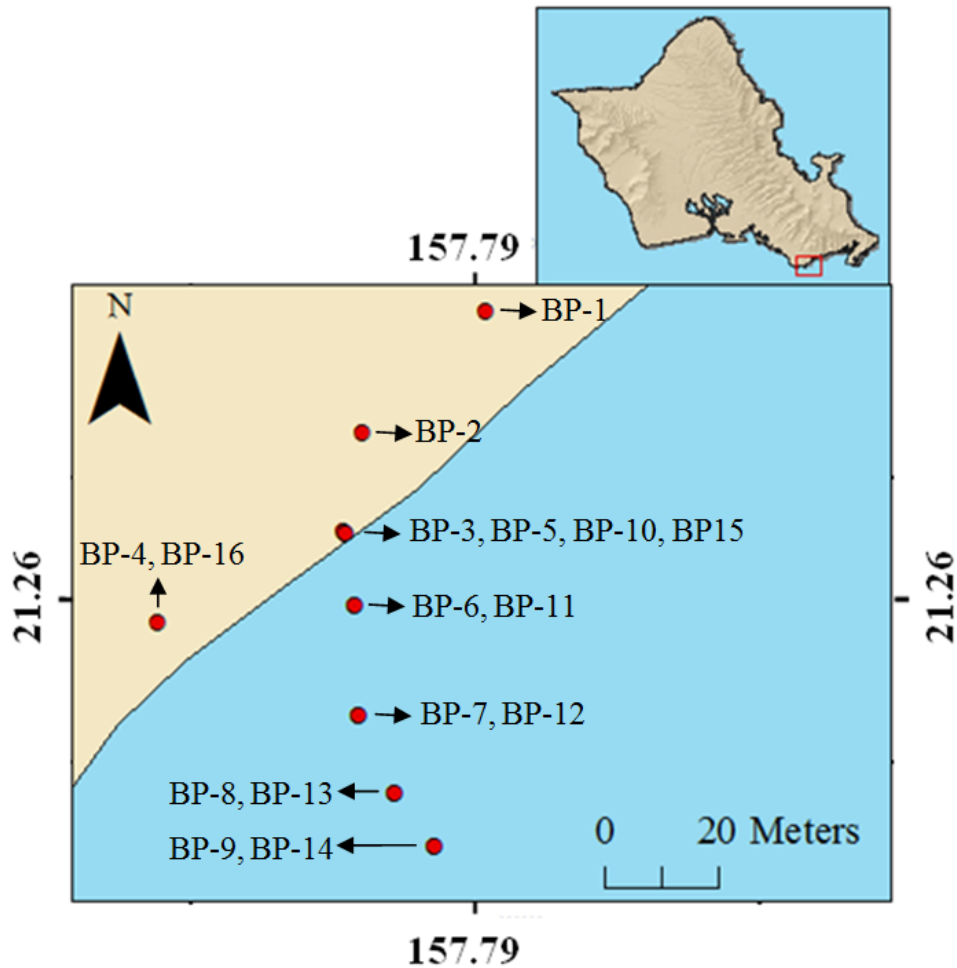


Figure 5: Map of Black Point with April and June 2010 nutrient sample sites, Ra sample sites, and Rn platform sites are indicated by solid red dots. Labels indicate sample names. Stationary radon time series stations were located at station BP-7 during April 2010 and at station BP-12 during June 2010. Nearshore groundwater vents were located at stations BP1-4 and BP15-16. The shoreline represents mean tide causing the samples collected along the shore line during low tide to be on land in this figure.

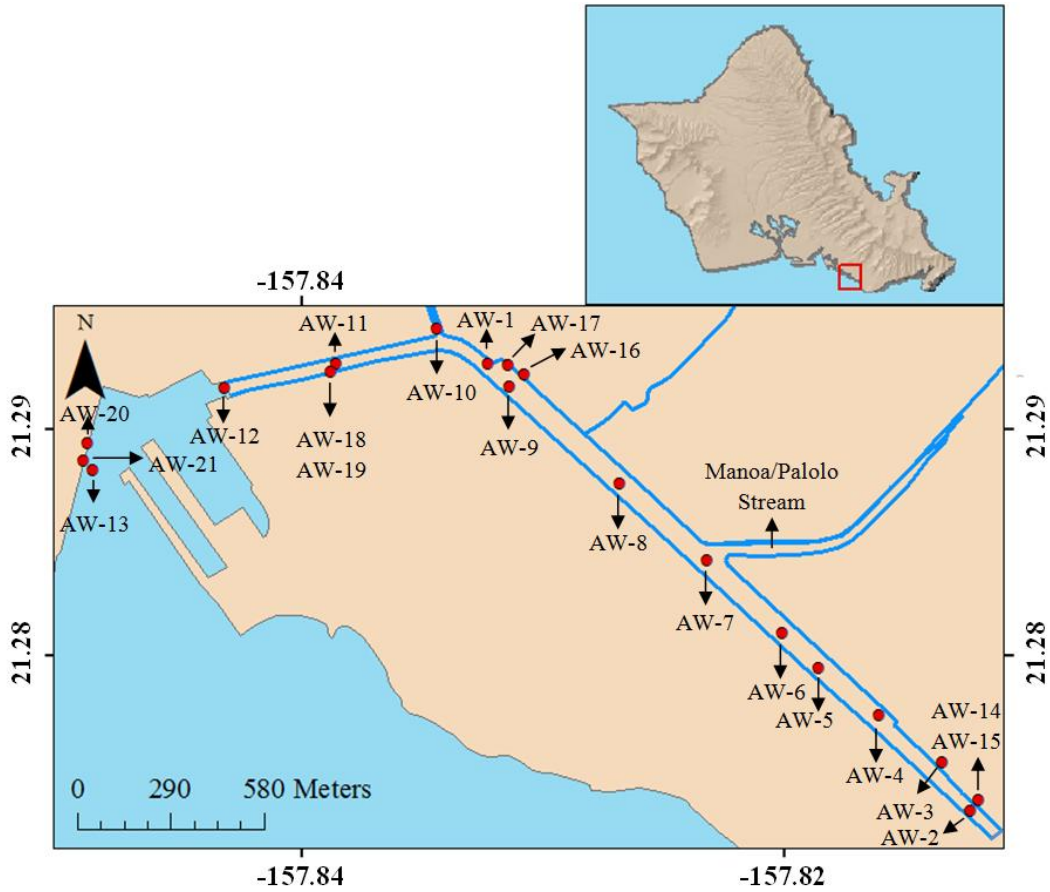


Figure 6: Map of the Ala Wai Canal with the July 2010 nutrient sample sites, Ra sample sites, photosynthetic carbon production sites, chlorophyll sample sites and Rn platform was located at station AW-1 during the July 2010 sampling period. The 2010 temperature and salinity survey shown in Figure 11 began in the Canal's back basin at station AW-2 and concluded at near the mouth of the Ala Wai Small Boat Harbor at station AW-13.

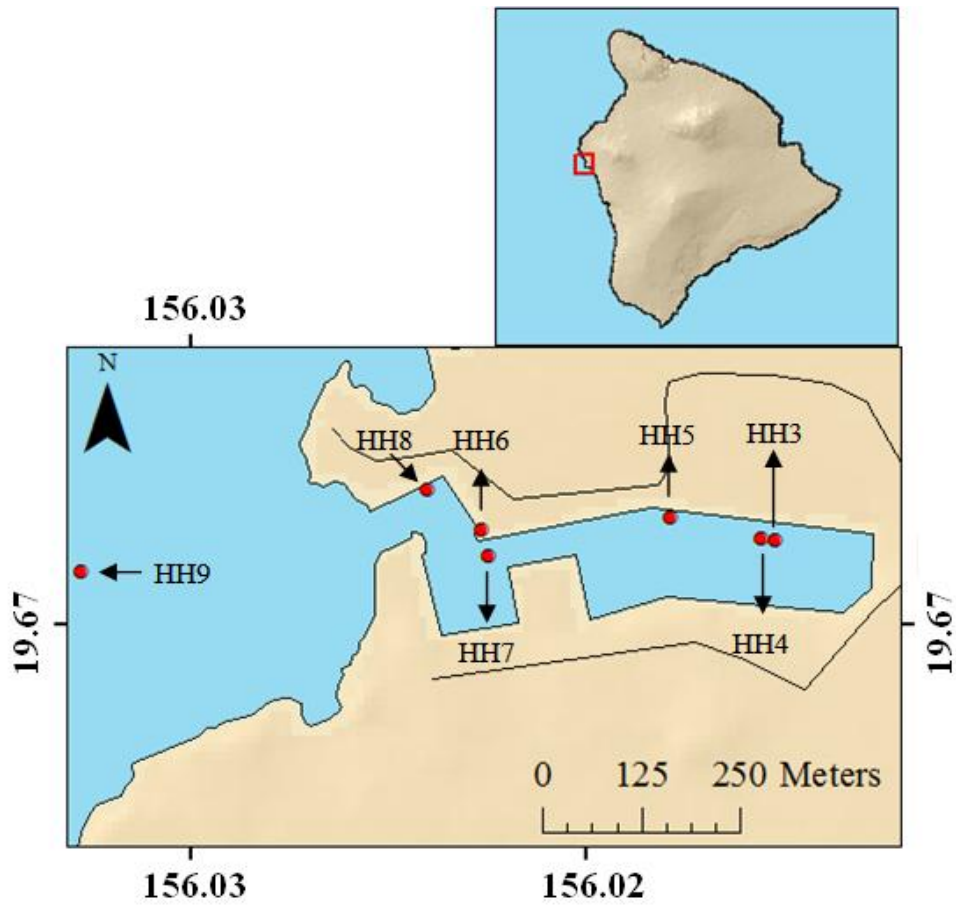


Figure 7: Map of Honokhau Harbor with 19 June 2010 nutrient sample site locations indicated by solid red dots. Labels indicate sample names.

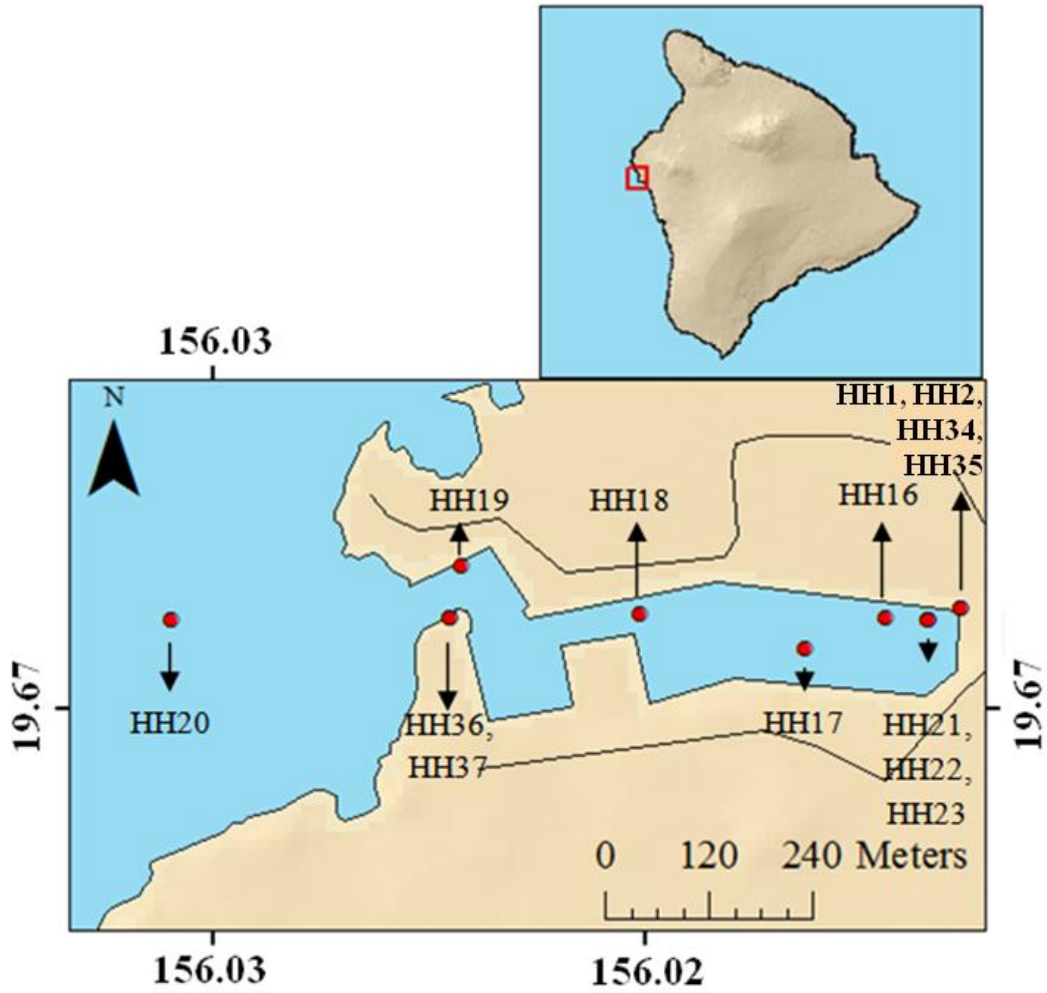


Figure 8: Map of Honokhau Harbor with June 2010 and September 2010 radon and radium sampling sites indicated by solid red dots. Labels indicate sample names. Stationary radon time series station locations at station HH1 during the June 2010 sampling period and station HH2 during the September 2010 Sampling period.

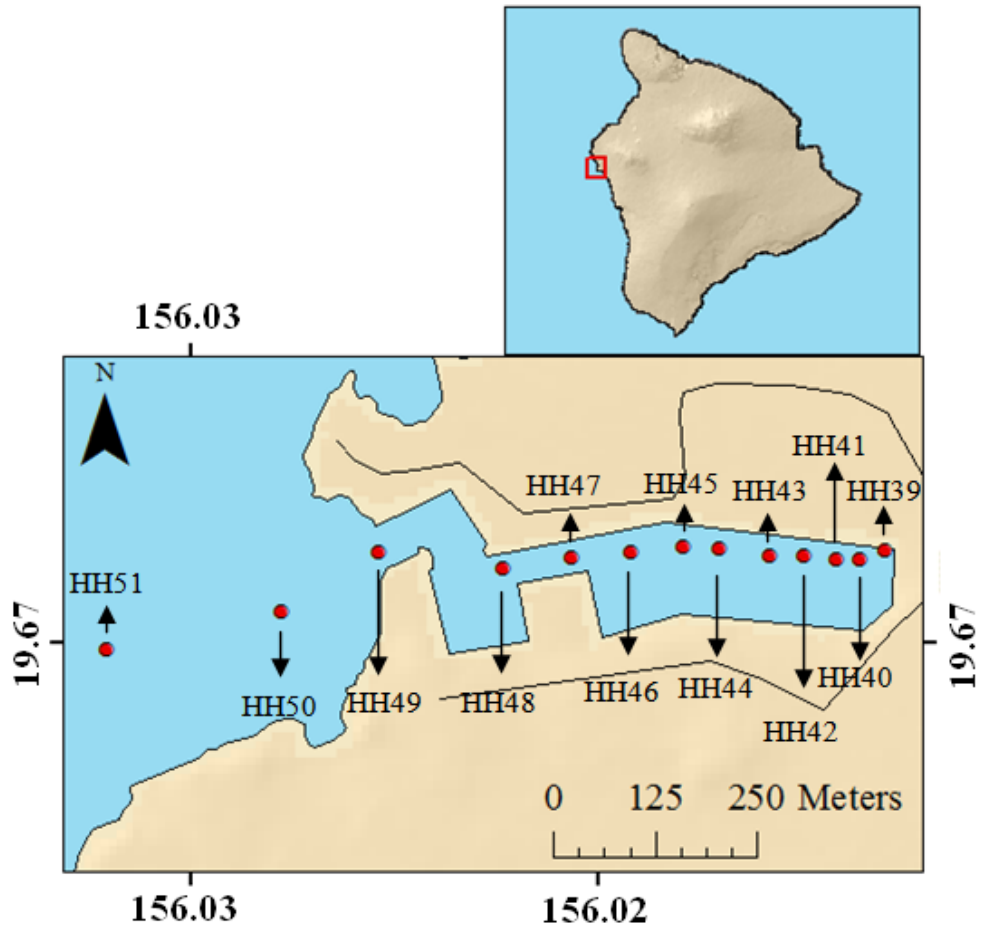


Figure 9: Map of Honokhau Harbor with 24 September 2010 temperature and salinity survey stations indicated by red dots. The salinity and temperature survey shown in Figure 12 started at site the back of the Harbor (HH39) and ended outside the Harbor mouth (HH51).

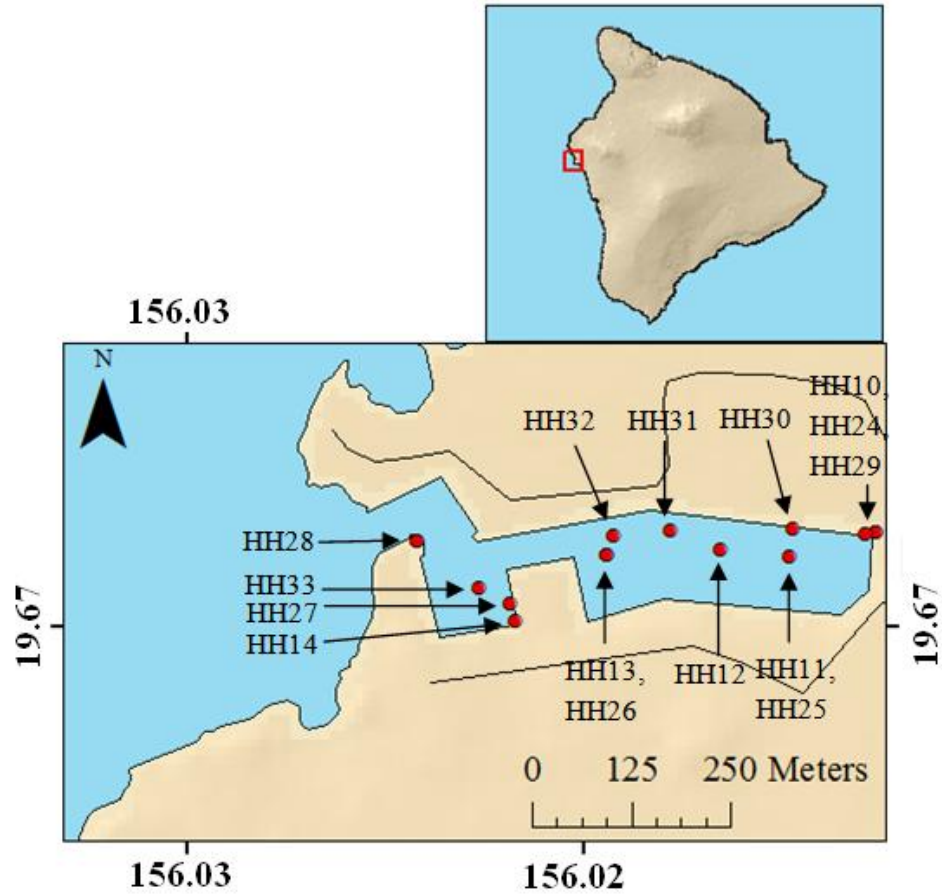


Figure 10: Map of Honokhau Harbor with June and September photosynthetic carbon production sampling sites indicated by solid red dots. Labels indicate sample names.

Radon as an SGD tracer

The geochemical tracer, ^{222}Rn , has proven to be an effective tool that can be used to estimate SGD within a coastal environment (e.g. Burnett et al., 1996, Burnett et al., 2003, Burnett and Dulaiova 2003, and Swarzenski 2007). Rn is a naturally occurring radioactive isotope and its concentration in groundwater can be three to four orders of magnitude higher than in seawater. Rn in groundwater is generated from a continuous decay of ^{226}Ra , which is part of the uranium decay series, present in the aquifer substrate. Due to the large concentration gradient between groundwater and seawater, areas of SGD can easily be identified based on elevated coastal Rn levels. The Rn inventory in these areas can then be converted to groundwater fluxes required to sustain the observed levels. In our study, we used continuous Rn measurements to calculate Rn inventories over several tidal cycles. A Rn inventory was then corrected at each study site to account for all source and loss terms that influence Rn in the water column: 1) in-situ production through the decay of ^{226}Ra , 2) input via diffusion from sediments, 3) input via groundwater advection, 4) removal due to mixing with open ocean waters, 5) removal due to evasion to the atmosphere, and 6) losses by radioactive decay. This mass balance can be expressed by

$$F_{SGD} = \frac{\left[\frac{(A - A_{ocn})z_{wc}}{T_w} \right] - \left[\Phi D_s \left(\frac{\partial A_{sed}}{\partial z_{sed}} \right) \right] + [e_g(A - A_{atm})] + [\lambda A]z_{wc}}{A_{gw}} \quad (1)$$

where F_{SGD} is the flux of SGD, A is the activity of ^{222}Rn (dpm m^{-3}), A_{ocn} is the ^{222}Rn activity of the ocean water, z_{wc} is the water column depth (m), T_w is the residence time of

the water (days), Φ is the sediment porosity, D_s is the diffusion coefficient of ^{222}Rn in pore waters (m^2/d), $\partial A_{\text{sed}}/\partial z_{\text{sed}}$ is the vertical gradient of the ^{222}Rn concentration in pore water, e_g is the air-sea piston velocity (m/d), A_{atm} is the ^{222}Rn concentration in marine boundary layer, λ is the decay constant (d^{-1}), and A_{gw} is the groundwater endmember ^{222}Rn activity (Charette et al., 2008). The procedure to apply this mass balance for a time series Rn model has been described in Burnett and Dulaiova (2003). Briefly, we 1) measured the ^{222}Rn concentrations in the water column and atmosphere as well as water temperature, water depth, air temperature, and wind speed in order to compile a Rn budget/inventory. 2) We accounted for excess ^{222}Rn by identifying ^{222}Rn within the water column that is unsupported by ^{226}Ra for each measurement period, 3) normalized ^{222}Rn inventory to tidal height and 4) corrected for losses to the budget due to atmospheric losses for each measurement period. The change in Rn inventory over time was used to estimate net ^{222}Rn fluxes or the flux of ^{222}Rn into the coastal zone during each measurement cycle. Minimum mixing losses to the inventory were estimated to be equal to maximum negative net flux. The sum of the minimum mixing loss and net flux for each time period resulted in the total Rn flux. The ^{222}Rn concentration of the advecting fluids (SGD) was estimated by identifying the concentrations of ^{222}Rn of groundwater vents and upland wells. The Rn total fluxes were divided by the Rn concentration of the advecting fluids to convert the Rn fluxes to water fluxes.

The derived advection rates represent fluxes of volume of groundwater per day. To scale measured rates to the area where SGD extends (area of SGD occurrence) one has to know how large of an area these time series Rn inventories represent. These were

identified using a coastal Rn survey where a Rn monitor (see below) was moved along the shoreline at low speed (3-4 km/h) while taking continuous measurements in 5-minute intervals. The representative area was then defined as the area within which the maximum Rn concentration observed during the time-series decreased by 5%. The advection rates were scaled to the areas of SGD occurrence in order to quantify the total groundwater discharge for each site.

In-situ Rn measurements to derive A in equation (1) were taken using a commercially available Rn in air monitor (RAD7, manufactured by DurrIDGE, Inc.) adapted to measure Rn in water, which was positioned on a floating platform, in our case an anchored small boat. At every site we monitored the Rn concentration over several tidal cycles with integrated measurements taken every fifteen to thirty minutes. The Rn measurement system consisted of a submersible pump, which continuously supplied surface water to an air-water exchanger that allowed the release of dissolved Rn into an air loop that was then transferred into the Rn-in-air monitor. These measurements were accompanied by sea level, salinity, water temperature and wind speed measurements that were used for the Rn mass balance calculations. In order to observe maximum flux of SGD within the coastal zones, platforms were deployed during periods when low tides were below the average sea level of the lowest of the low tides (Table 1).

Radium isotopes as tracers of coastal residence time

Ra can be useful in quantifying the brackish and salty water component of SGD as well as the apparent Ra age of the coastal components, which can be approximated as the residence time of groundwater-derived dissolved constituents within the coastal waters (Moore et al., 2000; Kelly and Moran, 2002; Dulaiova and Burnett, 2008). As brackish/saline water comes in contact with the aquifer substrate the common ions outcompete Ra from particle surfaces and Ra is desorbed enriching groundwater in significant quantities. Once Ra isotopes are desorbed from the particles and leave the aquifer, they are decoupled from their respective parent isotopes and decay based on their respective half-lives. There are four naturally occurring isotopes: ^{223}Ra ($T_{1/2} = 11.4$ days), ^{224}Ra ($T_{1/2} = 3.6$ days), ^{226}Ra ($T_{1/2} = 1600$ years), and ^{228}Ra ($T_{1/2} = 5.8$ years). By analyzing the concentration of the short lived Ra isotopes (^{224}Ra and ^{223}Ra) in the coastal waters, the apparent Ra age or residence time of components within the coastal environment can be determined. Because ^{224}Ra decays at a faster rate than ^{223}Ra the $^{224}\text{Ra}/^{223}\text{Ra}$ activity ratio changes at a predicted rate over time. Once an initial $^{224}\text{Ra}/^{223}\text{Ra}$ ratio is known, the residence time of the water parcel can be identified:

$$T_w = \ln \left(\frac{I \left(\frac{^{224}\text{Ra}}{^{223}\text{Ra}} \right)}{F \left(\frac{^{224}\text{Ra}}{^{223}\text{Ra}} \right)} \right) \times \left(\frac{1}{(\lambda^{224}\text{Ra} - \lambda^{223}\text{Ra})} \right) \quad (2)$$

where $I[^{224}\text{Ra}/^{223}\text{Ra}]$ is the initial activity ratio, $F[^{224}\text{Ra}/^{223}\text{Ra}]$ is the observed activity ratio, $\lambda^{224}\text{Ra}$ is the decay constant of the ^{224}Ra isotopes, and $\lambda^{223}\text{Ra}$ is the decay constant of ^{223}Ra (Dulaiova and Burnett 2008). To utilize this model it is assumed that 1) there is

only one source of the short-lived Ra isotopes into the coastal environments, which constantly supplied ^{224}Ra and ^{223}Ra . 2) The activities of ^{224}Ra and ^{223}Ra are in excess, which is derived from SGD (unsupported by thorium parent). 3) Losses to the Ra budget are only due to mixing and decay.

Ra samples were collected from wells, coastal surface water (< 0.5 m below the water surface), and nearshore groundwater vents at each study site. Water samples (< 100 L) of sample waters were collected in triple rinsed, Coleman expandable plastic 20 L containers. Exact volume was recorded for each sample and the water collected was passed through a column of manganese oxide-coated acrylic fibers at a rate equal to or less than 1 L/min to concentrate Ra (Moore, 1976). After the water was filtered through the fibers, the fibers were analyzed via Radium delayed coincidence counters in the laboratory (Moore and Arnold, 1996). The delayed coincidence counters measure the alpha particles from the decay of ^{220}Rn , ^{219}Rn , and their respective daughters. Since Rn is produced by Ra decay, the measured alpha particles can be used to calculate ^{224}Ra and ^{223}Ra . Samples are counted immediately after collection, ~1 week after collection, and ~1 month after collection. The immediate count allows for precise ^{224}Ra activities and the 1 week counts allow for more precise ^{223}Ra activity due to the partial decay of ^{224}Ra , which then results in lower coincidence count correction for ^{223}Ra . Samples are recounted at ~1 month to let any excess ^{224}Ra decay and the ^{228}Th supported ^{224}Ra to grow into equilibrium with Th. The latter is then subtracted from the total ^{224}Ra measured at the immediate count. By subtracting the ^{224}Ra -supported activity, the excess ^{224}Ra (provided by SGD) was estimated. Samples were counted at ~3 months to account for ^{223}Ra

supported by ^{227}Ac . However, ^{223}Ra ingrowth from ^{227}Ac was found to be negligible for our samples. Garcia-Solsona et al. (2008) identified relative uncertainties for ^{224}Ra activities and ^{223}Ra activities averaging 7% and 12%, respectively.

$\delta^{13}\text{C}$ values of organic carbon

To determine the relationship between SGD-derived nutrients and phytoplankton growth, the rate of photosynthetic carbon uptake was measured. For this study, phytoplankton photosynthetic carbon production rates were quantified from *in situ* surface waters, using the uptake of ^{13}C -labeled CO_2 (aq) Hama et al. 1983. Specifically, we determined the rate of ^{13}C uptake by particulate organic carbon (POC) over time by measuring the change in $\delta^{13}\text{C}$ values between the natural abundance water samples from the water sample incubated with ^{13}C labeled bicarbonate for ~24 hr. Because this method is completed within a closed system, any change in ^{13}C contents of particulate organic matter during the incubation is assumed to be the result of photosynthetic uptake. This change in the ^{13}C contents of particulate organic carbon (ΔC) can be determined by:

$$\Delta\text{C} = \text{C} \times \frac{(a_{\text{is}} - a_{\text{ns}})}{(a_{\text{ic}} - a_{\text{ns}})} \quad (3)$$

(Hama et al, 1983), where C is the concentration of particulate organic carbon (POC) at the end of the incubation, a_{is} is the ^{13}C activity of POC at the end of the incubation, a_{ns} is the ^{13}C activity of POC at the beginning of the experiment, and a_{ic} is activity of ^{13}C in $\text{CO}_2(\text{aq})$. The ΔC was divided by the hours of incubation (t) in order to measure the

photosynthetic carbon production (P) (Hama et al. 1983). See Appendix F for complete review of ΔC ($\mu\text{g/L}$) and P ($\mu\text{g/L/h}$) calculations.

Water samples for ^{13}C analyses were collected in transects perpendicular to the coastline, with multiple samples being collected within each transect. A dark bottle representative of the natural abundance of carbon before incubation and a light bottle that symbolized the abundance of carbon after incubation with ^{13}C label, respectively, were collected at each sampling site. The natural abundance water samples were collected in 2 L acid clean, triple rinsed, high density polyethylene brown bottles, while incubated water samples were collected in 2 L acid clean, triple rinsed, clear polycarbonate bottles. At each site, the dark bottle was filled with a 2 L volume of sample water, tightly sealed, and placed in a cooler for storage. No ^{13}C labeled inorganic carbon was added to the dark bottle. The clear (aka “light”) bottle was filled with a 2 L volume of sample to which a $\text{H}^{13}\text{CO}_3^-$ spike was added. The activity of the inorganic carbon spike was determined by isotope mass balance assuming that seawater has a content of 2,000 $\mu\text{mol/L}$ DIC and a $\delta^{13}\text{C}$ value of +1‰; as a result 2.28 μmol of $\text{H}^{13}\text{CO}_3^-$ (98 atom % ^{13}C) was added to 2 L of seawater to elevate the $\delta^{13}\text{C}$ value of seawater to 500‰ relative to Vienna-Pee Dee Belemnite. Once the $\text{H}^{13}\text{CO}_3^-$ was added, the incubated sample was tightly sealed and tied to floats in the surface of the seawater column at each study site to allow for *in situ* incubation for ~24 hours. The samples were filtered within 12 hours of removal from study site using precombusted 25 mm diameter glass fiber filters (Whatman GF/C, nominal porosity 1.2 μm). Filters were wrapped in precombusted aluminum foil and stored frozen at -20°C . At the Isotope Biogeochemistry Laboratory at the University of

Hawaii at Manoa, the filters were treated with 1 normal phosphoric acid in order to remove any inorganic carbon. The filters were dried in a dessicator for at least 24 hours. The carbon content and carbon isotopic composition of particulate organic carbon was determined using a Costech ECS 4010 Elemental Combustion System/Zero Blank Autosampler /ThermoFinnigan MAT Conflo IV/ThermoFinnigan DeltaXP with a respective error of 0.2%.

Chlorophyll-a

Chlorophyll-a plays an essential role in photosynthesis and is representative of most of the standing stock of photosynthesizing organisms within the coastal area. Individual water samples for measurement of the concentration of chlorophyll-a (either 250 or 500 mL) were taken at the beginning of the ^{13}C incubation experiments, described above, from within < 0.5 m of water surface. Water samples were collected in acid clean, triple rinsed, high-density polyethylene bottles and stored chilled in field coolers until the samples were filtered within < 24 hours. Water samples were filtered through precombusted 25 mm diameter glass fiber filters (Whatman GF/C, nominal porosity 1.2 μm). Once filtration was complete, the filters were wrapped in precombusted aluminum foil and frozen at -20°C . The filters were sent to the Marine Chemistry Laboratory at the University of Washington for chlorophyll-a determination analysis by Turner Model TD700 Fluorometer (Turner Designs, 1999) with a detection limit of 0.02 $\mu\text{g/L}$. Duplicates were not conducted so user error cannot be defined for the chlorophyll-measurements.

Nutrient uptake rates

Measured photosynthetic carbon production was converted to N and P uptake rates assuming that C/N and C/P ratios in the biomass were equal to the Redfield ratio, 106:16:1 (Redfield, 1958). The resulting N and P uptake were normalized to water volume, which is assumed to be the product of the area of SGD occurrence and depth of light penetration.

Chapter 3: Results

Vertical temperature and salinity profiles of the water column of the Ala Wai Canal and Honokohau Harbor

Vertical salinity and temperature water column profiles were taken along two partially enclosed embayments, the Ala Wai Canal and Honokohau Harbor, in order to define the plume structure of each embayment. Profiles of the transects of the water column for the Ala Wai Canal and Honokohau Harbor are shown in Figures 11 and 12, respectively. In the Ala Wai Canal, the range for temperature was 24.13-28.63°C while the salinity range was 4.2-34.2 (Table 14). At ~1260 m from the head of the canal we observed a five-fold decrease of salinity and a 1°C decrease in water temperature. The Ala Wai brackish water plume (salinity < 20) was derived from inputs of freshwater via both SGD and stream inputs from the Manoa/Palolo Stream and the Makiki Stream. During the 2010 study period, the plume extended ~1,100 m, with a depth of ~0.25 m. In the waters of Honokohau Harbor, a lower salinity groundwater plume was identified emanating from the back of the harbor. In the harbor, a temperature range of 20.54-

26.75°C and a salinity range of 20.7-34.7 were identified (Table 15) with the lowest observed temperature and salinity occurring at the back of the harbor. As distance from the back of the harbor increased the temperature and salinity of the water increased. The lower-salinity groundwater plume (which we arbitrarily defined as waters with salinity <30) extended to a distance of ~500 m from the back of the harbor with an average depth of 0.5 m.

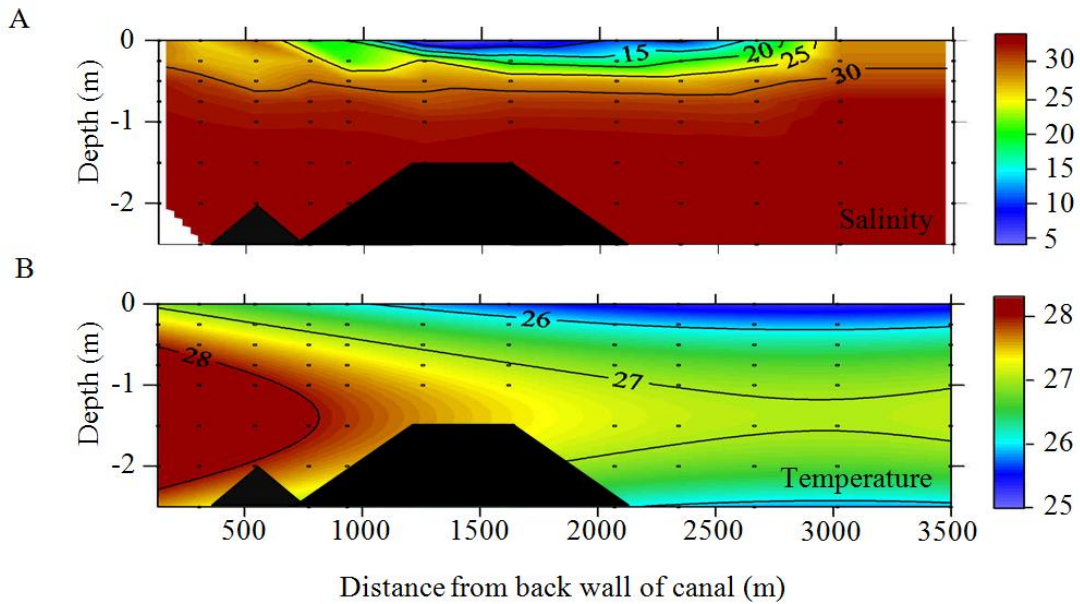


Figure 11: July 2010 water column salinity (A) and temperature (B) profiles for the Ala Wai Canal, Oahu. Black dots indicate survey stations (Figure 6; Table 14) where measurements were made. A major source of warm and relatively fresh surface waters enter the Canal from the Manoa-Palolo Drainage System at 1200 m seaward of the back of the canal, and flows seaward through the canal as a warm and brackish lid. A major sedimentary sill caused by sediment deposition by the Manoa/Palolo stream also occurs between the shown distances of ca. 1000 m and 2000, which historically has been known to restrict circulation towards its northeastern end (depicted as the left side of the figure) (cf. Glenn and McMurtry, 1995). This is perhaps also well reflected in the present study, as dissolved bottom water oxygen concentrations (as measured by the YSI % DO) were found to progressively decrease from ~82% near the mouth of the canal, to ~35% behind that sill at the rear of the canal (Table 14).

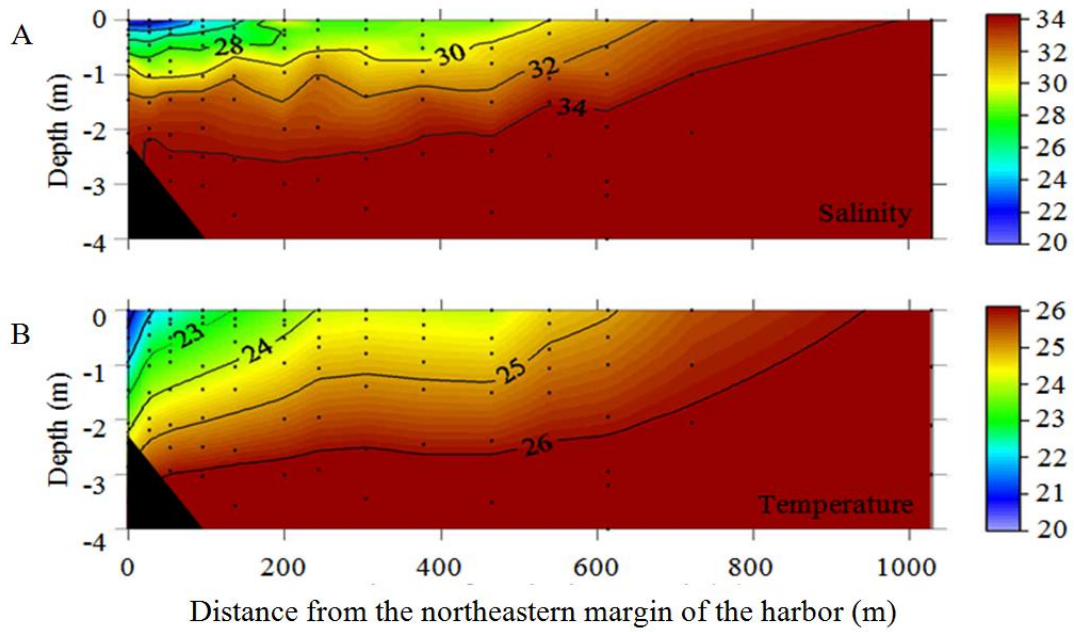


Figure 12: Water column salinity (A) and temperature (B) profiles for Honokohau Harbor, Hawaii during the September 2010, where x-axes are distance (m) from the back wall of the harbor and y-axes are depth below surface. Samples were taken during the transition from ebb tide to flood tide. Black dots are representative of sample sites (shown in Figure 9; Table15) where salinity and temperature recordings were made.

Nutrient characteristics of groundwater and coastal surface water

Nutrient concentration results plotted as a function of salinity are shown for the south shore of Oahu in Figure 13 and for Honokohau Harbor in Figure 14. Also shown on these figures are the respective zero-salinity nutrient concentration results from linear regressions and upland well waters analyzed from each island. The solid lines represent the linear regressions of coastal nutrients to a zero-salinity nutrient concentration, representing conservative mixing within the coastal areas. The dashed lines in these figures connect the average values of the nutrient concentrations of the upland well waters with a presumed average open ocean salinity of 35, and thus illustrates a simple line of seawater dilution if one assumes that all nutrients delivered to the coast were unmodified during aquifer transit to the coast. In the simplest interpretation, data which plots above this line represents the addition of nutrients to the coastal system that is in excess of that supplied from that observed in the upland wells, and data that falls below the line represents nutrient removal relative to the upland wells. Data that plots along the line should thus represent the situation where nutrients that were sourced at the wells were delivered to the ocean unmodified during transit in the aquifer, and simply diluted with open ocean seawater. While this is an obvious oversimplification, it is however instructive.

The upland wells, nearshore groundwater vents, and coastal water samples were analyzed for specific macronutrients. The average nutrient concentrations for upland wells along the south shore of Oahu were 2.43 $\mu\text{M PO}_4^{3-}$, 663.16 $\mu\text{M Si(OH)}_4$, and 50.15

$\mu\text{M NO}_3^-$ with an average $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratio of 37.33 (Figure 27; Table 1). Along the Kona Coast of Hawaii, average nutrient concentration of upland wells were 4.65 μM of PO_4^{3-} , 767.51 μM of $\text{Si}(\text{OH})_4$, and 74.70 μM of NO_3^- , respectively, with an average $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratio of 16.91 (Figure 31; Table 5). Nutrient samples along the south shore of Oahu were comprised of nearshore groundwater vents (salinity < 10) and coastal water (salinity > 10 in Wailupe and Black Point, salinity > 4 in the Ala Wai Canal). The average nutrient concentrations along the coastline of the south shore of Oahu were 0.96 μM of PO_4^{3-} , 265.45 μM of $\text{Si}(\text{OH})_4$, and 52.94 μM of NO_3^- (Figure 14; Table 2-4), with an average $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratio of 59.66 (Figure 28-30; Table 2-4). Nutrient samples within Honokohau Harbor were comprised of surface and subsurface coastal water samples (salinity > 15). The average concentrations of PO_4^{3-} , $\text{Si}(\text{OH})_4$, and NO_3^- during June coastal sampling within Honokohau Harbor were 2.86 μM of PO_4^{3-} , 211.74 μM of $\text{Si}(\text{OH})_4$, and 27.21 μM of NO_3^- , with an average $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratio of 10.85 (Table 5; Figure 14) On the other hand, nutrient concentrations within the harbor during September averaged 2.04 μM PO_4^{3-} , 185.65 μM $\text{Si}(\text{OH})_4$, and 23.52 μM NO_3^- (Figure 22; Table 6), with an average $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratio of 11.49 (Figure 32; Table 6).

Well Name	Well Number	Latitude	Longitude	Salinity	PO ₄ ³⁻ (μM)	Si(OH) ₄ (μM)	NO ₃ ⁻ (μM)	NO ₂ ⁻ (μM)	NH ₄ ⁺ (μM)	DIN/DIP
Waialae Golf Course	1646-01	21.27582	-157.77922		1.73	723.46	56.53	0.00	0.11	32.65
Aina Koa Well 1	1749-10	21.28365	-157.77857	0.14	1.42	654.85	34.70	0.00	0.03	41.35
Aina Koa Well 2	1746-04	21.29137	-157.77598	0.17	2.30	663.02	54.28	0.00	0.08	23.65
Palolo Well	1847-02	21.30703	-157.89117	0.21	1.69	717.14	53.02	0.00	0.00	24.49
Wilder Well	1849-14	21.30038	-157.82667	0.22	1.14	593.33	88.07	0.00	0.00	77.13
Kapalama Well	2052-13	21.33892	-157.86488	0.24	1.44	718.45	44.56	0.00	0.01	31.32
Moanalua Well	2153-11	21.35252	-157.89580	0.32	1.90	760.88	78.50	0.00	0.02	30.85

Table 1: Specific nutrient concentrations (μM) of upland wells along the south shore of Oahu, which were collected during the October 2010 study period. DIN/DIP ratios are representative of (NO₃⁻ + NH₄⁺) / PO₄³⁻ ratios

Sample Name	Sample Number	Latitude	Longitude	Date	Salinity	Total P (μM)	Total N (μM)	PO_4^{3-} (μM)	$\text{Si}(\text{OH})_4$ (μM)	NO_3^- (μM)	NO_2^- (μM)	NH_4^+ (μM)	DIN/DIP
Wailupe 1	W-1	21.27640	-157.76112	4/9/2010	4.78	2.06	57.98	1.30	631.98	31.17	0.56	0.80	24.60
Wailupe 2	W-2	21.27614	-157.76155	4/9/2010	15.02	2.33	63.21	1.23	186.31	4.94	0.09	0.02	4.04
Wailupe 3	W-3	21.27602	-157.76208	4/9/2010	8.45	1.60	13.19	1.59	336.30	31.00	0.12	0.06	19.53
Wailupe Boil 2	W-4	21.27590	-157.76210	4/12/2010	5.96	3.26	131.59	0.94	657.72	37.20	0.12	0.02	39.62
Wailupe Boil 3	W-5	21.27589	-157.76212	4/12/2010	5.90	3.33	136.60	1.27	671.50	52.37	0.12	0.08	41.22
Wailupe PP1 L	W-7	21.27543	-157.76248	5/30/2010	25.82	1.09	23.26	0.56	210.43	15.71	0.14	0.98	30.02
Wailupe PP2 L	W-8	21.28592	-157.79432	5/30/2010	34.98	0.52	10.35	0.23	21.57	0.48	0.10	0.52	4.28
Wailupe PP3 L	W-9	21.27545	-157.76247	5/30/2010	25.98	1.41	37.79	0.74	202.52	11.77	0.17	5.41	23.32
Wailupe PP4 L	W-10	21.27530	-157.76245	5/30/2010	33.51	1.09	18.54	0.09	42.46	0.44	0.13	0.74	13.04
Wailupe PP5 L	W-11	21.27520	-157.76240	5/30/2010	33.98	0.83	13.83	0.13	25.25	0.28	0.10	0.39	5.17
Wailupe PP1 H	W-12	21.27543	-157.76248	5/30/2010	35.13	0.84	17.92	0.12	7.71	0.08	0.10	0.28	3.02
Wailupe PP2 H	W-13	21.28592	-157.79432	5/30/2010	35.12	0.51	7.50	0.10	7.27	0.07	0.10	0.45	5.54
Wailupe PP3 H	W-14	21.27545	-157.76247	5/30/2010	35.14	0.73	12.96	0.13	7.94	0.03	0.13	0.50	4.41
Wailupe PP4 H	W-15	21.27530	-157.76245	5/30/2010	35.14	0.77	11.41	0.12	8.28	0.04	0.12	0.26	2.47
Wailupe PP5 H	W-18	21.27520	-157.76240	5/30/2010	35.15	0.86	14.74	0.10	6.40	0.02	0.11	0.17	1.92

Table 2: Specific nutrient concentrations (μM) of nearshore groundwater boils, beach, and coastal water samples along Wailupe Beach collected during the April and May 2010 study periods. L and H samples represent samples taken at low and high tide, respectively. DIN/DIP ratios are representative of $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratios

Sample Name	Sample Number	Latitude	Longitude	Date	Salinity	Total P (μM)	Total N (μM)	PO_4^{3-} (μM)	Si(OH)_4 (μM)	NO_3^- (μM)	NO_2^- (μM)	NH_4^+ (μM)	DIN/DIP
Black Point 1	BP-1	21.25933	-157.79039	4/12/2010	6.95	2.96	322.62	2.32	613.55	182.45	0.15	0.00	78.64
Black Point 2	BP-2	21.25914	-157.79060	4/12/2010	4.30	4.15	353.16	2.83	710.97	121.51	0.21	0.06	43.03
Black Point Boil 1	BP-3	21.25898	-157.79063	4/15/2010	8.92	3.54	253.96	2.69	604.79	169.87	0.16	0.06	61.51
Black Point Boil 2	BP-4	21.25887	-157.79062	4/15/2010	28.59	1.88	125.86	1.19	213.03	49.68	0.28	0.20	59.09
Black Point PP-1	BP-5	21.25898	-157.79063	4/15/2010	4.47	4.95	278.02	3.12	698.62	191.99	0.09	0.03	63.23
Black Point PP-2	BP-6	21.25887	-157.79062	4/15/2010	3.24	5.30	277.41	3.46	672.25	204.14	0.14	0.12	41.83
Black Point PP-3	BP-7	21.25881	-157.79067	4/15/2010	28.60	2.10	126.05	1.67	335.66	95.67	0.27	0.29	57.58
Black Point PP-4	BP-8	21.25857	-157.79055	4/15/2010	29.80	1.13	43.62	0.58	130.41	31.73	0.29	0.20	54.78
Black Point PP-5	BP-9	21.25848	-157.79048	4/15/2010	28.79			0.98	200.29	49.59	0.29	0.34	51.14
BP-BOIL 1	BP-10	21.25903	-157.79062	6/1/2010	3.20	5.80	262.03	3.17	615.29	196.97	0.09	0.02	62.19
BP-PP1	BP-11	21.25887	-157.79062	6/1/2010	21.40	2.46	140.27	1.26	301.18	80.12	0.24	1.26	64.82
BP-PP2	BP-12	21.25881	-157.79067	6/1/2010	28.20	2.01	112.84	0.85	190.84	53.00	0.21	0.69	63.07
BP-PP3	BP-13	21.25857	-157.79055	6/1/2010	28.40	1.19	48.30	0.43	95.19	24.57	0.17	0.84	58.80
BP-PP4	BP-14	21.25848	-157.79048	6/1/2010	31.20	1.07	41.12	0.31	77.82	18.27	0.13	0.51	60.58

Table 3: Specific nutrient concentrations (μM) of nearshore groundwater boils and coastal water samples along Black Point collected during the April and June 2010 study periods. DIN/DIP ratios are representative of $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratios

Sample Name	Sample Number	Latitude	Longitude	Date	Salinity	Total P (μM)	Total N (μM)	PO ₄ ³⁻ (μM)	Si(OH) ₄ (μM)	NO ₃ ⁻ (μM)	NO ₂ ⁻ (μM)	NH ₄ ⁺ (μM)	DIN/DIP
AW-PP1	AW-2	21.27571	-157.81847	7/23/2010	32.34	1.81	267.70	0.71	173.04	30.96	0.21	5.95	51.39
AW-T1	AW-3	21.27709	-157.81928	7/23/2010	26.11	1.65	94.28	0.99	189.92	94.99	0.64	5.72	101.48
AW-PP2	AW-4	21.27841	-157.82117	7/23/2010	31.30	1.69	125.75	0.34	146.60	17.51	0.39	4.63	68.78
AW-T2	AW-5	21.27975	-157.82295	7/23/2010	19.95	1.40	55.57	0.88	156.84	45.53	0.46	5.81	57.30
AW-PP3	AW-6	21.28073	-157.82405	7/23/2010	30.49	1.51	128.09	0.52	210.42	9.89	0.30	2.55	28.79
AW-T3	AW-7	21.28277	-157.82628	7/23/2010	4.20	1.69	45.66	0.72	143.88	46.32	0.45	5.18	67.58
AW-T4	AW-8	21.28496	-157.82889	7/23/2010	6.20	1.34	52.49		231.30	52.47	0.52	3.50	
AW-PP4	AW-9	21.28769	-157.83214	7/23/2010	22.33	2.41	130.44	0.53	190.87	14.82	0.37	3.35	34.74
AW-T5	AW-10	21.28930	-157.83430	7/23/2010	9.18	2.22	65.89	0.30	209.17	30.53	0.43	3.78	110.56
AW-PP5	AW-11	21.28837	-157.83733	7/23/2010	21.41	1.87	63.21	0.26	269.26	32.48	0.49	3.08	139.97
AW-T6	AW-12	21.28769	-157.84068	7/23/2010	18.99	2.15	56.65	0.33	167.41	23.17	0.39	2.96	80.68
AW-PP6	AW-13	21.28543	-157.84464	7/23/2010	29.21	1.49	53.03	0.07	228.36	40.09	0.53	3.16	583.15

Table 4: Specific nutrient concentrations (μM) of coastal water samples within the Ala Wai Canal collected during the July 2010 study period. DIN/DIP ratios are representative of (NO₃⁻ + NH₄⁺)/ PO₄³⁻ ratios

Well Name	Well Number	Latitude	Longitude	Salinity	Total P (μM)	Total N (μM)	PO_4^{3-} (μM)	Si(OH)_4 (μM)	NO_3^- (μM)	NO_2^- (μM)	NH_4^+ (μM)	DIN/DIP
Keei A	2753-01	19.45556	-155.89194	0.68	4.55	44.85	4.35	736.38	108.70	0.12	0.29	25.04
Keei C	2653-01	19.44306	-155.88611	0.14	4.83	198.06	3.71	799.67	156.66	0.13	0.00	42.19
Keei D	2753-03	19.46222	-155.88028	0.05	4.36	239.25	5.24	736.37	38.48	0.13	0.00	7.35
Halekii	3155-02	19.51806	-155.91611	0.07	5.28	118.38	4.78	762.19	53.97	0.13	0.00	11.29
Kahaluu Shaft	3557-05	19.58139	-155.95417	0.60	4.83	145.84	4.85	788.07	68.35	0.11	0.00	14.09
Kahaluu -A	3557-01	19.58306	-155.94972	0.29	5.19	148.51	5.08	724.76	62.40	0.10	4.30	13.14
Kahaluu-B	3557-02	19.58167	-155.94972	0.33	5.47	147.84	4.98	749.30	64.21	0.12	0.00	12.89
Kahaluu-C	3557-03	19.58278	-155.94944	0.23	5.62	148.18	4.78	797.10	64.31	0.12	0.00	13.47
Honokohau	4158-02	19.68222	-155.96444	0.22	5.40	149.18	4.50	829.37	61.31	0.12	0.00	13.63
Keahuloa QLT 1	4057-01	19.66525	-155.95806	0.08			4.27	751.87	68.61	0.13	0.01	16.06

Table 5: Specific nutrient concentrations (μM) of upland wells along the Kona Coast of Hawaii collected during the June 2010 study period. DIN/DIP ratios are representative of $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratios

Sample Name	Sample Number	Latitude	Longitude	Date	Salinity	Total P (μM)	Total N (μM)	PO ₄ ³⁻ (μM)	Si(OH) ₄ (μM)	NO ₃ ⁻ (μM)	NO ₂ ⁻ (μM)	NH ₄ ⁺ (μM)	DIN/DIP
HH-T2	HH-3	19.66918	-156.02228	6/19/2010	23.58	2.95	57.35	2.73	324.61	38.79	0.10	0.41	14.36
HH-T2 D	HH-4	19.66920	-156.02245	6/19/2010	30.88	2.49	48.76	2.02	249.17	29.74	0.12	0.38	14.92
HH-T3	HH-5	19.66946	-156.02353	6/19/2010	26.46	2.38	50.13	1.86	260.77	30.32	0.12	0.44	16.51
HH-T4	HH-6	19.66935	-156.02582	6/19/2010	29.37	4.13	44.93	3.93	169.81	24.53	0.12	0.42	6.34
HH-T4 D	HH-7	19.66906	-156.02574	6/19/2010	32.06	2.26	36.64	1.87	138.66	16.06	0.14	0.07	8.64
HH-T5	HH-8	19.66983	-156.02646	6/19/2010	29.92	2.06	38.64	1.53	173.99	19.18	0.12	0.45	12.82
HH-T7	HH-9	19.66895	-156.03065	6/19/2010	34.31	1.00	22.87	0.42	26.07	1.88	0.09	0.20	4.96
HH-PP1	HH-10	19.66927	-156.02105	6/20/2010	18.00	3.27	59.51	3.03	394.05	42.63	0.09	0.79	14.33
HH-PP2	HH-11	19.66900	-156.02210	6/20/2010	22.40	3.42	59.42	3.16	352.70	41.89	0.10	0.22	13.31
HH-PP3	HH-12	19.66907	-156.02428	6/20/2010	25.07	3.54	58.05	3.37	325.57	42.24	0.12	0.34	12.64
HH-PP4	HH-13	19.66907	-156.02430	6/20/2010	26.18	4.79	60.42	4.93	333.32	43.51	0.13	3.68	9.57
HH-PP5	HH-14	19.66853	-156.02547	6/20/2010	25.03	15.49	86.78	16.84	273.89	65.25	0.16	0.61	3.91
HH-D1	HH-21	19.66913	-156.02145	6/20/2010	29.76	1.79	41.94	1.19	134.42	14.56	0.14	1.11	13.11
HH-D2	HH-22	19.66913	-156.02145	6/20/2010	34.57	1.20	25.52	0.32	15.42	0.98	0.08	0.54	4.80
HH2-PP1	HH-24	19.66927	-156.02105	6/22/2010	23.19	3.21	58.16	2.73	400.47	41.70	0.15	0.88	15.60
HH2-PP5	HH-28	19.66927	-156.02658	6/22/2010	28.50	4.55	44.85	3.45	167.94	26.51	0.17	0.51	7.84
HH3-PP1	HH-29	19.66925	-156.02118	9/23/2010	23.49	3.00	59.42	2.73	332.92	39.67	0.16	0.53	14.74
HH3-PP2	HH-30	19.66933	-156.02205	9/23/2010	24.19	2.22	53.13	2.34	284.44	36.10	0.13	0.31	15.57

Table 6: Specific nutrient concentrations (μM) of coastal water samples within Honokohau Harbor collected during the June and September 2010 study periods. D samples are representative of samples taken at depth (~1 m below surface). DIN/DIP ratios are representative of (NO₃⁻ + NH₄⁺)/ PO₄³⁻ ratios

Sample Name	Sample Number	Latitude	Longitude	Date	Salinity	Total P (μM)	Total N (μM)	PO ₄ ³⁻ (μM)	Si(OH) ₄ (μM)	NO ₃ ⁻ (μM)	NO ₂ ⁻ (μM)	NH ₄ ⁺ (μM)	DIN/DIP
HH3-PP3	HH-31	19.66933	-156.02352	9/23/2010	27.39	1.81	51.39	1.83	194.48	23.88	0.13	0.27	13.21
HH3-PP4	HH-32	19.66925	-157.44800	9/23/2010	28.71	1.76	40.46	1.71	174.27	20.71	0.15	0.21	12.22
HH3-PP5	HH-33	19.66893	-157.54600	9/23/2010	29.26	4.48	49.73	4.79	144.45	31.78	0.16	0.10	6.66
HH3-Ra1	HH-34	19.66925	-156.02108	9/24/2010	24.23	2.43	50.25	2.12	275.85	32.59	0.12	2.96	16.77
HH3-Ra2	HH-35	19.66925	-156.02108	9/24/2010	31.77	0.94	14.70	0.78	116.94	10.14	0.10	0.28	13.31
HH3-Ra3	HH-36	19.66924	-156.02672	9/24/2010		3.55	32.30	3.59	158.77	26.17	0.09	0.14	7.33
HH3-Ra4	HH-37	19.66924	-156.02672	9/24/2010	35.14	0.50	7.71	0.34	17.30	1.90	0.13	0.03	5.62
HH3-S2	HH-38	19.66913	-156.02150	9/24/2010	21.42	2.55	55.49	2.57	302.13	38.65	0.22	0.24	15.12
HH3-S4	HH-39	19.66918	-156.02215	9/24/2010	24.88	2.05	37.19	2.04	251.73	30.40	0.20	0.12	14.93
HH3-S6	HH-40	19.66927	-156.02315	9/24/2010	26.91	1.83	31.13	1.74	219.96	24.87	0.19	0.10	14.34
HH3-S9	HH-47	19.66920	-156.02487	9/24/2010	28.68	2.28	28.04	2.23	183.05	22.49	0.20	0.10	10.11
HH3-S12	HH-50	19.66930	-156.02712	9/24/2010	31.02	1.60	20.00	1.53	106.52	12.28	0.16	0.18	8.12
HH3-S14	HH-52	19.66828	-156.03033	9/24/2010	34.21	0.48	9.05	0.26	21.93	1.13	0.06	0.00	4.27

Table 6: Honokohau Harbor nutrient samples continued.

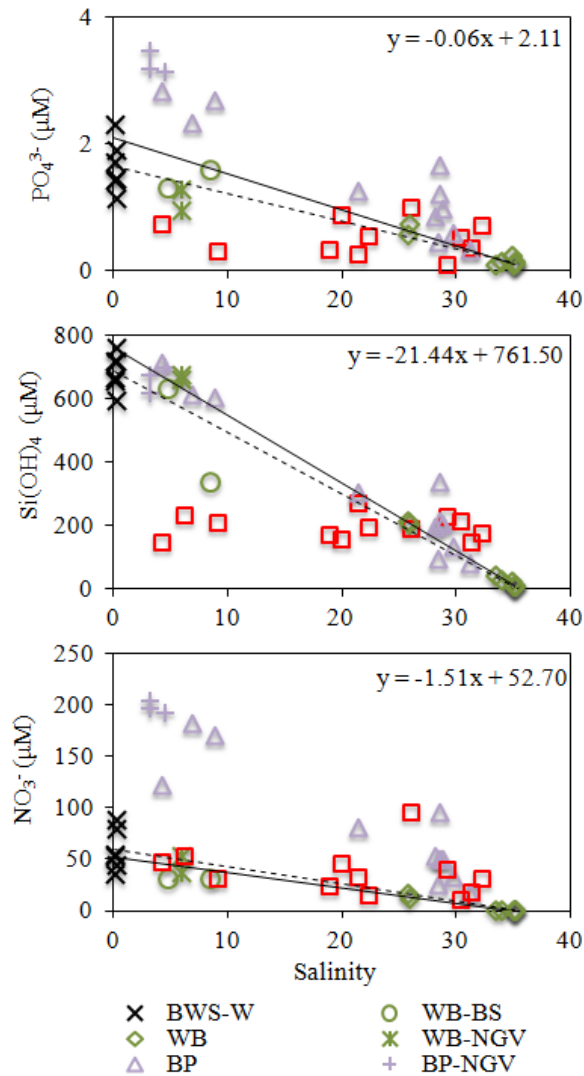


Figure 13: Dissolved nutrient concentrations along the southern shore of Oahu plotted against salinity. Upland groundwater wells samples (BWS-W), Wailupe Beach samples (WB), beach samples along Wailupe Beach samples (WB-BS), nearshore groundwater vents along Wailupe Beach samples (WB-NGV), Black Point samples (BP), nearshore groundwater vents along Black Point samples (BP-NGV), and the Ala Wai Canal samples (AW) are represented by x-marks, dots, diamonds, asterisks, triangles, plus signs, and squares, respectively. Solid lines and equations represent linear regression coefficients made by low nutrient, high salinity samples. Dashed lines represent mixing between the freshwater wells (salinity <1) along the south shore of Oahu and ambient ocean water (salinity >34), which represent the two end-members of our mixing model.

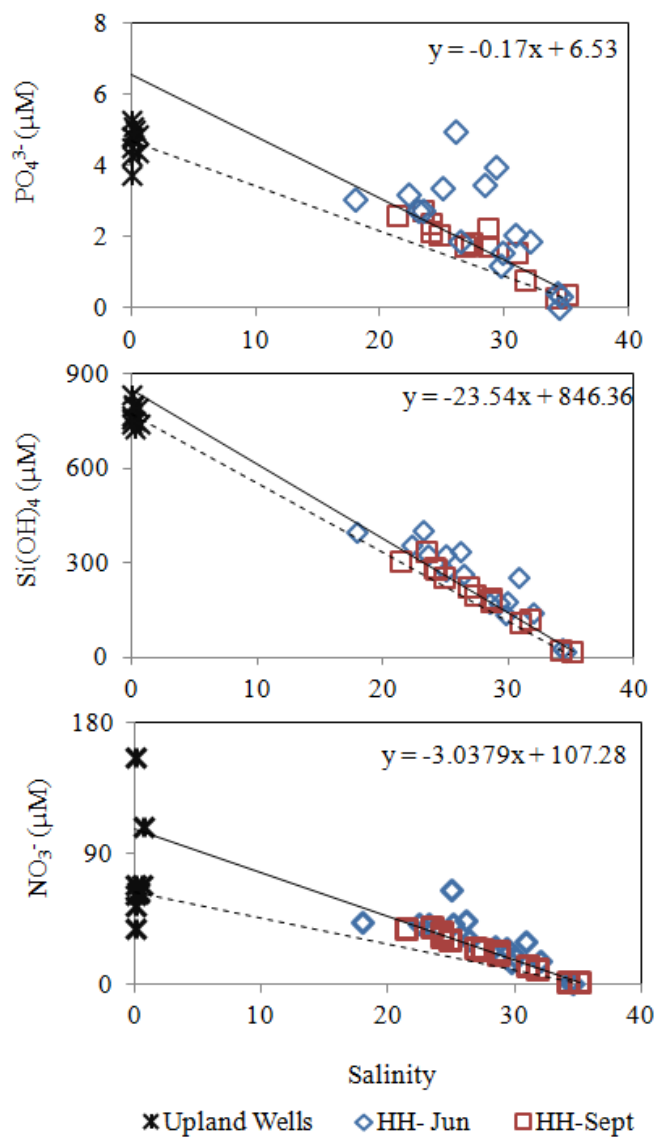


Figure 14: Dissolved nutrient concentrations of freshwater wells from the Kona coast of Hawaii and coastal samples within Honokohau Harbor, Hawaii vs. salinity. Upland wells, June 2010 harbor samples (HH-Jun.) and September 2010 harbor samples (HH-Sept.) are represented by asterisks, diamonds, and squares, respectively. Solid lines and equations represent linear regression coefficients made by low nutrient, high salinity samples. Dashed lines represent mixing between the average nutrient concentration of the freshwater wells and ambient ocean water. Note that the mixing lines were not fit through all data points but only ambient ocean water (salinities > 34) and average upland well nutrient concentrations.

²²²Radon and radon-derived SGD fluxes

²²²Rn concentrations were utilized to quantify the flux of SGD into coastal environments. Rn concentrations of upland groundwater wells along the south shore of Oahu ranged from 60,600-343,308 dpm/ m³, averaging 226,000 dpm/ m³. Along the Kona Coast of Hawaii, Rn concentrations of upland groundwater wells ranged from 1,556-77,819 dpm/m³, averaging 35,700 dpm/ m³. Rn concentrations in surface coastal waters observed at Wailupe Beach were 80-51,480 dpm/ m³ during April 2010 and 160-135,000 dpm/ m³ during May 2010, while Rn concentrations of nearshore groundwater vents observed at Wailupe Beach were 224,000 dpm/ m³ during both study periods (Figure 33-34; Table 18). Within Black Point's coastal zone, observed Rn concentrations were 7,990-320,170 dpm/ m³ during April 2010 and 830-130,440 dpm/ m³ during May 2010, while the Rn concentration observed at nearshore groundwater vents along Black Point were 907,000 dpm/ m³ for both sampling periods (Figure 35-36; Table 18). The Rn concentration observed within the Ala Wai Canal was 9,000-19,000 dpm/ m³ (Figure 37; Table 18). Within the waters of Honokohau Harbor, observed Rn concentrations were 3,000-25,000 dpm/ m³ during June 2010 and 9,000-23,000 dpm/ m³ during September 2010 (Figure 38-39; Table 18). At all study sites, the highest observed ²²²Rn concentrations were associated with ebb tides, while the lowest ²²²Rn concentrations were linked with flood tides (Figure 33-39). This is expected because at ebb tide hydraulic gradient between coastal ocean aquifers and the ocean are the greatest, allowing a greater influx of SGD. Also, as tides increase during flood tides, the groundwater concentration within the coastal zone is diluted.

The derived Rn inventories were corrected for atmospheric losses, Rn supported by dissolved ^{226}Ra in the water column, and mixing losses. Radon addition by diffusion was not accounted for in this study because it is a negligible. The corrected fluxes were then converted to groundwater advection rates by dividing the total corrected Rn flux by the Rn groundwater concentrations. In this study, advection rates of 121cm/d during April 2010 and 241cm/d during May 2010 along Wailupe Beach, 456 cm/d in April 2010 and 108 cm/d in June 2010 along Black Point, 67 cm/d in July 2010 within the Ala Wai Canal, and 54 cm/d in June 2010 and 27 cm/d in September 2010 within Honokohau Harbor were observed. Advection rates for each site, which are listed in Table 7, were extended to the area of SGD occurrence derived from spatial Rn surveys, which is defined as a 5% decrease in the maximum observed Rn concentration (Table 7). This upscaling significantly influenced the final SGD flux, but we felt that the area defined based on observed spatial Rn measurements was the best conservative approach to define the area of SGD occurrence. Along the south shore of Oahu, the average extent of area influenced by SGD was 29,884 m² while Honokohau Harbor, Hawaii's area of influence was 9,500 m² (as adapted from Johnson et al, 2008). The resulting range of the flux of SGD along the south shore of Oahu was 4,534-95,490 m³/d with an average SGD flux of 33,058 m³/d. In Honokohau Harbor, Hawaii, the range of the flux of SGD was 18,907-22,799 m³/d with an average flux of SGD 39,198 m³/d.

The flux of SGD determined by this study represents the flux of total SGD (fresh/brackish/salty), so exact salinities have not been determined for these fluxes. For example, nearshore groundwater vents at Wailupe Beach had a salinity of ~6, while

nearshore groundwater vents at Black Point had a salinity of 3-9. These vents show that the SGD is composed of both fresh groundwater and recirculated seawater. Due to this, these fluxes of SGD cannot be directly compared to freshwater fluxes derived based on hydrogeological models (e.g. Shade 1995; Shade and Nichols, 1996).

Site	Start Date	End Date	Advection Rates (cm/d)	Area (m ²)	SGD Flux (m ³ /d)
Wailupe Beach, Oahu	9 April 2010	12 April 2010	121.00	39,700	48,210
Wailupe Beach, Oahu	29 May 2010	31 May 2010	240.53	39,700	95,490
Black Point, Oahu	12 April 2010	15 April 2010	456.00	1,000	4,534
Black Point, Oahu	31 May 2010	2 June 2010	108.12	1,000	1,082
Ala Wai Canal, Oahu	23 July 2010	24 July 2010	66.51	24,019	15,974
Honokohau Harbor, Hawaii	19 June 2010	22 June 2010	53.65	94,875	22,799
Honokohau Harbor, Hawaii	23 September 2010	25 September 2010	26.91	94,875	18,907

Table 7: The advection rate, area of SGD influence, and SGD flux derived for each sampling period. The SGD flux was derived by multiplying the advection rate of each study site to the corresponding area of SGD influence. The advection rates were quantified via Rn budgets. The area of SGD influence is defined as the area in which the maximum Rn concentration observed decreases by 5%. See Appendix C for details of the calculations.

Groundwater-derived nutrient fluxes into the coastal areas

In order to quantify nutrient inputs from SGD, the radon-derived groundwater fluxes and upland well nutrient concentrations or those measured in nearshore groundwater vents were multiplied by the radon-derived SGD flux, which is shown in Figure 15. Within Wailupe Beach (Figure 13; Table 2) and Honokohau Harbor (Figure 14; Table 5), a conservative relationship was found between nutrient concentration and salinity. The conservative relationship between upland wells and coastal waters was previously identified along the Kona Coast by Knee et al. (2008). Due to conservative mixing, it is assumed there is little biogeochemical interactions along groundwater flow paths within the aquifers, making the upland wells a good representative groundwater endmember. Thus, the nutrient flux to Wailupe Beach, the Ala Wai Canal, and Honokohau Harbor were estimated by multiplying flux of SGD to the average nutrient concentration of upland wells. Within Black Point, nutrient concentrations of submarine groundwater vents (located < 3 m offshore) were three times more concentrated than nutrient concentrations of upland freshwater wells sampled along the south shore of Oahu (Figure 13). Therefore, it cannot be assumed that the sampled upland wells are the best representative groundwater end-member for Black Point. It is possible that groundwater exiting at Black Point has different flow-paths leading through volcanic ash and lava flows (Sterns, 1939; Sterns, 1940) and that nutrient additions occur along groundwater flow paths within the aquifer. However, because Rn is also elevated with respect to upland wells, the former scenario is more probable. Thus, nutrient fluxes within Black Point were estimated by multiplying the flux of SGD by nutrient concentrations of

nearshore groundwater vents. For simplicity, in all other nutrient flux calculations it is assumed that the SGD flux consists of only fresh water, which may not be the case.

Along the south shore of Oahu, average nutrient fluxes were 346 mol/d PO_4^{3-} , 83,500 mol/d Si(OH)_4 , and 19,514 mol/d NO_3^- . The nutrient fluxes for Honokohau Harbor were 182 mol/d PO_4^{3-} , 30,085 mol/d Si(OH)_4 , and 3,996 mol/d NO_3^- .

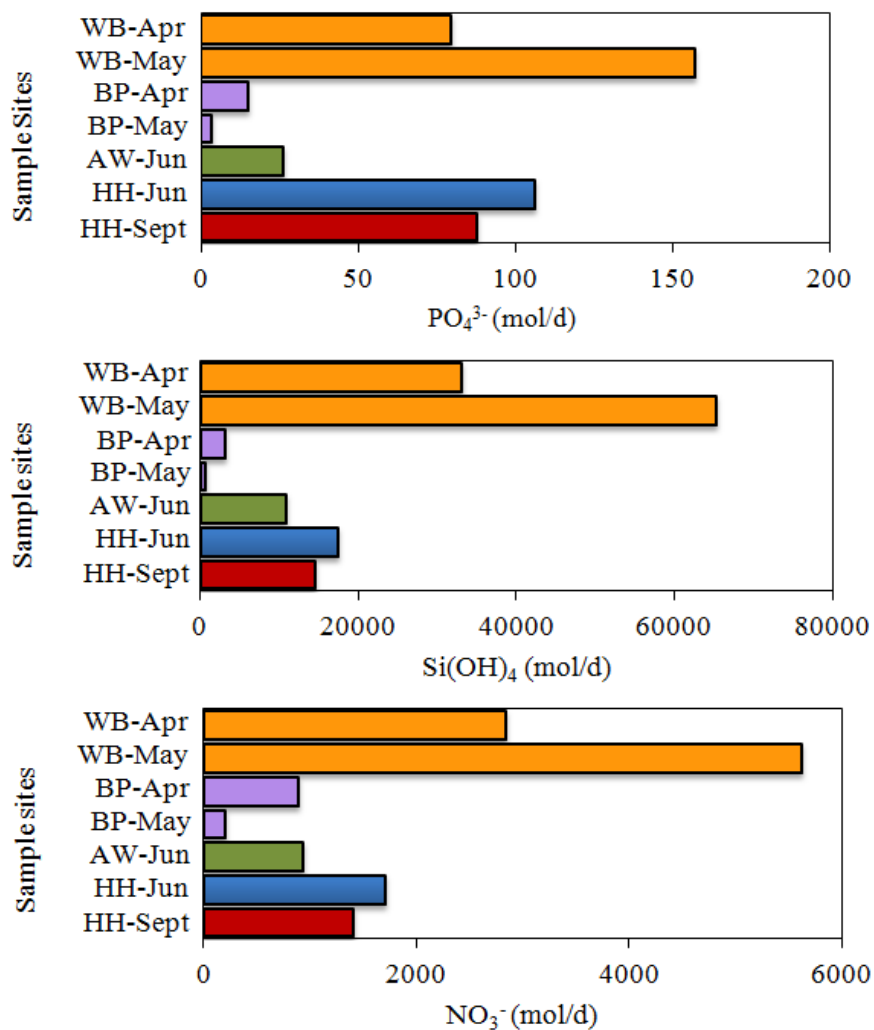


Figure 15: The SGD-derived nutrient fluxes (a product of nutrient concentrations and SGD flux) were defined for each area. Study sites are abbreviated to WB-Apr, WB-May, BP-Apr, BP-May, AW-Jun, HH-Jun, and HH-Sept which represent the Wailupe Beach April 2010 study, Wailupe Beach May 2010 study, Black Point April 2010 study, Black Point May 2010 study, the Ala Wai Canal 2010 study, Honokohau Harbor June 2010 study, and Honokohau Harbor September 2010 study

Coastal radium concentrations and apparent radium ages

We approximated coastal component residence times by apparent Ra ages, which represents the age of any conservative component traveling within that same water mass as the Ra isotopes. Ra samples were collected from upland wells, nearshore groundwater outcrops and within the nearshore coastal zone. The derived ^{224}Ra activities were plotted against the corresponding ^{223}Ra activities. As identified by Kelly and Moran (2002) the slope of ^{224}Ra vs. ^{223}Ra can be utilized as the best $^{224}\text{Ra}/^{223}\text{Ra}$ ratio due to the high correlation between the ^{224}Ra and ^{223}Ra activities (Figure 16-19). In order to define the residence time of each study area, the $^{224}\text{Ra}/^{223}\text{Ra}$ ratios were applied to the residence time equation used in Dulaiova and Burnett (2008).

To define the residence time the Ra ratios derived from upland wells and nearshore groundwater vents represent the original Ra ratios and the Ra ratios derived from the coastal zone represents the observed Ra ratios. The average Ra activities measured in water samples from upland wells along the south shore of Oahu were 0.20 dpm/m³ (range of 0-0.55 dpm/m³) for ^{223}Ra and 2.85 dpm/m³ (range of 1.04-4.29 dpm/m³) for ^{224}Ra (Table 19), but the data were too scattered to derive one best $^{224}\text{Ra}/^{223}\text{Ra}$ ratio. We instead thus derived the representative groundwater initial ratio by bracketing the observed data using the lower and upper $^{224}\text{Ra}/^{223}\text{Ra}$ ratios so all residence time estimates represent a range of most probable ages (Figure 16a, Figure 18a). The representative groundwater initial ratio was identified to be 3.2-10.3 for the south shore of Oahu. At Black Point, nearshore groundwater vents were utilized to define the initial

ratio. The nearshore groundwater vents along Black Point better represent the initial Ra ratio than the upland wells due to the ~60-fold enrichment in Rn concentrations and 2-3 fold nutrient enrichment observed in the groundwater vents within Black Point compared to upland wells. The average ^{223}Ra activities of the nearshore groundwater vents within the coastal zone of Black Point were 3.81 (range of 0.63-7.00 dpm/m³) during April and 7.83 dpm/m³ (range of 6.53-9.14 dpm/m³) during June, while average ^{224}Ra activities of 14.25 (range of 4.88-23.62 dpm/m³) during April and 7.83 (range of 26.26-45.23 dpm/m³) during June were observed (Table 21). The derived $^{224}\text{Ra}/^{223}\text{Ra}$ ratio was 3.4-3.8 during April and 4.6-5.0 during June. The representative groundwater $^{224}\text{Ra}/^{223}\text{Ra}$ ratios were 3.41 for the April sampling period and 4.64 for the June sampling period (Figure 17a). Within the coastal zone of Wailupe Beach, ^{223}Ra activities ranged between 0.58-80.76 dpm/m³ during April and 2.44-59.05 dpm/m³ during May. The ^{224}Ra activities observed within Wailupe Beach ranged between 10.65-68.63 dpm/m³ during April and 11.42-68.63 dpm/m³ during May (Table 20). However, the nearshore groundwater vents along Wailupe were depleted in ^{224}Ra relative to ^{223}Ra (<1 $^{224}\text{Ra}/^{223}\text{Ra}$), while coastal samples were enriched in ^{224}Ra relative to ^{223}Ra (>1 $^{224}\text{Ra}/^{223}\text{Ra}$). Along the Kona Coast, average observed ^{223}Ra activities ranged between 0-67.73 dpm/m³, while ^{224}Ra activities ranged between 0-68.89dpm/m³ (Table 23). The Ra activities of the Kona upland wells aligned along a linear trend, which allowed for one best $^{224}\text{Ra}/^{223}\text{Ra}$ ratio to be derived (Figure 19). The derived representative groundwater initial ratio was 10.36 (± 0.18). In Wailupe Beach, the prevailing coastal seepage signal had a presumably basaltic Ra ratio of less than 1, while the nearshore groundwater vents had a Ra ratio of greater than 1.

Due to the coastal seepage's Ra signal overwhelming the nearshore groundwater vents' Ra signal, the nearshore groundwater vents were not used for coastal residence time calculations. We therefore used the radium ratio range derived from the upland wells as initial Ra concentrations to account for the original Ra ratio. At Black Point, the observed ^{223}Ra activities ranged between 0.63-16.06 dpm/m³ in April and 2.65-9.14 dpm/m³ in June. The ^{224}Ra activities monitored along Black Point ranged between 4.88-37.41 dpm/m³ during April 2010 and 10.50-45.23 dpm/m³ during June 2010 (Table 21). Within the waters of the Ala Wai Canal, observed ^{223}Ra activities ranged between 11.14-48.87 dpm/m³ during July 2010, while the observed ^{224}Ra activities ranged between 26.68-137.46 dpm/m³ (Table 22). The ^{224}Ra vs. ^{223}Ra was well correlated indicating one characteristic Ra ratio for the Ala Wai Canal (Figure 18b). Within the waters of Honokohau Harbor, ^{223}Ra activities ranged between 2.69-35.84 dpm/m³ during June 2010 and 2.35-32.82 dpm/m³ during September 2010 (Table 24). Like south shore Oahu, the coastal samples within Honokohau Harbor aligned along a linear line when ^{224}Ra was plotted against ^{223}Ra , which indicated one characteristic ratio for each sampling period (Figure 19).

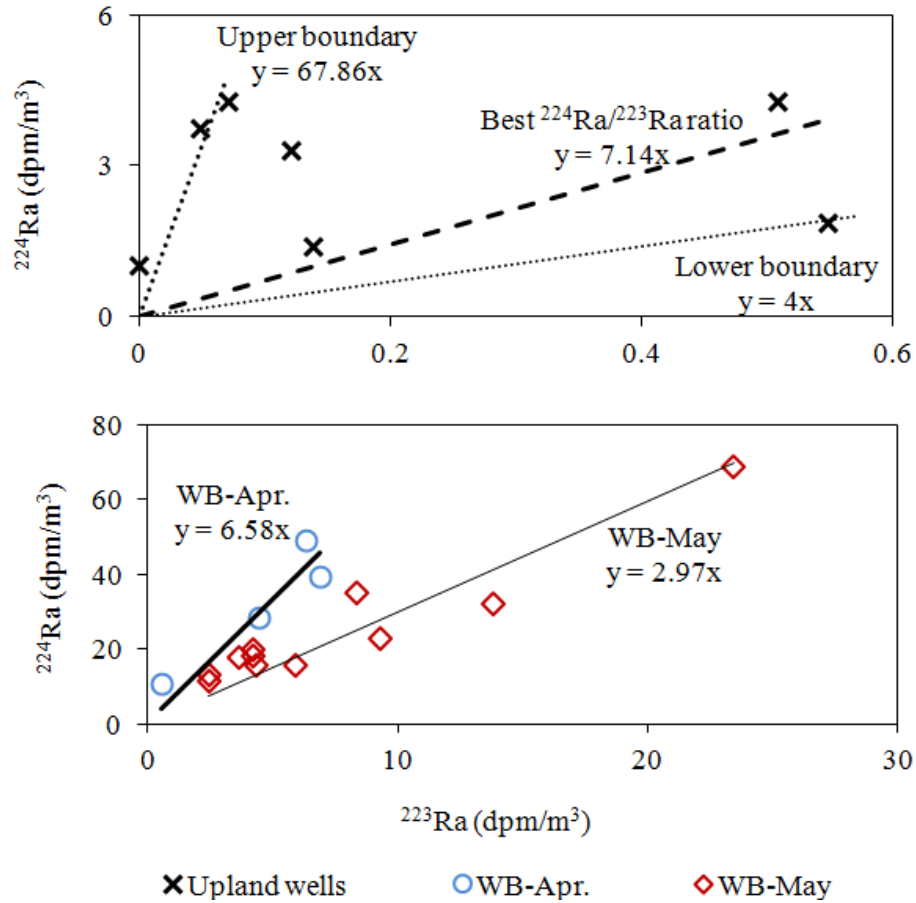


Figure 16: ^{224}Ra vs. ^{223}Ra activities measured in water samples from upland wells located in south shore Oahu (A) and coastal samples from Wailupe, Oahu (B). Upland wells, April 2010 Wailupe Beach coastal samples (WB-Apr.), and May 2010 Wailupe Beach coastal samples (WB-May) are represented by x-marks, dots, and diamonds, respectively. Upland well samples were bracketed by a lower boundary (thin dotted line) and an upper boundary (thick dotted line) to assess the best $^{224}\text{Ra}/^{223}\text{Ra}$ ratio, which is represented by a thick dashed line. Linear trends for WB-Apr. and WB-May are represented by a thick solid line and thin solid line, respectively. $^{224}\text{Ra}/^{223}\text{Ra}$ ratios (slopes) were derived from the linear trends and were utilized to define the residence time of SGD-derived Ra in Wailupe Beach during the April 2010 and May 2010 study periods.

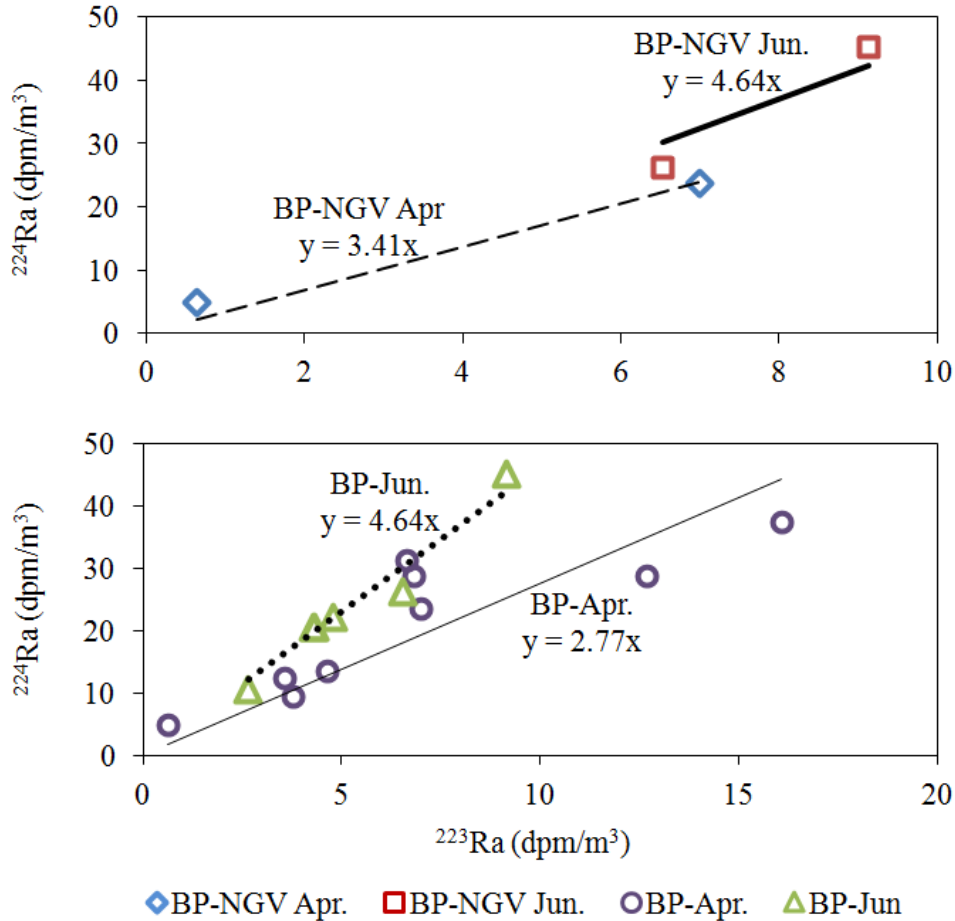


Figure 17: ^{224}Ra vs. ^{223}Ra activities measured in water samples from nearshore groundwater vents along Black Point (A) and coastal samples along Black Point (B). April 2010 nearshore groundwater vents samples (BP-NGV Apr.), June 2010 nearshore groundwater vents' samples (BP-NGV Jun.), April 2010 coastal samples (BP-Apr.), and June 2010 coastal samples (BP-Jun.) are represented by diamonds, squares, dots, and triangles, respectively. Linear trends for BP-NGV Apr., BP-NGV Jun., BP-Apr., and BP-Jun. are represented with a dashed line, a thick solid line, a thin solid line, and a dotted line, respectively. The slopes of the linear trends were utilized to define the residence time of Black Point during April and June 2010.

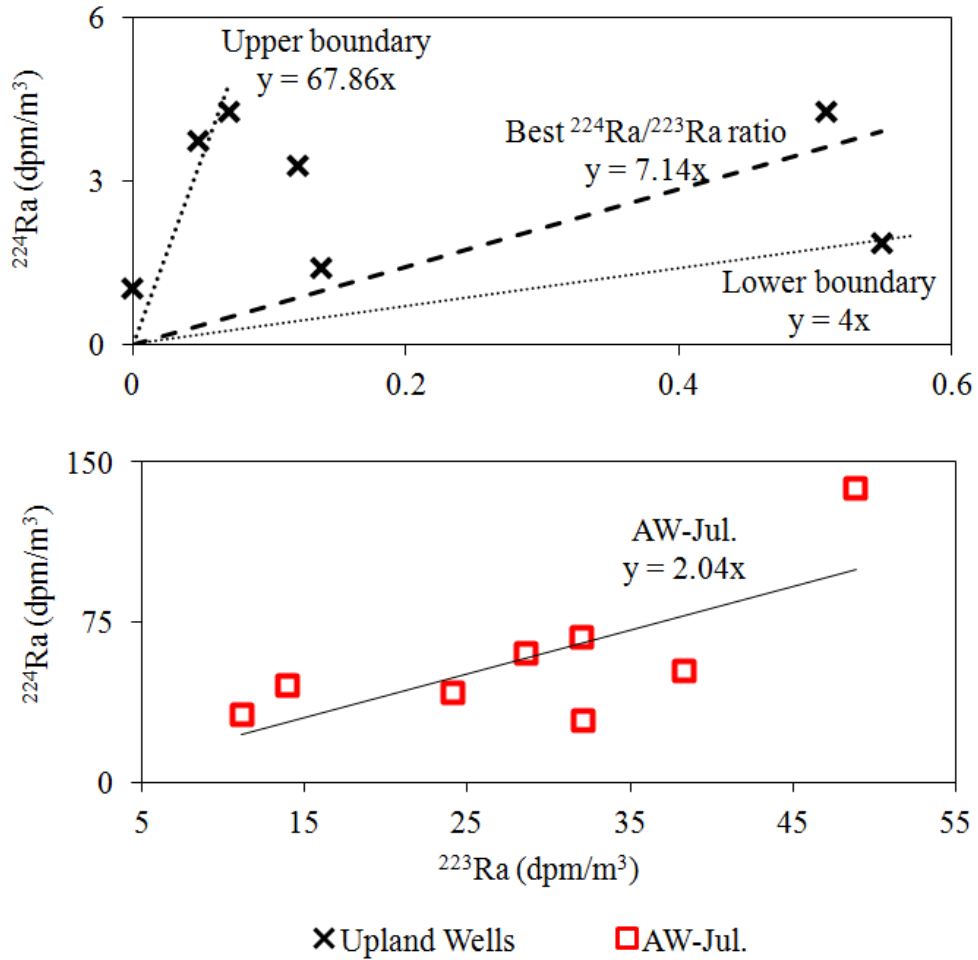


Figure 18: ^{224}Ra vs. ^{223}Ra activities measured in water samples from upland wells located in south shore Oahu (A) and coastal samples from the Ala Wai Canal (B). The upland wells and Ala Wai Canal samples are represented by x-marks and squares, respectively. Upland well samples were bracketed by upper (thick dotted line) and lower boundaries (thin dotted line) to enable the best $^{224}\text{Ra}/^{223}\text{Ra}$ ratio to be assessed, which is represented by the dashed line. The Ala Wai Canal is well mixed, which causes the scatter observed in the July 2010 Ra samples. The slopes of the linear trends were utilized to define the residence time of the Ala Wai Canal during July 2010.

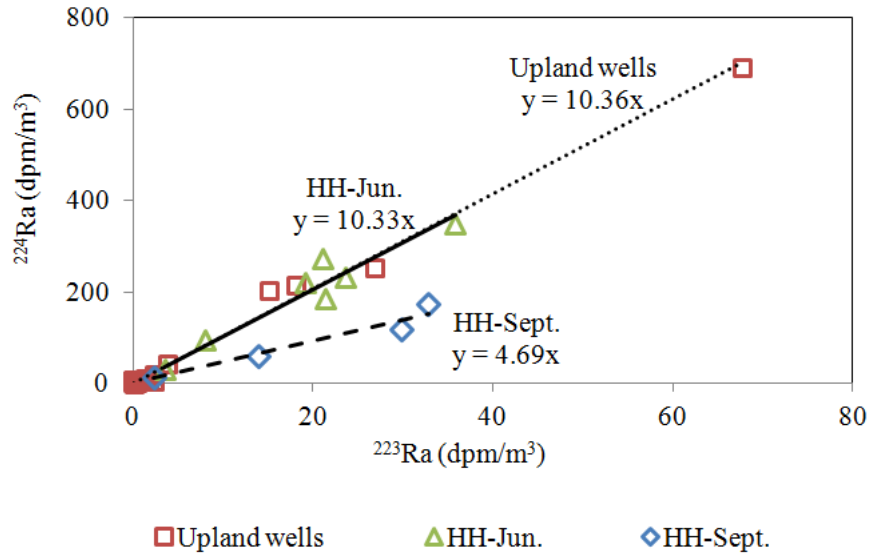


Figure 19: ^{224}Ra vs. ^{223}Ra activities measured in water samples from Kona upland wells and Honokohau Harbor, Hawaii. Kona upland well radium samples, June 2010 Honokohau Harbor radium samples (HH-Jun), and September 2010 Honokohau Harbor radium samples (HH-Sept) are represented by squares, triangles, and diamonds, respectively. Linear trends for the upland wells, HH-Jun, and HH-Sept are represented by a solid line, dotted line, and dashed line, respectively. The slopes of the linear trends represent the best Ra ratios, which were utilized to define the residence time of the SGD-derived Ra within the main harbor channel.

Coastal radium-derived residence time

Since radium is introduced to the coastal zone exclusively by SGD in all our sites except Ala Wai, apparent radium age represents the residence time of any conservative groundwater derived component and in addition the residence time of the groundwater plume itself. Groundwater-derived components residence times (Table 25) approximated by apparent radium ages derived from the $^{224}\text{Ra}/^{223}\text{Ra}$ ratios (e.g. Kelly and Moran, 2003) for both the south shore of Oahu and Honokohau Harbor were spatially and temporally variable, which is shown in Figure 20. For Oahu, the residence times of SGD-derived components varied from 1 to 13 days, the shortest observed at Black Point in April 2010 (0.75 days), while the longest residence time was observed at the Ala Wai Canal in July 2010 (10-13 days). Within Honokohau Harbor the residence times during the 2 sampling campaigns were 0.5 day and 6 days in June 2010 and September 2010 respectively.

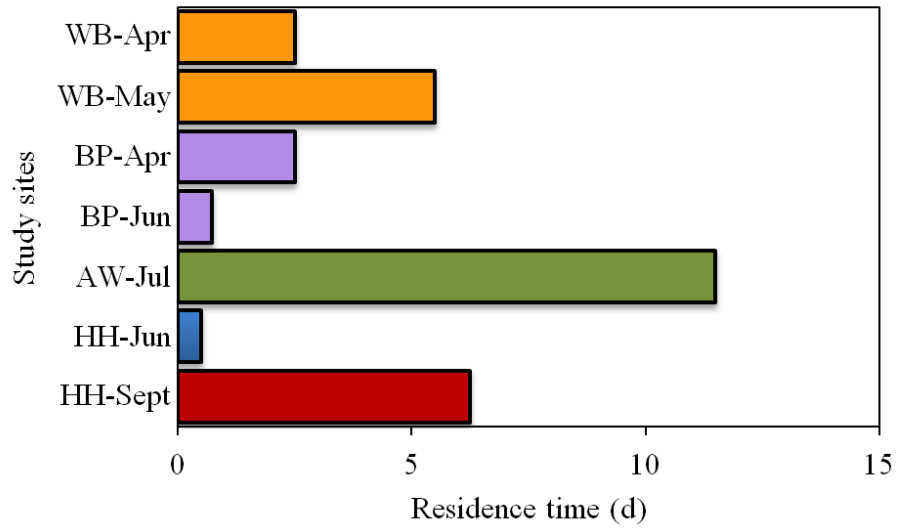
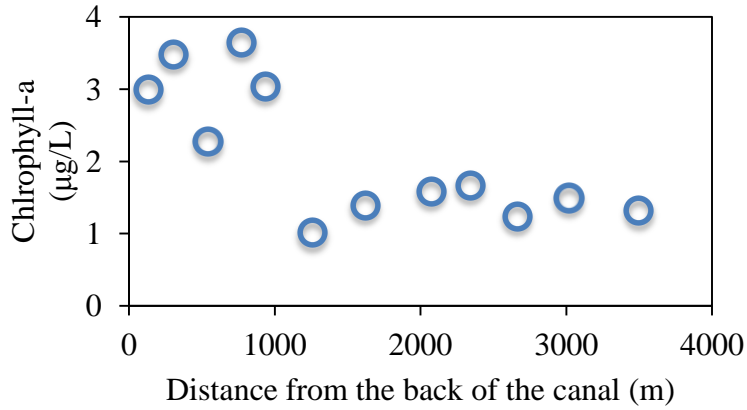


Figure 20: Radium-derived residence times observed during the 2010 study period with study sites shown on the y-axis. Study sites are abbreviated to WB-Apr, WB-May, BP-Apr, BP-Jun, AW-Jul, HH-Jun, and HH-Sept which represent the Wailupe Beach April 2010 study, Wailupe Beach May 2010 study, Black Point April 2010 study, Black Point May 2010 study, the Ala Wai Canal 2010 study, Honokohau Harbor June 2010 study, and Honokohau Harbor September 2010 study.

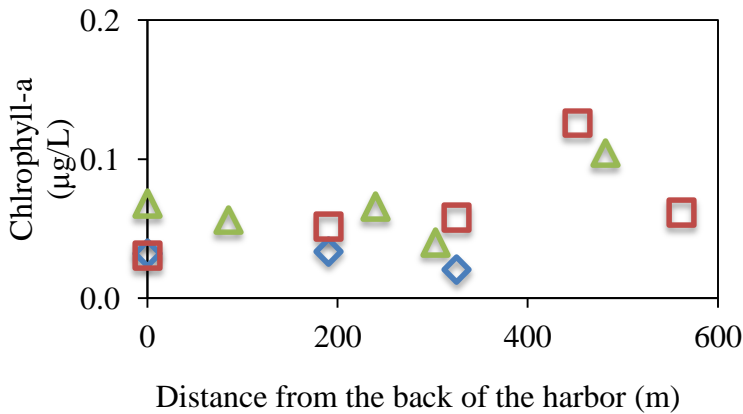
Chlorophyll-a of marine phytoplankton in the surface of the water column

Chlorophyll-a concentration were quantified for the Ala Wai Canal and Honokohau Harbor in order to compare the chlorophyll-a standing stock at the two embayments. The resulting chlorophyll-a concentrations of the Ala Wai Canal and Honokohau Harbor are shown in Figure 21 and Figure 22, respectively. Chlorophyll-a concentrations within the Ala Wai Canal ranged between 1.01-3.65 $\mu\text{g/L}$ (Table 26), with highest values found within ~1000 m distance from the back of the canal. Chlorophyll-a concentration decreased to 1.3 $\mu\text{g/L}$ at ~1257 m distance from the back of the canal (Figure 21). Low chlorophyll concentrations ($>1.7 \mu\text{g/L}$) were observed between ~1257 m distance from the back of the canal and the mouth of the canal. These results imply that relatively elevated standing stocks of marine phytoplankton inhabit the more saline surface waters that occur near the back of the Ala Wai Canal, behind the Manoa-Palolo Steam input and the canal's sedimentary sill (Figure 6 and 11). In contrast, the chlorophyll-a concentrations observed in Honokohau Harbor during the 2010 study period were near zero with the harbor's average chlorophyll-a concentration (0.06 $\mu\text{g/L}$) being 36 times less than the Ala Wai Canal's average chlorophyll-a concentration (2.10 $\mu\text{g/L}$). In the harbor, chlorophyll-a concentrations ranged from 0.02-0.13 $\mu\text{g/L}$ (Figure 22; Table 27). The maximum observed chlorophyll a concentrations (~0.11 $\mu\text{g/L}$) were found outside the main harbor channel. Within the main harbor channel no distinct trends can be identified when chlorophyll a concentrations were compared to distance from the back wall of the harbor.



○ 23 July 2010

Figure 21: Chlorophyll-a concentrations observed in the Ala Wai Canal during the July 2010 study period. Maximum surface water chlorophyll-a concentrations were measured from the backmost, landlocked portion of the Ala Wai Canal, while the lowest observed chlorophyll-a concentrations were observed at the input of the Manoa-Palolo Stream.



◇ 20 June 2010 □ 22 June 2010
 △ 23 September 2010

Figure 22: Surface water chlorophyll-a concentrations within Honokohau Harbor during the 2010 study period. The chlorophyll-a concentrations observed along the main harbor channel were near-zero. Relative to the Ala Wai canal, the average chlorophyll-a concentration of Honokohau Harbor was 36 times less than the chlorophyll-a of the Ala Wai Canal.

Particulate organic carbon isotope compositions of coastal water

The carbon isotopic composition of POC measured for surface water samples within the Ala Wai Canal, Oahu and Honokohau Harbor, Hawaii are shown in Table 30 and Table 31, respectively. Within the Ala Wai Canal, the $\delta^{13}\text{C}$ values for unincubated (natural abundance) samples ranged from -24.0 to -21.1‰, while those for incubated samples ranged from -12.0 to 4.4‰ corresponding to a ^{13}C enrichments of 12.0 to 27.3‰. In the Ala Wai Canal, the largest ^{13}C enrichment occurred in samples incubated at the most seaward site. In Honokohau Harbor, the isotopic composition measured in the harbor differed between 20 June 2010 and 22 June 2010. During the 20 June 2010 study, the $\delta^{13}\text{C}$ values for incubated samples ranged from 1.9 to 4.3‰ while during the 22 June 2010 study the $\delta^{13}\text{C}$ for incubated samples ranged from 1.2 to 7.2‰.

Photosynthetic carbon production of phytoplankton in the surface of coastal waters

Photosynthetic carbon production rates were calculated for the Ala Wai Canal (Table 28) and Honokohau Harbor (Table 29). The calculated photosynthetic carbon production rates for the July 2010 study within the Ala Wai ranged between 0.92-1.95 $\mu\text{g/L/h}$. The lowest photosynthetic carbon production rates were observed at sites of freshwater inputs (SGD and stream) (Figure 23). Within Honokohau Harbor, the photosynthetic carbon production rates varied between 0.04-0.11 and 0.04-3.98 $\mu\text{g/L/h}$ on 20 June 2010 and 22 June 2010 respectively. Like the Ala Wai Canal, no correlation was found between photosynthetic carbon production and salinity. On the other hand, an

exponential decrease in photosynthetic carbon production is apparent along the main axis of the harbor (Figure 24).

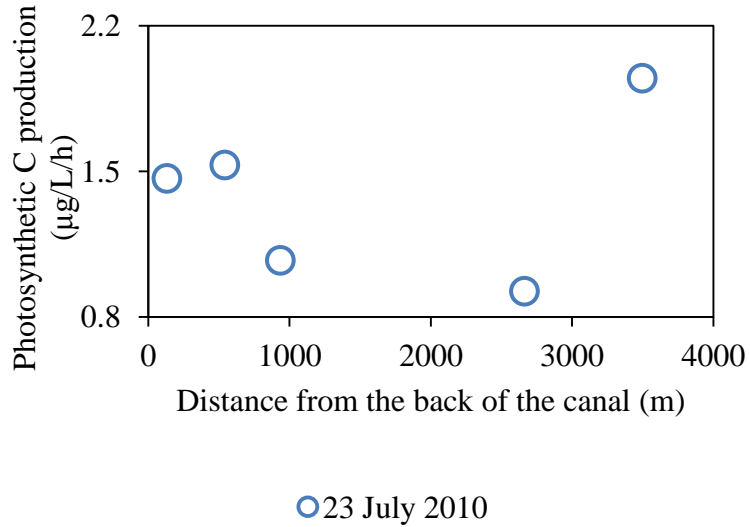


Figure 23: Results from surface water photosynthetic C production rate calculations for the Ala Wai Canal during the July 2010 study period. The highest production rates were quantified near the mouth of the Ala Wai Canal, while the lowest production rates were quantified at sites of freshwater input.

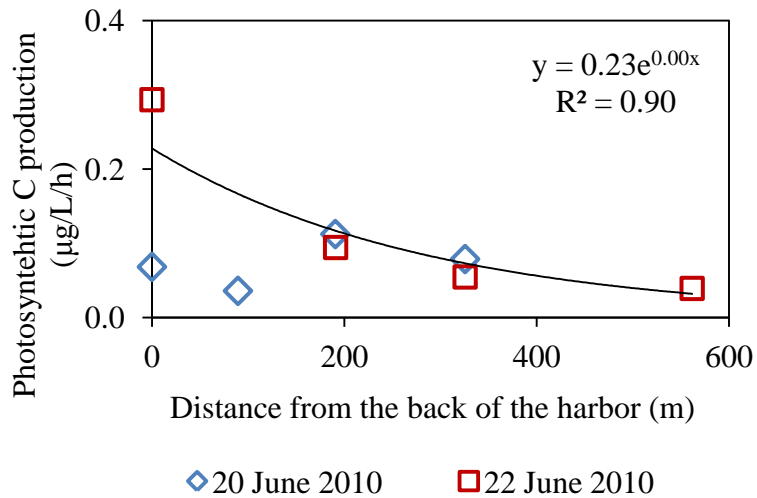


Figure 24: Results from surface water photosynthetic C production rate calculations for Honokohau Harbor for the June 2010 and September 2010 study periods. The exponential line includes 6 of the 8 production rates, excluding the production rates quantified within 200 m distance of the back wall of the harbor during June 2010. The equation of the line corresponds to the exponential line.

Phosphorus and nitrogen uptake by phytoplankton in the surface of coastal water

The phosphorus (P) and nitrogen (N) uptake rates by phytoplankton were quantified for the Ala Wai Canal and Honokohau Harbor, which are shown in Table 8 and Table 9, respectively. In the Ala Wai Canal, P and N uptake by phytoplankton ranged from 0.32 to 0.68 mol/d P and 11.48 to 24.22 mol/d N, respectively (Table 32). During both study periods within Honokohau Harbor, P and N uptake by phytoplankton ranged from range from 0.03 to 0.23 mol/d P and 1.00 to 8.16 mol/d N, respectively (Table 33). Average nutrient uptake rates by phytoplankton in the Ala Wai canal were 0.49 mol/d P and 17 mol/d N, while phytoplankton within the surface of the water column in Honokohau Harbor utilized on average 0.09 mol/d P and 3 mol/d N.

Site	Date	PO ₄ ³⁻ (μM)	SGD flux (m ³ /d)	PO ₄ ³⁻ flux (mol/d)	P Uptake (mol/d)
Ala Wai Canal, Oahu	23 July 2010	2.68	15,974	26	0.49
Honokohau Harbor, Hawaii	20 June 2010	6.27	22,799	106	0.06
	22 June 2010	3.09	22,799	106	0.09

Table 8: Comparison of average PO₄³⁻, SGD flux, PO₄³⁻ flux, and P uptake by phytoplankton within Ala Wai Canal and Honokohau Harbor during the 2010 study period. The P uptake of phytoplankton within the surface water of the Ala Wai Canal was higher 5-8 times higher than the P uptake of phytoplankton within the surface water of Honokohau Harbor. The uptake rate of phytoplankton in both study sites was less than 2% of the nutrient flux observed during the 2010 study period.

Site	Date	NO ₃ ⁻ (μM)	SGD flux (m ³ /d)	NO ₃ ⁻ flux (mol/d)	N Uptake (mol/d)
Ala Wai Canal, Oahu	23 July 2010	30.43	15,974	934	17
Honokohau Harbor, Hawaii	20 June 2010	47.10	22,799	1713	2
	22 June 2010	34.11	22,799	1713	3

Table 9: Comparison of average NO₃⁻, SGD flux, NO₃⁻ flux, and N uptake by phytoplankton within Ala Wai Canal and Honokohau Harbor during the 2010 study period. The N uptake of phytoplankton within the surface water of the Ala Wai Canal was higher 6-9 times higher than the N uptake of phytoplankton within the surface water of Honokohau Harbor. The uptake rate of phytoplankton in both study sites was less than 2% of the nutrient flux observed during the 2010 study period.

Chapter 4: Discussion

Vertical salinity and temperature profile of two partially enclosed embayments

The temperature and salinity in the Ala Wai Canal were influenced by the input of freshwater from both streams and SGD. As identified by the vertical profiles of temperature and salinity of the water column of the canal (taken during a flood tide) shown in Figure 11, a low-density lens of brackish water resides on top of a more saline water mass, resulting in a stratified water column. This finding agrees well with the water column characteristics observed from past studies (Laws et al., 1993). Within the upper 1 m of the water column a dramatic decrease in salinity and a 1°C decrease in temperature occurred at the confluence of the Manoa/Palolo Stream with the Ala Wai canal (~1,260 meters). The higher temperature and water observed before the Manoa/Palolo Stream and associated drop in salinity are in agreement with the findings of Gonzalez (1971). The low salinity signatures continue from the input of the Manoa/Palolo stream to the mouth of the canal due to inputs from the Manoa/Palolo Stream as well as fresh water inputs from the Makiki Stream and SGD.

In Honokohau Harbor a cool and brackish plume of SGD water flowed continuously through Honokohau Harbor (Figure 12). This cool, brackish plume is persistent spatially and temporally (e.g. Bienfang 1980; Johnson et al, 2008). The plume extends past the back wall of the harbor to form a thin (~0.5 m thick), nutrient-rich layer that resides on a warmer and denser saltwater mass, which flows into the harbor from

below. Water circulation in Honokohau mimics that of an estuary, but one where the freshwater component is brackish SGD, rather than river water.

Nutrient characteristics of groundwater and coastal surface water

Conservative mixing between nutrient rich groundwater and nutrient poor ocean water was found along the south shore of Oahu (Figure 13) and in Honokohau Harbor (Figure 14). Dissolved nutrient concentrations measured in the coastal zone of Wailupe Beach generally fell along a conservative mixing line. Brackish groundwater flowing from the nearshore groundwater vents (located < 5 m offshore), however, were enriched in PO_4^{3-} and depleted in $\text{Si}(\text{OH})_4$ relative to this hypothetical mixing line. Although the reason for this deviation was not investigated, it presumably reflects a difference in the source waters and flow paths that those waters take or that different biogeochemical processes occur in different regions of the aquifer. The assumption of variable flow-path for the Wailupe site is reasonable because the presence of groundwater with different chemical compositions was observed. Significantly lower $^{224}\text{Ra}/^{223}\text{Ra}$ activity ratios (~0.64) were found in nearshore groundwater vents compared to offshore coastal water (~5.33). This enrichment in ^{223}Ra activities in comparison to ^{224}Ra may be due to the groundwater conduits through Pleistocene karst caprock that occurs along the south shore of Oahu (Hunt, 1996), which have higher high uranium/thorium ratios than basalt; thus, groundwater entering the coastal zone flowed through different rock types than the groundwater supplied to the nearshore groundwater vents. The $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratios observed along the coastal zone of Wailupe Beach (Table 2) were depleted in comparison

to the upland wells located along the south shore of Oahu (Table 1). During the April 2010 sampling period the $(\text{NO}_3^- + \text{NH}_4^+)$ and PO_4^{3-} of coastal water samples taken along Wailupe Beach were ~2 times less than the $(\text{NO}_3^- + \text{NH}_4^+)$ and PO_4^{3-} of upland wells, while during May 2010 the $(\text{NO}_3^- + \text{NH}_4^+)$ and PO_4^{3-} of coastal water samples were 15 and 7 times less than the $(\text{NO}_3^- + \text{NH}_4^+)$ and PO_4^{3-} of upland wells, respectively. The coastal samples are assumed to be depleted in both the $(\text{NO}_3^- + \text{NH}_4^+)$ and PO_4^{3-} compared to the upland wells because of mixing with nutrient poor ambient ocean water. Greater mixing was observed in May, which is indicated by high salinity (>34) and low nutrient levels (<1 μM $(\text{NO}_3^- + \text{NH}_4^+)$ and PO_4^{3-}).

Dissolved PO_4^{3-} and NO_3^- concentrations measured in the nearshore groundwater vents within Black Point were three times higher than that of the freshwater upland wells (Figure 13). Thus, additional nutrients must be supplied to the aquifer between the upland wells and the coastal zone. In addition, during April 2010 the average $(\text{NO}_3^- + \text{NH}_4^+)$ and PO_4^{3-} concentrations of coastal zone along Black Point (Table 3) were enriched compared to the $(\text{NO}_3^- + \text{NH}_4^+)$ and PO_4^{3-} concentration of upland wells (Table 1), while in June 2010 the average $(\text{NO}_3^- + \text{NH}_4^+)$ concentration of coastal samples (Table 3) were enriched compared to the $(\text{NO}_3^- + \text{NH}_4^+)$ concentration of upland wells (Table 1). The average $(\text{NO}_3^- + \text{NH}_4^+) / \text{PO}_4^{3-}$ ratios (Figure 29; Table 3) observed in the coastal waters was ~double the average $(\text{NO}_3^- + \text{NH}_4^+) / \text{PO}_4^{3-}$ ratio of upland wells (Table 1). The enrichment of $(\text{NO}_3^- + \text{NH}_4^+)$ in the coastal waters compared to upland wells further supports the assumption of secondary nutrient, mostly N inputs entering the aquifer between the upland wells and Black Point's coastal zone. Black Point is a highly populated area and

local leakage from cesspools have been reported (Oki and Brasher, 2003; Hunt 2004). In addition, there is a golf course and some parks within the region. Thus, although we did not analyze the chemistry of cesspools or fertilizers, it seems reasonable to assume that anthropogenic sources are the cause of these the high nutrient concentrations of the Black Point SGD. But this hypothesis requires further investigation, which is beyond the scope of this project.

Overall, inputs of freshwater and tidal mixing caused variations in the nutrient concentrations in the Ala Wai canal during the study period. Dissolved nutrients in the Ala Wai Canal behaved nonconservatively compared to a conservative mixing line established for the south shore of Oahu (Figure 13). In addition, sample sites located within the area impacted by the Manoa/Paolo Stream (as inferred from surface salinities), were depleted in nutrients in comparison to the conservative mixing line established for the south shore of Oahu (Figure 13). When compared to upland wells, the average $(\text{NO}_3^- + \text{NH}_4^+)$ of the Ala Wai Canal water samples (Table 4) were ~1.4 times less than the average $(\text{NO}_3^- + \text{NH}_4^+)$ of upland wells (Table 1), while the average PO_4^{3-} of coastal water (Table 4) was ~3 times less than the average PO_4^{3-} of upland wells (Table 1). The average $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratio observed within the Ala Wai (Figure 29; Table 4) was three times higher than the $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ ratio observed in upland wells (Figure 27; Table 1), due to the large decrease in $(\text{NO}_3^- + \text{NH}_4^+)$ between upland wells and coastal water samples. This decrease is assumed to be due to biogeochemical changes to the nutrients within the water column along the pathway from upland wells to the canal.

In Honokohau Harbor both June 2010 and September 2010 samples were enriched in PO_4^{3-} and NO_3^- compared to the conservative mixing line (Figure 14). The 2-3 times enrichment of PO_4^{3-} and NO_3^- is assumed to be due to nutrient inputs from a wastewater injection site located ~ a mile away from the harbor, which is further validated by $(\text{NO}_3^- + \text{NH}_4^+) / \text{PO}_4^{3-}$ ratios (Table 6) of 3-4 similar to the $(\text{NO}_3^- + \text{NH}_4^+) / \text{PO}_4^{3-}$ ratio of the wastewater injection plant (~3) (Johnson, 2008) being measured in the harbor. However, this assumption is an oversimplification because it assumes no biogeochemical transformation of P or N.

A comparison of the nutrient concentrations measured in Honokohau Harbor in this study with those reported by Johnson et al. (2008) are shown in Figure 25, which suggests that nutrient inputs or uptake in the harbor vary seasonally. The highest nutrient concentrations were observed during February 2006. There was greater variability with the nutrient concentrations during February 2006 causing the samples to be enriched compared to the conservative mixing line. The lowest concentrations were observed during September 2010 and August 2010. In addition, during the two studies the $(\text{NO}_3^- + \text{NH}_4^+) / \text{PO}_4^{3-}$ ratio ranged between 9-12 with the lowest ratio was observed during February 2006 (Johnson et al., 2008).

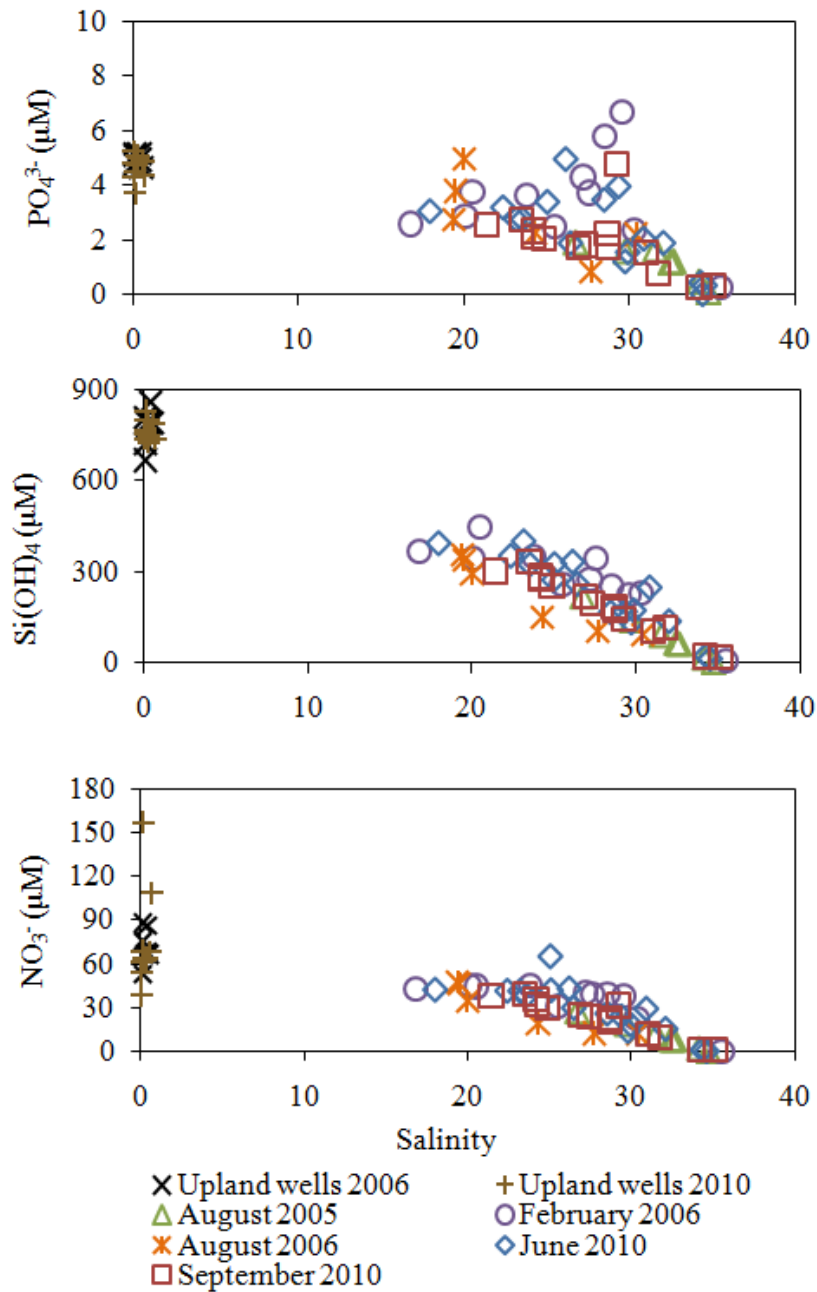


Figure 25: Seasonal and interannual surface water nutrient variability within Honokohau Harbor, Hawaii. Circles, asterisks, diamonds, and squares represent nutrient concentrations from Johnson et al. (2008), upland wells, June 2010 sampling, and September 2010 sampling, respectively.

Radon and radon-derived SGD fluxes in the coastal zone

This work demonstrates that Rn is an applicable tracer in Hawaii and we observed Rn concentrations ranging from 2,000-300,000 dpm/m³ with the highest Rn concentrations being observed within the coastal zone of Black Point (Table 18). The rate of 4 m/d in Black Point is very high indicating significant groundwater movement through the nearshore groundwater vents. However, SGD within Black Point was constrained to an area of 1000 m² where nearshore groundwater vents were observed, which caused the SGD flux in Black Point to be the smallest flux from the sites we investigated (Figure 26). Due to the Wailupe Beach's large area of SGD occurrence, the largest SGD flux (95,490 m³/d) was quantified for the May sampling period.

The observed Rn concentrations and SGD flux observed along the south shore of Oahu and Honokohau Harbor changed during the study periods. Between the April 2010 and May 2010 study periods, the SGD flux within Wailupe Beach showed a ~two-fold increase while Black Point decreased ~four-fold. Differenced in the geology of Wailupe Beach and Black Point play an important role in the differences observed in the flux of Rn in the two areas. Diamondhead lava and marine sediments comprise the geology of Wailupe (Sterns 1939), while Black Point lava and ash comprise the geology of Black Point (Sterns 1939; Sterns 1940). The uranium (U) concentrations of Black Point lava (2 ppm) is 4 times greater than the U concentration of Diamondhead lava (0.5 ppm) (Rubin, K. personal communication). Thus, the higher Rn concentrations were observed in Black Point than Wailupe due to Black Point rocks having higher U concentration than Wailupe

Beach. In Honokohau Harbor, a decrease in flux was observed between June 2010 and September 2010. The decrease in the flux of SGD to the harbor is attributed to a 50% decrease in normal precipitation rates during the study periods (National Oceanic and Atmospheric Administration).

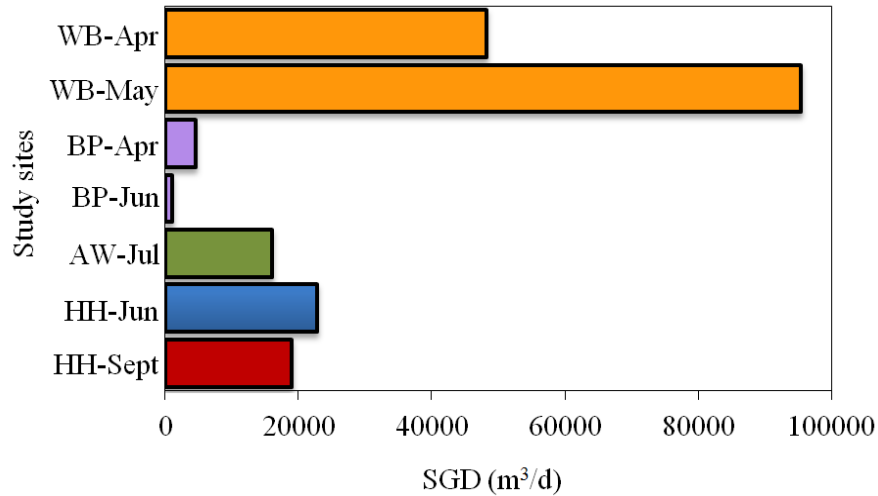


Figure 26: Comparison of derived fluxes of SGD for the 2010 study period. Study sites are abbreviated to WB-Apr, WB-May, BP-Apr, BP-Jun, AW-Jul, HH-Jun, and HH-Sept which represent the Wailupe Beach April 2010 study, Wailupe Beach May 2010 study, Black Point April 2010 study, Black Point May 2010 study, the Ala Wai Canal 2010 study, Honokohau Harbor June 2010 study, and Honokohau Harbor September 2010 study

During this study, the observed fluxes of SGD are classified as “magnitude 2 springs” (discharge of 2,445-244,538 m³/d) on the Floridian Magnitude Scale (Rosenau et al., 1977). The highest flux observed within this study (flux of 95,490 m³/d within Wailupe Beach) was ~21 times less than the flux of SGD observed at Silver Springs (located in Florida), which is called the largest spring in the United States (Rosenau et al., 1977). Examples of other magnitude 2 springs can be identified along Town Cove,

Massachusetts where a 43,000 m³/d flux of SGD was observed (Giblin and Gaines, 1990) as well as along Kahana Bay, Oahu where a 90,000 m³/d flux of SGD was measured (Garrison et al., 2003). Past studies have quantified the flux of SGD to Honokohau Harbor to be ~12,000 m³/d flux of (Knee et al., 2008; Peterson et al., 2008), which qualified Honokohau Harbor as a magnitude 2 spring. However, the flux of SGD observed during the 2010 study period experiences a ~1.5-fold increase compared to the flux measured by Peterson et al (2008). To compare the flux of SGD to Honokohau Harbor observed by the different studies, we applied the water, salt, and Rn mass balances utilized by Peterson et al. (2009) to define the flux of SGD during the June 2010 and September 2010 study periods. Peterson et al.'s (2009) mass balance utilized Rn concentrations and salinities of groundwater endmembers, coastal endmembers, and ocean endmembers in order to define salinity, radon, and volume mass balances; the endmembers utilized by Peterson et al., (2009) and the endmembers utilized by this study are shown in Table 10. The resulting fluxes of total SGD for June 2010 and September 2010 were 13,872 m³/d and 10,811 m³/d, respectively. Thus, the flux of SGD quantified for June 2010 and September 2010 brackets the flux of SGD quantified by Peterson et al., (2009)

Study	GW Rn (dpm/m ³)	GW Salinity	Average Coastal Rn (dpm/m ³)	Average Coastal Salinity	Ocean Rn (dpm/m ³)	Ocean Salinity	Flux of SGD (m ³ /d)
Peterson et al., (2008)	4,980	6.4	10,103	25.56	62	35.46	12,000
This study: HH-June	357,000	0.26	19,462	24.01	64.3	35.46	13,872
This study: HH-Sept	357,000	0.26	14,262	22.96	64.3	35.46	10,811

Table 10: Comparison of the groundwater (GW), coastal, and ocean endmembers utilized to quantify the SGD flux of Honokohau Harbor during the February 2006 Peterson et al., (2008) study and the June 2010 and September 2010 study. The flux of SGD quantified for this study bracketed the flux of SGD quantified by Peterson et al., (2008) with the highest flux observed during the June 2010 study period.

SGD-derived nutrient flux to the coastal environments in Hawaii

This study clearly demonstrates and reconfirms that nutrients are introduced to the coastal environments of Hawaii via SGD. During the 2010 study period, SGD supplied 281 mol/d PO_4^{3-} , 113,015 mol/d Si(OH)_4 , and 10,505 mol/d NO_3^- to the coastal zone along the south shore of Oahu (total of 5 studies), and that SGD supplied 194 mol/d PO_4^{3-} , 31,998 mol/d Si(OH)_4 , and 3,123 mol/d NO_3^- to Honokohau Harbor (total of 2 studies). The highest SGD-derived nutrient fluxes were observed within the coastal area of Wailupe Beach during May 2010, and the lowest SGD-derived nutrient fluxes were measured along the coastal zone at Black Point (Figure 26). In order to compare the nutrient fluxes to each other and to SGD rates documented in previous studies, the nutrient fluxes were scaled to meter of shoreline by dividing the fluxes by the width of shoreline. With this shoreline length scaling applied, the largest flux of SGD-derived nutrients were observed at Black Point, which is shown in Table 11. In general, the SGD nutrient fluxes quantified by this study were generally greater than previous studies (Table 11). This variability between studies and sites is believed to be due to differences in SGD flux and nutrient concentrations used by each study to estimate the nutrient flux. For example, our study utilized upland wells to define the nutrient flux for Honokohau Harbor, while Johnson et al. (2008) used nutrient concentrations measured within 100 m distance from the back wall of Honokohau Harbor.

To address the variability in nutrient concentrations due to differences in methods we quantified the nutrient flux to Wailupe Beach and Honokohau Harbor using different

nutrient flux methods. In both Wailupe Beach and Honokohau Harbor, regression lines were applied to the nutrient concentrations and corresponding salinity data observed in the coastal zones to define the zero-salinity nutrient concentration, which is shown in Figure 13 and Figure 14, respectively. The zero-salinity nutrient concentrations were then multiplied by the flux of SGD in order to define the SGD-derived nutrient flux. In Honokohau Harbor we utilized the product of the average nutrient concentrations observed within 100 m inland of the harbor defined by Johnson (2008) and the flux of SGD to define the flux of SGD-derived nutrients to the harbor. The resulting SGD-derived nutrient fluxes estimated from the different methods were compared in Figure 12. Along Wailupe Beach the PO_4^{3-} flux and Si(OH)_4 flux estimated by the zero-salinity nutrient concentrations were less than the PO_4^{3-} flux and Si(OH)_4 flux estimated by the upland wells, while the NO_3^- flux estimated by the zero-salinity nutrient concentration was less than the NO_3^- flux estimated by the upland wells. Due to the conservative mixing of nutrients within Wailupe Beach we assume that the zero-salinity nutrient concentration method is the best approach to estimate the SGD-derived nutrient flux to Wailupe Beach. In Honokohau Harbor, the largest nutrient fluxes were estimated using the zero-salinity nutrient concentrations. Since Honokohau Harbor is impacted by nutrient additions from the waste water injection plant, the average upland well nutrient concentrations method and the brackish ponds nutrient concentrations method are the best approach for estimating the SGD-derived nutrient flux for the harbor. Thus, the best SGD-derived nutrient flux is dependent on the study area and available nutrient data.

Site and Study	SGD (m ³ /d/m)	Si(OH) ₄ (mol/d/m)	PO ₄ ³⁻ (mol/d/m)	NO ₃ ⁻ (mol/d/m)
Wailupe Beach, Oahu (4/10) This study	121	83.14	0.20	7.15
Wailupe Beach, Oahu (5/10) This study	241	164.67	0.40	14.16
Black Point, Oahu (4/10) This study	453	310.76	1.49	89.83
Black Point, Oahu (6/10) This study	108	66.57	0.34	21.31
Ala Wai Canal, Oahu (7/10) This study	29	374.00	0.05	35.69
Honokohau Harbor, Hawaii (6/10) This study	61	46.66	0.28	4.57
Honokohau Harbor, Hawaii (9/10) This study	50	38.67	0.23	3.76
Keahou Bay, Hawaii Dollar and Atkinson, 1992	23	17.30	0.09	1.70
Waikola, Hawaii Dollar and Atkinson, 1992	13	11.30	0.02	1.00
Kahana Bay, Oahu Garrison et al., 2003	0	0.00	0.00	0.00
Honokohau Harbor, Hawaii Johnson et al., 2008	32	15.90	0.17	1.70
Kahauloa Bay, Hawaii Johnson et al., 2008	34	24.90	0.15	6.40
Kailua Bay, Hawaii Johnson et al., 2008	101	75.20	0.45	14.40
Kiholo Bay, Hawaii Johnson et al., 2008	87	69.60	0.21	6.10
Manini Beach, Hawaii Johnson et al., 2008	51	39.00	0.24	8.40
Queen's Bath, Hawaii Johnson et al., 2008	88	64.40	0.33	8.20
Hanalei, Kauai Knee et al., 2008		0.17	0.00	0.07
Kalolo Point, Hawaii Street et al., 2008	456-5180	227.3-258	1.23-1.4	20.4-23.2

Table 11: Comparison of SGD-derived nutrient flux quantified in this study to past studies within the Hawaiian Islands.

Study Site	Nutrient Flux Method	PO ₄ ³⁻ (μM)	Si(OH) ₄ (μM)	NO ₃ ⁻ (μM)	SGD flux (m ³ /d)	PO ₄ ³⁻ Flux (mol/d)	Si(OH) ₄ Flux (mol/d)	NO ₃ ⁻ Flux (mol/d)
WB-Apr.	Average upland wells nutrient concentration × SGD	1.66	690.16	58.52	48,210	37.85	15,734.99	1,334.26
WB-Apr.	Zero-salinity nutrient concentration × SGD	2.10	761.50	52.70	48,210	47.88	17,361.44	1,201.51
WB-May	Average upland wells nutrient concentration × SGD	1.66	690.16	58.52	95,490	31.39	13,048.88	1,106.49
WB-May	Zero-salinity nutrient concentration × SGD	2.10	761.50	52.70	95,490	39.70	14,397.68	996.40
HH-Jun.	Average upland wells nutrient concentration × SGD	4.65	767.51	74.7	22,799	106.02	17,498.46	1,703.09
HH-Jun.	Zero-salinity nutrient concentration × SGD	6.55	846.36	107.28	22,799	149.38	19,296.16	2,445.88
HH-Jun.	Average nutrient concentration within 100 m inland × SGD	5.40	497.00	54.00	22,799	123.11	11,331.10	1,231.15
HH-Sept.	Average upland wells nutrient concentration × SGD	4.65	767.51	74.7	18,907	87.92	14,511.31	1,412.35
HH-Sept.	Zero-salinity nutrient concentration × SGD	6.55	846.36	107.28	18,907	123.88	16,002.13	2,028.34
HH-Sept.	Average nutrient concentration within 100 m inland × SGD	5.40	497.00	54.00	18,907	102.10	9,396.78	1,020.98

Table 12: Comparison of different methods utilized to quantify the flux of SGD-derived nutrients to Wailupe Beach and Honokohau Harbor. WB-Apr., WB-May, HH-Jun, and HH-Sept. represent the April 2010 Wailupe Beach study, the May 2010 Wailupe Beach study, the June 2010 Honokohau Harbor study, and the September 2010 Honokohau Harbor study, respectively. The zero-salinity nutrient concentrations were identified through linear regressions of the coastal nutrient samples at each site. The average nutrient concentrations within 100 m inland of Honokohau Harbor were collected in brackish ponds by Johnson (2008).

Variability in residence time of the coastal areas

The residence times for the coastal water bodies studied were found to vary between each other as well as between sampling periods, which is shown in Table 13. At Wailupe Beach, water residence times increased between April and May, while at Black Point the residence time decreased. Along Wailupe Beach the average wind speed, flux of SGD, and residence time increased between the April 2010 and May 2010 sampling periods. Currents caused by physical forces besides wind, which were not measured during this study, may cause the variability in the residence time seen in Wailupe Beach. At Black Point, average wind speed increased between sampling periods. Thus, when the wind speed increases the surface water will be mixed more quickly causing the residence time of the SGD dissolved constituents to decrease. In Honokohau Harbor, the residence time observed in June 2010 agrees well with the residence time of 1.6 days or less, which was quantified by both Street et al. (2008) and Knee et al. (2008). During the June 2010 and September 2010, average wind speed observed for the harbor was ~ 3 m/s (Table 13) causing no apparent relationship between residence time and wind speed. However, an inverse relationship was quantified between SGD and residence time of SGD-derived constituents during the 2010 study period. Since wind speed was not variable between the study periods we assume that decreased SGD flux was a major factor in the increased residence time of the SGD-derived components in the harbor. It is important to note that for this study, the residence time quantified by SGD-derived R_a is assumed to be representative to the residence time of nutrients. Since the Ala Wai Canal demonstrated the highest residence time (10-13 days), the canal also has the highest nutrient residence

time. Thus, nutrients within the Ala Wai Canal were available for uptake longer than the other study sites.

Study Site	Date	Residence Time (d)	SGD (m ³ /d)	Average Wind Speed (m/s)
Wailupe Beach, Oahu	April 2010	2.5	48,210	4.55
Wailupe Beach, Oahu	May 2010	5.5	95,490	5.64
Black Point, Oahu	April 2010	2.50	4,534	3.17
Black Point, Oahu	June 2010	0.72	1,082	7.56
Ala Wai Canal, Oahu	July 2010	11.5	15,974	1.2
Honokohau Harbor, Hawaii	June 2010	0.5	22,799	2.95
Honokohau Harbor, Hawaii	Sept. 2010	6.25	18,907	3.2

Table 13: Comparison of residence time, flux of SGD, and average wind speed observed at each study site during the 2010 study period. Of the study areas, Black Point was the only site where an inverse relationship between residence time and average wind speed was observed. Honokohau Harbor was the only study site where an inverse relationship between residence time and SGD flux was observed.

Chlorophyll-a and photosynthetic carbon production rates of marine phytoplankton

We used chlorophyll-a concentrations and the rate of photosynthetic ^{13}C uptake to investigate potential relationships between phytoplankton photosynthetic carbon production and SGD-derived nutrients. In the Ala Wai Canal, the lowest chlorophyll-a concentrations (Figure 21; Table 26) and photosynthetic carbon production rates (Figure 23; Table 28) were measured between ~ 1,260 m and 3,500 m distance from the back of the canal, where stream water inputs decreased the salinity and temperature of the surface of the water column. Past studies have identified decreased chlorophyll-a concentrations and gross photosynthesis in these areas of fresh water input (Laws et al., 1993). From the data it seems that phytoplankton located at the sites of SGD inputs were unable to adequately take up the nutrients provided by SGD. This may be due to phytoplankton being unable to utilize the nutrients to full efficiency due to higher nutrient flushing rates and decreased salinity at the sites impacted by fresh water inputs. We do acknowledge that multiple factors such as phytoplankton species (Beach et al., 1995) and grazing affect photosynthetic production rates and that without more data these interpretations are over simplified. However, for this study we are limiting our scope to SGD-derived nutrients in order to conduct a first case assessment on the impact of SGD on phytoplankton so we did not need to incorporate species segregation.

Within Honokohau Harbor, highest chlorophyll-a concentrations were identified at locations exterior to the main harbor channel (Figure 22; Table 27). There is restricted circulation in areas not located within the main channel; thus, the chlorophyll

concentrations observed in these areas do not represent the standing stock of the main harbor channel. There was a lack of variability between the standing stock measured in the harbor between the sampling periods, and similarly low chlorophyll-a concentrations (0.06-0.7 $\mu\text{g/L}$) were observed within the surface waters of the harbor during past studies (Bienfang 1980.)

Variability was observed within less than two hundred meters distance of the back of the harbor when the photosynthetic carbon production rates measured during the 2010 study period were compared to distance from the back wall, which is shown in Figure 24. At greater than 200 m distance from the back of the harbor, phytoplankton photosynthetic carbon production rates of 20 June 2010 were well correlated with the phytoplankton photosynthetic carbon production rates of 22 June 2010. The variability observed within the <200 m distance could be caused by a change in physical factors expressed as an increase in salinity ~21 during 20 June 2010 to ~24 during 22 June 2010.

Chlorophyll-a concentrations and photosynthetic carbon production rates measured in the Ala Wai Canal were much greater than that of Honokohau Harbor (Figures 20 and 21). On average, the chlorophyll-a concentrations within the Ala Wai Canal were ~30 times more than chlorophyll-a concentrations in Honokohau Harbor, while the photosynthetic carbon production rates in the Ala Wai were ~12 times greater. The chlorophyll-a concentrations of this study are comparable to chlorophyll-a concentrations identified within other coastal regions within Hawaii. The average chlorophyll-a of the Ala Wai Canal (0.0-0.13 μg) and Honokohau Harbor (1-4 μg) fall

within ranges of chlorophyll-a concentrations observed within the coastal zones of Lahina, Maui (.50-5.1 $\mu\text{g/L}$) and Kihei, Maui (0.2-2 $\mu\text{g/L}$) (Laws et al., 2004). The chlorophyll-a concentrations ($\sim 0.10 \mu\text{g/L}$) and photosynthetic carbon concentrations (0.12 $\mu\text{g/L/h}$) observed off Kahe Point, Oahu during 1980-1981 (Bienfang, et al. 1984) are comparable to the average chlorophyll-a concentrations ($\sim 0.06 \mu\text{g/L}$) and photosynthetic carbon production rates ($\sim 0.10 \mu\text{g/L/h}$) observed within Honokohau Harbor during the 2010 study period. In Darwin Harbor, Australia (a macro-tropical estuary impacted by freshwater inputs), chlorophyll-a concentrations within a range of 1.58-1.69 were identified during a 2004 study period (Burford et al., 2008), which falls between the chlorophyll-a ranges observed within the Ala Wai Canal and Honokohau Harbor. The chlorophyll-a concentration measured within this study were lower than chlorophyll-a concentrations observed in other areas impacted by SGD such as the Yucatan Peninsula, where a range of 2.7-7.1 $\mu\text{g/L}$ in chlorophyll-a was observed in the 2000-2001 study period (Alvarez-Gongora and Herrera-Silveira, 2006). The findings of Alvarez-Gongora and Herrera-Silveira (2006) and this study indicate that standing stock and productivity of a water body is based on many factors including nutrient availability and water parameters such as temperature and salinity.

Phosphorus and nitrogen uptake of marine phytoplankton in Hawaii

The uptake of P and N by phytoplankton was identified in both the Ala Wai Canal and Honokohau Harbor in order to quantify if the phytoplankton were nutrient limited or not. Our calculations suggest that in the Ala Wai Canal, phytoplankton utilized < 2% of the P and N supplied to the canal via SGD. For the 2010 Honokohau Harbor studies, we estimated that phytoplankton utilized < 1% of the P and N supplied to the harbor by SGD. Thus, phytoplankton within the Ala Wai Canal and Honokohau Harbor were not limited by bioavailable nutrients during the 2010 study periods. Previous studies within Hawaii have identified uptake rates of phytoplankton using alternate methods (Dollar and Atkinson, 1992). To quantify the uptake rate of carbon by phytoplankton, Dollar and Atkinson (1992) assumed a carbon/chlorophyll-a ratio of 50. This resulted in 1 mmol planktonic C/m³. Marine Redfield C/N (7) and C/P (106) ratios, a specific growth rate of 2 day⁻¹, and a respiration rate of 15% were utilized to convert the calculated planktonic Carbon concentration to uptake rates. In Keauhou Bay, Hawaii, phytoplankton were estimated to be utilizing at ≤ 2% of the SGD-derived P and N (Dollar and Atkinson, 1992). Despite the use of different methods, the P and N uptake rates assessed by this method and Dollar and Atkinson (1992) show good agreement.

Chapter 5: Conclusions

From continuous measurements of ^{222}Rn , a correlation with SGD and tides was identified. At each site, high Rn concentrations were correlated with low tide, which translated into high SGD fluxes at low tides. SGD fluxes measured within the four study sites were spatially and seasonally variable. We found significant SGD rates (1,082-95,490 m^3/d) and our measurements added more evidence to the already existing literature that confirm that Pacific oceanic islands have significant SGD fluxes as predicted by hydrological models and coastal typology by Zekster (2000).

The residence times of SGD-derived constituents at each study site were dependent on SGD flux and mixing of the groundwater plume with oceanic water. Due to the open shoreline environments of Wailupe Beach and Black Point, physical factors play a dominant role in the mixing of surface water, thus, these physical factors play a dominant roles in the residence time of SGD-dissolved constituents. In the relatively sheltered environment of Honokohau Harbor, the residence time was inversely correlated with SGD flux. This inverse relationship between SGD and residence time likely maintains the harbor's volume. We can generally conclude that coastal mixing by physical forces such as wind, currents, and waves are the dominant controls on residence time in areas of open coastal environments, while SGD flux is the dominant control on residence time within semi-enclosed embayments. The Ra-derived residence times for the groundwater plume in Honokohau Harbor differed between June (0.5 days) and September (6 days) sampling periods (Table 3), and this groundwater plume residence

time increased with a decreasing SGD flux. The circulation in Honokohau Harbor is acting like an estuary, where the SGD flushes the surface water lens (composed of both SGD and ocean water) out of the harbor while sea water invades the harbor (Bienfang 1980). SGD flux, therefore, appears to drive the present circulation and flushing of this harbor, although winds and currents may also be important. The Ala Wai Canal experienced a greater nutrient flux (SGD-derived nutrients + stream-derived nutrients) than Honokohau Harbor. In addition, the residence time and SGD-derived nutrient inventory of the Ala Wai Canal was greater than the residence time and SGD-derived nutrient inventory of Honokohau Harbor. It is likely that due to this, the Ala Wai Canal was ~twelve times more productive than Honokohau Harbor. We believe these results are extendable throughout Hawaii, and to elsewhere, and conclude that wherever a significant SGD influx is present, that SGD influx must be considered as a potentially important variable and possible control on the residence time of a coastal system's water masses, nutrient flux, and biota.

Phytoplankton within the Ala Wai Canal and Honokohau Harbor utilized less than 2% of the supply of SGD-derived PO_4^{3-} and NO_3^- ; suggesting that phytoplankton growth within these embayments were not limited by nutrient supply. The bioavailable nutrients within the Ala Wai Canal remained within the canal for 10-13 days while the bioavailable nutrients within Honokohau Harbor were flushed from the harbor in less than 0.5-6 days. Consequently, phytoplankton within the Ala Wai Canal were able to utilize bioavailable nutrient over a longer length of time. We assume that photosynthetic carbon production rates within Honokohau Harbor will increase with an increase in the residence time of

bioavailable nutrients. We view this result to be highly significant with respect to future harbor development or expansion, which could cause both the residence time of the SGD-derived constituents and the photosynthetic carbon production rates to increase. This is especially important along the majority of West Hawaii coastlines due to the widespread occurrence of SGD plumes along the coasts of Hawaii (e.g. Johnson et al. 2008) due to the relationship between SGD and nutrient loadings.

Appendix A: Vertical salinity and temperature profiles

Table 14: Vertical profiles of the Ala Wai Canal. Profiles were completed on July 23 2010. Temperature, salinity, and dissolved oxygen (DO) were measured via an YSI multiparameter probe.

Station Number	Latitude	Longitude	Distance from head (m)	Depth from surface (m)	Temperature (°C)	Salinity	DO (%)
AW-2	21.27571	-157.81847	131.79	0.00	28.18	29.41	66.2
				0.25	28.26	29.22	66.2
				0.50	28.58	32.56	76.0
				0.75	28.63	32.94	69.6
				1.00	28.55	33.11	59.0
				1.50	28.07	33.41	45.4
				2.00	27.63	33.61	36.0
AW-3	21.27709	-157.81928	304.73	0.00	27.38	26.11	69.2
				0.25	27.60	27.42	35.5
				0.50	27.93	31.33	71.4
				0.75	28.13	32.58	71.6
				1.00	28.34	33.01	69.8
				1.50	27.91	33.50	70.4
				2.00	27.64	33.65	50.3
AW-4	21.27841	-157.82117	541.58	0.00	26.66	29.97	68.8
				0.25	27.03	26.45	67.1
				0.50	27.08	28.15	67.4
				0.75	28.01	31.88	81.7
				1.00	28.16	32.90	72.7
				1.50	27.86	33.44	50.1
				2.00	27.52	33.67	35.9
AW-5	21.27975	-157.82295	772.25	0.00	25.81	19.95	79.0
				0.25	25.92	27.63	75.6
				0.50	27.25	29.95	78.4
				0.75	27.93	32.07	81.4
				1.00	28.03	32.92	72.3
				1.50	27.80	33.44	58.1
				2.00	27.61	33.64	56.7
	2.50	27.44	33.71	52.4			

Table 14: Vertical profiles of the Ala Wai Canal, continued

Station Number	Latitude	Longitude	Distance from head (m)	Depth from surface (m)	Temperature (°C)	Salinity	DO (%)
AW-6	21.28073	-157.82405	934.7	0.00	25.50	20.10	82.0
				0.50	27.07	29.14	80.4
				0.75	27.87	32.29	80.7
				1.00	28.00	32.87	75.0
				1.50	27.88	33.44	65.7
				2.00	27.60	33.62	57.0
				2.50	27.49	33.68	48.7
AW-7	21.28277	-157.82628	1257.65	0.00	24.24	4.20	85.0
				0.25	25.82	25.50	77.7
				0.50	26.74	29.16	80.0
				0.75	27.27	30.73	86.9
				1.00	28.04	32.52	86.3
				1.50	27.81	33.44	63.3
AW-8	21.28496	-157.82889	1620.66	0.00	24.33	6.20	98.5
				0.25	25.38	18.57	73.4
				0.50	26.68	28.40	76.9
				0.75	27.77	31.62	76.2
				1.00	27.95	32.85	62.5
				1.50	27.31	33.71	51.0
AW-9	21.28769	-157.83214	2071.43	0.00	24.13	10.48	78.6
				0.25	25.11	16.73	73.8
				0.50	26.81	27.81	82.3
				0.75	27.79	31.50	90.7
				1.00	28.24	32.73	68.5
				1.50	26.25	33.87	78.1
				2.00	26.61	34.05	79.0
AW-10	21.28930	-157.83430	2340.61	0.00	26.63	9.18	75.5
				0.25	25.00	19.88	67.9
				0.50	26.40	27.14	73.4
				0.75	27.62	31.31	89.2
				1.00	27.92	32.61	84.8
				1.50	26.82	33.79	75.0
				2.00	26.59	34.06	72.4
			2.50	26.45	34.15	64.3	

Table 14: Depth and vertical profiles of Honokohau Harbor, Hawaii. Profiles were completed on September 24 2010 between 1502 and 1727. Temperature, salinity, and dissolved oxygen (DO) were measured via an YSI multparameter probe.

Station Number	Latitude	Longitude	Distance from head (m)	Depth from surface (m)	Temperature (°C)	Salinity	DO (%)
HH39	19.66922	-156.02120	0.00	0.000	20.54	20.79	89.2
				0.171	21.43	23.85	91.8
				0.265	22.18	25.59	91.1
				0.513	22.62	26.75	93.0
				0.736	23.91	29.71	100.9
				1.033	24.28	30.69	102.7
				1.461	25.52	32.67	113.9
				2.073	26.11	33.67	125.5
				2.433	26.11	33.72	124.5
				HH40	19.66913	-156.02150	26.98
0.123	22.13	22.73	91.9				
0.221	22.52	24.65	91.5				
0.452	22.79	26.44	92.1				
0.727	23.52	28.30	95.6				
1.011	23.90	29.72	101.1				
1.508	25.20	32.44	113.8				
1.978	26.09	33.65	121.1				
2.192	26.47	34.07	126.0				
2.938	26.49	34.12	126.4				
HH41	19.66912	-156.02177	53.39	0.000	22.20	22.27	95.4
				0.163	22.68	24.18	95.6
				0.248	23.06	25.89	95.6
				0.499	23.54	28.01	95.7
				0.753	23.81	29.12	96.2
				0.947	23.83	29.35	96.4
				1.450	25.66	32.98	115.2
				2.097	26.28	33.83	121.9
				2.505	26.45	34.07	122.8
				2.941	26.58	34.31	124.3
			3.296	26.65	34.39	124.9	

Table 15: Depth and vertical profiles of Honokohau Harbor, Hawaii continued

Station Number	Latitude	Longitude	Distance from head (m)	Depth from surface (m)	Temperature (°C)	Salinity	DO (%)
HH42	19.66918	-156.02215	95.44	0.000	22.65	24.88	124.5
				0.121	22.88	25.07	95.2
				0.241	23.29	26.39	96.2
				0.462	23.35	27.63	95.5
				1.023	24.04	30.19	103.2
				1.450	25.48	32.98	113.5
				1.965	25.99	33.65	118.5
				2.502	26.42	34.06	123.8
				3.031	26.62	34.32	124.5
				4.027	26.73	34.55	125.8
				4.251	26.73	34.56	126.3
HH43	19.66918	-156.02255	136.06	0.000	23.02	25.25	96.1
				0.153	23.26	26.61	95.7
				0.279	23.32	26.49	96.1
				0.575	24.15	29.56	102.8
				1.030	25.22	31.89	110.1
				1.446	25.54	32.76	114.1
				2.558	26.30	34.09	118.5
				3.569	26.73	34.70	124.7
				4.020	26.75	34.59	125.8
HH44	19.66927	-156.02315	200.01	0.000	23.58	29.91	99.4
				0.178	23.92	28.05	99.5
				0.269	24.04	28.19	99.4
				0.513	24.15	28.48	99.8
				0.955	24.64	30.61	104.0
				1.990	25.65	33.24	115.5
				3.001	26.68	34.51	123.8
				4.009	26.72	34.64	126.2
4.318	26.73	34.64	126.5				

Table 15: Honokohau Harbor, Hawaii depth profile continued.

Station Number	Latitude	Longitude	Distance from head (m)	Depth from surface (m)	Temperature (°C)	Salinity	DO (%)
HH45	19.66930	-156.02357	243.35	0.000	24.05	28.10	103.0
				0.174	24.16	28.30	102.1
				0.500	24.31	29.44	104.2
				0.665	25.11	31.14	108.7
				1.062	25.18	32.29	110.9
				1.961	25.77	33.23	112.6
				2.920	26.70	34.59	123.5
				4.030	26.72	34.68	124.9
				4.064	26.72	34.68	124.9
HH46	19.66925	-156.02417	304.21	0.000	24.14	28.18	130.0
				0.161	23.99	28.28	99.6
				0.496	24.50	29.76	102.0
				0.788	24.67	30.29	103.4
				1.394	25.07	31.98	106.3
				2.525	26.40	34.21	121.6
				3.449	26.74	34.70	126.3
				3.451	26.74	34.70	
				0.000	24.08	28.68	99.9
HH47	19.66920	-156.02487	377.42	0.265	24.15	28.93	98.9
				0.509	24.17	28.93	99.0
				0.936	24.90	31.01	11.3
				1.447	25.99	33.01	105.1
				2.446	26.54	34.51	120.5
				4.390	26.71	34.72	124.9
				0.000	24.00	28.41	105.3
HH48	19.66910	-156.02567	464.99	0.508	25.05	30.43	104.8
				0.793	25.23	30.81	106.6
				1.502	25.80	32.59	113.2
				2.388	26.61	34.58	121.6
				3.516	26.66	34.71	124.1
				5.433	26.70	34.73	

Table 15: Honokohau Harbor, Hawaii depth profile continued.

Station Number	Latitude	Longitude	Distance from head (m)	Depth from surface (m)	Temperature (°C)	Salinity	DO (%)
HH49	19.66930	-156.02640	539.04	0.000	24.67	30.01	106.7
				0.243	25.09	30.78	105.9
				0.708	25.40	31.78	109.4
				1.062	25.82	33.01	113.4
				1.495	26.40	33.96	117.0
				2.478	26.62	34.57	121.4
				5.916	26.63	34.74	
HH50	19.66930	-156.02712	613.74	0.000	24.93	31.02	108.3
				0.491	25.56	32.10	112.1
				0.993	25.85	32.71	114.5
				1.950	26.63	34.58	119.4
				2.946	26.58	34.53	119.8
				3.211	26.57	34.53	
HH51	19.66865	-156.02828	721.57	0.000	25.52	32.73	118.3
				0.997	26.45	34.04	119.7
				2.062	26.59	34.48	119.1
				7.080	26.28	34.71	117.1
							0

Appendix B: Regional nutrient samples

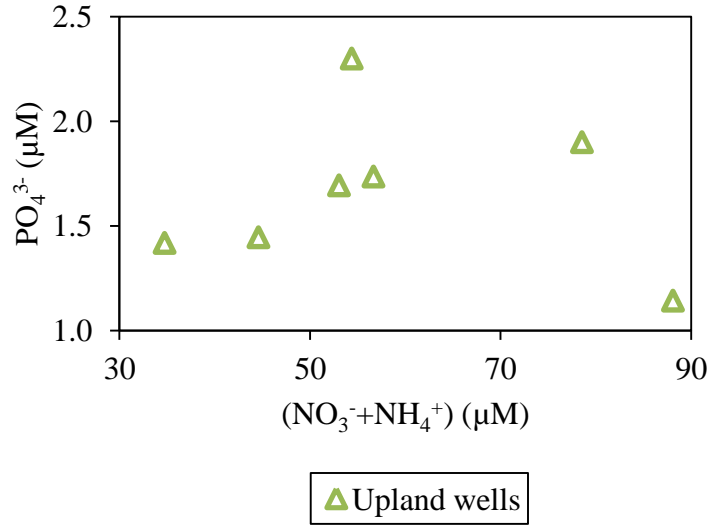


Figure 27: $(NO_3^- + NH_4^+)$ vs. PO_4^{3-} for upland wells along south shore Oahu during October 2010.

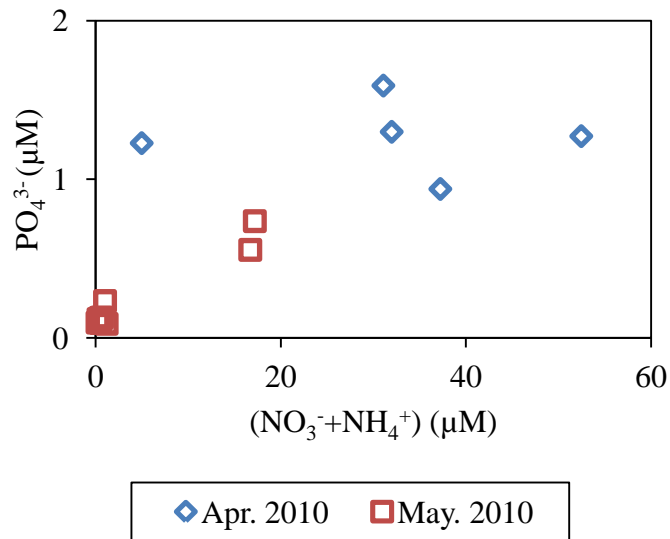


Figure 28: $(NO_3^- + NH_4^+)$ vs. PO_4^{3-} for groundwater vents and coastal water samples along Wailupe Beach, Oahu during April and May 2010.

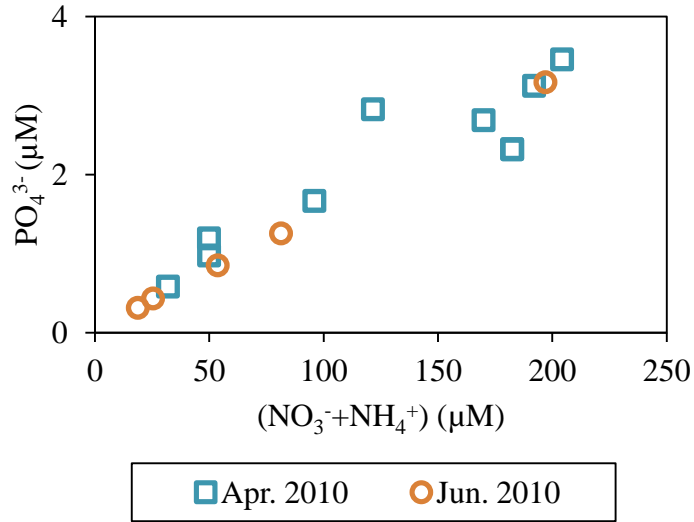


Figure 29: $(\text{NO}_3^- + \text{NH}_4^+)$ vs. PO_4^{3-} for groundwater vents and coastal water samples along Black Point, Oahu during April and June 2010.

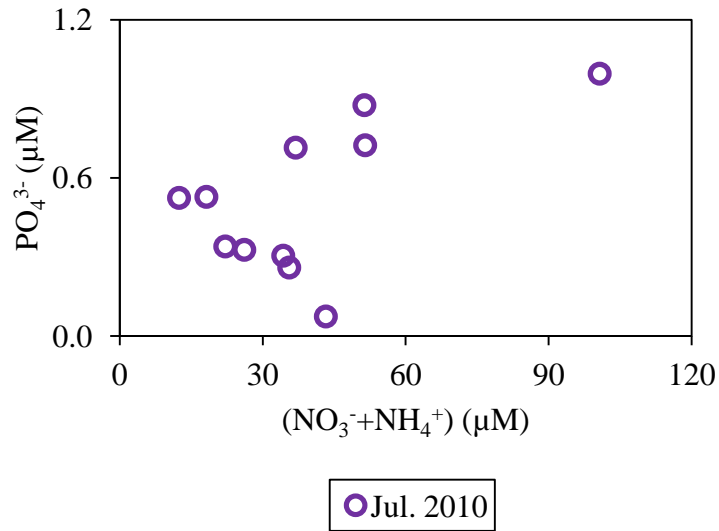


Figure 30: $(\text{NO}_3^- + \text{NH}_4^+)$ vs. PO_4^{3-} for coastal water samples within the Ala Wai Canal, Oahu during July 2010.

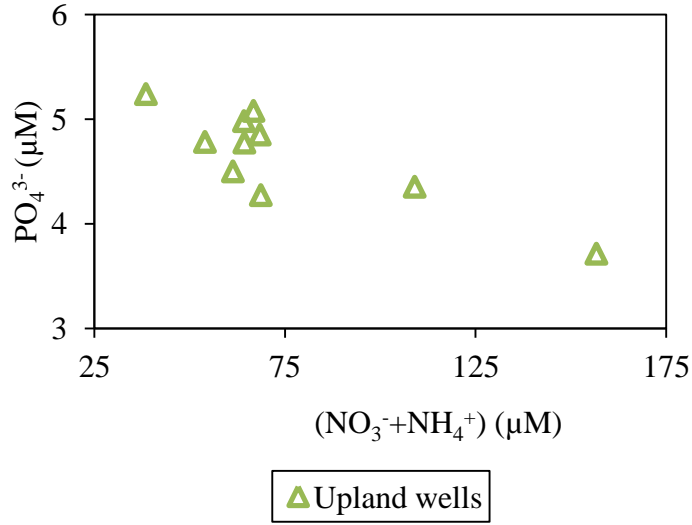


Figure 31: $(\text{NO}_3^- + \text{NH}_4^+)$ vs. PO_4^{3-} for upland wells along the Kona Coast of Hawaii during June 2010.

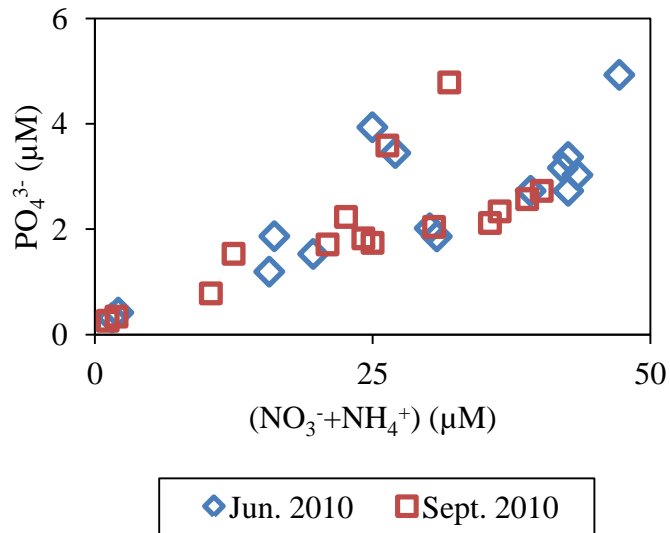


Figure 32: $(\text{NO}_3^- + \text{NH}_4^+)$ vs. PO_4^{3-} for coastal water samples within Honokohau Harbor, Hawaii during June and September 2010.

Table 16: ^{222}Rn concentrations measured in upland wells along the south shore of Oahu.

Well Name	Well Number	Latitude	Longitude	Date	^{222}Rn (dpm/m ³)	STDEV (dpm/m ³)
Waialae Golf Course	1646-01	21.27582	-157.77922	10/27/2010	343,307.64	2,3842.68
Palolo Well 2	1847-02	21.30703	-157.89117	10/27/2010	229,415.83	3,9690.68
Wilder Well 1	1849-14	21.30038	-157.82667	10/27/2010	425,161.55	4,4871.29
Aina Koa Well 2	1746-04	21.29137	-157.77598	10/27/2010	60,600.26	9,842.625
Kapalama Well 1	2052-13	21.33892	-157.86488	10/27/2010	72,973.16	14,853.75

Table 17: ²²²Rn concentrations measured in upland wells along the Kona Coast of Hawaii.

Well Name	Well Number	Latitude	Longitude	Date	²²² Rn (dpm/m ³)	STDEV (dpm/m ³)
Keei A	2753-01	19.45556	-155.89194	6/21/2010	5,973.092	4,896.673
Keei C	2653-01	19.44306	-155.88611	6/21/2010	17,008.99	3,164.463
Keei D	2753-03	19.46222	-155.88028	6/21/2010	17,342.48	13,000.89
Halekii	3155-02	19.51806	-155.91611	6/21/2010	43,327.88	18,032.26
Kahaluu Shaft	3557-05	19.58139	-155.95417	6/21/2010	15,55.955	3,111.911
Kahaluu -A	3557-01	19.58306	-155.94972	6/21/2010	62,081.06	24,198.2
Kahaluu-B	3557-02	19.58167	-155.94972	6/21/2010	38,895.61	18,385.25
Kahaluu-C	3557-03	19.58278	-155.94944	6/21/2010	77,819.6	22,176.75
Honokohau	4158-02	19.68222	-155.96444	6/21/2010	59,860.37	14,730.06
Keahuloa QLT 1	4057-01	19.66525	-155.95806	6/21/2010	33,416.92	9,936.456

Table 18: Comparison of the derived SGD flux for study sites. In situ ^{222}Rn concentrations were measured by the closed-system Rn monitoring equipment (discussed more thoroughly in methods chapter). Terrestrial endmember ^{222}Rn concentrations were quantified for Wailupe Beach and Black Point were derived from ^{222}Rn concentrations measured in groundwater outcrops (located > 5 m offshore) while terrestrial endmember ^{222}Rn concentrations for the Ala Wai Canal and Honokohau Harbor were quantified from upland wells. A concentration of 86 dpm/m^3 (Street et al., 2008) was utilized for the ^{226}Ra ocean endmember concentration and 64 dpm/m^3 (Peterson et al., 2009) was utilized for the ^{222}Rn ocean endmember concentration. The in situ ^{222}Rn concentrations were corrected to in situ water level, temperature, salinity, water density (Macintyre et al., 1995), wind speed, groundwater ^{222}Rn concentrations, and ocean endmember concentration in order to derive the advection rate at each site. Advection rates were multiplied by the area of SGD influence defined for each site in order to derive the SGD flux.

Study Site	Station Number	Start Date	Latitude	Longitude	Minimum In situ ^{222}Rn (dpm/m^3)	Maximum In situ ^{222}Rn (dpm/m^3)	Ground-water ^{222}Rn (dpm/m^3)	Advection Rate (cm/d)	Area of SGD Occurrence (m^2)	SGD Flux (m^3/d)
Wailupe Beach, Oahu	W-10	Apr. 2010	21.27545	-157.76247	80	51,480	224,000	128	39,700	48,210
Wailupe Beach, Oahu	W-15	May 2010	21.27545	-157.76247	160	135,000	224,000	182	39,700	95,490
Black Point, Oahu	BP-7	Apr. 2010	21.25881	-157.76067	7,990	320,170	750,000	44201	1,000	4,534
Black Point, Oahu	BP-12	Jun. 2010	21.25881	-157.76067	830	130,440	750,000	127	1,000	1,082
Ala Wai Canal, Oahu	AW-1	Jul. 2010	21.28831	-157.83281	9,000	19,000	15,261	64	24,019	15,974
Honokohau Harbor, Hawaii	HH-1	Jun. 2010	19.66925	-156.02108	3,000	25,000	131,000	56	94,875	22,799
Honokohau Harbor, Hawaii	HH-2	Sept. 2010	19.66925	-156.02108	9,000	23,000	131,000	25	94,875	18,907

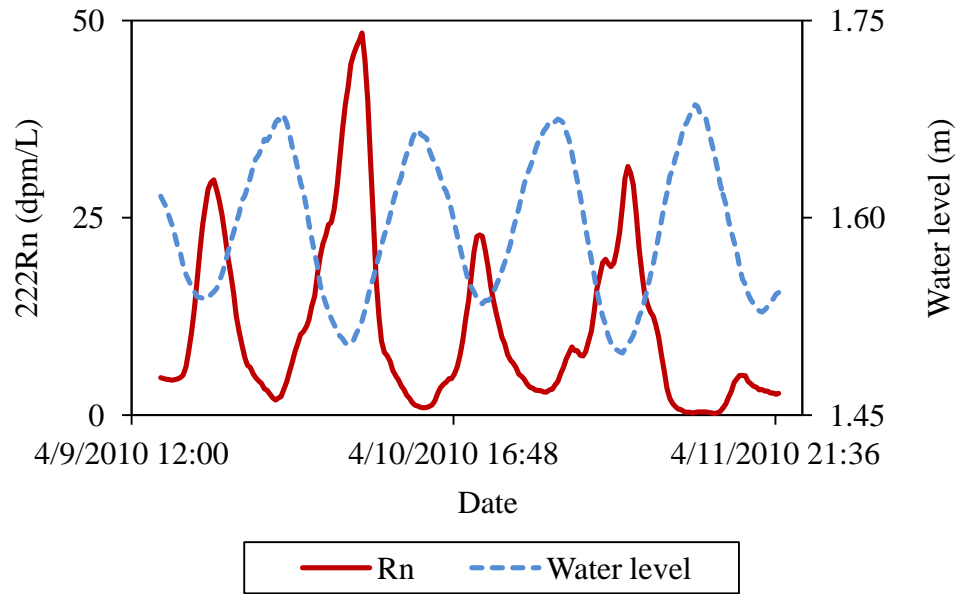


Figure 33: Continuous ^{222}Rn plotted along with water level in Wailupe Beach, Oahu (station number W-10) during April 9, 2010 to April 11, 2010. During the measurement period a range of ^{222}Rn of 80-51,480 dpm/ m^3 was measured.

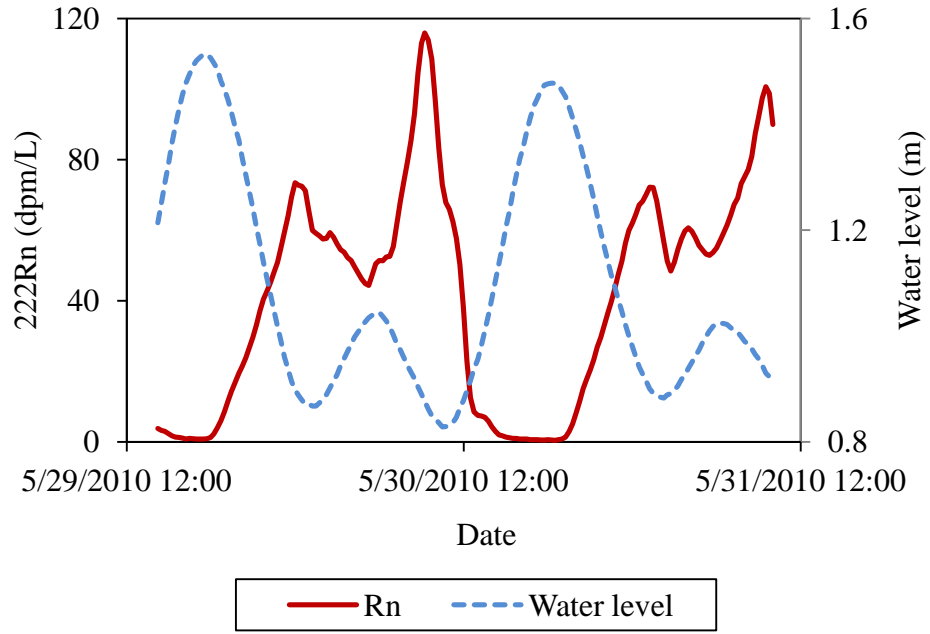


Figure 34: Continuous ^{222}Rn plotted along with water level in Wailupe Beach, Oahu (station number W-15) during May 29, 2010 to May 31, 2010. During the measurement period a range of ^{222}Rn of 160-135,000 dpm/ m^3 was measured

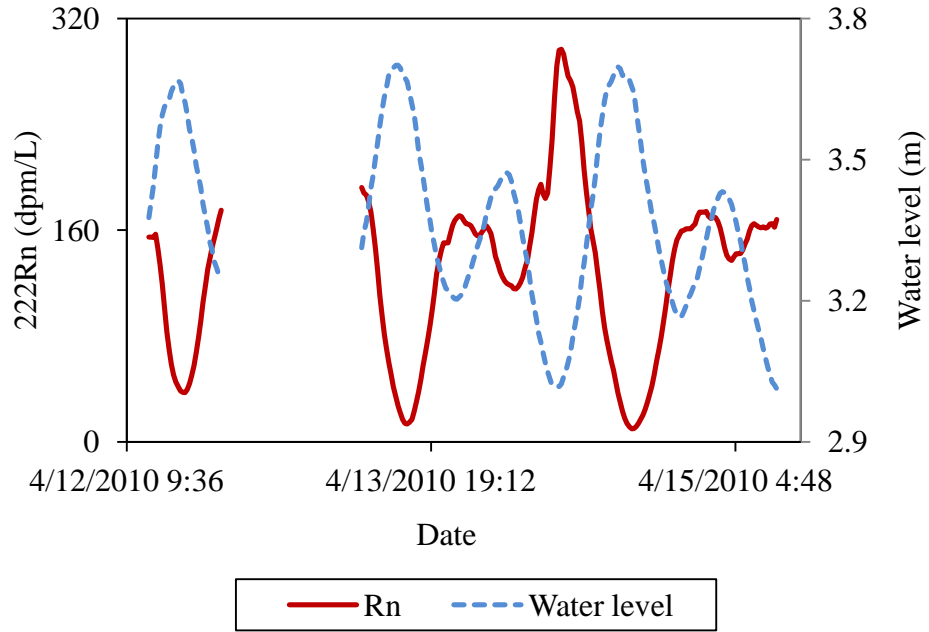


Figure 35: Continuous ²²²Rn plotted along with water level in Black Point, Oahu (station BP-7) during April 12, 2010 to April 15, 2010. Missing data is due to failure of the monitoring equipment, which was solved on site. During the measurement period a range of ²²²Rn of 7,990-320,170 dpm/ m³ was measured.

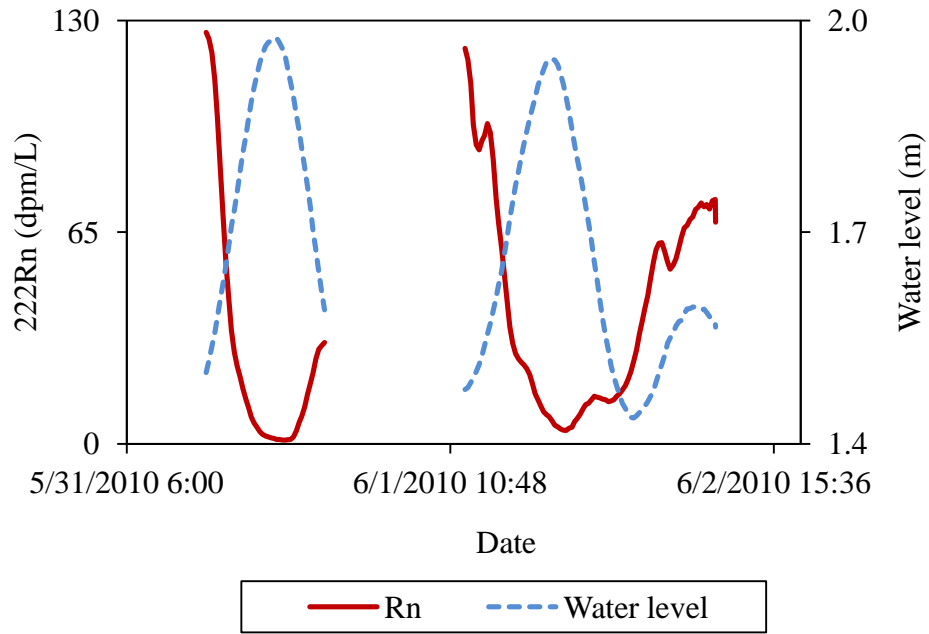


Figure 36: Continuous ²²²Rn plotted along with water level in Black Point, Oahu (station BP-12) during May 31, 2010 to June 2, 2010. Missing data is due to failure of the monitoring equipment, which was solved on site. During the measurement period a range of ²²²Rn of 830-130,440 dpm/ m³ was measured.

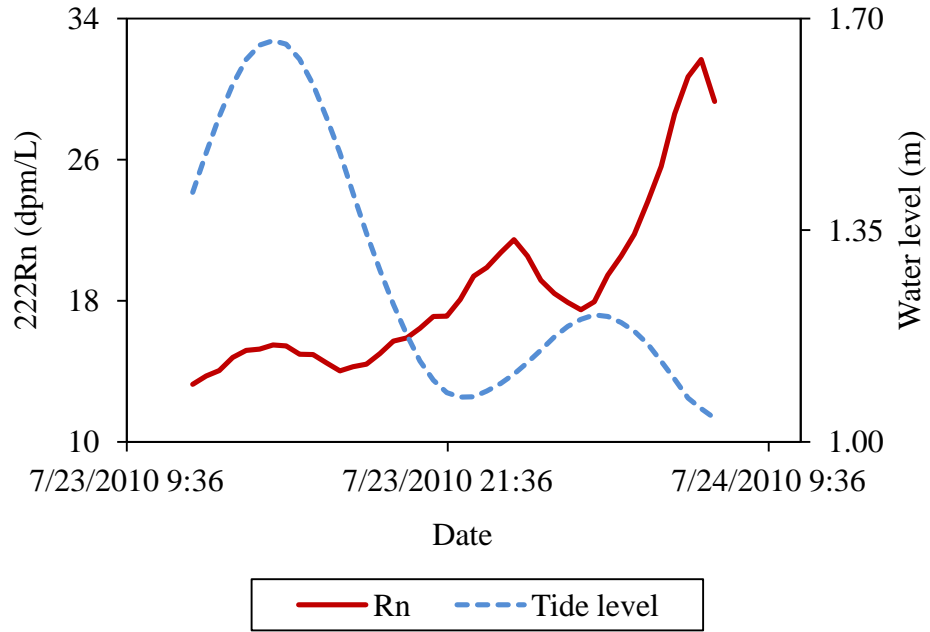


Figure 37: Continuous ^{222}Rn plotted along with water level in the Ala Wai Canal, Oahu (station AW-1) during July 23, 2010 to July 24, 2010. During the measurement period a range of ^{222}Rn of 9,000-19,000 dpm/ m^3 was measured.

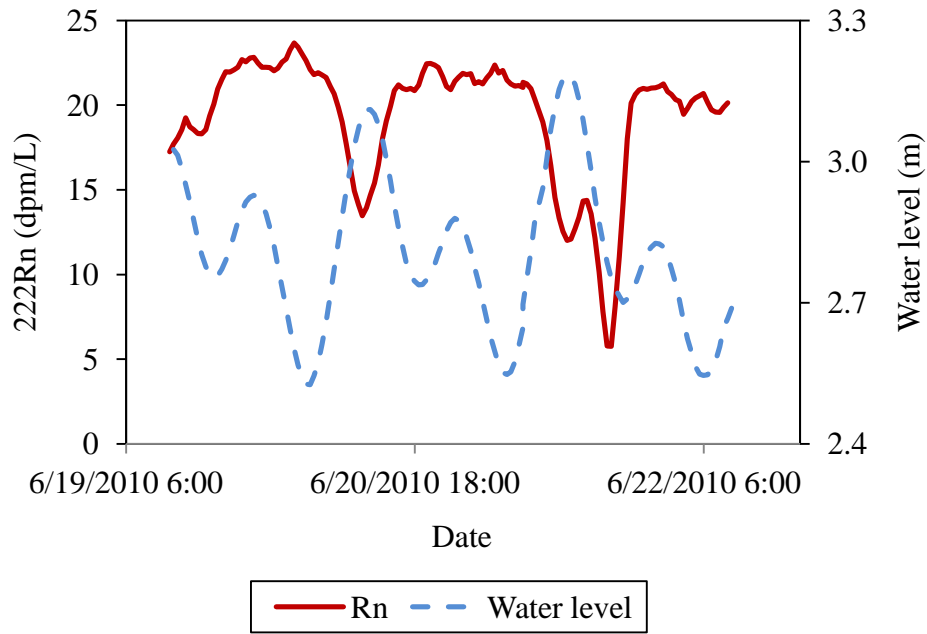


Figure 38: Continuous ²²²Rn plotted along with in Honokohau Harbor, Hawaii (station HH-1) during June 19, 2010 to June 22, 2010. During the measurement period a range of ²²²Rn of 3,000-25,000 dpm/ m³ was measured.

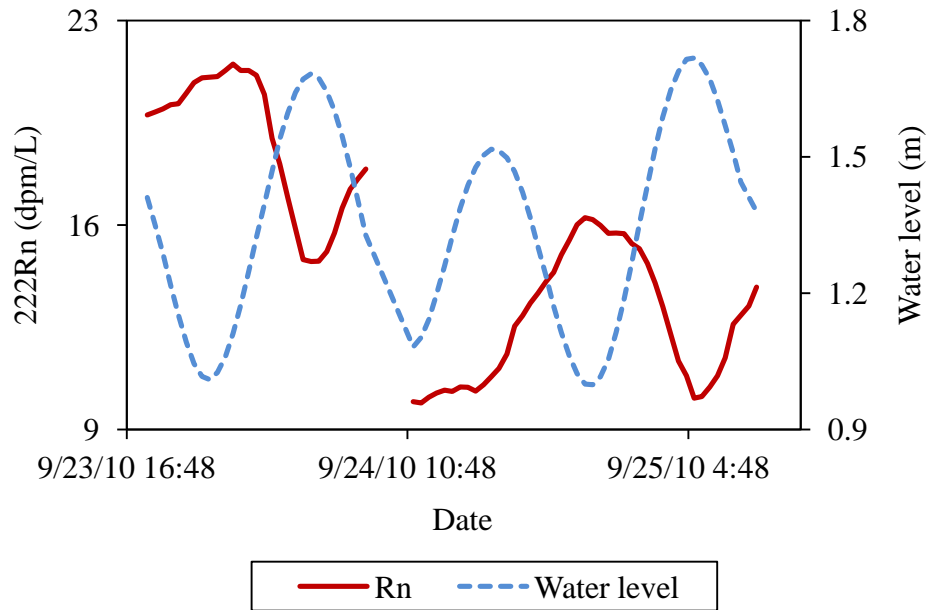


Figure 39: Continuous ²²²Rn plotted along with in Honokohau Harbor, Hawaii (station HH-1) during September 23, 2010 to September 24, 2010. During the measurement period a range of ²²²Rn of 9,000-23,000 dpm/ m³ was measured.

Table 19: ^{223}Ra and ^{224}Ra activities measured in upland wells along the south shore of Oahu. Samples were collected during the October 2010 sampling period.

Well Name	Well Number	Latitude	Longitude	Date	^{223}Ra (dpm/m ³)	^{224}Ra (dpm/m ³)	$^{224}\text{Ra}/^{223}\text{Ra}$
Waialae Golf Course	1646-01	21.27582	-157.77922	10/27/2010	0.51	4.29	8.44
Aina Koa Well 1	1749-10	21.28365	-157.77857	10/27/2010	0.55	1.87	3.41
Palolo Well 2	1847-02	21.30703	-157.89117	10/27/2010	0.14	1.42	10.27
Wilder Well 1	1849-14	21.30038	-157.82667	10/27/2010	0.00	1.04	0.00
Kapalama Well 1	2052-13	21.33892	-157.86488	10/27/2010	0.05	3.74	77.41
Moanalua Well 2	2153-11	21.352517	-157.8958	10/27/2010	0.12	3.30	27.32

Table 20: ^{223}Ra and ^{224}Ra activities measured in nearshore groundwater vents, beach pore water, and coastal water samples along Wailupe Beach. Samples were collected during the April 2010 and May 2010 sampling periods. L and H samples represent samples collected during low tide and high tide, respectively.

Sample Name	Sample Number	Latitude	Longitude	Date	^{223}Ra (dpm/m ³)	^{224}Ra (dpm/m ³)	$^{224}\text{Ra}/^{223}\text{Ra}$
Wailupe	W-1	21.27610	-157.76146	4/5/2010	6.38	48.98	7.68
Wailupe 1	W-2	21.27640	-157.76112	4/9/2010	6.92	39.34	5.68
Wailupe 2	W-3	21.27614	-157.76155	4/9/2010	4.47	28.15	6.29
Wailupe 3	W-4	21.27602	-157.76208	4/9/2010	0.58	10.65	18.25
Wailupe Boil 1	W-5	21.27593	-157.76208	4/12/2010	80.76	37.99	0.47
Wailupe Boil 3	W-6	21.27589	-157.76212	4/12/2010	65.00	46.48	0.72
Wailupe PP1 L	W-8	21.27543	-157.76248	5/30/2010	13.83	32.18	2.33
Wailupe PP2 L	W-9	21.28592	-157.79432	5/30/2010	9.32	22.84	2.45
Wailupe PP3 L	W-10	21.27545	-157.76247	5/30/2010	23.43	68.63	2.93
Wailupe PP4 L	W-11	21.27530	-157.76245	5/30/2010	8.38	34.82	4.16
Wailupe PP5 L	W-12	21.27520	-157.76240	5/30/2010	5.94	15.61	2.63
Wailupe PP1 H	W-13	21.27543	-157.76248	5/30/2010	4.25	19.92	4.69
Wailupe PP2 H	W-14	21.28592	-157.79432	5/30/2010	4.34	15.65	3.61
Wailupe PP3 H	W-15	21.27545	-157.76247	5/30/2010	4.24	18.24	4.30
Wailupe PP4 H	W-16	21.27530	-157.76245	5/30/2010	2.44	11.42	4.67
Wailupe PP5 H	W-17	21.27593	-157.76208	5/30/2010	59.05	43.60	0.74
Far Site	W-18	21.27447	-157.76227	5/30/2010	3.64	17.80	4.89
W Boil 1	W-19	21.27520	-157.76240	5/30/2010	2.48	13.20	5.32

Table 21: ^{223}Ra and ^{224}Ra activities measured in nearshore groundwater vents and coastal water samples along Black Point. Samples were collected during the April 2010 and June 2010 sampling periods.

Sample Name	Sample Number	Latitude	Longitude	Date	^{223}Ra (dpm/m ³)	^{224}Ra (dpm/m ³)	$^{224}\text{Ra}/^{223}\text{Ra}$
Black Point 1	BP-3	21.25933	-157.79039	4/12/2010	16.06	37.41	2.33
Black Point 2	BP-4	21.25914	-157.79060	4/12/2010	6.81	28.82	4.23
Black Point Boil 1	BP-5	21.25898	-157.79063	4/15/2010	7.00	23.62	3.38
Black Point Boil 2	BP-6	21.25887	-157.79062	4/15/2010	0.63	4.88	7.75
Black Point PP1	BP-7	21.25898	-157.79063	4/15/2010	6.66	31.24	4.69
Black Point PP2	BP-8	21.25887	-157.79062	4/15/2010	12.67	28.82	2.27
Black Point PP3	BP-9	21.25881	-157.79067	4/15/2010	3.79	9.49	2.50
Black Point PP4	BP-10	21.25857	-157.79055	4/15/2010	3.56	12.46	3.51
Black Point PP5	BP-11	21.25848	-157.79048	4/15/2010	4.63	13.57	2.93
BP PP1	BP-12	21.25887	-157.79062	6/1/2010	4.77	22.06	4.62
BP PP2	BP-13	21.25881	-157.79067	6/1/2010	4.33	20.52	4.74
BP PP3	BP-14	21.25857	-157.79055	6/1/2010	4.28	20.56	4.80
BP PP4	BP-15	21.25848	-157.79048	6/1/2010	2.65	10.50	3.96
BP Boil 1	BP-16	21.25903	-157.79062	6/1/2010	9.14	45.23	4.95
BP Boil 2	BP-17	21.25884	-157.79095	6/2/2010	6.53	26.26	4.02

Table 22: ^{223}Ra and ^{224}Ra activities measured in coastal water samples within the Ala Wai Canal. Samples were collected during the April 2010 and May 2010 sampling periods. L and H samples represent samples collected during low tide and high tide, respectively.

Sample Name	Sample Number	Latitude	Longitude	Date	^{223}Ra (dpm/m ³)	^{224}Ra (dpm/m ³)	$^{224}\text{Ra}/^{223}\text{Ra}$
AW Ra 1 Low	AW-14	21.27562	-157.76242	7/23/2010	11.14	31.90	2.86
AW Ra 2 Low	AW-15	21.28830	-157.83217	7/23/2010	48.87	137.46	2.81
AW Ra 3 Low	AW-16	21.28813	-157.84492	7/23/2010	24.10	41.83	1.74
AW Ra 4 Low	AW-17	21.28568	-157.81823	7/23/2010	28.63	60.30	2.11
AW Ra 1 High	AW-18	21.27593	-157.83173	7/23/2010	38.27	51.94	1.36
AW Ra 2 High	AW-19	21.28800	-157.84480	7/23/2010	32.08	28.68	0.89
AW Ra 3 High	AW-20	21.28813	-157.83745	7/23/2010	13.94	45.24	3.25
AW Ra 4 High	AW-21	21.28613	-157.83747	7/23/2010	32.02	67.95	2.12

Table 23: ^{223}Ra and ^{224}Ra activities measured in upland wells along the Kona Coast of Hawaii. Samples were collected during the June 2010 sampling period.

Well Name	Well Number	Latitude	Longitude	Date	^{223}Ra (dpm/m ³)	^{224}Ra (dpm/m ³)	$^{224}\text{Ra}/^{223}\text{Ra}$
Honokohau	4158-02	6/21/2010	19.68222	-155.96444	0.94	6.12	6.52
Kahaluu-B	3557-02	6/21/2010	19.58167	-155.94972	0.00	3.75	0.00
Kahaluu-C	3557-03	6/21/2010	19.58278	-155.94944	0.58	3.63	6.22
Keei C	2653-01	6/21/2010	19.44306	-155.88611	0.32	3.51	10.89
Kahaluu -A	3557-01	6/21/2010	19.58306	-155.94972	0.11	0.00	0.00
Keahuloa QLT 1	4057-01	6/21/2010	19.66525	-155.95806	0.00	1.65	0.00
Kahaluu Shaft	3557-05	6/21/2010	19.58139	-155.95417	0.74	9.02	12.11
Keei A	2753-01	6/21/2010	19.45556	-155.89194	0.12	7.03	57.02
Halekii	3155-02	6/21/2010	19.51806	-155.91611	0.47	1.02	2.15
Keei D	2753-03	6/21/2010	19.46222	-155.88028	3.79	42.64	11.24
Kaupulehu Irrigation 1	4757-01	6/23/2010	19.79528	-155.95944	0.15	8.69	57.90
Kaupulehu Irrigation 5	4856-01	6/23/2010	19.77861	-155.95361	1.38	9.50	6.91
Kaupulehu Irrigation 6	4856-02	6/23/2010	19.77972	-155.94972	15.21	204.12	13.42
Hualai Salt #1	4959-01	6/24/2010	19.82910	-155.99077	18.10	215.73	11.92
King's Pond	-	6/24/2010	19.82938	-155.99090	67.63	693.12	10.25
Hualalai #2	-	6/24/2010	19.66907	-156.02429	0.07	3.07	41.03
Kaupulehu Potable 1	4658-01	6/23/2010	19.77500	-155.96583	1.79	11.60	6.46
Kaupulehu Irrigation 2	4757-02	6/23/2010	19.79528	-155.95778	0.00	8.21	0.00
Kaupulehu Potable 5	4657-03	6/23/2010	19.77861	-155.95360	2.44	18.34	7.51
Kaupulehu Potable 6	4656-01	6/23/2010	19.77972	-155.94972	0.00	4.01	0.00
Big Island Country Club 1	4950-01	6/26/2010	19.82216	-155.84306	2.40	6.15	2.56
Puu Waawaa	4950-02	6/26/2010	19.77905	-155.84148	26.81	254.69	9.50
Hualalai #1	-	6/24/2010	19.66907	-156.04290	26.81	254.69	9.50

Table 24: ^{223}Ra and ^{224}Ra activities measured in coastal waters within Honokohau Harbor. Samples were collected during the June 2010 and September 2010 sampling periods.

Sample Name	Sample Number	Latitude	Longitude	Date	^{223}Ra (dpm/m ³)	^{224}Ra (dpm/m ³)	$^{224}\text{Ra}/^{223}\text{Ra}$
HHPP6-Ra	HH-15	19.66928	-156.02980	6/19/2010	2.69	12.60	4.69
HHPP1-Ra	HH-16	-	-	6/20/2010	35.84	349.02	9.74
HHPP2-Ra	HH-17	19.67427	-156.02272	6/20/2010	21.15	274.37	12.98
HHPP3-Ra	HH-21	19.66885	-156.02280	6/20/2010	23.60	233.48	9.89
HHPP4-Ra	HH-22	19.66925	-156.02463	6/20/2010	19.10	219.98	11.51
HHPP5-Ra	HH-23	19.66978	-156.02660	6/20/2010	21.38	187.48	8.77
HH-D2	HH-25	19.66913	-156.02145	6/20/2010	7.97	96.43	12.09
HH-D3	HH-26	19.66913	-156.02145	6/20/2010	3.56	31.09	8.74
HH3-Ra1	HH-35	19.66925	-156.02108	9/24/2010	32.82	175.61	5.35
HH3-Ra2	HH-36	19.66925	-156.02108	9/24/2010	14.00	59.01	4.22
HH3-Ra3	HH-37	19.66924	-156.02672	9/24/2010	29.88	118.82	3.98
HH3-Ra4	HH-38	19.66924	-156.02672	9/24/2010	2.35	14.31	6.09

Table 25: The residence time of Ra and conservative SGD-dissolved constituents for each study site and period. The initial activity ($^{223}\text{Ra}/^{224}\text{Ra}$ (I)) was derived by defining the rate of decay of ^{224}Ra in relation of the rate of decay of ^{223}Ra within upland wells. The observed activity ($^{223}\text{Ra}/^{224}\text{Ra}$ (F)) was quantified by defining the rate of decay of ^{224}Ra in relation of the rate of decay of ^{223}Ra within the coastal waters. The initial Ra activity and observed Ra activity quantified for each site were applied to the residence time equation (Dulaiova and Burnett 2008). The uncertainty of the residence time was defined by applying the statistical uncertainty analysis to the possible error of both the initial Ra ratio and the observed Ra ratio.

Sample Site	Date	I $\frac{(^{224}\text{Ra})}{(^{223}\text{Ra})}$	F $\frac{(^{224}\text{Ra})}{(^{223}\text{Ra})}$	Residence Time (d)	Error (\pm d)
Wailupe Beach, Oahu	April 2010	7.14	6.61	1-4	0.57
Wailupe Beach, Oahu	May 2010	7.14	4.34	4-7	0.27
Black Point, Oahu	April 2010	4.64	3.21	1-2	0.28
Black Point, Oahu	June 2010	3.41	4.22	0.7	0.17
Ala Wai Canal, Oahu	July 2010	7.14	2.04	10-13	0.27
Honokohau Harbor, Hawaii	June 2010	10.36	10.31	0.5	0.51
Honokohau Harbor, Hawaii	September 2010	10.36	4.69	6	0.39

Appendix E: Chlorophyll-a of phytoplankton

Table 26: Chlorophyll-a concentrations in the surface water of the Ala Wai Canal, Oahu.

Sample Name	Sample Number	Latitude	Longitude	Date	Salinity	Chlorophyll-a ($\mu\text{g/L}$)
AW-PP1	AW-2	21.27571	-157.81847	7/23/2010	32.34	2.993
AW-T1	AW-3	21.27709	-157.81928	7/23/2010	26.11	3.481
AW-PP2	AW-4	21.27841	-157.82117	7/23/2010	31.30	2.271
AW-T2	AW-5	21.27975	-157.82295	7/23/2010	19.95	3.647
AW-PP3	AW-6	21.28073	-157.82405	7/23/2010	30.49	3.038
AW-T3	AW-7	21.28277	-157.82628	7/23/2010	4.20	1.011
AW-T4	AW-8	21.28496	-157.82889	7/23/2010	6.20	1.395
AW-PP4	AW-9	21.28769	-157.83214	7/23/2010	22.33	1.585
AW-T5	AW-10	21.28930	-157.83430	7/23/2010	9.18	1.671
AW-PP5	AW-11	21.28837	-157.83733	7/23/2010	21.41	1.241
AW-T6	AW-12	21.28769	-157.84068	7/23/2010	18.99	1.492
AW-PP6	AW-13	21.28543	-157.84464	7/23/2010	29.21	1.315

Table 25: Chlorophyll-a concentrations of the surface water of Honokohau Harbor during the June 2010 and September 2010 study periods.

Sample Name	Sample Number	Latitude	Longitude	Date	Salinity	Chlorophyll-a (µg/L)
HH-PP1	HH-10	19.66927	-156.02105	6/20/2010	22.11	0.032
HH-PP2	HH-11	19.66900	-156.02210	6/20/2010	21.68	0.304
HH-PP3	HH-12	19.66907	-156.02428	6/20/2010	21.83	0.034
HH-PP4	HH-13	19.66907	-156.02430	6/20/2010	22.06	0.021
HH-PP5	HH-14	19.66853	-156.02547	6/20/2010	23.50	0.324
HH2-PP1	HH-24	21.41087	-156.02213	6/22/2010	23.19	0.031
HH2-PP2	HH-25	19.67427	-156.02272	6/22/2010	24.01	0.051
HH2-PP3	HH-26	19.66885	-156.02280	6/22/2010	25.09	0.058
HH2-PP4	HH-27	19.66925	-156.02463	6/22/2010	25.70	0.126
HH2-PP5	HH-28	19.66978	-156.02660	6/22/2010	28.50	0.062
HH3-PP1	HH-29	19.66925	-156.02118	9/23/2010	23.49	0.068
HH3-PP2	HH-30	19.66933	-156.02205	9/23/2010	24.19	0.056
HH3-PP3	HH-31	19.66933	-156.02352	9/23/2010	27.39	0.066
HH3-PP4	HH-32	19.66925	-157.44800	9/23/2010	28.71	0.040
HH3-PP5	HH-33	19.66893	-157.54600	9/23/2010	29.26	0.104

Table 28: Derived photosynthetic carbon production for the Ala Wai Canal, Oahu during 23 July 2010. The natural abundance samples were filtered immediately after collection while the incubated samples remained in the canal for 10 hours. The calculated isotopic composition and carbon concentrations were used to quantify the change in carbon. The change in carbon over time resulted in the rate of photosynthetic carbon production at each sampling

Sample Name	Sample Number	Latitude	Longitude	Date	Natural Abundance C ($\mu\text{g/L}$)	Incubated C ($\mu\text{g/L}$)	Natural Abundance ‰	Incubated ‰	ΔC ($\mu\text{g/L}$)	h	P ($\mu\text{g/L/h}$)
AW-PP1	AW-2	21.27571	-157.81847	7/23/2010	625.2	587.4	-21.8	-9.4	14.66	10	1.47
AW-PP2	AW-4	21.27841	-157.82117	7/23/2010	701.0	403.9	-21.1	-2.3	15.31	10	1.53
AW-PP3	AW-6	21.28073	-157.82405	7/23/2010	561.7	343.6	-21.8	-6.3	10.72	10	1.07
AW-PP5	AW-11	21.28837	-157.83733	7/23/2010	461.2	384.0	-24.0	-12.0	9.23	10	0.92
AW-PP6	AW-13	21.28543	-157.84464	7/23/2010	478.1	355.3	-22.9	4.4	19.48	10	1.95

Table 29: Derived photosynthetic carbon production for the Honokohau Harbor, Hawaii during 20 June 2010 and 22 June 2010. The natural abundance samples were filtered immediately after collection while the incubated samples remained in the canal for 10 hours. The calculated isotopic composition and carbon concentrations were used to quantify the change in carbon. The change in carbon over time resulted in the rate of photosynthetic carbon production at each sampling site.

Sample Name	Sample Number	Latitude	Longitude	Date	Natural Abundance C ($\mu\text{g/L}$)	Incubated C ($\mu\text{g/L}$)	Natural Abundance ‰	Incubated ‰	ΔC ($\mu\text{g/L}$)	h	P ($\mu\text{g/L/h}$)
HH-PP1	HH-10	19.66927	-156.02105	6/20/2010	90.5	144.3	-22.5	-19.7	0.82	12	0.07
HH-PP2	HH-11	19.66900	-156.02210	6/20/2010	89.5	114.0	-21.9	-20.0	0.43	12	0.04
HH-PP4	HH-13	19.66907	-156.02430	6/20/2010	59.6	127.7	-23.1	-20.5	1.35	12	0.11
HH-PP5	HH-15	19.66853	-156.02547	6/20/2010	57.8	109.7	-20.5	-16.2	0.95	12	0.08
HH2-PP1	HH-24	21.41087	-156.02213	6/22/2010	78.7	241.9	-22.4	-15.2	3.52	12	0.29
HH2-PP2	HH-25	19.67427	-156.02272	6/22/2010	62.2	83.1	-23.3	-16.5	1.13	12	0.09
HH2-PP3	HH-26	19.66885	-156.02280	6/22/2010	80.1	105.7	-22.0	-18.9	0.66	12	0.05
HH2-PP5	HH-28	19.66978	-156.02660	6/22/2010	91.4	146.3	-22.1	-20.9	0.47	12	0.04

Table 30: Derived organic C and N concentrations within the Ala Wai Canal, Oahu during the 23 July 2010 study period.

Sample Name	Sample Number	Latitude	Longitude	Date	Natural Abundance C (µg/L)	Natural Abundance N (µg/L)	Incubated N (µg/L)
AW-PP1	AW-2	21.27571	-157.81847	7/23/2010	625.2	587.4	55.4
AW-PP2	AW-4	21.27841	-157.82117	7/23/2010	701.0	403.9	116.9
AW-PP3	AW-6	21.28073	-157.82405	7/23/2010	561.7	343.6	94.1
AW-PP5	AW-11	21.28837	-157.83733	7/23/2010	461.2	384.0	148.1
AW-PP6	AW-13	21.28543	-157.84464	7/23/2010	478.1	355.3	89.4

Table 31: Derived organic C and N concentrations within Honokohau Harbor, Hawaii during the 20 July 2010 and 22 July 2010 study periods.

Sample Name	Sample Number	Latitude	Longitude	Date	Natural Abundance C (µg/L)	Natural Abundance N (µg/L)	Incubated N (µg/L)
HH-PP1	HH-10	19.66927	-156.02105	6/20/2010	90.5	9.5	24.7
HH-PP2	HH-11	19.66900	-156.02210	6/20/2010	89.5		23.5
HH-PP4	HH-13	19.66907	-156.02430	6/20/2010	59.6	8.4	15.5
HH-PP5	HH-15	19.66853	-156.02547	6/20/2010	57.8	10.5	16.1
HH2-PP1	HH-24	21.41087	-156.02213	6/22/2010	78.7	0	36.7
HH2-PP2	HH-25	19.67427	-156.02272	6/22/2010	62.2	8.8	10.0
HH2-PP3	HH-26	19.66885	-156.02280	6/22/2010	80.1	10.6	12.3
HH2-PP5	HH-28	19.66978	-156.02660	6/22/2010	91.4	10.5	0

Table 32: Derived P and N uptake rates for the surface water of the Ala Wai Canal, Oahu during the 23 July 2010 study period.

Sample Name	Sample Number	Latitude	Longitude	Date	Photosynthetic C Production ($\mu\text{g/L/h}$)	P uptake (mol/day)	N uptake (mol/day)
AW-PP1	AW-2	21.27571	-157.81847	7/23/2010	1.47	0.51	18.22
AW-PP2	AW-4	21.27841	-157.82117	7/23/2010	1.53	0.54	19.03
AW-PP3	AW-6	21.28073	-157.82405	7/23/2010	1.07	0.38	13.33
AW-PP5	AW-11	21.28837	-157.83733	7/23/2010	0.92	0.32	11.49
AW-PP6	AW-13	21.28543	-157.84464	7/23/2010	1.95	0.68	24.22

Table 33: Derived P and N uptake rates for the surface water of Honokohau Harbor, Hawaii during the 20 June 2010 and 22 June 2010 study periods.

Sample Name	Sample Number	Latitude	Longitude	Date	Photosynthetic C Production ($\mu\text{g/L/h}$)	P Uptake (mol/d)	N Uptake (mol/d)
HH-PP1	HH-10	19.66927	-156.02105	6/20/2010	0.07	0.13	4.74
HH-PP2	HH-11	19.66900	-156.02210	6/20/2010	0.04	0.07	2.50
HH-PP4	HH-13	19.66907	-156.02430	6/20/2010	0.11	0.22	7.81
HH-PP5	HH-15	19.66853	-156.02547	6/20/2010	0.08	0.15	5.47
HH2-PP1	HH-24	21.41087	-156.02213	6/22/2010	0.29	0.58	20.39
HH2-PP2	HH-25	19.67427	-156.02272	6/22/2010	0.09	1.73	61.22
HH2-PP3	HH-26	19.66885	-156.02280	6/22/2010	0.05	0.11	3.80
HH2-PP5	HH-28	19.66978	-156.02660	6/22/2010	0.04	0.08	2.73

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