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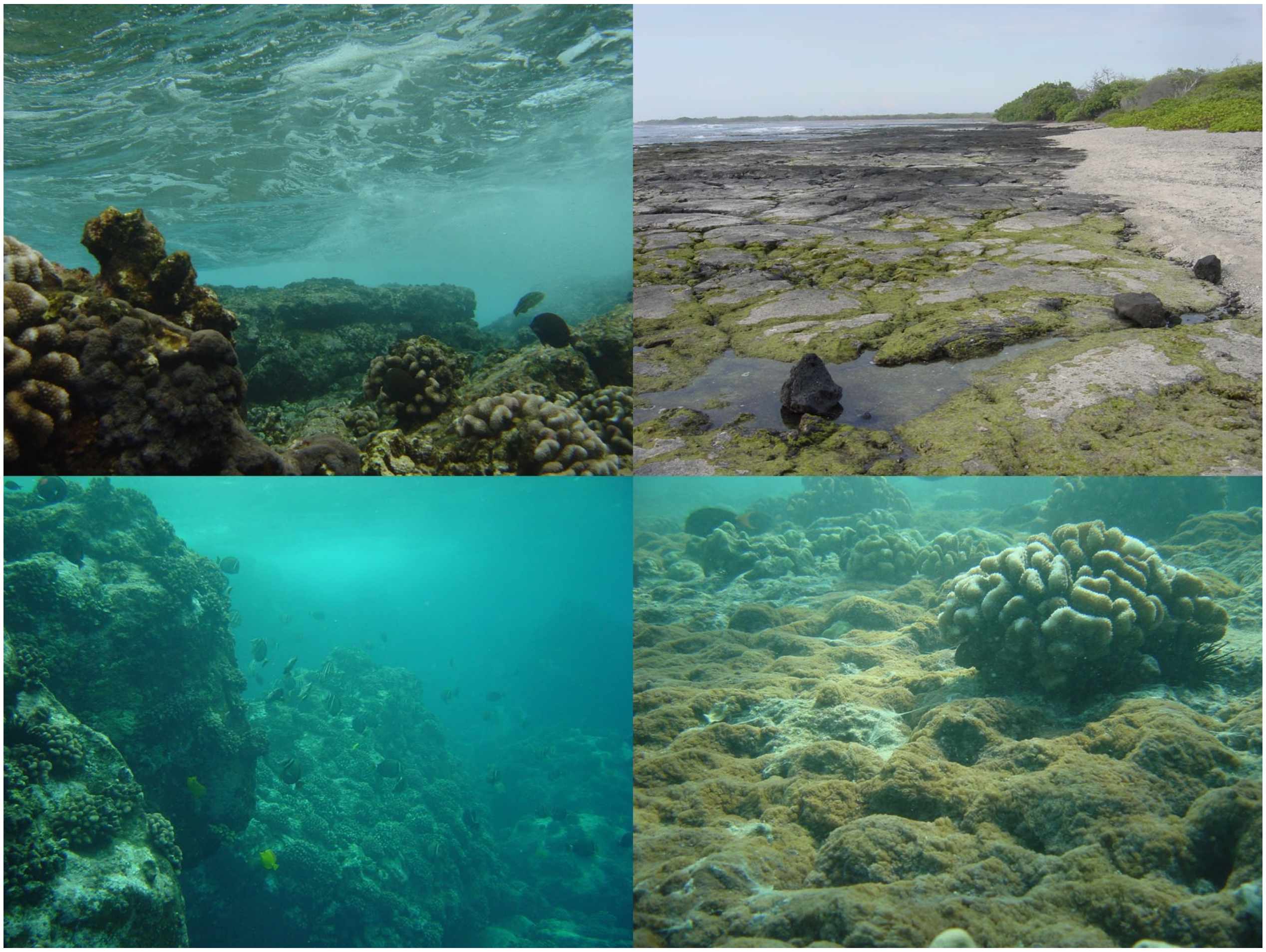
Part 2, Spatial and Temporal Variations in Salinity, Radium-Isotope Activity, and Nutrient Concentrations in Coastal Waters, December 2003–April 2006



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FRONT COVER—From upper left hand moving clockwise: (1) Shallow, wave-scoured intertidal platform of north Kaloko-Honokōhau National Historical Park with sparse stoutly branching coral *Pocillopora meandrina*; (2) algae-covered intertidal platform of central Kaloko-Honokōhau National Historical Park, common where submarine groundwater discharge is persistent; (3) dense cover of soft coral *Sarcothelia* sp. (Anthelia) common of submarine groundwater seeps, central Kaloko-Honokōhau National Historical Park; (4) complex basalt topography with thin veneer of dense in north Kaloko-Honokōhau National Historical Park. (USGS photos by Eric Grossman.)

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Submarine Ground-Water Discharge and Fate Along the Coast of Kaloko-Honokōhau National Historical Park, Island of Hawaiʻi

Part 2, Spatial and Temporal Variations in Salinity, Radium-Isotope Activity, and Nutrient Concentrations in Coastal Waters, December 2003-April 2006

By Karen L. Knee[1,2], Joseph H. Street[1,2], Eric E. Grossman, and Adina Paytan[2]

Abstract

The aquatic resources of Kaloko-Honokōhau National Historical Park, including rocky shoreline, fishponds, and anchialine pools, provide habitat to numerous plant and animal species and offer recreational opportunities to local residents and tourists. A considerable amount of submarine groundwater discharge was known to occur in the park, and this discharge was suspected to influence the park's water quality. Thus, the goal of this study was to characterize spatial and temporal variations in the quality and quantity of groundwater discharge in the park. Samples were collected in December 2003, November 2005, and April 2006 from the coastal ocean, beach pits, three park observation wells, anchialine pools, fishponds, and Honokōhau Harbor. The activities of two Ra isotopes commonly used as natural ground-water tracers (^{223}Ra and ^{224}Ra), salinity, and nutrient concentrations were measured. Fresh ground water composed a significant proportion (8–47 volume percent) of coastal-ocean water. This percentage varied widely between study sites, indicating significant spatial variation in submarine groundwater discharge at small (meter to kilometer) scales. Nitrate + nitrite, phosphate, and silica concentrations were significantly higher in nearshore coastal-ocean samples relative to samples collected 1 km or more offshore, and linear regression showed that most of this difference was due to fresh ground-water discharge. High-Ra-isotope-activity, higher-salinity springs were a secondary source of nutrients, particularly phosphate, at Honokōhau Harbor and Aiopio Fishtrap. Salinity, Ra-isotope activity, and nutrient concentrations appeared to vary in response to the daily tidal cycle, although little seasonal variation was observed, indicating that submarine ground-water discharge may buffer the park's water quality against the severe seasonal changes that would occur in a system where freshwater inputs were dominated by rivers and runoff. Ra-isotope-activity ratios indicated that the residence time of water in the coastal ocean at the study sites was less than 1.6 days. We calculated water and nutrient fluxes into the coastal ocean at each study site. This study provides a baseline description of submarine ground-water discharge in Kaloko-Honokōhau National Historical Park and its effect on the park's aquatic resources. We hope that it will allow park managers to better assess potential future changes in ground-water quality and quantity and conserve the park's valuable resources.

Introduction

Kaloko-Honokōhau National Historical Park: Water Resources and Habitats

Kaloko-Honokōhau National Historical Park spans 1,161 acres on the Kona, or west, coast of the island of Hawaiʻi (fig. 1). The park's aquatic resources, including anchialine pools (landlocked bodies of water hydrologically connected to both the ocean and fresh ground water), two 11-acre fishponds, and 596 acres of coral reefs, are among its most significant natural and cultural assets. Myriad species of fish, mammals, birds, reptiles, invertebrates, and plants rely upon the park's aquatic resources for their survival (see http://www.nps.gov/kaho).

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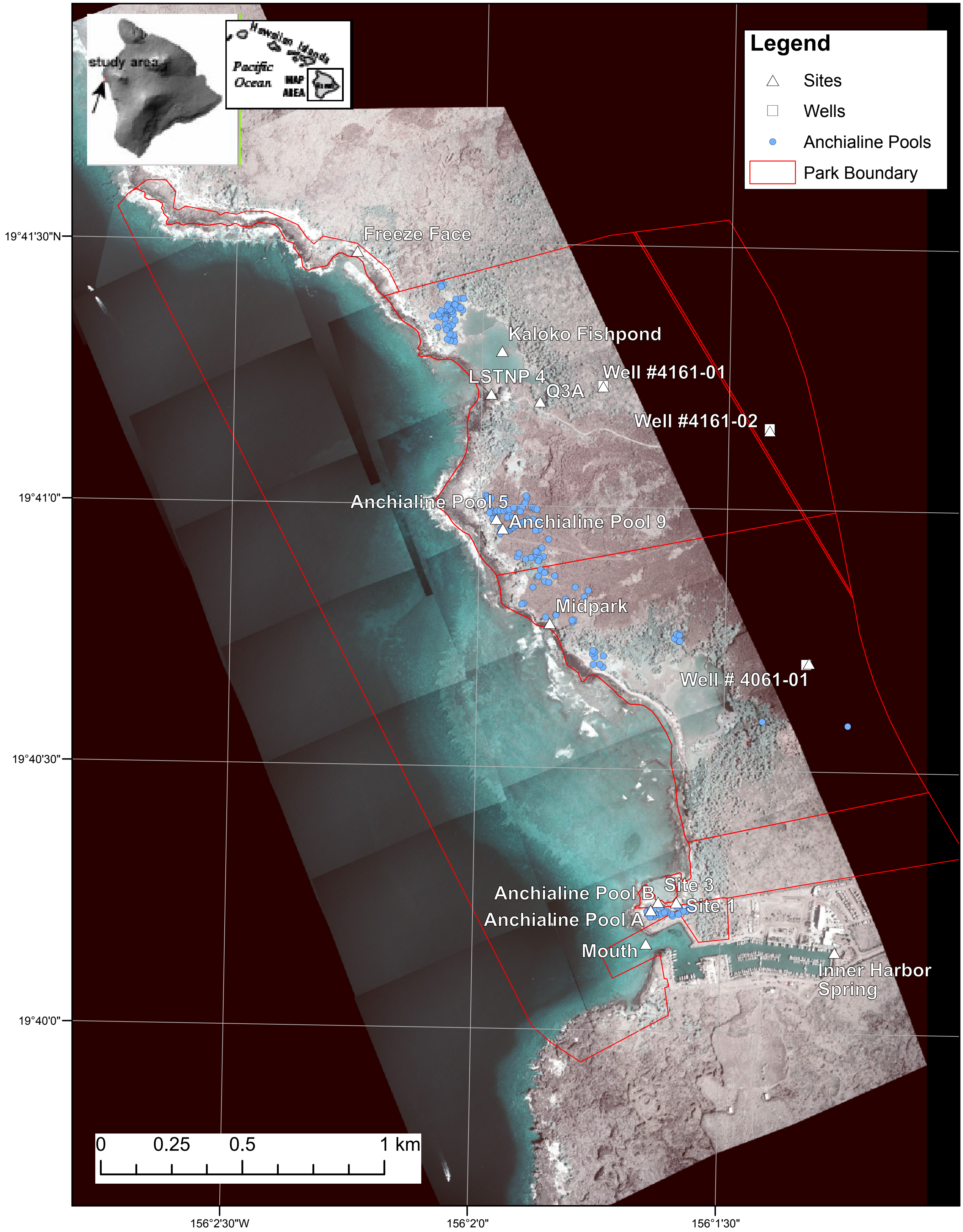

Figure 1. Kaloko-Honokōhau National Historical Park, western Island of Hawai‘i, showing locations of sample sites.

The park’s aquatic resources and the ecosystems that depend on them are heavily influenced by ground water. Despite the area’s low mean annual rainfall of 50 to 75 cm (Oki and others, 1999) and the absence of perennial streams, most water bodies in the park are considerably fresher than seawater, indicating the presence of ground water, which originates in the rainy central part of the island, flows through the highly porous basalt aquifer, and discharges at the coast. Oki and others showed that increasing ground-water withdrawals for urban development since 1978 likely have decreased ground-water flux to the coast by 50 percent. During the same period, contaminants and residential land use upslope of the park have impaired ground-water quality (Oki and others, 1999). More development on the west coast of Hawai‘i, adjacent to the park, is planned in the near future.

Submarine Ground-Water Discharge

Submarine ground-water discharge occurs when ground water in the coastal aquifer flows down a hydraulic gradient and enters the ocean (Taniguchi and others, 2002). Ground water can discharge in distinct springs, generally defined by fractures, faults, or lava tubes, or in diffuse seepage at the shoreline or offshore (Church, 1996; Swarzenski and others, 2001; Moore, 2003). The quantity of ground-water discharge is influenced by rainfall in aquifer-recharge areas inland of the park, permeability of the geologic substrate and water consumption by pumping, waves, and tides, whereas the quality of the discharged water is influenced by land use, chemical characteristics of the geologic substrate, and pumping, which can lead to saltwater intrusion (Burnett and others, 2006).

Submarine ground water discharge can include both fresh and saline ground water (Moore, 1999; Taniguchi and others, 2002; Kim and others, 2003). Fresh ground water, which is of meteoric origin, may flow underground for long distances, taking tens or hundreds of years to travel from the recharge zone to the sea. In contrast, saline ground water is generally seawater that has undergone wave and tide-driven circulation through the coastal aquifer on a time scale of days to months; it may also include the deep, saline ground water underlying the fresh-ground-water lens in coastal areas (Horn, 2002; Burnett and others, 2006; Robinson and others, 2007). Submarine ground-water discharge can affect various aspects of water quality, including temperature, salinity, and the concentrations of nutrients and other chemicals. In Kaloko-Honokōhau National Historical Park, ground-water discharge is particularly important because it is the only significant hydrologic connection between land and sea.

Several methods have been developed for quantifying submarine ground-water discharge, including seepage-meters, natural tracers, and hydrogeologic modeling. Seepage-meters are devices constructed by embedding a chamber into sea-floor sediment, attaching a bag to the top of the chamber, and collecting the ground-water that seeps out into the bag (Lee, 1977; Lewis, 1987; Matson, 1993). Concentrations of natural tracers, such as silica, radium, radon, and methane, generally are much higher in ground-water than in surface waters and so can be used to identify areas of ground-water influence. When certain other parameters are known or estimated, natural tracers can be incorporated into a mass-balance approach to calculate ground-water fluxes. In hydrogeologic modeling, a ground-water flow model, incorporating such parameters as hydraulic head at different sites, rainfall, evapotranspiration, and aquifer transmissivity, is constructed (Smith and Nield, 2003).

Natural tracers were used to measure submarine ground-water discharge in this study for several reasons. Seepage-meters cannot be installed in rocky or wave-dominated coastal areas, which are common in the park. The natural-tracer approach also provides a more integrated estimate of submarine ground-water discharge over a scale of tens to hundreds of meters and so is not as likely to be influenced by small-scale heterogeneity (Burnett and others, 2006). Previous studies have shown that both the fresh and brackish or saline components of ground water can affect the nutrient budgets of coastal systems (Kim and others, 2003; Boehm and others, 2006; Beck and others, 2007). Because hydrogeologic modeling typically addresses only the fresh component of ground water, we decided that the natural-tracer approach, which can measure both fresh and brackish or saline ground water, was more appropriate.

Use of Radium Isotopes as Ground-Water Tracers

The use of Ra isotopes to study submarine ground-water discharge and coastal mixing processes was pioneered by Moore (1976, 1999) and has since been applied in numerous studies (for example, Krest and others, 2000; Charette and others, 2001; Kim and others, 2003; Moore, 2003; Hwang and others, 2005). The four naturally-occurring isotopes of Ra, ^{223}Ra ($t_{1/2}$=11.6 d), ^{224}Ra ($t_{1/2}$=3.7 d), ^{226}Ra ($t_{1/2}$=1600 yr), and ^{228}Ra ($t_{1/2}$=5.8 yr), are all products of the uranium and thorium radioactive decay series and thus occur naturally in most rocks on Earth. In a subterranean estuary (Moore, 1999), where fresh and saline waters mix underground, the observed Ra-isotope activity depends on the concentrations of Ra parents in the geological substrate, the free surface area of the substrate, the salinity of the ground water, and the time scale on which circulation occurs (Webster and others, 1995). Ra is continually being produced by the decay of its parent isotopes; however, in the presence of freshwater it remains sorbed onto rock or particle surfaces. As salinity rises, Ra begins to desorb and dissolve, eventually reaching full desorption at a salinity of 15 to 35 practical salinity units, depending on grain size. Coarser sediment reaches full desorption at lower salinities (Webster and others, 1995).

The four Ra isotopes exhibit chemically identical behavior but decay at vastly different rates, making them useful for characterizing mixing processes occurring on a wide range of time scales. Because this study focused on nearshore processes occurring on a time scale of hours to days, only the shorter lived isotopes, ^{223}Ra and ^{224}Ra, were used.

Study goals

The goals of this study were: (1) to characterize the quality of the park's water resources (ground water, nearshore water, anchialine pools, and fishponds) in terms of temperature, salinity, radium-isotope activity, and nutrient concentrations for later use as a baseline to assess the impact of development on water quality; (2) to characterize patterns of spatial and temporal variation in water quality; (3) to estimate ground-water-related fluxes of water and nutrients into the coastal ocean at the park using Ra isotopes and salinity as natural tracers; and (4) to assess the effect of submarine groundwater discharge on the park's water resources in terms of nutrient subsidies.

Methods

Survey Description

We surveyed all types of water that occur within and adjacent to Kaloko-Honokōhau National Historical Park, including anchialine pools, springs, fishponds, coastal and offshore water, Honokōhau Harbor, wells, and the ground water directly underneath the beach face (fig. 1). Coastal surface water was sampled along cross-shore transects at the following sites: Honokōhau Harbor, Honokōhau Beach/Aiopio Fishtrap, the beach near Aimakapa Fishpond, midpark, and the beach near Kaloko Fishpond ("the Cut"). At beach sites, three to five samples were collected at evenly spaced intervals from the shoreline out to an approximate depth of 1.5 m; the depth and distance from shore of each sample were recorded. In Honokōhau Harbor, samples were collected from the upper 1 m of the water column along a transect extending from the inner-harbor spring to the harbor mouth. The inner-harbor spring, which emerged from the inner-harbor wall about 2 m below the water's surface, created a visible disturbance at the water's surface and was noticeably colder and fresher than the surrounding water. Several samples were also collected at least 1 km offshore to provide information about the marine end-member. Samples suspected to be tidally influenced (anchialine pools, ground water directly below the beach, and nearshore areas) were sampled at high and low tides. Most study sites were sampled during three periods (December 2003, November 2005, and April 2006) to characterize seasonal variation (table 1).

Table 1. Study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i.

[X, sampled; –, not sampled]

Study site	Dec. 2003	Nov. 2005	Apr. 2006
Anchialine pools	X	X	X
Park observation wells	–	X	X
Park pits	–	X	X
Kaloko Fishpond	X	X	X
Aimakapa Fishpond	X	X	X
Beach near Aimakapa Fishpond	X	–	X
Beach near Kaloko Fishpond	X	X	–
Aiopio Fishtrap/Honokōhau Beach	X	X	X
Honokōhau Harbor	X	X	X
Midpark	–	X	–
Freeze Face Cove	–	X	–

Water-Quality Measurements

Ra-Isotope Activities

For each sample, 100 L of water was collected into a clean plastic trashcan, using either a small bilge pump or a collection funnel and 20-L plastic water carriers. In the field, the water in each trashcan was filtered through a column containing 10 to 20 g (dry weight) of manganese-coated fiber, prepared according to the procedure of Moore (1976), at a flow rate lower than 1.5 L/min to quantitatively strip Ra from the samples. A plug of plain acrylic fiber was placed in the column above the manganese-coated fiber to filter out sediment and prevent contamination.

After filtration, each sample was rinsed with freshwater, squeezed dry, and shipped back to the laboratory at Stanford University (Stanford, CA), where it was analyzed on a RaDeCC delayed-coincidence counter (Moore and Arnold, 1996) within a week of collection. The RaDeCC system measures the activities of ^{219}Rn and ^{220}Rn, which are daughter isotopes of ^{223}Ra and ^{224}Ra. ^{223}Ra and ^{224}Ra activities were calculated from the raw RaDeCC data, as described by Moore and Arnold (1996). The counting error associated with this method, which is equal to the square root of the total number of raw counts, averaged 18 percent for ^{223}Ra and 6 percent for ^{224}Ra. The error between duplicate runs was typically about 10 percent. A subset of samples was run for a second time 3 to 6 weeks after collection to correct for the contribution of ^{228}Th to the original ^{224}Ra value. Samples that were not rerun for Th correction were corrected by subtracting the average Th correction from those samples that were rerun. The Th correction was typically about 5 percent of the original total ^{224}Ra value.

Differences in ^{224}Ra/^{223}Ra isotope-activity ratios between the ground-water source (represented by wells, springs, and anchialine pools) and the water bodies into which it is discharging (such as fishponds, the coastal ocean, and Honokōhau Harbor) were used to constrain the time scales of coastal-mixing processes, following the approach of Moore (2000), which takes advantage of the different half-lives of these two isotopes. Once ground water has discharged and lost contact with the aquifer (the Ra source), the abundance of the shorter lived ^{224}Ra ($t_{1/2}$=3.6 days) will decrease relative to that of the longer lived ^{223}Ra ($t_{1/2}$=11.4 days), resulting in a lower isotope-activity ratio in nearshore compared to groundwater samples. Assuming that (1) ground water has a distinct and uniform isotope-activity ratio, (2) the only source of Ra to the coastal area is submarine groundwater discharge, and (3) the Ra behaves conservatively (except for decay) once released into the nearshore zone, the average time that the Ra has been separated from its source can be calculated. This value corresponds to the average residence time of water within the defined volume of the coastal ocean.

Salinity and Temperature

The salinity and temperature of each sample were measured in the field using a YSI 85/50 hand-held probe, which is accurate to approximately 0.1 salinity units and 0.1°C. More precise salinities were obtained by filtering 10 mL of each sample through a 0.2- or 0.45-µm syringe filter into a centrifuge tube and measuring the density of the water on an Anton-Paar density-meter at Stanford University. The density-meter brings all samples to the same temperature (20°C) before measurement, and so temperature has no effect on measured density. The densities were converted into salinities, using the UNESCO equation of state for seawater (Foffonoff, 1985). The Anton-Paar density-meter is accurate to within 0.0001 g/cm^3, corresponding to approximately 0.001 parts per thousand (ppt). When duplicate samples were run, the difference between duplicates was within this analytical error.

Nutrient Concentrations

Nutrients (nitrate, nitrite, silica, ammonium and phosphate) were analyzed on 30 mL of each sample that had been filtered through a 0.2- or 0.45-µm syringe filter and kept frozen in acid-washed amber high-density polyethylene bottles until analysis. The goal of nutrient sample filtration was to remove (1) any organic material that might decay and release nutrients during storage, and (2) any organisms that might consume nutrients already present. Because both pore sizes are adequate for these purposes, and freezing the samples promptly was an additional safeguard against biologic activity, filter-pore size would not be expected to cause any systematic error in nutrient concentrations. Samples were analyzed in the laboratory at Oregon State University (Corvallis, OR) using a continuous-segmented-flow system with components of a Technicon Autoanalyzer II and an Alpkem RFA 300. The average combined analytical, sampling, and natural-variation errors determined from 89 duplicate samples were 8, 13, 10 and 31 percent for phosphate, nitrate+nitrite, silica, and ammonium, respectively. The large error between duplicate ammonium samples appears to be due to the typically low concentrations of this nutrient. In samples with ammonium concentrations greater than 1 µM, the average difference between duplicates was 11 percent.

Results

Salinity

A depression in salinity, relative to the offshore value of approximately 35 ppt, was observed at every nearshore site sampled, as well as at Kaloko and Aimakapa Fishponds, all the anchialine pools, and Honokōhau Harbor (table 2; appendix). The salinity distributions at each sample site during each trip are presented in figure 2. The volume percentage of freshwater in each sample can be calculated from the salinity as (S_o-S_s)/S_o, where S_o is the salinity of offshore seawater and S_s is the salinity of the sample. The average salinity of Kaloko Fishpond (n=46) was 21.1 ppt, corresponding to 40 volume percent freshwater, whereas that of Aimakapa Fishpond (n=16) was 12.2 ppt (65 volume percent freshwater). The difference may be due to the fact that Kaloko Fishpond has an open connection to the sea, whereas Aimakapa Fishpond does not. The average salinity of all the anchialine pools sampled (n=42) was 16.6 ppt (53 volume percent freshwater), whereas that of Honokōhau Harbor (n=15) was 28.6 ppt (18.3 volume percent freshwater). Salinity ranges observed in fishponds and anchialine pools were as follows: Aimakapa Fishpond, 11.8 to13.2; Kaloko Fishpond, 10.9 to 32.6; and anchialine pools, 8.2 to 25.0, higher at pools near Honokōhau Harbor relative to those near Kaloko Fishpond.

Average salinities at nearshore sites ranged from 18.6 ppt (47 volume percent freshwater) at Freeze Face Cove to 32.3 ppt (8 volume percent fresh water), at the beach immediately seaward of Aimakapa Fishpond. Because no rivers or streams were present in the study area (except for a small intermittent stream in December 2003), we can conclude that the source of this freshwater is ground water.

Additionally, in April 2006 we conducted an informal salinity survey of the park's coastline in an attempt to find a high salinity "control" site where little or no submarine ground-water discharge was occurring. The highest salinity site we were able to locate was the beach near Aimakapa Fishpond, which had a shoreline salinity of 30 ppt, indicating that ground-water discharge, although spatially varying, is pervasive throughout the park.

Radium-Isotope Activity

Isotope activities of both ^{223}Ra (fig. 3) and ^{224}Ra (fig. 4) in park sites including wells, anchialine pools, fishponds, beach-pits, and nearshore samples were high relative to activities at offshore sites (table 2). Anchialine pools had the highest average ^{223}Ra-isotope activities (3.3 decays per minute per 100 L of water, or dpm/100 L), followed by Honokōhau Harbor (1.6 dpm/100 L), nearshore sites (0.6-1.5 dpm/100 L), beach-pits (1.4 dpm/100 L), Kaloko Fishpond (1.1 dpm/100 L) and Aimakapa Fishpond (0.3 dpm/100 L). The highest average ^{224}Ra-isotope activities were also measured in anchialine pools (39.5 dpm/100 L), followed by Honokōhau Harbor

(23.7 dpm/100 L), nearshore sites (8.0–20.3 dpm/100 L), beach-pits (12.4 dpm/100 L), Kaloko Fishpond (9.8 dpm/100 L), and Aimakapa Fishpond (5.8 dpm/100 L). Among nearshore sites, the highest activities of both isotopes were measured at Freeze Face Cove, whereas the lowest were measured at the beach near Aimakapa Fishpond. Although sample sites varied considerably in Ra-isotope activity, we did not note any significant inter-site differences in ^{224}Ra/^{223}Ra-isotope activity ratio (fig. 5). The pattern observed appears to represent random scatter around an average isotope-activity ratio of about 12.

At nearshore sites, ^{224}Ra-isotope activity and salinity were inversely related, with the freshest nearshore samples generally having the highest ^{224}Ra-isotope activities (fig. 6). ^{223}Ra showed the same relation, although the results are not shown here. This relation indicates that the nearshore can be conceptualized as a mixing zone with two end-members: high-salinity, low-Ra-isotope-activity seawater (represented by offshore samples) and lower-salinity, higher-Ra-isotope-activity ground water (represented by anchialine pools). Fishponds spanned the same salinity range as nearshore samples but generally had lower Ra-isotope activities and a less pronounced relation between salinity and Ra-isotope activity.

Following the approach of Moore (2000), as described in the section above entitled “Methods”, we estimated the maximum residence time of water in the nearshore zone at our study sites, using the ^{224}Ra/^{223}Ra-isotope activity ratio. The nearshore zone was defined as a triangular prism (“box”) with the following dimensions: a length equivalent to transect length (typically, 25 m), a width of 1 m (approximating the width of the area in which water was collected), and a depth equivalent to the maximum transect depth (typically, 1.5 m). At Honokōhau Harbor, we estimated ground-water discharge into the entire surface layer of the harbor. We calculated the volume of this surface layer by estimating the surface area of the harbor from a map and defining the depth of the surface layer to be 1 m. We did not note any significant difference in ^{224}Ra/^{223}Ra-isotope activity ratio between ground water and nearshore water at any study site (fig. 5), suggesting that the residence time of water at all nearshore sites sampled was less than 1.6 days, most likely much smaller (Street and others, 2007).

Nutrients

Combined Nitrate and Nitrite

The highest nitrate + nitrite concentrations were measured in park observation wells (82.6 µM, *n* = 6), followed by anchialine pools (51.2 µM, *n* = 42), beach-pits (35.5 µM, *n* = 36), nearshore areas (3.0-45.9 µM, *n* = 100), Honokōhau Harbor (22.3 µM, *n* = 15), Kaloko Fishpond (22.0 µM, *n* = 46), and Aimakapa Fishpond (9.2 µM, *n* = 16) (fig. 7). Notably, the site types expected to represent the ground-water end-member (wells, anchialine pools, and beach-pits) had the highest nitrate + nitrite concentrations. The lowest nitrate + nitrite concentrations were measured offshore (0.7 µM, *n* = 5), as expected. Among nearshore sites, the highest nitrate + nitrite concentrations were measured at Freeze Face Cove (45.9 µM, *n* = 3), followed by midpark (24.4 µM, *n* = 12), the beach near Kaloko Fishpond (24.0 µM, *n* = 26), Honokōhau Beach/Aiopio Fishtrap (17.5 µM, *n* = 51), and the beach near Aimakapa Fishpond (3.0 µM, *n* = 8). Note that all nutrient concentrations were measured on the same samples, and so the number of samples in each group (*n*) is the same for all other nutrients as for nitrate + nitrite, and is omitted in the rest of this section to avoid redundancy. In nearshore samples, we noted a strong, inverse relationship between salinity and combined nitrate + nitrite concentration (fig. 8), indicating a groundwater nitrogen source, because groundwater is the only freshwater entering the coastal ocean.

Phosphate

The highest phosphate concentrations were measured in wells (4.3 µM), followed by anchialine pools (2.6 µM), Honokōhau Harbor (2.4 µM), beach-pits (2.3 µM), nearshore sites (0.4–2.0 µM), Kaloko Fishpond (1.3 µM), Aimakapa Fishpond (1.3 µM), and offshore (0.2 µM). Again, samples expected to represent the ground-water end-member tended to have the highest phosphate concentrations. Among nearshore sites, Freeze Face Cove had the highest phosphate concentration (2.0 µM), followed by the beach near Kaloko Fishpond (1.6 µM), midpark (1.2 µM), Aiopio Fishtrap (1.0 µM), and the beach near Aimakapa Fishpond (0.4 µM) (fig. 9). As with nitrate + nitrite, a strong, inverse relation between salinity and phosphate concentration was noted in nearshore samples (fig. 8). However, some samples fell considerably above the mixing line, with much higher phosphate concentrations than would be expected on the basis of salinity, possibly indicating another phosphate source, in addition to fresh ground water. Possible generation of brackish or saline groundwater by the recirculation of seawater through the coastal aquifer will be explored further in the sections below entitled “Results: Cross-Shore Transects” and “Discussion”. Alternatively, cleansers or other chemicals used in the vicinity of Honokōhau Harbor may provide localized phosphate inputs.

Silica

The highest silica concentrations were measured in wells (574 µM), followed by Aimakapa Fishpond (530 µM), anchialine pools (463 µM), nearshore areas (65 – 412 µM), Kaloko Fishpond (327 µM), beach-pits (236 µM) and Honokōhau Harbor (181 µM), and the lowest silica concentrations were measured offshore (6 µM). Among nearshore samples, the highest silica concentrations were measured at Freeze Face Cove (412 µM), followed by the beach near Kaloko Fishpond (281 µM), midpark (231 µM), Aiopio Fishtrap (184 µM), and the beach near Aimakapa Fishpond (65 µM) (fig. 10). In nearshore samples, we noted a very strong inverse correlation between salinity and silica concentration, indicating a groundwater silica source (fig. 8).

Table 2. Means and standard deviations (σ) of salinity; ^{223}Ra and ^{224}Ra isotope activity; ^{224}Ra/^{223}Ra isotope-activity ratio; and nitrate + nitrite, phosphate, silica, and ammonium concentrations at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawaiʻi (fig. 1) during December 2003, November 2005, April 2006, and all seasons combined.

Date	Site	n	Salinity (ppt)		^{223}Ra isotope activity (dpm/100 L)		^{224}Ra isotope activity (dpm/100 L)	
			Mean	σ	Mean	σ	Mean	σ
Dec. 2003	Anchialine pools	5	13.8	0.3	4.2	1.6	43.4	11.2
	Kaloko Fishpond	4	26.2	2.9	0.5	0.1	9.4	2.6
	Aimakapa Fishpond	2	12.6	0.9	0.5	0.1	8.8	0.5
	Beach near Aimakapa Fishpond	2	34.3	0.1	0.5	0.5	5.1	0.2
	Beach near Kaloko Fishpond	7	24.4	6.9	2.1	1.3	27.9	17.7
	Aiopio Fishtrap/Honokōhau Beach	10	28.7	5.1	1.6	1.0	20.3	13.0
	Honokōhau Harbor	3	24.9	3.7	2.9	0.5	39.1	4.4
Nov. 2005	Anchialine pools	13	13.6	3.1	2.1	1.0	30.0	10.1
	Park observation wells	3	8.0	3.3	0.7	0.6	10.4	6.3
	Park pits	31	23.4	7.2	1.1	0.9	10.8	7.8
	Kaloko Fishpond	34	20.5	7.0	0.7	0.7	10.0	6.5
	Aimakapa Fishpond	7	12.2	0.2	0.2	0.1	4.7	2.7
	Beach near Aimakapa Fishpond	2	32.7	1.4	0.5	0.2	7.5	4.9
	Beach near Kaloko Fishpond	19	23.9	4.4	1.0	0.4	15.2	6.0
	Aiopio Fishtrap/Honokōhau Beach	14	26.1	5.7	1.5	1.0	16.1	9.6
	Honokōhau Harbor	5	28.2	4.0	1.3	0.8	19.6	15.4
	Midpark	12	25.7	5.0	1.0	0.5	14.4	6.1
	Freeze Face Cove	4	18.6	5.2	1.5	0.8	20.3	7.1
	Offshore	4	34.9	0.1	0.0	0.0	0.2	0.5
Apr. 2006	Anchialine pools	24	18.7	4.8	3.8	2.6	43.8	8.8
	Park observation wells	3	8.0	3.4	0.6	0.5	10.8	8.7
	Park pits	3	16.1	0.5	3.2	2.9	26.3	21.4
	Kaloko Fishpond	10	20.5	6.0	0.6	0.2	9.5	3.7
	Aimakapa Fishpond	8	12.0	0.0	0.3	0.1	5.8	0.7
	Beach near Aimakapa Fishpond	4	30.8	1.0	0.7	0.4	9.8	2.2
	Aiopio Fishtrap/Honokōhau Beach	12	27.4	3.9	1.9	1.0	20.6	10.6
	Honokōhau Harbor	12	28.5	4.2	1.1	1.3	20.1	23.3
All	Anchialine pools	42	16.6	4.9	3.3	2.2	39.5	11.3
	Park observation wells	6	8.1	3.0	0.7	0.5	10.6	6.8
	Park pits	36	23.3	7.2	1.4	1.2	12.4	10.0
	Kaloko Fishpond	46	21.1	6.7	1.1	1.9	9.8	5.7
	Aimakapa Fishpond	16	12.2	0.3	0.3	0.1	5.8	2.1
	Beach near Aimakapa Fishpond	8	32.3	1.7	0.6	0.4	8.0	3.1
	Beach near Kaloko Fishpond	26	24.5	5.0	1.2	0.8	18.1	10.9
	Aiopio Fishtrap/Honokōhau Beach	51	27.4	4.6	1.6	1.0	18.0	10.5
	Honokōhau Harbor	15	28.6	4.3	1.6	1.2	23.7	18.6
	Midpark	12	25.7	5.0	1.4	1.5	14.1	6.5
	Freeze Face Cove	3	18.6	5.2	1.5	0.8	20.3	7.1
	Offshore	5	34.8	0.1	0.0	0.0	0.4	0.6

Table 2. Means and standard deviations (σ) of salinity; ^{223}Ra and ^{224}Ra isotope activity; ^{224}Ra/^{223}Ra isotope-activity ratio; and nitrate + nitrite, phosphate, silica, and ammonium concentrations at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, April 2006, and all seasons combined—Continued.

Date	Site	^{224}Ra/^{223}Ra isotope-activity ratio		Nitrate + nitrite (µmol/L)		Phosphate (µmol/L)	
		Mean	σ	Mean	σ	Mean	σ
Dec. 2003	Anchialine pools	10.9	2.3	43.6	23.6	2.3	0.8
	Kaloko Fishpond	20.5	6.2	5.2	6.9	0.5	0.5
	Aimakapa Fishpond	16.4	2.8	51.0	n/a	4.1	n/a
	Beach near Aimakapa Fishpond	24.2	25.6	1.3	0.4	0.3	0.0
	Beach near Kaloko Fishpond	16.3	8.0	23.9	17.9	1.6	1.0
	Aiopio Fishtrap/Honokōhau Beach	13.3	2.8	14.4	14.0	1.0	0.7
	Honokōhau Harbor	13.8	1.6	30.2	8.2	3.2	1.9
Nov. 2005	Anchialine pools	16.4	8.3	60.6	19.5	3.0	0.5
	Park observation wells	18.4	5.7	85.1	15.1	4.4	0.4
	Park pits	9.9	3.7	32.5	16.8	2.1	1.7
	Kaloko Fishpond	16.3	5.7	24.8	18.5	1.5	0.9
	Aimakapa Fishpond	30.2	14.3	11.6	14.2	1.5	1.0
	Beach near Aimakapa Fishpond	13.2	4.2	2.9	1.0	0.3	0.1
	Beach near Kaloko Fishpond	17.0	5.0	24.7	11.2	1.6	0.6
	Aiopio Fishtrap/Honokōhau Beach	12.5	4.7	17.5	12.9	0.9	0.5
	Honokōhau Harbor	14.0	2.8	23.5	16.0	2.8	2.8
	Midpark	15.9	4.0	24.7	16.8	1.2	0.7
	Freeze Face Cove	14.4	5.4	45.9	17.9	2.0	0.8
	Offshore	n/a	n/a	0.7	0.3	0.2	0.1
Apr. 2006	Anchialine pools	13.1	3.9	47.7	26.4	2.5	0.9
	Park observation wells	16.3	1.1	80.1	30.7	4.2	0.8
	Park pits	8.3	2.0	73.2	3.5	2.1	1.1
	Kaloko Fishpond	17.0	3.6	17.8	23.4	1.0	1.2
	Aimakapa Fishpond	20.5	8.7	1.8	3.1	0.8	0.4
	Beach near Aimakapa Fishpond	15.6	5.4	4.3	1.6	0.4	0.1
	Aiopio Fishtrap/Honokōhau Beach	11.2	3.3	20.0	13.5	1.0	0.4
	Honokōhau Harbor	15.6	7.8	17.2	14.1	1.6	1.1
All	Anchialine pools	13.9	5.7	51.2	24.5	2.6	0.8
	Park observation wells	17.3	3.8	82.6	21.8	4.3	0.6
	Park pits	9.4	3.7	35.5	19.6	2.3	1.8
	Kaloko Fishpond	15.5	6.9	22.0	19.6	1.3	1.0
	Aimakapa Fishpond	23.2	11.2	9.2	15.3	1.3	1.1
	Beach near Aimakapa Fishpond	17.2	11.3	3.0	1.7	0.4	0.1
	Beach near Kaloko Fishpond	16.6	5.7	24.0	12.7	1.6	0.7
	Aiopio Fishtrap/Honokōhau Beach	12.5	4.0	17.5	13.1	1.0	0.5
	Honokōhau Harbor	14.6	5.1	22.3	14.1	2.4	2.1
	Midpark	14.7	5.6	24.4	15.5	1.2	0.6
	Freeze Face Cove	14.4	5.4	45.9	17.9	2.0	0.8
	Offshore	n/a	n/a	0.7	0.3	0.2	0.0

Table 2. Means and standard deviations (σ) of salinity; ^{223}Ra and ^{224}Ra isotope activity; ^{224}Ra/^{223}Ra isotope-activity ratio; and nitrate + nitrite, phosphate, silica, and ammonium concentrations at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, April 2006, and all seasons combined—Continued.

Date	Site	Silica (µmol/L)		Ammonium (µmol/L)	
		Mean	σ	Mean	σ
Dec. 2003	Anchialine pools	478	54	1.5	2.2
	Kaloko Fishpond	188	70	0.8	1.0
	Aimakapa Fishpond	532.4	15.7	2.0	n/a
	Beach near Aimakapa Fishpond	22	1	0.3	0.3
	Beach near Kaloko Fishpond	254	181	0.6	0.3
	Aiopio Fishtrap/Honokōhau Beach	157	132	0.4	0.2
	Honokōhau Harbor	259	89	0.6	0.1
Nov. 2005	Anchialine pools	513	54	1.3	1.8
	Park observation wells	531	98	0.8	0.4
	Park pits	227	151	0.7	0.6
	Kaloko Fishpond	335	170	1.0	0.7
	Aimakapa Fishpond	543	16	0.6	0.3
	Beach near Aimakapa Fishpond	64	24	0.7	0.1
	Beach near Kaloko Fishpond	296	115	1.1	0.4
	Aiopio Fishtrap/Honokōhau Beach	194	113	1.0	0.4
	Honokōhau Harbor	167	112	0.8	0.8
	Midpark	233	131	0.8	0.2
	Freeze Face Cove	412	136	0.8	0.5
	Offshore	6	5	0.6	0.4
Apr. 2006	Anchialine pools	433	106	0.5	0.4
	Park observation wells	616	54	0.2	0.1
	Park pits	423	89	0.4	0.1
	Kaloko Fishpond	340	148	0.8	0.7
	Aimakapa Fishpond	518	15	0.4	0.2
	Beach near Aimakapa Fishpond	93	24	0.7	0.1
	Aiopio Fishtrap/Honokōhau Beach	183	93	1.0	0.4
	Honokōhau Harbor	157	121	0.6	0.3
All	Anchialine pools	463	94	0.9	1.3
	Park observation wells	574	85	0.5	0.4
	Park pits	236	156	0.7	0.6
	Kaloko Fishpond	327	163	0.9	0.7
	Aimakapa Fishpond	530	19	0.6	0.4
	Beach near Aimakapa Fishpond	65	36	0.6	0.2
	Beach near Kaloko Fishpond	281	131	1.0	0.5
	Aiopio Fishtrap/Honokōhau Beach	184	111	0.9	0.4
	Honokōhau Harbor	181	112	0.7	0.5
	Midpark	231	121	0.9	0.3
	Freeze Face Cove	412	136	0.8	0.5
	Offshore	6	4	0.5	0.4

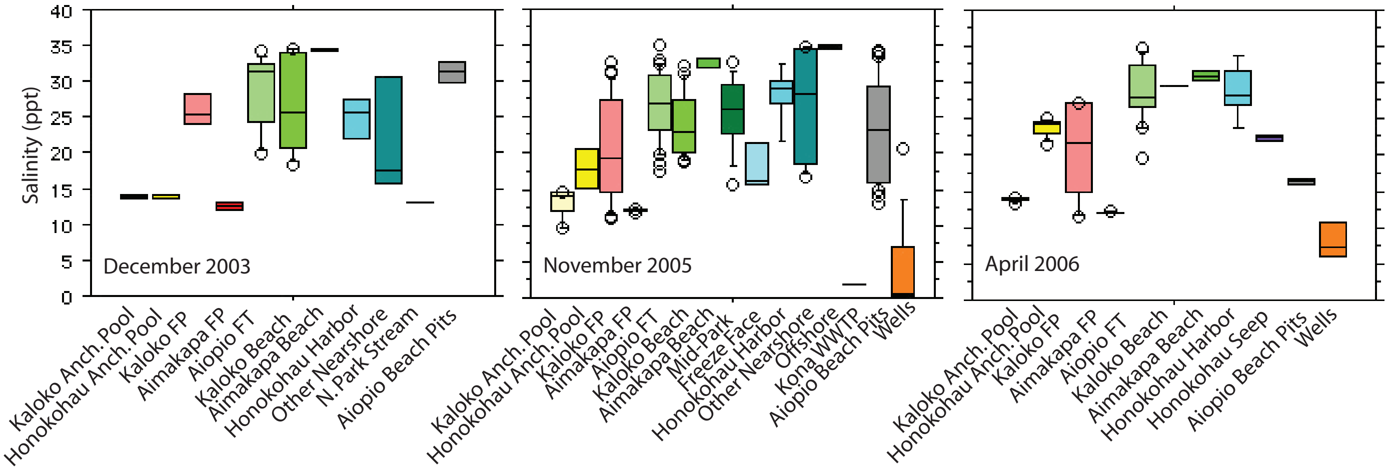

Figure 2. Salinity at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, and April 2006. Each color represents the same sample site in all plots (including those for other water quality parameters), although not all sample sites appear in all plots because they were not sampled in all seasons.

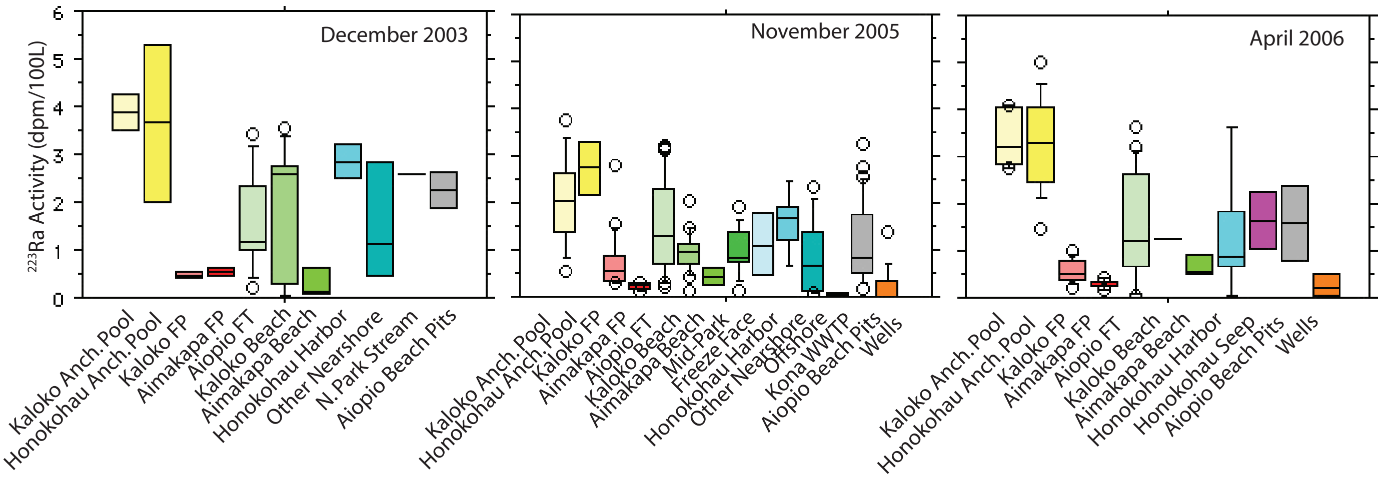

Figure 3. ^{223}Ra-isotope activity at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, and April 2006.

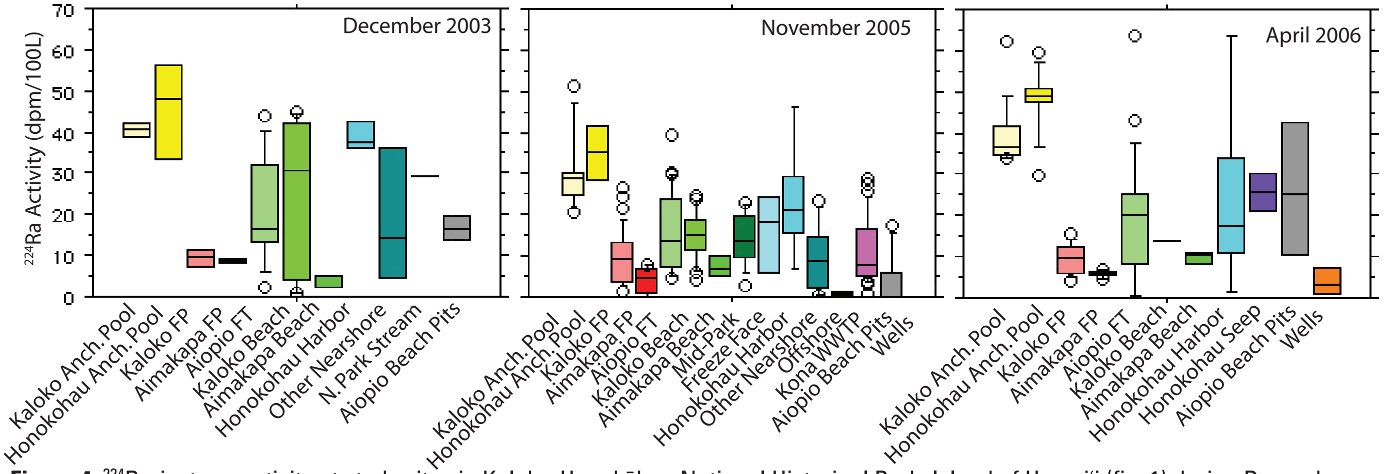

Figure 4. ^{224}Ra-isotope activity at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, and April 2006.

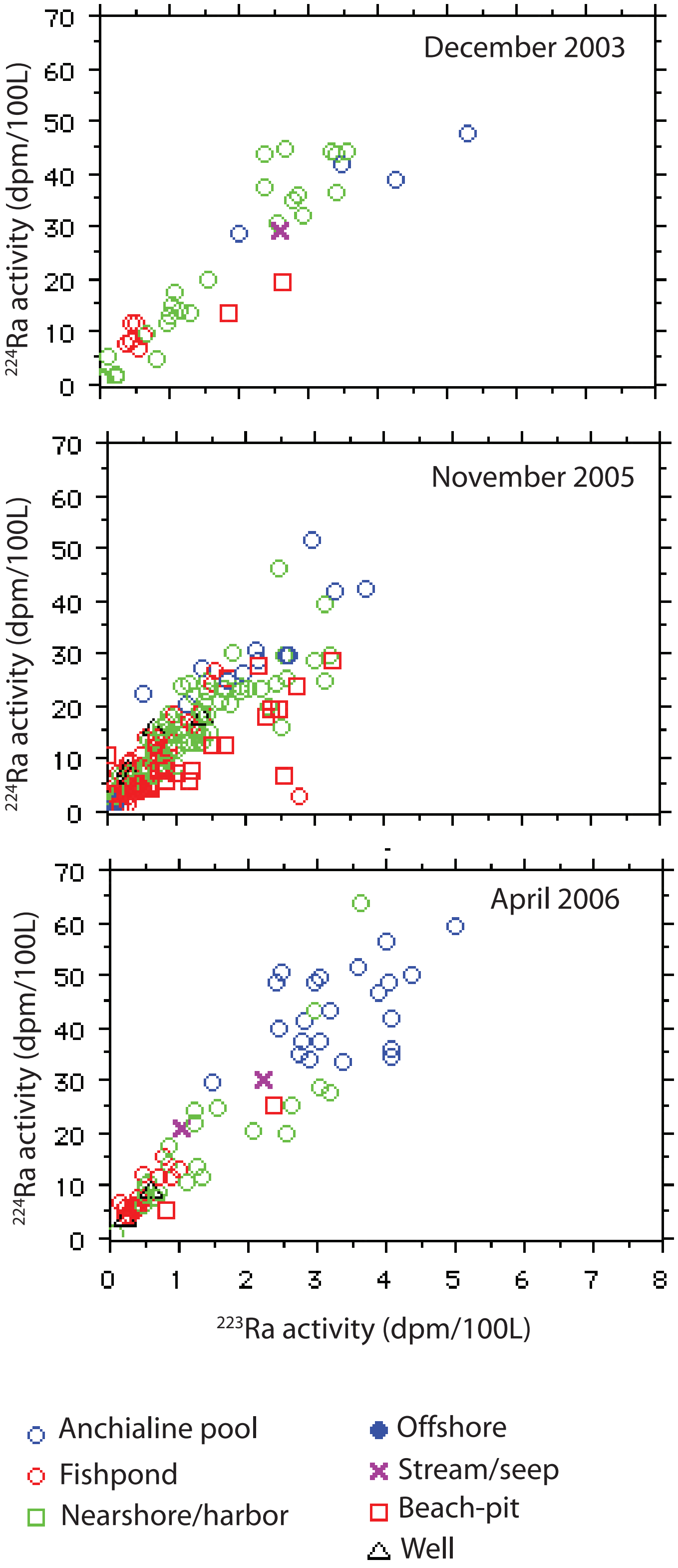

Figure 5. ^{224}Ra/^{223}Ra-isotope activity ratio at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, and April 2006.

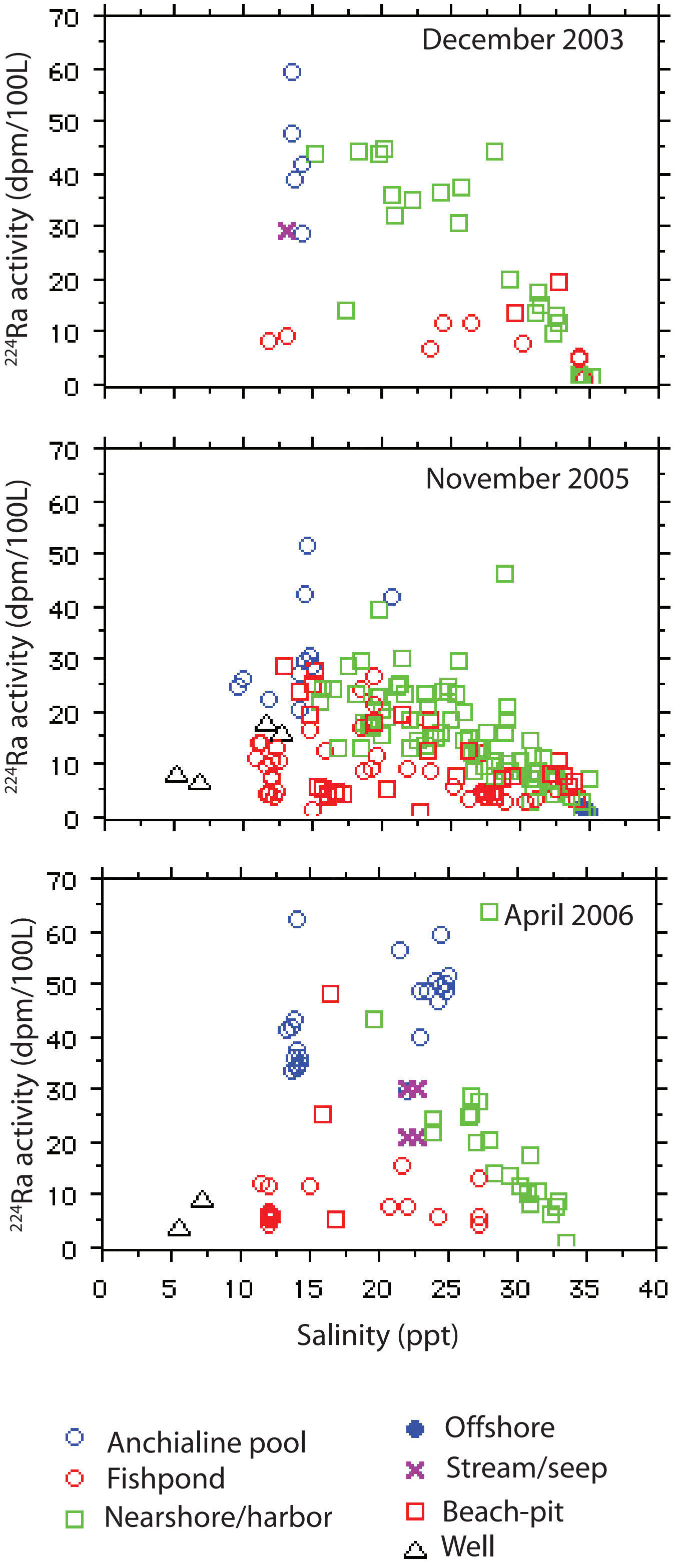

Figure 6. ^{224}Ra-isotope activity vs. salinity at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, and April 2006, showing patterns of mixing within coastal aquifer and nearshore ocean.

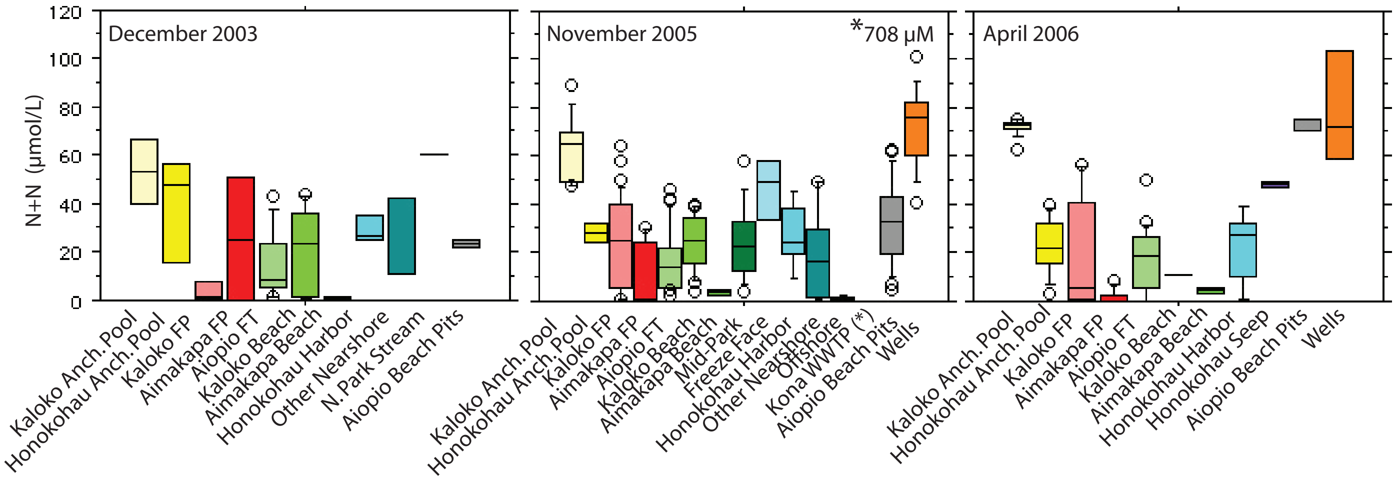

Figure 7. Combined nitrate + nitrite (N + N) concentrations study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, and April 2006. Nitrite concentrations were generally negligible relative to nitrate.

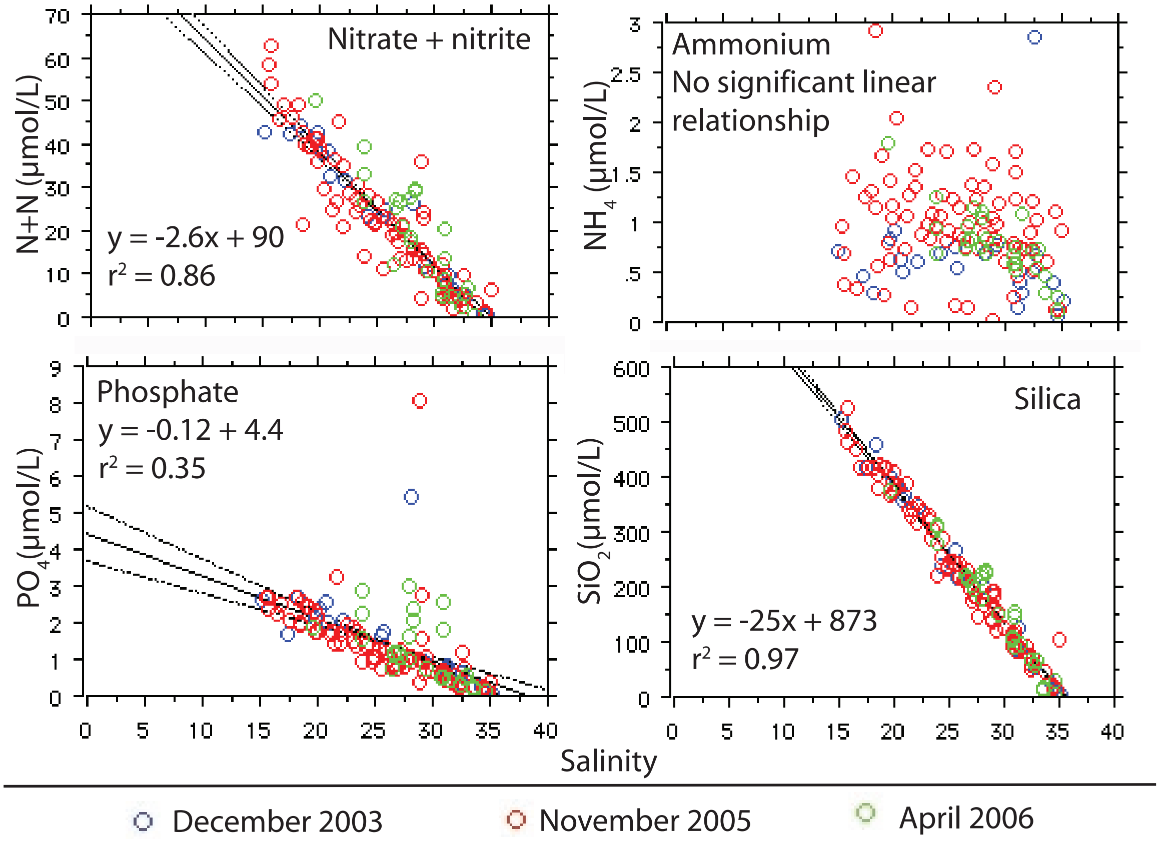

Figure 8. Nitrate + nitrite (N + N), phosphate (PO_4), ammonium (NH_4), and silica (SiO_2) concentrations versus salinity at coastal-ocean sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1). Solid black lines indicate statistically significant ($p < 0.05$) linear regressions, and dotted black lines represent the 95-percent confidence intervals about them.

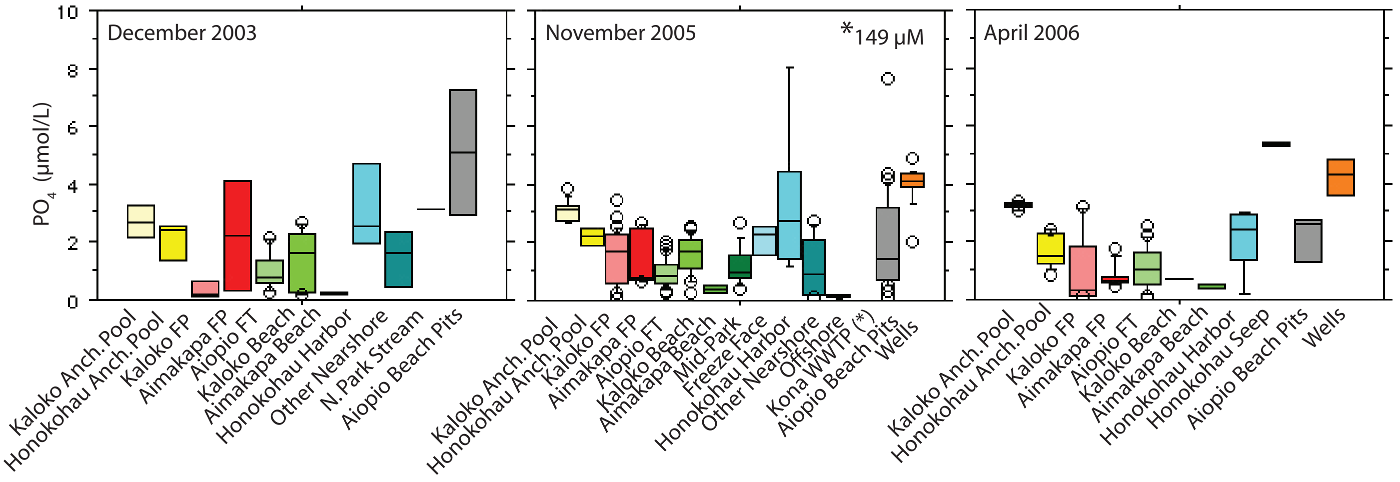

Figure 9. Phosphate concentration at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, and April 2006.

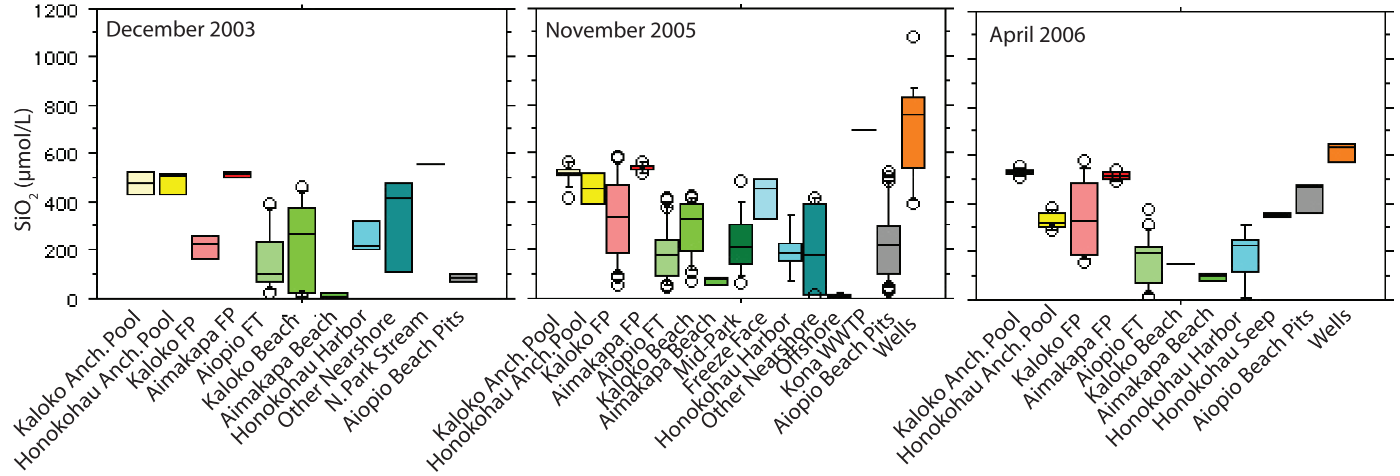

Figure 10. Silica concentration at study sites in Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, and April 2006.

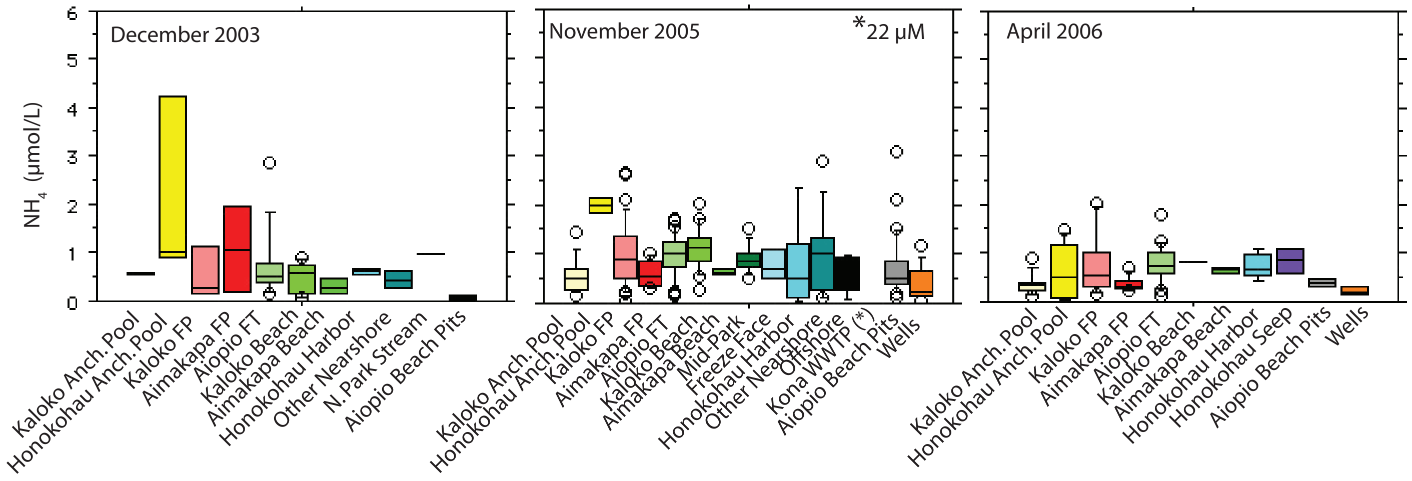

Figure 11. Ammonium concentration at study sites in Kaloko-Honokōhtau National Historical Park, Island of Hawai‘i (fig. 1) during December 2003, November 2005, and April 2006.

Ammonium

Ammonium concentrations in water bodies throughout the park were generally less than 1 μM. We did not note any significant differences in ammonium concentration (fig. 11), or any correlation between salinity and ammonium concentration in nearshore samples (fig. 8), indicating a low, randomly varying ammonium background with no distinct source.

Spatial Variation: Cross-Shore Transects

Samples were collected along cross-shore transects at Honokōhau Harbor, the beaches near both fishponds, Aiopio Fishtrap/Honokōhau Beach, and midpark. Gradients observed along these transects generally supported the idea of cold, low-salinity, high-Ra-isotope-activity, high-nutrient-concentration ground water discharging at the shoreline and being diluted by seawater in the coastal ocean. Thus, the lowest salinities and temperatures, and the highest Ra-isotope activities and nutrient concentrations, were measured closest to shore. Salinity and temperature increased, and Ra-isotope activities and nutrient concentrations decreased, with distance offshore.

At Honokōhau Harbor (fig. 12), fresh ground water composed an average of 40 volume percent of the total surface water near the inner-harbor spring, decreasing to an average of 6 volume percent near the harbor mouth. Salinity and temperature increased steadily with distance from the inner-harbor spring, displaying only a slight dip at 500 m away. However, the activities of both Ra isotopes showed strong mid-harbor peaks, much higher than those measured at the inner-harbor spring, indicating distinct, high-Ra-isotope-activity springs in mid-harbor. In November 2005, we noted peaks in nitrate + nitrite, phosphate, and ammonium concentrations corresponding to the peak in Ra-isotope-activity. Interestingly, these peaks were much less pronounced in April 2006, indicating that nutrient enrichment in the mid-harbor spring(s) varies sporadically or seasonally.

Samples along the cross-shore transect near Aimakapa Fishpond (fig. 13) had salinities of 30 ppt (14 volume percent fresh ground water) at the shoreline and a salinity of 32.5 ppt (7 volume percent fresh groundwater) 25 m offshore. Nutrient concentrations showed the typical pattern (decreasing offshore) except that the ammonium concentration increased offshore. At the transect near Kaloko Fishpond (fig.14), both salinity and temperature increased offshore and were lower at low tide and higher at high tide. Ra-isotope activities fluctuated considerably along the transect and generally increased at the end of the transect near the fishpond mouth, indicating Ra inputs from the fishpond. Nitrate + nitrite, phosphate, and silica concentrations decreased offshore, whereas ammonium concentration increased, indicating that the spring at the shoreward end of the transect was the main source of nitrate + nitrite, phosphate, and silica, whereas ammonium originated either from the fishpond or from another offshore source, or is produced in the nearshore zone.

Along the Aiopio Fishpond transect (fig.15), the fresh ground-water component at the shoreline ranged from 14–49 volume percent, decreasing to 3–6 volume percent at 200 m from shore. Both salinity and temperature increased steadily offshore. However, in November 2005 and April 2006 at low tide, peaks in Ra-isotope-activity and nutrient concentrations were measured in the middle of the fish trap, 10 to 50 m from shore, possibly indicating a distinct high-salinity, high-Ra-isotope-activity, high-nutrient-concentration ground-water end-member discharging slightly offshore, perhaps the same end-member already noted in Honokōhau Harbor. Along the mid-park transect (fig. 16), fresh groundwater composed as much as 54 volume percent of the water at the shoreline, decreasing to 9–14 volume percent at 25 m from shore. All water-quality parameters displayed the typical trends, except that ammonium concentration peaked at 5 m from shore rather than at the shoreline.

Spatial Variation: Fishponds

Kaloko and Aimakapa Fishponds differed in their water quality (table 2). On average, Kaloko Fishpond was much more saline (21.1 ppt, *n* =46) than Aimakapa Fishpond (12.2 ppt, *n* =16) —not surprising, because Kaloko Fishpond has an open connection to the sea, whereas Aimakapa Fishpond has no outlet. Salinity was remarkably constant at Aimakapa Fishpond, varying by less than 0.5 ppt over all three sampling periods. Kaloko Fishpond was generally warmer than Aimakapa Fishpond, a difference that was more pronounced in winter (Dec. 2003 and Nov. 2005) than in summer (Apr. 2006). Average isotope activities of ^{223}Ra and ^{224}Ra were higher in Kaloko Fishpond (1.1 and 9.8 dpm/100 L, respectively) than in Aimakapa Fishpond (0.3 and 5.8 dpm/100 L, respectively). Phosphate concentrations in the two fishponds were nearly the same, whereas nitrate + nitrate concentrations were higher in Kaloko Fishpond, leading to a higher N:P ratio and possibly indicating differences in nutrient cycling and limitation between the two ponds. For example, because Aimakapa Fishpond does not have an open connection to the ocean, the residence time of water in that pond is likely longer than in Kaloko Fishpond, possibly resulting in more complete nitrogen consumption.

Temporal Variation: Tidal Cycle

In addition to sampling cross-shore transects and fishponds during high and low tides, a subset of study sites was also sampled every 4 hours over a 24-hour period to better understand variation in water quality related to the tidal cycle: in November 2005, Kaloko Fishpond and Honokōhau Beach/Aiopio Fishtrap; and in April 2006, four anchialine pools (two near Kaloko Fishpond and two near Honokōhau Beach) and Honokōhau Beach/Aiopio Fishtrap. At each sample site, some degree of variation in water quality was observed over the course of the tidal cycle; however, the rela-

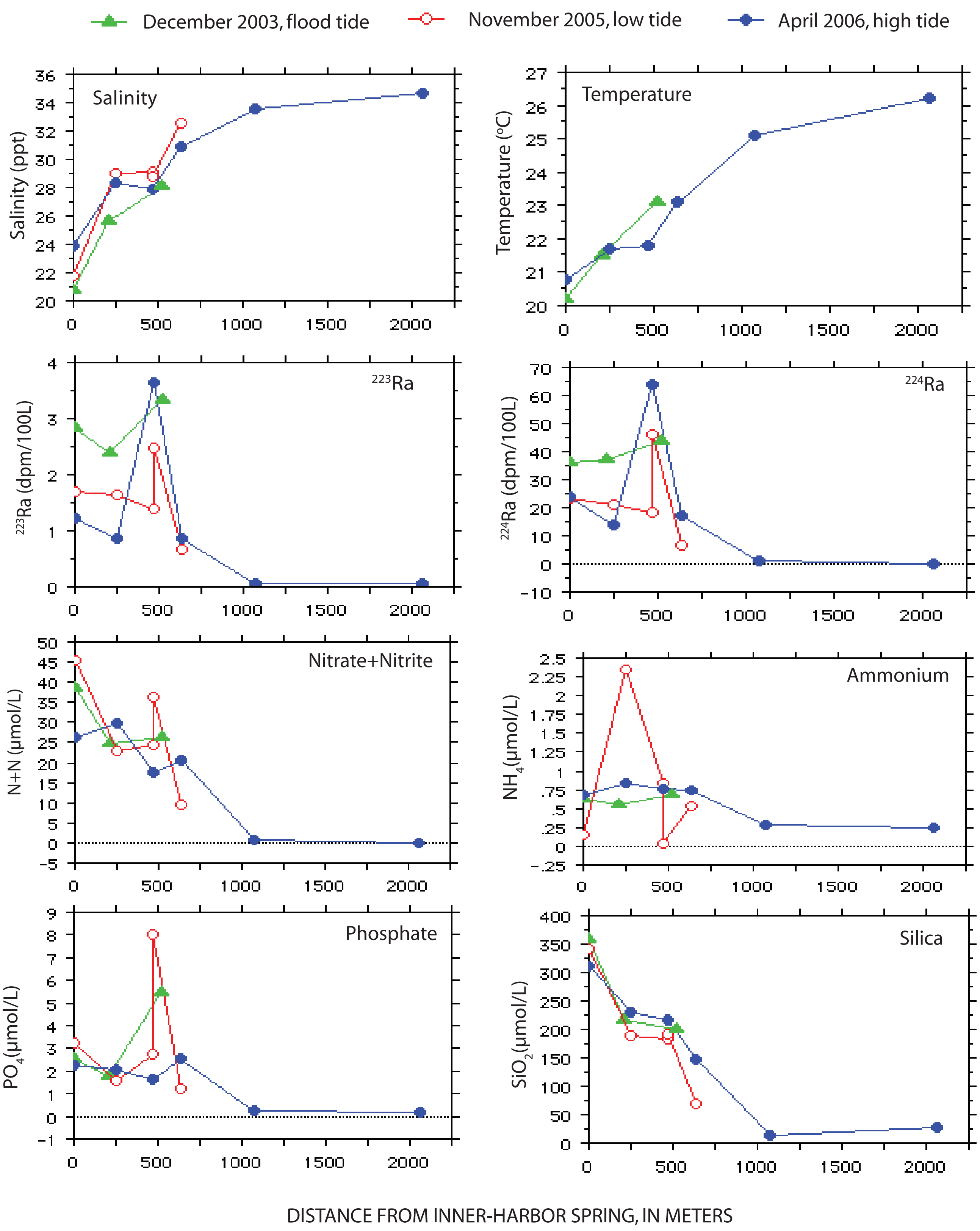

Figure 12. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations along Honokōhau Harbor coastal-ocean transect, Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1).

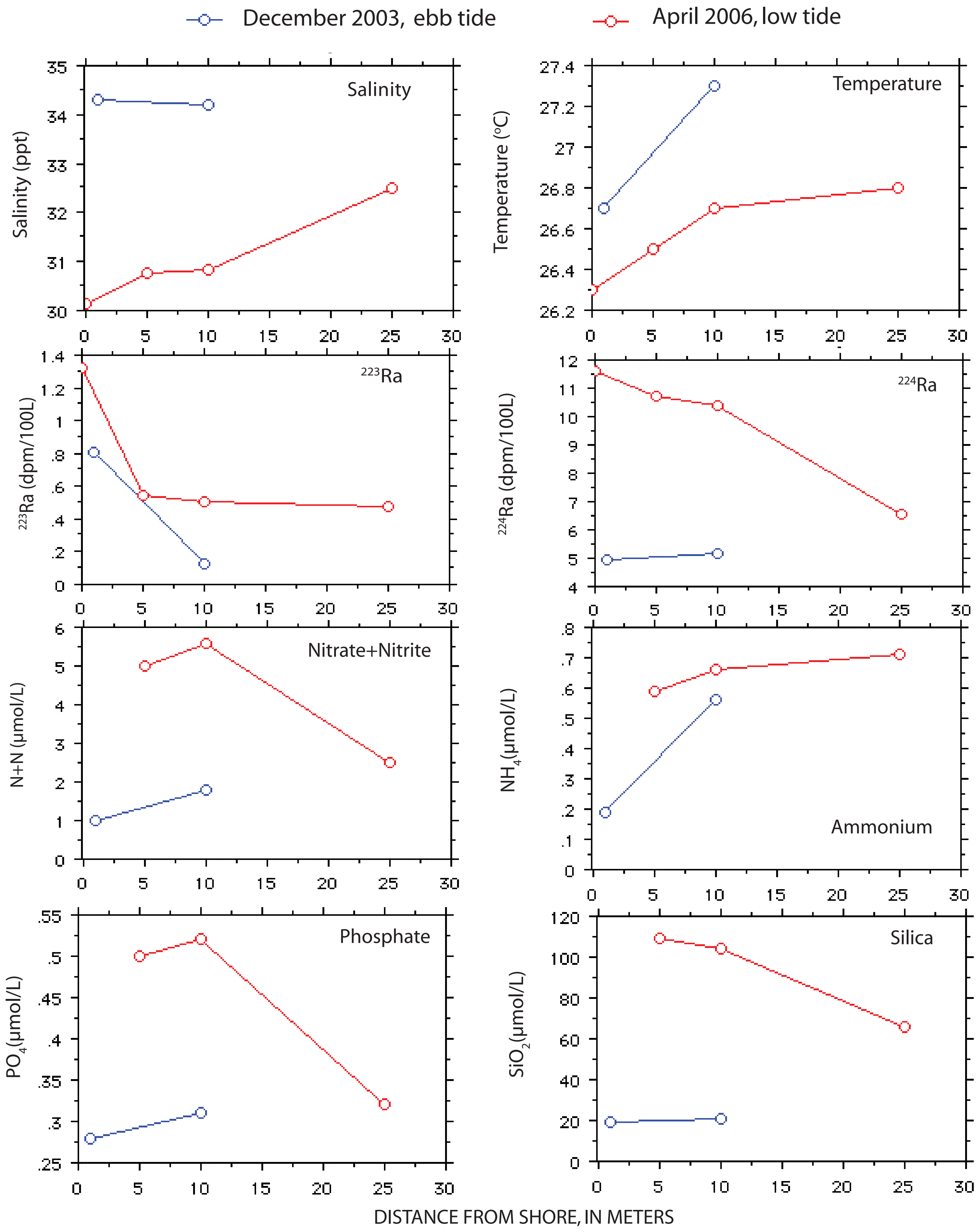

Figure 13. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations along Aimakapa coastal-ocean transect, Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1).

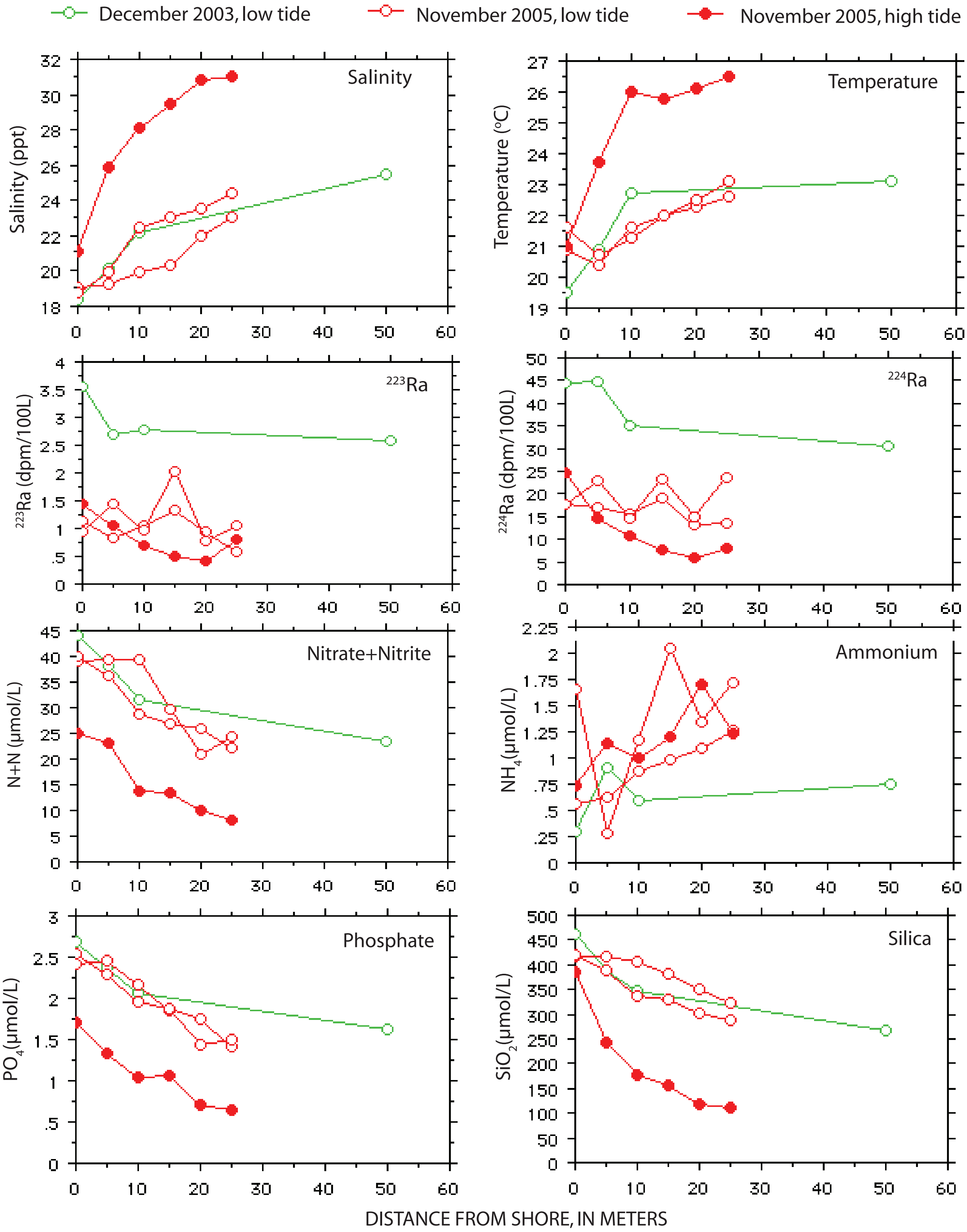

Figure 14. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations along Kaloko coastal-ocean transect, Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1).

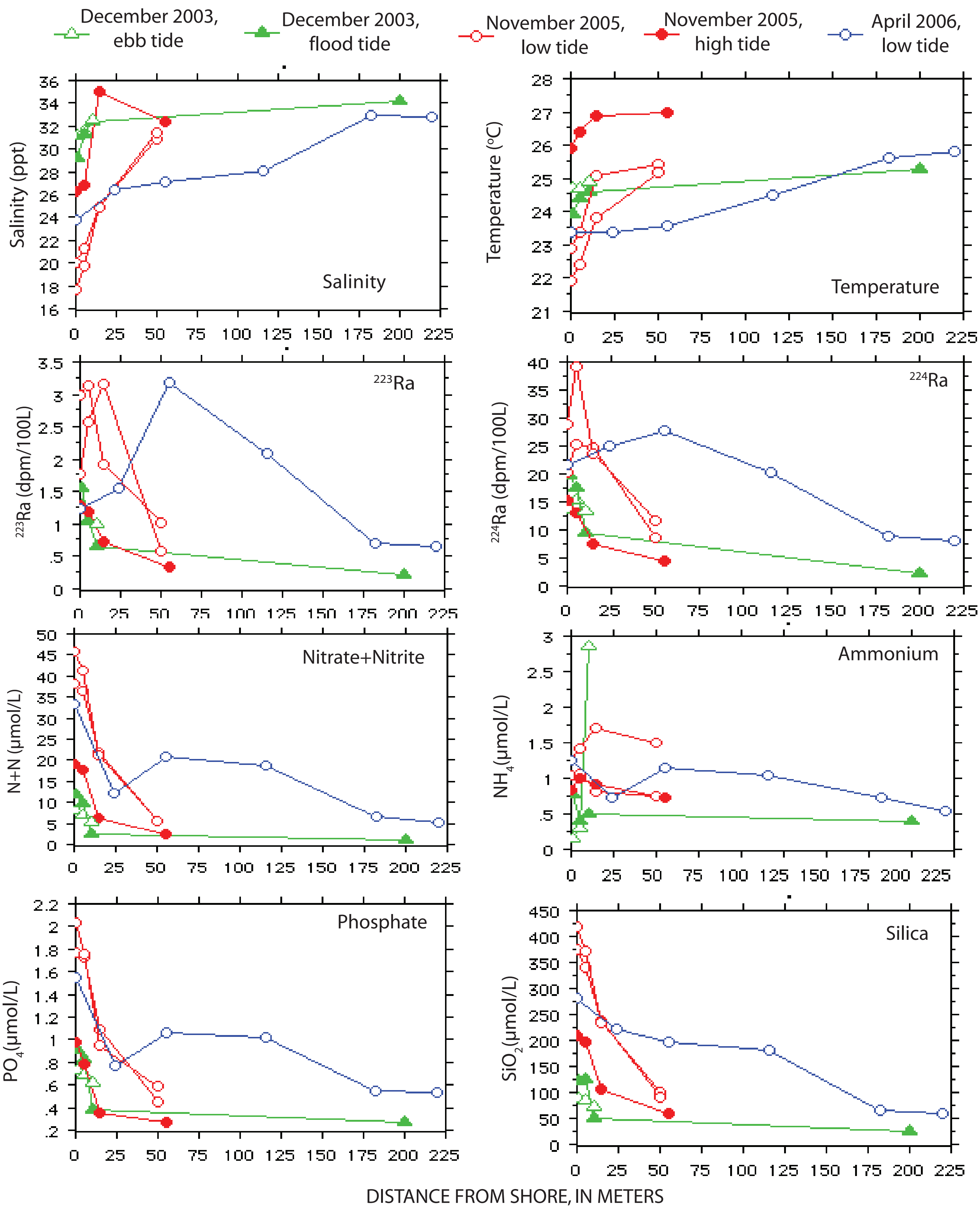

Figure 15. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations along Aiopio Fishtrap coastal-ocean transect, Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1).

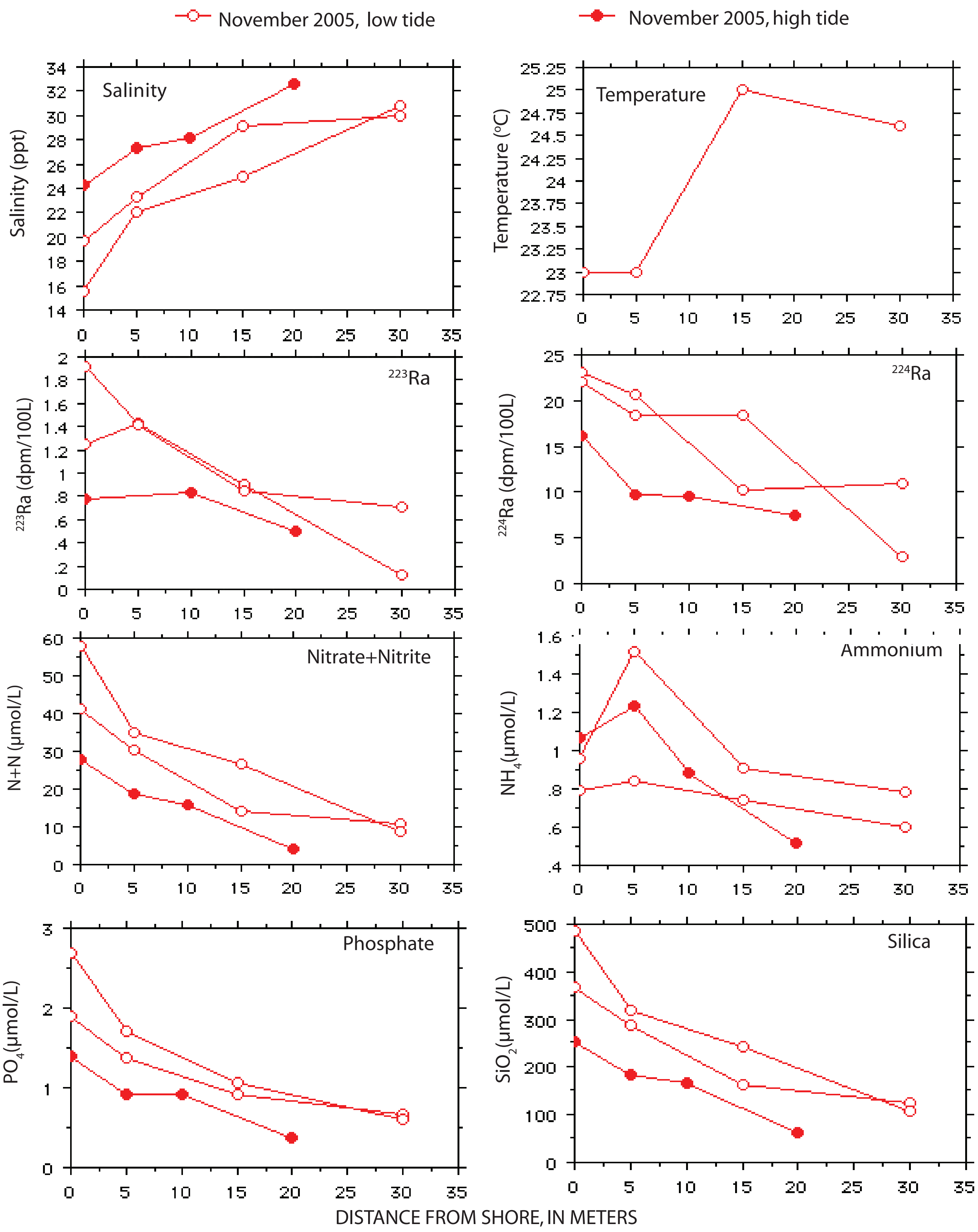

Figure 16. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations along mid-park coastal-ocean transect, Kaloko-Honokōhau National Historical Park, Island of Hawaiʻi (fig. 1).

tion of this variation to tide level was clearer at some sample sites than at others.

At Kaloko Fishpond, two springs (LSTNP, Q3A, fig.1) were sampled (fig. 17). Neither spring displayed any tidal variation in salinity, ^{223}Ra-isotope activity or silica concentration. ^{224}Ra-isotope activity and nitrate + nitrite, phosphate, and ammonium concentrations all displayed possible tidal variation. Interestingly, the two springs seemed to respond in opposite ways to tidal forcing. For example, the nitrate + nitrite concentration at spring LSTNP increased at high tide, whereas that at spring Q3A decreased, possibly indicating a difference in lag-times between forcing and response, or truly different responses.

At Aiopio Fishtrap, two sites (fig.1; figs 18,19) were sampled in November 2005; site 1 (fig. 20) was also sampled in April 2006. At each sample site, water was sampled from a beach-pit and from the coastal ocean at the shoreline. As expected, both salinity and temperature were highest at high tide in the coastal-ocean sample, indicating a lower volume percentage of cold, fresh ground water at that time. The salinity and temperature of water collected from the beach-pit did not appear to be tidally influenced, except possibly at sample site 3. Isotope activities of both ^{223}Ra and ^{224}Ra were negatively correlated with tide level; that is, they were higher at low tide. This result is expected, because Ra-isotope activities are higher in ground water than in ocean water, and submarine ground-water discharge is expected to be greater at low tide because of the steeper hydraulic gradient between the water table and sea level. In November 2005 at sample site 1, the Ra signal of water from the beach-pit seemed to lag behind that of the ocean sample; however, at sample site 3, the Ra signal of the ocean sample seemed to lag behind that of the beach-pit. In April 2006, both the beach-pit and ocean samples responded simultaneously to the tidal signal.

The relation of nutrient concentrations to tidal level at Aiopio Fishtrap was complex. In April 2006 (fig. 20), concentrations of all nutrients in both the beach-pit and ocean samples showed the expected, inverse relation to tidal level, except for nitrate + nitrite in the beach-pit, which remained almost constant over the sampling period. This result is consistent with the hypothesis that submarine ground-water discharge, which occurs to a greater degree at low tide, is the main source of nutrients to the coastal ocean. In November 2005 at sample site 3 (figs. 1,19), nitrate + nitrite, phosphate, and silica concentrations in the ocean sample showed the expected inverse relation to tidal level; however, the relation between tidal level and the concentrations of these nutrients in the beach-pit was unclear. Ammonium concentration in the ocean sample was positively correlated with tidal level. At sample site 1 (figs. 1,18), nitrate + nitrite, phosphate, and silica concentrations in the beach-pit sample showed an inverse relation to tidal level, whereas in the ocean sample they did not appear to be related to tidal level.

The relation of water-quality parameters to tidal level in anchialine pools varied. Both of the anchialine pools near Kaloko Fishpond that were sampled appeared to be tidally influenced; however, the timing of their tidal responses differed despite their close proximity, likely owing to variations in hydraulic conductivity (fig. 21). Salinity and temperature at both pools varied directly with tidal level, although a greater lag-time was apparent at pool 9 (fig. 9). Ra-isotope activity in both pools appeared to vary inversely with tidal level. Ammonium, phosphate, and silica concentrations in pool 5 (fig.1) were inversely correlated with tidal level, whereas nitrate + nitrite concentration remained fairly constant over the sampling period. In pool 9 (fig. 1), ammonium and silica concentrations were negatively correlated with tidal level, whereas nitrate + nitrite and phosphate concentrations appeared to be positively correlated. Interestingly, the magnitude of tidal variation in salinity, temperature, Ra-isotope activity and nutrient concentration in anchialine pools was not especially large and was generally lower than in coastal ocean samples collected at the shoreline.

In the two anchialine pools near Aiopio Fishtrap (fig. 22), salinity at one pool (A, fig.1), and temperature at both pools appeared to be positively correlated with tidal level. The relation of Ra-isotope activity to tidal level in these pools was unclear, possibly because the Kona coast has a mixed semidiurnal tidal pattern, with four distinct tides (high high, high low, low high, and low low) each day. Nutrient concentrations in both pools appeared to be positively correlated with tidal level, but the patterns of variation in nutrient concentrations may have resulted from other sources (for example, diurnal patterns of photosynthesis and respiration by organisms inhabiting the pools) that approximately coincided with tidal variation during the study period. The magnitudes of response were much greater in these anchialine pools than in those near Kaloko Fishpond, possibly because they are influenced to a greater degree by ocean water. This hypothesis is supported by the higher salinity of the Honokōhau anchialine pools and their closer proximity to the shoreline.

Temporal Variation: Seasonal

No striking seasonal variations in water quality at Kaloko-Honokōhau National Historical Park were observed in this study, although some water-quality parameters did vary at certain study sites over the three sampling trips (figs. 1–4, 7, 9–11; table 2). No notable seasonal variations in salinity were observed at any study site. Isotope activities of ^{223}Ra and ^{224}Ra displayed similar patterns of seasonal variation. Ra-isotope activities in anchialine pools were higher in December 2003 and April 2006 relative to November 2005. At the beach near Kaloko Fishpond, Aiopio Fishtrap, and Honokōhau Harbor, the highest Ra-isotope activities were measured in December 2003. Aimakapa Fishpond had much higher nitrate + nitrite, ammonium, and phosphate concentrations in December 2003 than at any other time. Nutrient concentrations in other water bodies did not vary considerably. The general seasonal stability of water quality in the park distinguishes it from many other coastal areas, where significant seasonal changes in water quality, occur commonly resulting from seasonal variation in precipitation and runoff.

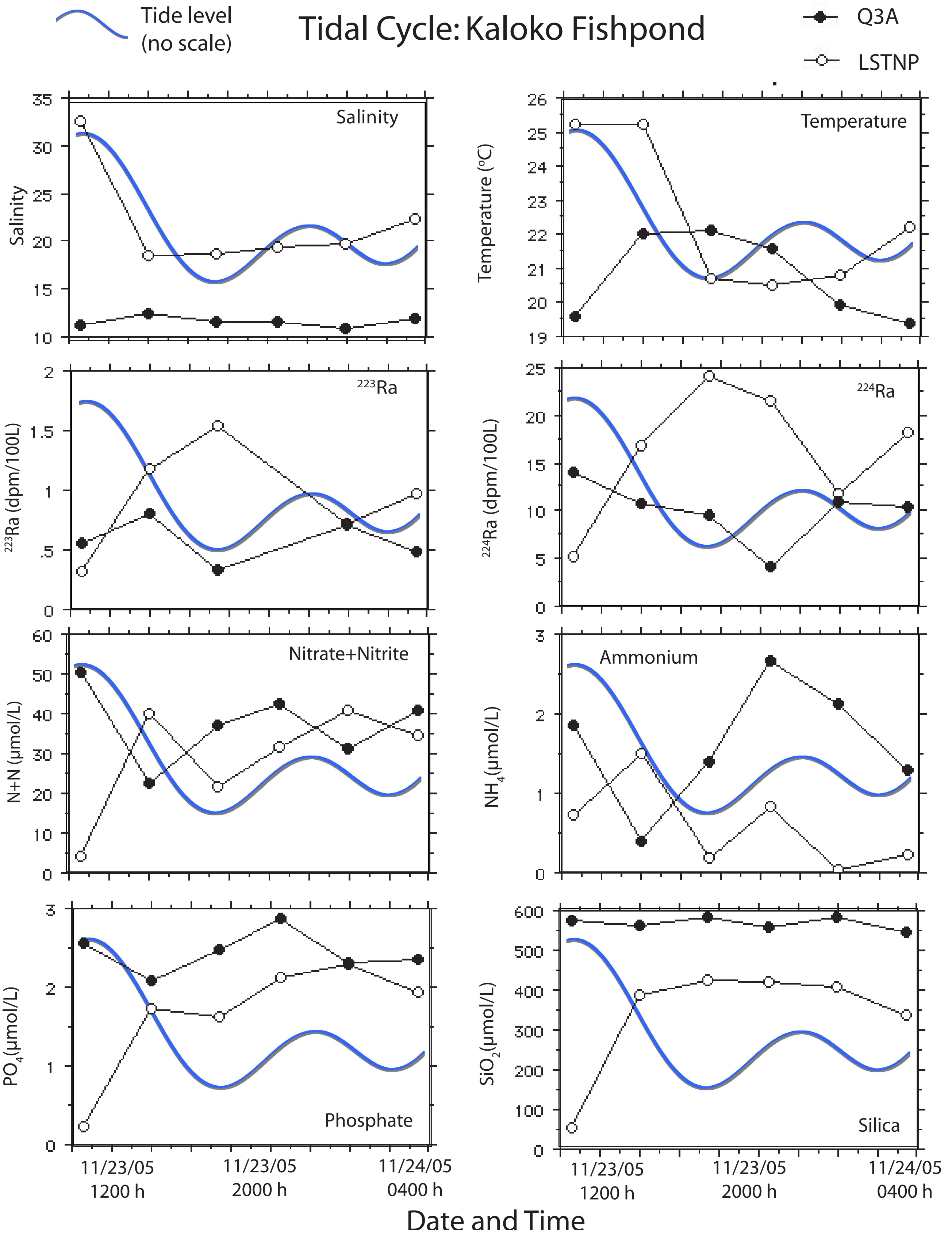

Figure 17. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations over one complete tidal cycle in November 2005 at two springs in Kaloko Fishpond, Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig.1).

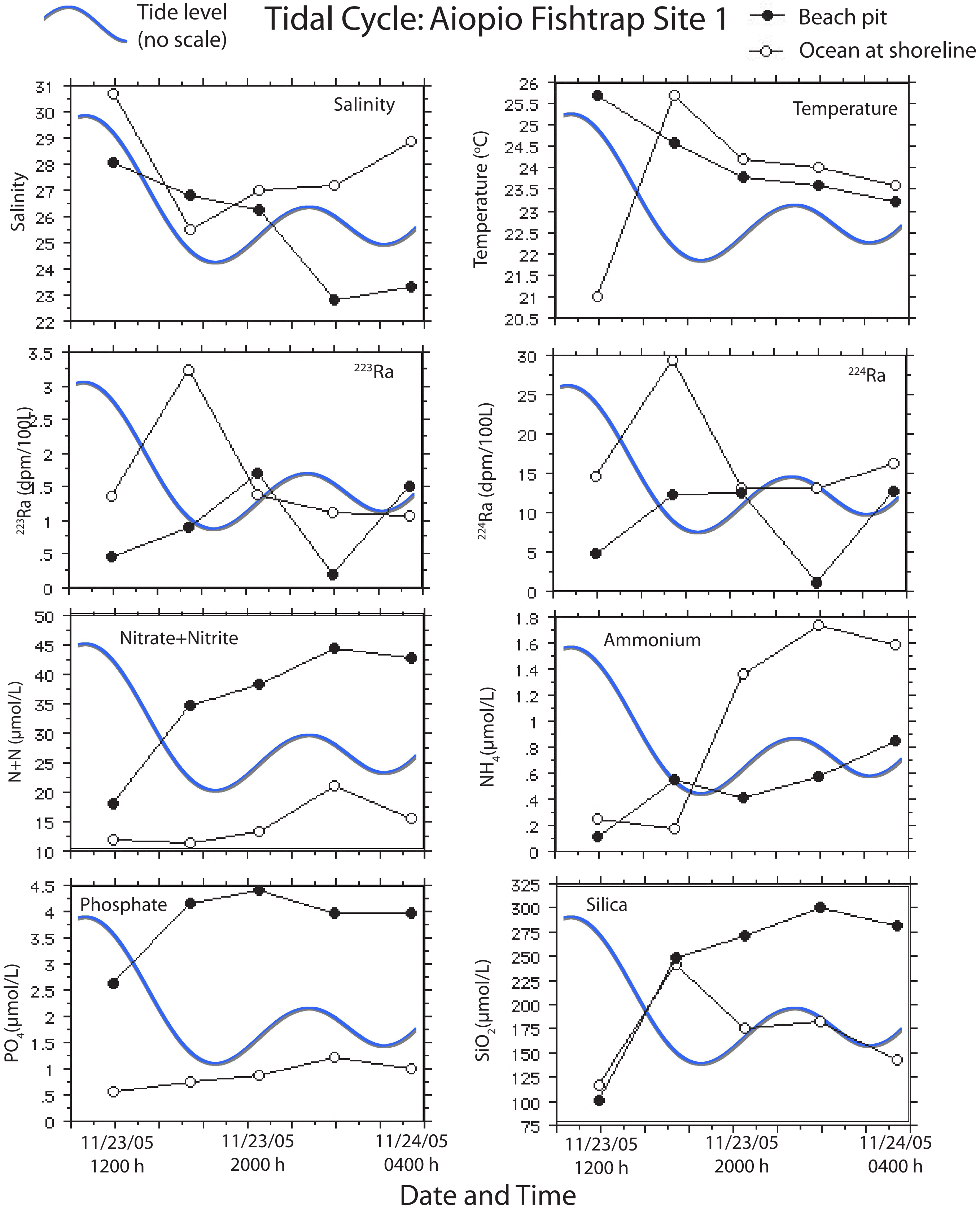

Figure 18. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations over one complete tidal cycle in November 2005 in coastal ocean at shoreline and in a beach-pit at Aiopio Fishtrap (sample site 1), Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1).

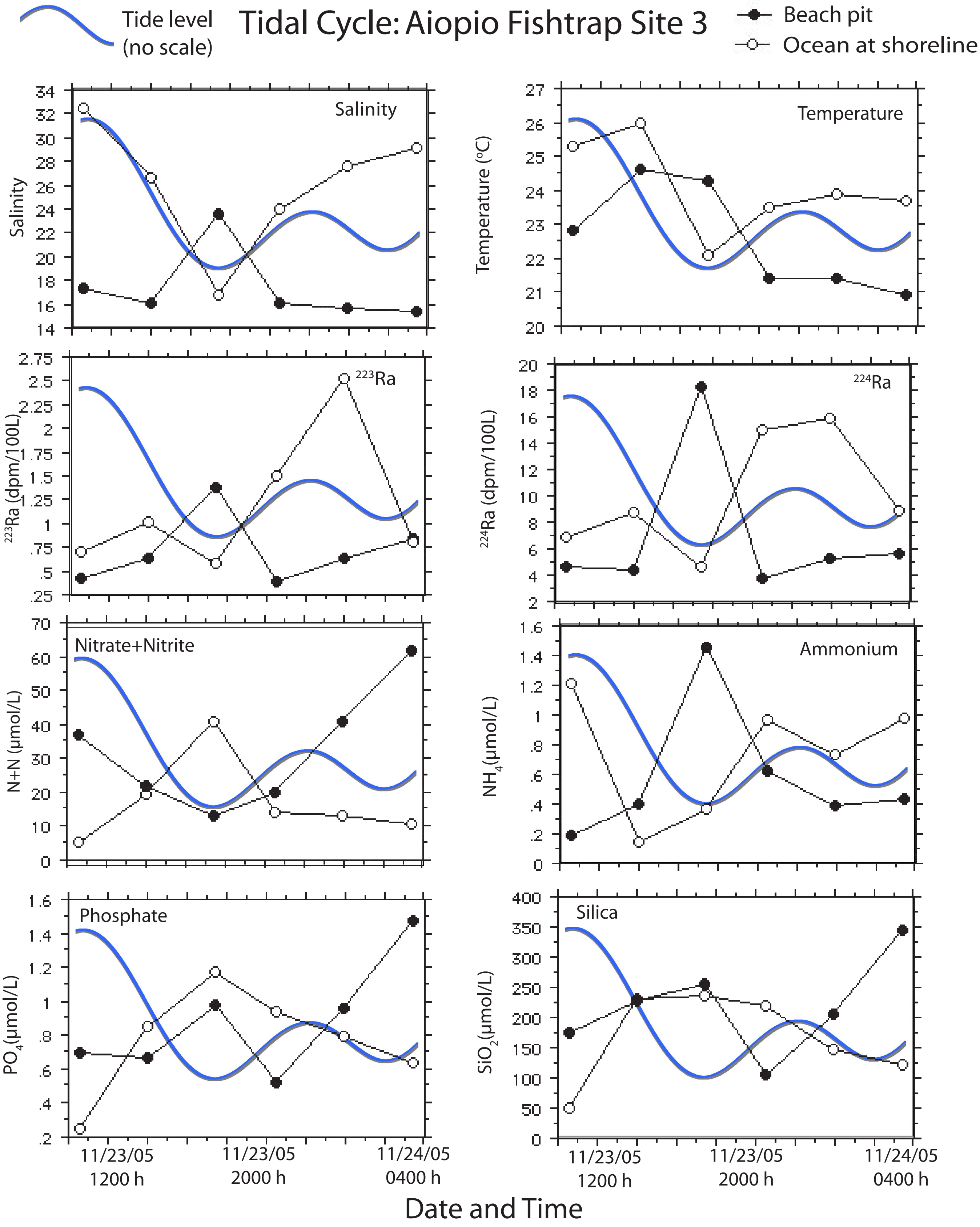

Figure 19. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations over one complete tidal cycle in November 2005 in coastal ocean at shoreline and in a beach-pit at Aiopio Fishtrap (sample site 3). Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1).

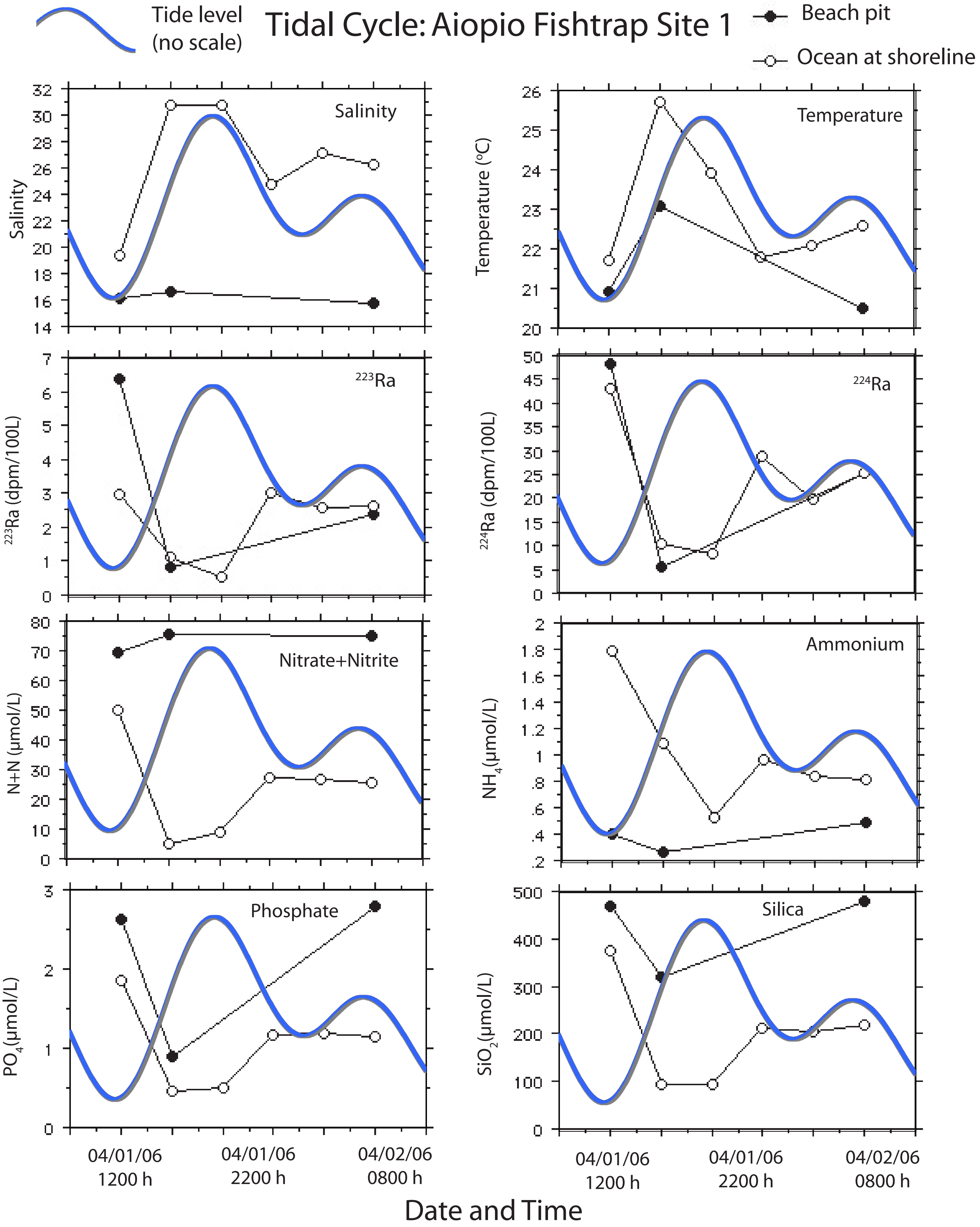

Figure 20. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations over one complete tidal cycle in April 2006 in coastal ocean at shoreline and in a beach-pit at Aiopio Fishtrap (sample site 1). Kaloko-Honokōhau National Historical Park, Island of Hawai'i (fig. 1).

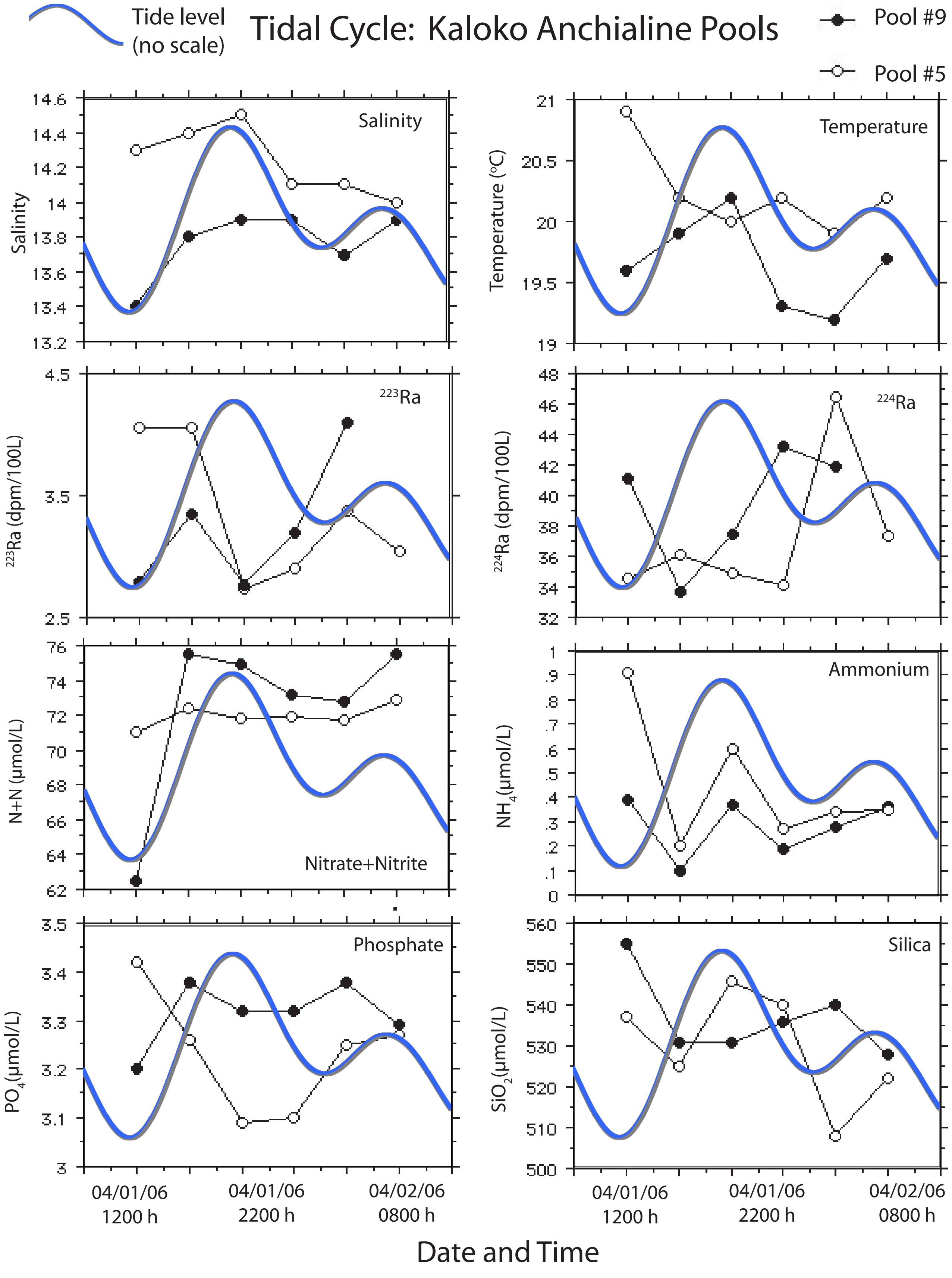

Figure 21. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations over one complete tidal cycle in April 2006 at two anchialine pools near Kaloko Fishpond, Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1).

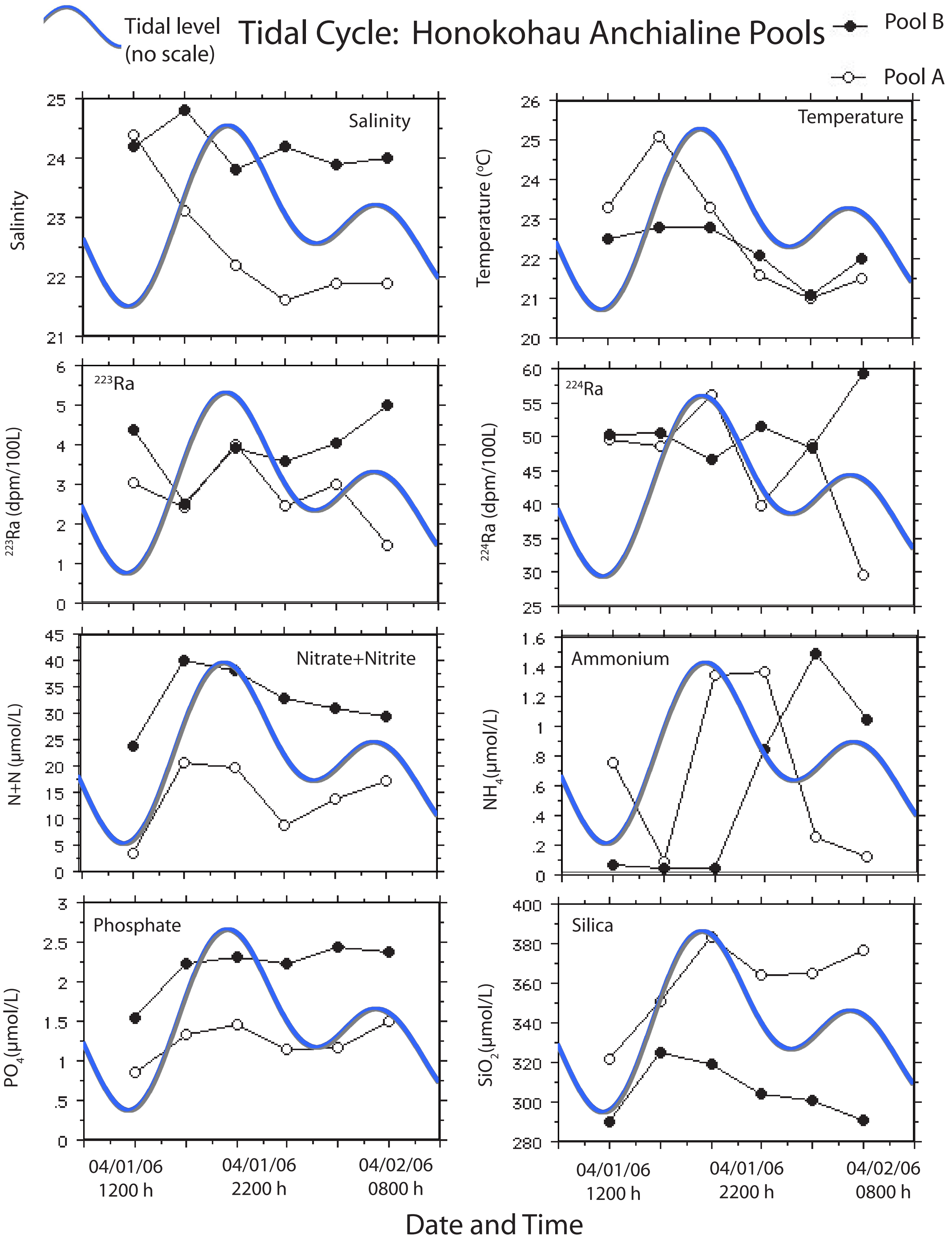

Figure 22. Salinity, temperature, isotope activities of ^{223}Ra and ^{224}Ra, and nutrient concentrations over one complete tidal cycle in April 2006 at two anchialine pools near Aiopio Fishtrap, Kaloko-Honokōhau National Historical Park, Island of Hawai‘i (fig. 1).

Submarine Ground-Water Discharges into the Coastal Ocean

Because salinity and Ra-isotope activity had a linear, inverse relation in the coastal ocean, mixing in that zone can be conceptualized as a two-end-member system, with high-salinity, low-Ra-isotope-activity seawater as the first end-member and lower salinity, higher Ra-isotope-activity ground water as the second. On the basis of plots of ^{224}Ra-isotope activity versus salinity (fig. 6), anchialine pools, with salinities of 15 to 25 ppt and ^{224}Ra-isotope activities of 50 to 70 dpm/100 L, appear to be representative of this ground-water end-member. Although the park's ground water had a brackish salinity (15–25 ppt), the fresh component of ground water was the main determinant of nutrient concentrations in the nearshore zone (fig. 8). In those instances where the saline ground-water component did appear to influence coastal-water quality (that is, Honokōhau Harbor and Aiopio Fishtrap), this component was representative of a distinct end-member, not of the saline component of the typical ground-water end-member. Thus, only the fresh component of submarine ground-water discharge was estimated.

Submarine ground-water discharges into the nearshore zone at each cross-shore transect site were calculated by using a simple box model. First, the volume of the nearshore "box" was calculated as $V_b = L_t \times W_t \times D_t$, where V_b is the volume of the box, L_t is the length of the transect, W_t is the width of the transect, and D_t is the average depth of the transect area. For Honokōhau Harbor (fig. 1), only the upper 1 m of the harbor was considered because this is the only part of the harbor that was sampled and exploratory salinity and temperature measurements indicated that the harbor was stratified, with cooler, fresher water on top and warmer, more saline water at the bottom. The surface area of the harbor was estimated from a map by using Google Earth software, and the volume of the box was calculated as the surface area multiplied by a surface layer thickness of 1 m. The flux of fresh ground water into the box was calculated as $SGD_f = [(S_o\text{-}S_b)/S_o] \times V_b/T_r$ where SGD_f is the flux of freshwater into the box (in liters per hour), S_o is the salinity of offshore seawater, S_b is the salinity of water in the box, V_b is the volume of the box (in liters) and T_r is the residence time of water in the box (in hours).

Because the precise residence time of water in the coastal boxes could not be calculated by using Ra-isotope-activity ratios, submarine groundwater discharges were calculated by using the maximum residence time (1.6 d or 39 h). We also present calculations of potential submarine groundwater discharges given residence times of 1 and 10 hours, to show the ranges that would be expected under feasible coastal-circulation conditions (table 3).

SGD_f values calculated using a maximum, conservative residence time of 1.6 days fell within the range 1–22 m^3/d per meter shoreline, with the highest SGD_f value occurring at Aiopio Fishtrap and the lowest at Aimakapa Beach. Using a 10-hour residence time, an approximately four-fold increase

Table 3. Estimates of fresh-submarine-ground-water discharge along coastal-ocean transects and in Honokōhau Harbor, using a maximum residence time of 1.6 days and potentially feasible times of 1 and 10 hours.

Site	Date	Length (m)	Width (m)	Depth (m)	Salinity (ppt)	Fresh Submarine ground-water discharge (m^3/d)		
						1 h	10 h	1.6 d
Aimakapa Beach	Apr-06	25	1	1.5	30.8	54	5	1
Kaloko Beach	Dec-03	70	1	1.5	24.4	382	38	10
	Nov-05	25	1	1	23.9	95	10	2
Aiopio Fishtrap/	Dec-03	10	1	1.5	28.1	35	4	1
Honokōhau Beach	Nov-05	50	1	1.5	26.1	229	23	6
	Apr-06	220	1	1.5	27.4	860	86	22
Midpark	Nov-05	30	1	1.5	25.7	143	14	4
Honokōhau Harbor	Dec-03	650	105	1	24.9	4.73E+05	4.73E+04	1.21E+04
	Nov-05	650	105	1	28.2	3.18E+05	3.18E+04	8.16E+03
	Apr-06	650	105	1	28.5	3.04E+05	3.04E+04	7.80E+03

in the estimated SGD_f value is calculated, and using a 1-hour residence time a forty-fold increase is calculated. Using the 1.6-day residence time, the SGD_f value for Honokōhau Harbor was calculated to be 8,000 to 12,000 m^3/d. Assuming that this discharge eventually leaves the harbor by the approximately 100-m wide mouth, the discharge rate at the harbor would be 80 to120 m^3 per meter per day, considerably higher than the rest of the park shoreline.

Ground-Water-Derived Nutrient Fluxes into the Nearshore Zone

Ground-water-derived fluxes of nitrate + nitrite, phosphate, and silica at each study site were estimated by multiplying the concentration of each nutrient in the fresh-ground-water end-member by the volumetric flux of fresh ground water (table 4). The nutrient concentrations of the fresh-ground-water end-member were calculated by using simple linear regression between salinity (x) and nutrient concentration (y) in nearshore or harbor samples, respectively. Nearshore samples from all study sites and all sampling trips were pooled together to calculate the nutrient concentrations of the fresh-ground-water end-member because no systematic difference in the relation between salinity and nutrient concentration was noted between sites or sampling trips. The estimated nitrate + nitrite concentration in the fresh-ground-water end-member was 90 µM for coastal transects ($r^2 = 0.91$, $n = 114$) and 109 µM for Honokōhau Harbor ($r^2 = 0.84$, $n = 15$); the estimated phosphate concentrations were 4.4 µM ($r^2 = 0.91$) and 7.9 µM ($r^2 = 0.16$); and the estimated silica concentrations were 872 µM ($r^2 = 0.98$) and 910 µM ($r^2 = 0.95$) for coastal transects and Honokōhau Harbor, respectively. Because no relation between NH_4 concentration and salinity was noted in nearshore or harbor samples and ammonium was not enriched in ground-water (anchialine pool, well, and beach-pit) samples relative to nearshore or harbor samples, we concluded that ground water is not an important source of ammonium to the coastal ocean, and so no ammonium concentration was calculated for the fresh-ground-water end-member.

Using the conservative residence-time estimate of 1.6 days, nitrate + nitrite fluxes ranged from 0.08 to 2 mol/d per meter of shoreline; ranges for phosphate and silica fluxes were 0.04 to 0.1 and 0.9 to 19 mol/d per meter of shoreline, respectively. In Honokōhau Harbor, nitrate + nitrite fluxes ranged from 850 to 1300 mol/d, phosphate fluxes from 62 to 96 mol/d, and silica fluxes from 7,100 to 11,000 mol/d (table 4). These fluxes vary in response to residence time in exactly the same way as do submarine-ground-water fluxes, and so if the residence time were shorter, they would be greater.

Table 4. Estimates of nutrient inputs from submarine fresh-ground-water discharge along coastal-ocean transects and in Honokōhau Harbor using a maximum residence time of 1.6 days and potentially feasible residence times of 1 and 10 hours.

Site	Date	Nitrate + nitrite flux (mol/d)			Phosphate flux (mol/d)			Silica flux (mol/d)		
		1 h	10 h	1.6 d	1 h	10 h	1.6 d	1 h	10 h	1.6 d
Aimakapa Beach	Apr-06	4.9E+00	4.9E-01	1.1E-01	2.40E-01	2.40E-02	6.10E-03	4.70E+01	4.70E+00	1.20E+00
Kaloko Beach	Dec-03	3.4E+01	3.4E+00	8.8E-01	1.70E+00	1.70E-01	4.30E-02	3.30E+02	3.30E+01	8.50E+00
	Nov-05	8.6E+00	8.6E-01	2.2E-01	4.20E-01	4.20E-02	1.10E-02	8.30E+01	8.30E+00	2.10E+00
Aiopio Fishtrap/ Honokōhau Beach	Dec-03	3.2E+00	3.2E-01	8.0E-02	1.60E-01	1.60E-02	4.00E-03	3.10E+01	3.10E+00	7.90E-01
	Nov-05	2.1E+01	2.1E+00	5.3E-01	1.00E+00	1.00E-01	2.60E-02	2.00E+02	2.00E+01	5.10E+00
	Apr-06	7.7E+01	7.7E+00	2.0E+00	3.80E+00	3.80E-01	9.70E-02	7.50E+02	7.50E+01	1.90E+01
Midpark	Nov-05	1.3E+01	1.3E+00	3.0E-01	6.30E-01	6.30E-02	1.60E-02	1.30E+02	1.30E+01	3.20E+00
Honokōhau Harbor	Dec-03	5.20E+04	5.20E+03	1.30E+03	3.70E+03	3.70E+02	9.60E+01	4.30E+05	4.30E+04	1.10E+04
	Nov-05	3.50E+04	3.50E+03	8.90E+02	2.50E+03	2.50E+02	6.40E+01	2.90E+05	2.90E+04	7.40E+03
	Apr-06	3.30E+04	3.30E+03	8.50E+02	2.40E+03	2.40E+02	6.20E+01	2.80E+05	2.80E+04	7.10E+03

Discussion

Submarine ground-water discharge is a pervasive phenomenon in Kaloko-Honokōhau National Historical Park, affecting every water body sampled, including anchialine pools, fishponds, Honokōhau Harbor, and coastal ocean sites. Salinity was generally a good indicator of submarine ground-water discharge. At most study sites in the coastal ocean, salinity was well correlated to other submarine ground-water discharge indicators (Ra-isotope activity and silica concentration) as well as to nitrate + nitrite and phosphate concentrations. This observation indicates that at most study sites, fresh ground water is simply being diluted by seawater as it moves through the coastal aquifer (and acquiring an elevated Ra-isotope activity as a result of its brackish salinity). No distinct saline or brackish ground-water end-member is present.

At Honokōhau Harbor and Aiopio Fishtrap, however, mid-transect peaks in Ra-isotope activity and the concentrations of certain nutrients indicated the presence of a distinct, high-salinity, high-Ra-isotope-activity, high-nutrient-concentration ground-water end-member, which discharges slightly offshore. This end-member could be a spring or a system of springs with unique chemical properties, or it could result from wave or tide-driven circulation of seawater through the aquifer, if this recirculation caused an alteration in water chemistry. At Honokōhau Harbor, phosphate and ammonium concentrations in the high-salinity ground-water end-member appeared to be high, affecting concentrations of these nutrients to a greater extent than did inputs from the fresh inner-harbor spring (fig. 12). Further research is needed to assess the source of this high-salinity, high-Ra-isotope-activity ground-water end-member and to determine its importance to the nutrient budgets of the sites where it discharges.

Although submarine ground-water discharge occurred ubiquitously throughout the park, considerable spatial variation was observed. Aimakapa Fishpond and Kaloko Fishpond differed in salinity and nutrient concentrations, possibly indicating differences in biologic-nutrient uptake and cycling. Fresh-ground-water input also varied between coastal-ocean sites. The proportion of fresh ground water in samples collected at the shoreline ranged from 8 volume percent at the beach near Aimakapa Fishpond to 47 volume percent at Freeze Face Cove, with values of 30–40 volume percent most common. Salinity increased with distance from shore at every coastal site, indicating that fresh ground-water discharge was occurring at the shoreline and the fresh ground water was being diluted with seawater with increasing distance from shore.

Across all nearshore sites, nitrate + nitrite, phosphate, and silica concentrations were inversely correlated with salinity, and this linear relationship was constant between sites, indicating that nutrient concentrations in the fresh-ground-water end-member did not vary between study sites and that the chief factor causing variation in coastal-water quality was the quantity of fresh ground water present. The linear relation between salinity and nutrient concentrations in the coastal ocean also indicates that nutrients are behaving conservatively. Specifically, biologic uptake by algae, phytoplankton, or other organisms is not rapid enough to change nutrient concentrations within 25 to 50 m of the shore. Although phosphate concentration generally was conservatively related to salinity, several data points from Honokōhau Harbor and Aiopio Fishtrap fell well above the mixing line (fig. 8). As already discussed, these two sites were influenced by a distinct high-salinity ground-water end-member.

No consistent pattern of seasonal variation in salinity or other water-quality parameters was observed in this study, suggesting that the quality of the park's water bodies is generally stable on seasonal time scales. In contrast to rivers and streams, which can deliver freshwater that varies widely in quantity and quality, the groundwater discharging at the park's coastline represents the integration of many years or decades of rainfall over a large inland area. Thus, neither the quality nor the quantity of submarine ground-water discharge is likely to change quickly owing to natural processes (although human activity, such as pumping, waste disposal, or development could have rapid, severe effects). The fact that ground water dominates freshwater inputs to the park's coastal waters may buffer these waters from significant seasonal changes in water quality. However, we note that the study design (three 1-2-week sampling trips spread over a 3-year period) was not ideal for capturing seasonal variation, especially if such variation is related to environmental factors, such as rain or swells, which may occur at different times and with different intensities each year.

Tidal-cycle variation in salinity, Ra-isotope activity, and nutrient concentrations were observed at coastal-ocean sites, beach-pits, in Kaloko Fishpond, and in anchialine pools. Along coastal transects, salinity and temperature were lower, and Ra-isotope activities and nutrient concentrations were higher, at low tide than at high tide (figs. 12–16). However, both the extent of variation, and the timing of the response to the tidal signal, differed between study sites and sampling times. When a subset of study sites were sampled over an entire tidal cycle (24 hours), no consistent, predictable relation between tidal height and water quality was observed. Because variation in water quality related to tidal fluctuations occurs, but is difficult to predict, it would be prudent for future sampling to cover the full tidal range at each study site in order to obtain both representative averages and measures of variation that can be used for inter-site comparisons.

The box model used to calculate water and nutrient fluxes from submarine ground-water discharge into coastal areas in this study should be considered a first-order approximation because much uncertainty is associated with the calculated values. The main source of this uncertainty is the residence time of water in the coastal areas under study. Using the ^{224}Ra/^{223}Ra isotope-activity ratio, we determined that the residence time of coastal surface water at all study sites was less than 1.6 days; however, the range of feasible residence times less than 1.6 days spans an order of magnitude (1–39 hours), introducing a comparably large uncertainty into the flux calculations.

An associated issue is that the uncertainty surrounding the flux calculations makes spatial or temporal comparisons of submarine ground-water discharges difficult. In this report, we presented flux calculations based on a maximum residence time of

1.6 days, as well as potentially feasible coastal residence times of 1 and 10 hours. Both the residence time of coastal water and the ground-water flux probably vary by site and season, and so flux estimates based on the assumption of a uniform residence time should be compared cautiously, if at all. Much research on water circulation in the park's coastal areas has already been done by Storlazzi and Presto (2005); however, no residence times that are applicable to the shallow "box" areas 0 to 50 m from the shoreline have been estimated. We note that if coastal residence times at the study sites in this report were determined with greater precision, more precise fluxes could be calculated with little or no additional water-quality sampling required.

Conclusions

A total of more than 300 water samples were collected from fishponds, anchialine pools, observation wells, coastal-ocean sites in Kaloko-Honokōhau National Historical Park, and Honokōhau Harbor between December 2003 and April 2006. Key observations from this study included:

- Fresh ground water is present in all the park's water bodies, commonly composing at least 30 volume percent of the total water in the coastal ocean.

- Fresh ground water is the main source of nitrate, phosphate, and silica to the coastal ocean in the park.

- Nutrient concentrations in the fresh ground-water end-member are similar throughout the park.

- Honokōhau Harbor and, to a lesser extent, Freeze Face Cove are "hot spots" for submarine ground-water discharge. The volume of fresh ground water entering the coastal ocean at Honokōhau Harbor's mouth is more than ten times that from an equivalent length (~100 m) of park shoreline. Any change in quality or quantity of submarine ground-water discharge from Honokōhau Harbor would likely affect adjacent coastal areas in the park.

- Brackish or saline ground water is not an important source of nutrients except at Honokōhau Harbor and Aiopio Fishtrap. At these study sites, high-Ra-isotope-activity, high-salinity springs appeared to discharge slightly offshore. These springs were sporadically enriched in nitrate+nitrite, phosphate and ammonium concentrations.

- Tidal variation in submarine ground-water discharge was observed, but the relation was inconsistent across study sites and sampling times. No significant seasonal variation in submarine ground-water discharge was observed.

These data provide a detailed characterization of certain important aspects of water quality in the park, including the extent of ground-water influence on water resources. They can also be used as a baseline to assess the effect of future changes, such as development or climate variation, on the park's water resources.

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Additional Project Information

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[Appendix available only online at http://pubs.usgs.gov/sir/2008/5128/appendix]

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