

## Nutrient inputs to the coastal ocean from submarine groundwater discharge in a groundwater-dominated system: Relation to land use (Kona coast, Hawaii, U.S.A.)

Karen L. Knee,<sup>a,b,\*</sup> Joseph H. Street,<sup>a,b</sup> Eric E. Grossman,<sup>c</sup> Alexandria B. Boehm,<sup>d</sup> and Adina Paytan<sup>b</sup>

<sup>a</sup>Department of Geological and Environmental Sciences, Stanford University, Stanford, California

<sup>b</sup>Institute of Marine Sciences, University of California, Santa Cruz, California

<sup>c</sup>United States Geological Survey, Pacific Science Center, Santa Cruz, California

<sup>d</sup>Environmental and Water Studies, Department of Civil and Environmental Engineering, Stanford University, Stanford, California

### Abstract

We evaluated the magnitude and composition (in terms of salinity,  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  activity, and nutrient concentrations) of submarine groundwater discharge (SGD) fluxes at 11 sites on the Kona coast of Hawaii. Discharging groundwater was typically brackish to saline and had high Ra activity relative to ocean water and fresher, inland groundwater. Brackish SGD fluxes, estimated using a mass-balance approach based on excess coastal ocean  $^{224}\text{Ra}$  activity, ranged from 3 to 1300 L m<sup>-1</sup> of coastline min<sup>-1</sup>. Fluxes of the freshwater component of SGD, calculated based on salinity, ranged from 2 to 310 L m<sup>-1</sup> min<sup>-1</sup>. Nutrient fluxes into coastal waters from SGD varied by up to three orders of magnitude among sites. Nitrate + nitrite (N + N), phosphate, and silica concentrations showed strong, inverse linear correlations with salinity in coastal seawater and groundwater. These correlations were consistent with previous work that documented conservative mixing between fresh, high-nutrient groundwater and saline, low-nutrient seawater at a few coastal ocean sites. We extend this conservative relationship to more coastal ocean sites and to groundwater in the coastal aquifer. N + N concentrations in the fresh component of discharging groundwater were higher at sites near golf courses and those with a greater percentage of bare land within a 5-km radius, and silica concentrations in the fresh component of discharging groundwater were higher at sites with more bare land and lower population densities. However, neither urbanization nor agriculture was significantly correlated with groundwater nutrient concentrations on this relatively undeveloped coast.

The Kona coast of the island of Hawaii is unusual among coastal areas in that it has negligible stream flow combined with large submarine groundwater discharge (SGD) fluxes into the coastal ocean (Kay et al. 1977; Oki 1999). SGD that is considerably fresher and higher in nutrients than the receiving seawater has been documented at multiple locations on the Kona coast (Bienfang 1980; Peterson et al. 2007; Johnson et al. 2008), and SGD fluxes have been estimated for a few discrete locations (Street et al. 2008; Peterson et al. 2009), as well as for the entire coastline (Kay et al. 1977; Oki 1999). Although it has been suggested that development over the past several decades has affected water quality (Parsons et al. 2008), the relationship between land use and water quality on the Kona coast has not been investigated.

Land use and water quality are pressing issues on the Kona coast, where population growth and economic development are occurring rapidly (State of Hawaii Department of Business, Economic Development and Tourism 2007), and are expected to keep increasing in the future. Numerous studies (Eckhardt and Stackelberg 1995; Cole et al. 2006; Bowen et al. 2007) have shown that urbanization, agriculture, and dense human populations are associated with higher nutrient concentrations in groundwater. Land use on the watershed scale has been correlated with groundwater nutrient concentrations (Cole et al. 2006), and golf courses have also been associated with

high groundwater nutrient concentrations in various locations (Wong et al. 1998; King et al. 2007).

On the Kona coast, previous work by Dollar and Atkinson (1992) suggested that fertilizer additions to golf courses could provide significant subsidies of nitrogen and phosphorus to groundwater. The kiawe tree (*Prosopis pallida*), a nitrogen-fixing species abundant in Hawaii, has also been suggested as one factor contributing to high groundwater nitrogen concentrations in the area (Kay et al. 1977; Brock et al. 1987; Street et al. 2008).

High nutrient concentrations in coastal ocean waters have been associated with decreased coral abundance and diversity and increased macroalgal abundance at many locations (Fabricius 2005; Lapointe et al. 2005), including the Kona coast (Parsons et al. 2008). Nutrient additions can also fuel toxic dinoflagellate blooms (Townsend et al. 2001; Anderson et al. 2002). Because SGD is the dominant pathway by which terrestrial nutrients enter the coastal ocean in this area, characterizing SGD fluxes is necessary to maintain the health of Kona's coral reefs, beachgoers, and tourism-based economy.

To address this need, this study sought to (1) evaluate the magnitude and composition (in terms of salinity, Ra activity, and nutrient concentrations) of SGD at multiple sites on the Kona coast; (2) investigate how SGD in this area varies in space and time; and (3) assess the relations between land use or land cover and groundwater nutrient concentrations. The relations between land use, groundwater nutrient concentrations, and SGD-related nutrient

\*Corresponding author: klknee@stanford.edu

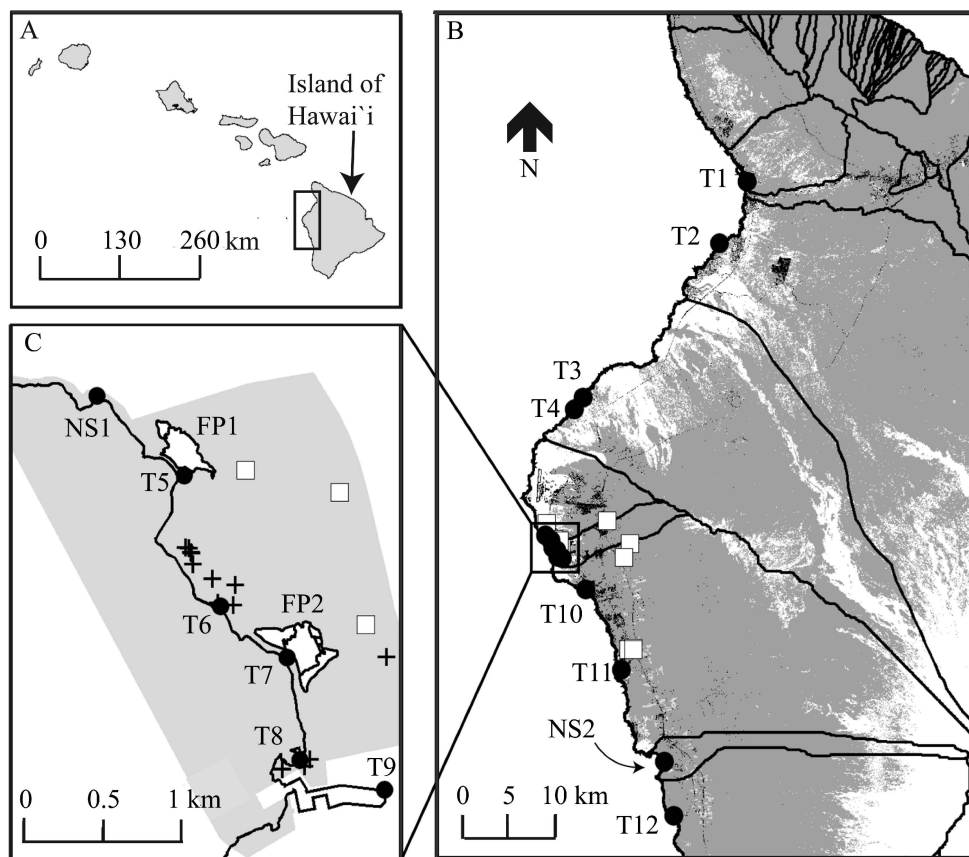


Fig. 1. Map of study sites. (A) Hawaiian archipelago, with study area indicated by a black rectangle. (B) Kona, or western, coast of the island of Hawaii. Black dots indicate coastal ocean sampling sites. White squares indicate wells. Black lines indicate watershed boundaries. Shading indicates land use: black is developed, dark gray is forested or natural, light gray is agricultural, and white is bare land, unconsolidated shore, and water. (C) Kaloko-Honokohau National Historical Park. Light gray shading indicates the park boundary. Black dots and white squares have the same meaning as in (B); black crosses indicate anchialine pools.

inputs to the coastal ocean will likely become more important as development continues in the future.

## Methods

**Study sites and sampling design**—The study area spanned approximately 90 km of the Kona coast, from 19°25.35' N, 155°54.64' W to 20°1.43' N, 155°49.37' W (Fig. 1). The maximum tidal range in this area is approximately 1 m. Samples were collected from 10 coastal ocean sites (T3–11, NS1), two fishponds (FP1–2), 14 wells (including monitoring and water-supply wells), 14 anchialine pools (small brackish pools with hydrologic connections to both the ocean and groundwater), and the Kealahou wastewater treatment plant (WWTP; primary treated effluent) in December 2003, November 2005, and April 2006 (Fig. 1; Table 1). A total of 405 samples, 73 of which were included in a previous paper (Street et al. 2008) were collected. Including these previously reported samples, which were all collected in December 2003, allowed us to incorporate four additional coastal ocean sites (T1, T2, T12, NS2) and investigate potential seasonal variability at sites that were

sampled both in December 2003 and in November 2005 and/or April 2006 (FP1, FP2, T5, T8, T9, T11).

Surface water (depth < 1 m) at coastal ocean sites was collected along shore-perpendicular transects (denoted T1, T2, etc.) 100–2000 m in length. Between 6 and 51 samples were collected along each transect during one or more sampling events. At two other nearshore sites (NS1 and NS2) where transect sampling was not possible, multiple ( $n = 4$ –7) surface water samples were collected within 25 m from shore. Various types of coastal ocean sites, including exposed shoreline (T3, T4, T6, T7), shoreline within natural semi-enclosed bays (T1, T2, T5, T8, T10, T11, T12, NS1, NS2), and one man-made harbor (T9), were sampled.

To characterize the chemistry of the subterranean estuary, or zone within the unconfined coastal aquifer where fresh groundwater and entrained seawater mix (Moore 1999), we collected 113 groundwater samples (see Web Appendix, [www.aslo.org/lo/toc/vol\\_55/issue\\_3/1105a.html](http://www.aslo.org/lo/toc/vol_55/issue_3/1105a.html)) ranging in salinity from < 1 to > 35. Groundwater sampling sites included nine fresh (salinity  $\leq 1$ ) water supply wells located 2–7 km inland of the coastline (hereafter referred to as “inland freshwater wells”), three brackish monitoring wells

Table 1. List of sampling sites. Site locations are shown in Fig. 1. Numbers in columns corresponding to each trip indicate the number of samples collected. Letters indicate tidal stage: E for ebb, F for flood, H for high, and L for low. High and low tide samples were collected within 2 h of the corresponding tide; ebb and flood samples were collected more than 2 h after a high or low tide, respectively.

| Site  | Full name                                       | Transect length (m) | Dec 2003   | Nov 2005        | Apr 2006       | Total |
|-------|-------------------------------------------------|---------------------|------------|-----------------|----------------|-------|
| T1    | Spencer Beach Park                              | 500                 | 6E         | —               | —              | 6     |
|       | Spencer Beach Park pit                          | —                   | 1E         | —               | —              | 1     |
|       | Spencer Beach Park spring                       | —                   | 1E         | —               | —              | 1     |
| T2    | Puako                                           | 1000                | 10E        | —               | —              | 10    |
|       | Puako beach pit                                 | —                   | 1E         | —               | —              | 1     |
| T3    | Kekaha Kai State Park                           | 300                 | —          | 9L              | —              | 9     |
|       | Kekaha Kai State Park beach pit                 | —                   | —          | 1L              | —              | 1     |
| T4    | Ka'upulehu (Four Seasons Hualalai Resort Beach) | 1000                | —          | 6H, 14L         | —              | 20    |
|       | Ka'upulehu beach pit                            | —                   | —          | 2H, 2L          | —              | 4     |
| NS1   | Freeze Face (KAHO)                              | —                   | —          | 4L              | —              | 4     |
| FP1   | Kaloko Fishpond (KAHO)                          | —                   | 4E         | 18H, 16L        | 4E, 3F, 3L     | 48    |
| T5    | Kaloko Beach (KAHO)                             | 300                 | 6L         | 7H, 14L         | 2F             | 29    |
| T6    | Mid-park (KAHO)                                 | 800                 | —          | 4H, 10L         | —              | 14    |
| FP2   | Aimakapa Fishpond (KAHO)                        | —                   | 1E, 1H     | 7L              | 4H, 4L         | 17    |
| T7    | Aimakapa Beach (KAHO)                           | 500                 | 2E, 1H     | 3L              | 4L             | 10    |
| T8    | Honokohau Beach (KAHO)                          | 220                 | 3E, 4H, 3L | 8E, 1F, 8H, 12L | 7E, 1F, 2H, 2L | 51    |
|       | Honokohau beach pit                             | —                   | 1E, 1H     | 7E, 2F, 12H, 8L | 1E, 1F, 1L     | 34    |
| AP    | Anchialine pools (KAHO)                         | —                   | 1E, 3H, 1L | 7E, 1H, 5L      | 4E, 4F, 8H, 8L | 42    |
| T9    | Honokohau Harbor                                | 2000                | 2F         | 5L              | 5H             | 12    |
|       | Honokohau Harbor springs                        | —                   | 1F         | 1L              | 3H             | 5     |
| T10   | Kailua Bay                                      | 600                 | —          | 10E, 12L        | —              | 22    |
|       | Kailua Bay beach pit                            | —                   | —          | 1E, 2L          | —              | 3     |
|       | Kailua Bay spring                               | —                   | —          | 1L              | —              | 1     |
| T11   | Keauhou Bay                                     | 1000                | 6L         | 10E             | 5H, 5L         | 26    |
|       | Keauhou Bay beach pit                           | —                   | —          | 1L              | 1H, 1L         | 3     |
| NS2   | Kealakekua Bay                                  | —                   | 7L         | —               | —              | 7     |
| T12   | Pu'uhoonua O Honaunau (City of Refuge)          | 100                 | 6H         | —               | —              | 6     |
|       | National Historical Park                        | —                   | —          | —               | —              | —     |
| Wells | Various                                         | —                   | —          | 14              | 3              | 17    |
| WWTP  | Kealakehe Wastewater Treatment Plant            | —                   | —          | 1               | —              | 1     |
| Total |                                                 |                     | 73         | 246             | 86             | 405   |

KAHO, Kaloko-Honokohau National Historical Park.

(salinity 5–15), and 14 anchialine pools (salinity 7–25) in Kaloko-Honokohau National Historical Park. Anchialine pools are small ponds located within about 1 km of the shoreline, with hydrologic connections to both the ocean and inland groundwater. Additionally, we sampled groundwater from the unconfined surficial aquifer at coastal ocean sites by sampling beach pits (at T1, T2, T3, T4, T8, T10, T11, NS2) and/or springs (at T1, T5, T9, T10) as close as possible to the shoreline, which we assumed to be the groundwater discharge location. Beach pits were sampled by excavating a hole in the sand 10–30 cm deeper than the water table, installing a screened bucket, and pumping out the water that filled the bucket. At four sites (T6, T7, T12, NS1) it was impossible to sample discharging groundwater because little or no sand overlaid the basalt bedrock and we could not locate any springs.

Because tidal differences in SGD and water quality on the Kona coast have been noted previously (Bienfang 1980; Street et al. 2008), we investigated temporal variability in water quality and SGD fluxes over the daily tidal cycle and seasonally. Both fishponds (FP1 and FP2), several anchia-

line pools, and six coastal ocean transect sites (T4, T5, T6, T8, T10, T11) were sampled at different points in the tidal cycle on one or more trips. Additionally, both fishponds, several anchialine pools, and four coastal ocean transect sites (T5, T7, T8, T11) were resampled at the same approximate point in the tidal cycle during at least two different trips (Table 1) to investigate seasonal or inter-annual variability.

*Salinity and temperature*—Water temperatures were measured in the field using a YSI 85/50 handheld probe, which is accurate to 0.1°C. Density was measured on filtered samples in the lab using an Anton-Paar Density Meter Analyzer 4500 with an SH-3 sample-handling unit, accurate to 0.0001 g cm<sup>-3</sup> and converted to salinity values using the United Nations Educational, Scientific, and Cultural Organization equation of state for seawater (Fofonoff 1985). The instrument error, in terms of final calculated salinity, is approximately 0.1, and calculated salinities of samples run in duplicate fell within this error range.

Table 2. Land use and land cover within a 5-km radius and distance to the nearest golf course for each coastal ocean site. Water, unconsolidated shore, and unclassified land use were excluded from analysis. For the five sites within Kaloko-Honokhau National Historical Park (NS1, T5–8) and T9, land use within a 5-km buffer of the park is reported because the buffers for individual sites overlapped significantly; however, because a golf course is located on one side of the park, distance to the nearest golf course is reported for each individual site.

| Site | Distance to nearest golf course (km) | Population density (km <sup>-2</sup> ) | Developed | Cultivated | Forested or natural | Kiawe | Bare |
|------|--------------------------------------|----------------------------------------|-----------|------------|---------------------|-------|------|
| T1   | 2.5                                  | 3.0                                    | 5%        | 0%         | 71%                 | 4%    | 24%  |
| T2   | 2.0                                  | 4.5                                    | 2%        | 0%         | 35%                 | 14%   | 63%  |
| T3   | 3.1                                  | <1                                     | 7%        | 0%         | 38%                 | 11%   | 54%  |
| T4   | 0.5                                  | <1                                     | 2%        | 0%         | 29%                 | 8%    | 70%  |
| NS1  | 4.6                                  | 81                                     | 16%       | 1%         | 51%                 | 6%    | 33%  |
| T5   | 3.8                                  | 81                                     | 16%       | 1%         | 51%                 | 6%    | 33%  |
| T6   | 3.1                                  | 81                                     | 16%       | 1%         | 51%                 | 6%    | 33%  |
| T7   | 2.5                                  | 81                                     | 16%       | 1%         | 51%                 | 6%    | 33%  |
| T8   | 2.1                                  | 81                                     | 16%       | 1%         | 51%                 | 6%    | 33%  |
| T9   | 1.6                                  | 81                                     | 16%       | 1%         | 51%                 | 6%    | 33%  |
| T10  | 1.1                                  | 190                                    | 17%       | 1%         | 69%                 | 5%    | 12%  |
| T11  | 0.3                                  | 81                                     | 8%        | 6%         | 84%                 | 2%    | 3%   |
| NS2  | 10.1                                 | 83                                     | 4%        | 4%         | 84%                 | 1%    | 7%   |
| T12  | 15.7                                 | 27                                     | 2%        | 6%         | 89%                 | 1%    | 3%   |

<sup>223</sup>Ra and <sup>224</sup>Ra activity—The activities of <sup>223</sup>Ra and <sup>224</sup>Ra were measured using the same methods described by Street et al. (2008) and Knee et al. (2008), based on techniques developed by Moore (1976) and Moore and Arnold (1996). Ra activities in samples from Kealahou WWTP effluent and inland freshwater wells were not measured because Ra is almost entirely particle-bound at the low (< 1) salinities characterizing these samples (Webster et al. 1995). Activities are presented in mBq (100 L)<sup>-1</sup>. One mBq is equivalent to 0.06 decays per minute.

A subset of samples (88% and 40% in November 2005 and April 2006, respectively) was rerun 3–6 weeks after collection to correct for <sup>228</sup>Th-supported <sup>224</sup>Ra activity. The average Th correction was 3.9% of the original total <sup>224</sup>Ra activity in November 2005 and 3.0% in April 2006; the average correction for each trip was applied to those samples that were not rerun. The error associated with each <sup>223</sup>Ra and <sup>224</sup>Ra activity measurement was calculated using the method of Garcia-Solsona et al. (2008). The average errors, expressed as percentages of sample Ra activity, were 28% for <sup>223</sup>Ra and 8% for <sup>224</sup>Ra. The relatively high error associated with <sup>223</sup>Ra activity is the result of low activity; because the error associated with <sup>224</sup>Ra was much lower, this isotope was used to calculate brackish SGD fluxes.

*Nutrient concentrations*—Nutrient samples were collected and analyzed using the same methods employed by Street et al. (2008). During the combined sampling periods, a total of 100 nutrient samples were collected in duplicate. The average errors between duplicates (the absolute value of their difference expressed as a percentage of the mean concentration of the two samples) were 19% for combined nitrate and nitrite (N + N), 9% for phosphate (PO<sub>4</sub><sup>3-</sup>), 11% for silica (Si), and 35% for ammonium (NH<sub>4</sub><sup>+</sup>).

*Land use and land cover*—The Hawaii Land Cover 2001 data set (National Oceanographic and Atmospheric Ad-

ministration Coastal Services Center; <http://www.csc.noaa.gov/crs/lca/hawaii.html>), consisting of analyzed, field-validated Landsat Enhanced Thematic Mapper (ETM) data from 2001, was used for land use analysis. The data set has a 30-m resolution and divides land cover into 22 categories, which we aggregated into four groups: developed (including high- and low-intensity developed land), agricultural (corresponding to the cultivated land classification), forested or natural (including all forest, grassland, and wetland classifications), and bare land. Areas classified as water, unconsolidated shore, or unclassified were excluded from analysis. Data on population density from the 2000 census were obtained from the Hawaii Statewide Geographic Information System Program website (<http://hawaii.gov/dbedt/gis/>).

In addition to the land use classes listed above and population density, we also considered two specific types of land cover suspected to affect groundwater nutrient concentrations: golf courses and kiawe (*P. pallida*) trees. No “golf course” land use classification existed in the Hawaii Land Cover 2001 data set, so data on golf course locations were obtained from the Hawaii State Golf Association (<http://www.hawaiistategolf.org>) and street addresses were converted to geographical coordinates using Yahoo! maps (<http://maps.yahoo.com>). Data on kiawe tree range were obtained from the University of Idaho’s Gap Analysis Program website (<ftp://ftp.gap.uidaho.edu/products/Hawaii>), and consist of automated classifications from 2001–2004 ETM images that were edited using ancillary data.

Land use analysis was performed using ArcGIS software. The percentages of developed, agricultural, forested or natural, and bare land cover; the population density; the percentage of land occupied by kiawe trees; and the number of golf courses in the vicinity of each sampling site were calculated at two spatial scales: a 5-km radius surrounding the site (Table 2), and the entire watershed in which the site

Table 3. Number of samples and 95% confidence intervals for salinity, Ra isotope activity, and nutrient concentrations at coastal ocean sites, fishponds, anchialine pools, beach pits, wells, springs, the Kealakehe Wastewater Treatment Plant (WWTP), and the offshore ocean. In the *n* column, the number outside the parentheses is the total number of samples, and the number inside is the number of samples collected by Street et al. (2008). Concentrations were classified as below the detection limit (b.d.) if their 95% confidence interval included 0.

| Site       | <i>n</i> | Salinity  | <sup>223</sup> Ra activity<br>(mBq [100 L] <sup>-1</sup> ) | <sup>224</sup> Ra activity<br>(mBq [100 L] <sup>-1</sup> ) | N+N<br>(μmol L <sup>-1</sup> ) | PO <sub>4</sub> <sup>3-</sup><br>(μmol L <sup>-1</sup> ) | Si<br>(μmol L <sup>-1</sup> ) | NH <sub>4</sub> <sup>+</sup><br>(μmol L <sup>-1</sup> ) |
|------------|----------|-----------|------------------------------------------------------------|------------------------------------------------------------|--------------------------------|----------------------------------------------------------|-------------------------------|---------------------------------------------------------|
| T1         | 6 (6)    | 29.1–31.6 | 1.7–5.0                                                    | 32–63                                                      | 0.2–11                         | 0.2–0.4                                                  | b.d.                          | 0.2–0.3                                                 |
| T2         | 10 (10)  | 30.0–33.9 | 1.7–5.0                                                    | 22–47                                                      | b.d.                           | b.d.                                                     | b.d.                          | 0.2–0.6                                                 |
| T3         | 9        | 34.8–34.9 | 0.0–1.7                                                    | 6.7–17                                                     | 0.1–0.5                        | 0.1–0.2                                                  | 6–8                           | 0.3–0.5                                                 |
| T4         | 20       | 32.7–34.0 | b.d.                                                       | 28–52                                                      | 3.1–19                         | 0.2–0.6                                                  | 25–120                        | 0.4–1.2                                                 |
| NS1        | 4        | 13.5–23.7 | 10–40                                                      | 200–470                                                    | 28–63                          | 1.2–2.9                                                  | 280–550                       | 0.4–1.3                                                 |
| T5         | 29 (6)   | 23.2–27.3 | 13–25                                                      | 220–350                                                    | 17–27                          | 1.2–1.8                                                  | 210–320                       | 0.8–1.1                                                 |
| T6         | 14       | 24.0–30.0 | 8.3–18                                                     | 130–280                                                    | 12–30                          | 0.7–1.4                                                  | 130–270                       | 0.7–1.0                                                 |
| T7         | 10 (3)   | 31.4–33.7 | 5.0–13                                                     | 80–160                                                     | 1.4–4.0                        | 0.3–0.4                                                  | 30–84                         | 0.4–0.7                                                 |
| T8         | 51 (10)  | 26.3–28.8 | 22–32                                                      | 250–350                                                    | 14–21                          | 0.9–1.2                                                  | 150–210                       | 0.8–1.0                                                 |
| T9         | 17       | 26.5–30.9 | 17–35                                                      | 230–550                                                    | 15–29                          | 1.4–3.5                                                  | 130–240                       | 0.4–1.0                                                 |
| T10        | 22       | 30.5–33.0 | 6.7–12                                                     | 110–200                                                    | 7.0–18                         | 0.6–1.0                                                  | 64–120                        | 0.6–0.9                                                 |
| T11        | 26 (6)   | 29.5–32.2 | 1.7–5.0                                                    | 42–70                                                      | 14–32                          | 0.4–1.1                                                  | 67–140                        | 0.8–1.7                                                 |
| NS2        | 7 (7)    | 33.7–34.4 | 1.7–5.0                                                    | 25–35                                                      | 0.8–2.7                        | 0.2–0.3                                                  | 9–26                          | 0.1–0.2                                                 |
| T12        | 6 (6)    | 24.6–33.3 | 3.3–5.0                                                    | 28–83                                                      | 2.5–20                         | 0.4–1.5                                                  | 34–260                        | 0.3–0.8                                                 |
| FP1        | 48 (4)   | 19.2–23.0 | 8.3–12                                                     | 150–200                                                    | 16–28                          | 1.1–1.6                                                  | 280–370                       | 0.8–1.1                                                 |
| FP2        | 17 (2)   | 12.0–12.3 | 3.3–6.7                                                    | 78–110                                                     | 1.7–17                         | 0.8–1.8                                                  | 520–540                       | 0.4–0.8                                                 |
| Beach pits | 47 (4)   | 21.5–26.2 | 13–25                                                      | 130–220                                                    | 28–51                          | 1.6–2.6                                                  | 180–280                       | 0.4–1.4                                                 |
| Anchialine |          |           |                                                            |                                                            |                                |                                                          |                               |                                                         |
| Pools      | 42 (5)   | 14.9–17.9 | 43–65                                                      | 580–700                                                    | 45–60                          | 2.4–2.9                                                  | 440–510                       | 0.5–1.4                                                 |
| Wells      | 17*      | 2.1–7.9   | 5.0–15                                                     | 110–270                                                    | 66–83                          | 3.8–4.4                                                  | 590–770                       | 0.2–0.5                                                 |
| Springs    | 7        | 7.3–22.1  | 6.7–45                                                     | 150–530                                                    | 36–89                          | 2.0–5.2                                                  | 350–670                       | 0.3–0.9                                                 |
| WWTP       | 1        | 1.8       | —                                                          | —                                                          | 710                            | 150                                                      | 700                           | 22                                                      |
| Offshore   | 20       | 33.7–34.8 | 0.0–1.7                                                    | 3.3–22                                                     | 1.4–6.0                        | 0.2–0.4                                                  | 11–32                         | 0.4–1.3                                                 |

\* *n* = 6 for <sup>223</sup>Ra and <sup>224</sup>Ra measurements.

was located. A 5-km radius was chosen because smaller radii often contained mainly bare rock and did not capture inland land uses that would be expected to affect groundwater quality, whereas larger radii, such as 10 km, overlapped to a significant extent. Because coastal ocean sites in Kaloko-Honokohau National Historical Park, including NS1 and T5–T8, were located very close to each other and to T9, land cover statistics were calculated for a 5-km buffer zone around the entire park and applied to these six sites.

**Statistical analysis**—Statistical analyses were performed using Microsoft Excel, Igor Pro, and SPSS (originally, Statistical Package for the Social Sciences). To compare groups of data, a *t*-test was used either when data in both groups were normally distributed, or when each group contained at least 40 measurements (Moore and McCabe 2003). When these conditions were not met, the nonparametric Wilcoxon rank-sum test was used. Paired *t*-tests were used to test for tidal and seasonal differences. Relations between normally distributed variables were assessed using simple linear regression. The significance of linear correlations was tested using a *t*-statistic. When variables were not normally distributed, the nonparametric Spearman rank correlation coefficient was used. A multiple linear regression model with interaction effects (Neter et al. 1990) was used to test whether the slopes and y-intercepts of two linear regressions were significantly different from each other at the 95% confidence level.

## Results

**Salinity**—Salinities measured at coastal ocean sites and fishponds were significantly lower than those measured in the offshore ocean, 200–2000 m from the shoreline (Table 3). At all coastal ocean sites except T2 (Puako), salinities were lower nearshore and increased offshore (Fig. 2). Groundwater samples (pits, wells, springs, and anchialine pools) had lower salinities than coastal ocean water (Table 3). The 95% confidence intervals (CIs) for well, spring, beach pit, and anchialine pool salinities were 2.1–7.9, 7.3–22.1, 21.5–26.2, and 14.9–17.9, respectively, whereas those for coastal ocean sites ranged from 13.5–23.7 at NS1 to 34.8–34.9 at T3.

**<sup>223</sup>Ra and <sup>224</sup>Ra activities and activity ratios**—Activities of both <sup>223</sup>Ra and <sup>224</sup>Ra were highest in anchialine pools; intermediate in beach pits, coastal ocean sites, and wells; lower in fishponds FP1 and FP2; and lowest in offshore samples (Table 3). Ten samples from freshwater-supply wells were excluded from Ra analysis, so well Ra activities are representative of brackish wells with salinities of 5–21. Activities of both <sup>223</sup>Ra and <sup>224</sup>Ra varied among coastal ocean sites (Table 3) from maximum values of 10–40 and 200–470 mBq (100 L)<sup>-1</sup>, respectively, at NS1 (Freeze Face), to minimum values of 0–1.7 and 6.7–17 mBq (100 L)<sup>-1</sup>, respectively, at T3 (Kekaha Kai State Park).

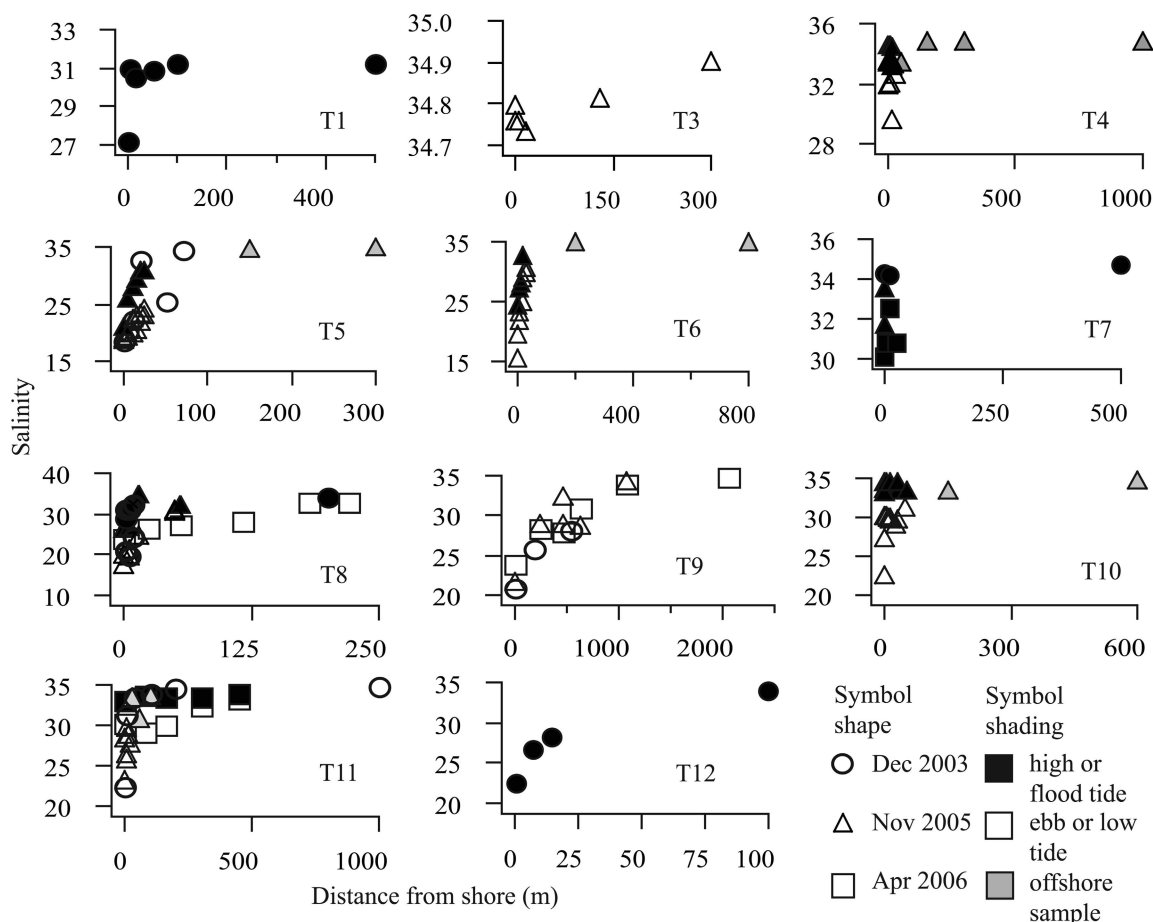


Fig. 2. Relation between salinity and distance from shore at coastal transects, showing low salinities nearshore and increasing salinities offshore. T2, which did not display this pattern, is not shown.

Activities of both Ra isotopes were positively correlated with salinity in anchialine pools, wells, and springs, suggesting salinity-dependent desorption in the coastal aquifer. In coastal ocean and fishpond samples the correlation was inverse, suggesting dilution with low-Ra, high-salinity seawater. No correlation between salinity and Ra activity was observed in beach pits (Fig. 3), which may reflect the combined influences of desorption and dilution.

Across all site types, activities of  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  displayed a positive correlation to each other (Fig. 4). We tested for differences in  $^{224}\text{Ra}:^{223}\text{Ra}$  activity ratio (AR) among site types (well, anchialine pool, fishpond, beach pit, spring, harbor, coastal ocean, and offshore) and individual sampling sites by assessing whether the slopes of the linear relations between  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  activity differed significantly ( $p < 0.05$ ) among sites or site types. No significant differences in  $^{224}\text{Ra}:^{223}\text{Ra}$  AR were observed. The average AR over all sites and site types was 10 (Fig. 4).

**Estimation of coastal ocean water residence time**—The difference in  $^{224}\text{Ra}:^{223}\text{Ra}$  AR between groundwater and nearshore samples at a given site can be used to calculate the residence time of water in the nearshore zone, assuming that discharging groundwater has a particular AR (Moore 2000). This method is best suited for situations where  $^{224}\text{Ra}$

in the coastal ocean has decayed such that the coastal ocean  $^{224}\text{Ra}:^{223}\text{Ra}$  AR is well below that of groundwater. If the nearshore AR falls within the error envelope of the groundwater AR, the following reasoning can be used to calculate a maximum residence time. The AR of discharged groundwater in the nearshore zone would begin to diverge immediately from that of the groundwater source as  $^{224}\text{Ra}$  decayed faster than  $^{223}\text{Ra}$ . However, because of analytical error associated with the measurement of these isotopes, the new (nearshore) ratio would still fall within the error envelope of the original (groundwater) ratio for a certain period of time. This time ( $t$ ) depends on the relative errors associated with  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  ( $d^{223}\text{Ra}$  and  $d^{224}\text{Ra}$ ) and the decay constants of the two Ra isotopes ( $\lambda_{223}$  and  $\lambda_{224}$ ) as follows:

$$t = \frac{\ln(1 - \sqrt{(d^{223}\text{Ra})^2 + (d^{224}\text{Ra})^2})}{\lambda_{223} - \lambda_{224}} \quad (1)$$

Because we observed no significant difference in AR between groundwater and coastal ocean samples at any site, we used the average analytical errors of 8% and 28% for  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  activity, respectively, to calculate a maximum residence time of 65 h (2.7 d) for all coastal

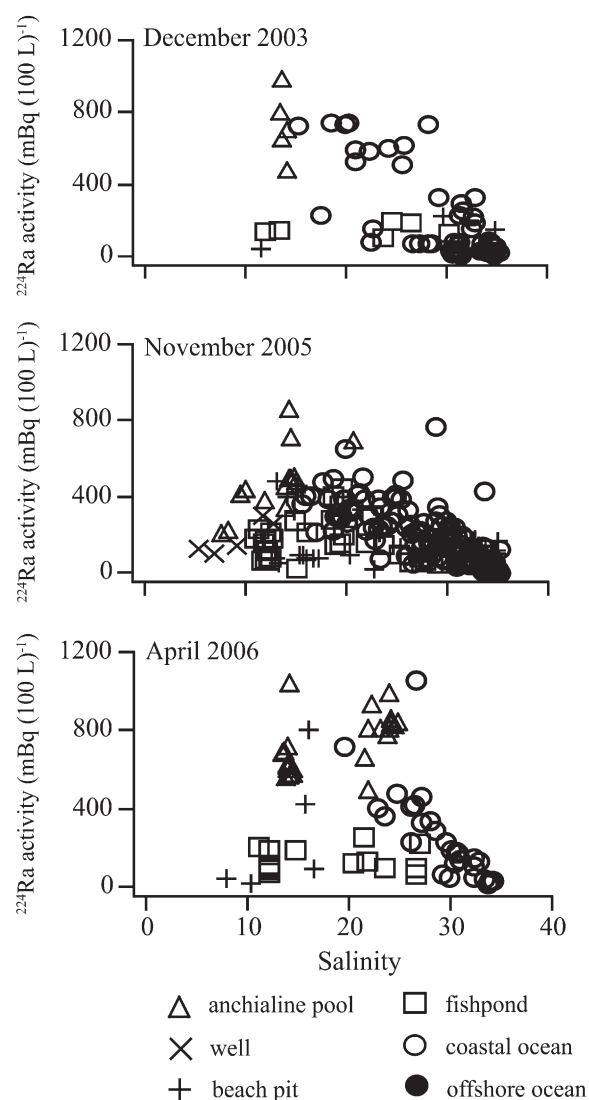


Fig. 3. Relation between  $^{224}\text{Ra}$  activity and salinity in anchialine pools, wells, beach pits, fishponds, coastal ocean, and offshore ocean samples.  $^{223}\text{Ra}$  (not shown) had a similar pattern.

ocean sites. This means that if the residence time had been longer than 65 h, we would have been able to detect a significant difference between the groundwater and near-shore ARs.

The actual residence times at coastal ocean sites are likely much shorter than 65 h, but they cannot be determined more precisely using the AR method. Thus, other available data were used to better constrain the residence time. A drogue study conducted at T9 (Gallagher 1980) provided an independent estimate of the residence time of water in the harbor of 12 h, and data from a more recent study (Peterson et al. 2009) were used to estimate residence times for T9 and T10 of 18 and 38 h, respectively. Additionally, shallow current meter measurements at a subset of sites indicated residence times of 6–12 h (E. E. Grossman unpubl. data). Thus, literature residence time values were used in flux calculations for T9 and T10, and minimum and maximum residence time estimates (6 and

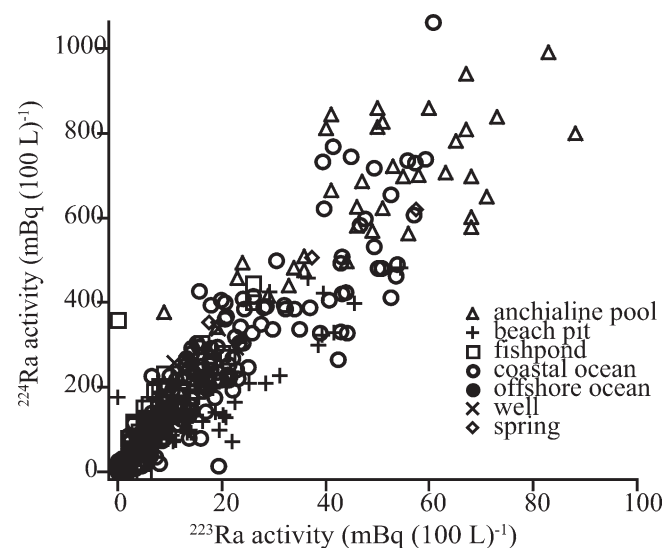


Fig. 4.  $^{224}\text{Ra} : ^{223}\text{Ra}$  activity ratio (AR).

65 h, respectively) were used to generate a corresponding SGD flux range for all other sites.

**Nutrient concentrations in coastal ocean water and groundwater**—Well, spring, and anchialine pool samples had the highest concentrations of  $\text{N} + \text{N}$ ,  $\text{PO}_4^{3-}$ , and Si. Concentrations in beach pits, the coastal ocean, and fishponds were intermediate, and the lowest concentrations were measured offshore. Coastal ocean sites varied considerably in terms of nutrient concentrations (Table 3). In general, concentrations of  $\text{N} + \text{N}$ ,  $\text{PO}_4^{3-}$ , and Si decreased with distance offshore along coastal ocean transects (Fig. 5). Concentrations of  $\text{NH}_4^+$  were generally lower than  $1.5 \mu\text{mol L}^{-1}$  at all sites and less variable than those of the other nutrients. No significant differences in  $\text{NH}_4^+$  concentration among site types were observed, and differences among coastal ocean sites, although at times statistically significant, were small (Table 3).

Strong, inverse linear relationships between salinity and the concentrations of  $\text{N} + \text{N}$ ,  $\text{PO}_4^{3-}$ , and Si, similar to those reported for T9, T10, and NS2 by Johnson et al. (2008), were observed at most coastal ocean sites during all three sampling trips (Fig. 6; Table 4). A salient exception occurred at T9 (Honokohau Harbor), where high levels of  $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$ , and  $\text{PO}_4^{3-}$  (Fig. 5) were measured in the middle of the harbor approximately 500 m from the inner harbor spring, whereas salinity increased steadily from the inner harbor spring to the harbor mouth (Fig. 2). No significant relations ( $p < 0.01$ ) between salinity and  $\text{NH}_4^+$  concentration were observed except at T8 and FP1 (Honokohau Beach and Kaloko Fishpond; see Table 4); both these relations were inverse.

Concentrations of  $\text{N} + \text{N}$ ,  $\text{PO}_4^{3-}$ , and Si in groundwater samples from all sites showed an inverse, linear correlation with salinity (Fig. 7), suggesting conservative mixing in the coastal aquifer. Two exceptions to the linear trend between salinity and  $\text{N} + \text{N}$  concentrations in groundwater samples (pits, springs, wells, and anchialine pools) were observed. Beach pits sampled at T11 (Keauhou Bay) fell well above

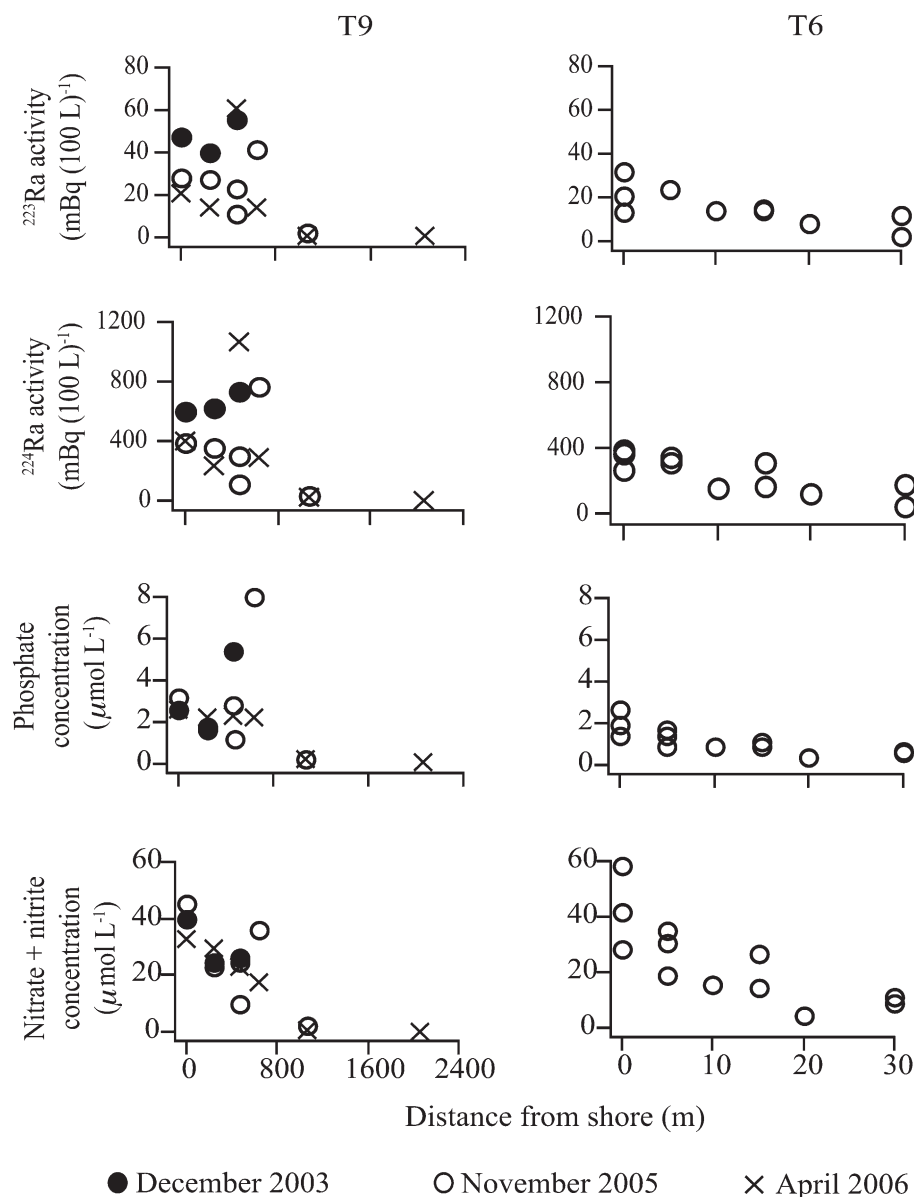


Fig. 5. Gradients of  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  activity,  $\text{PO}_4^{3-}$ , and  $\text{N} + \text{N}$  concentrations at T9 (Honokohau Harbor) and T6 (mid-Kaloko-Honokohau National Historical Park). The gradients at T6 were typical of patterns observed at most sites, whereas those at T9 indicated one or more brackish, high-Ra, high-nutrient springs discharging in the middle of the harbor.

the mixing line, and inland freshwater wells fell below it (Fig. 7).

Groundwater  $\text{PO}_4^{3-}$  concentrations also showed an inverse linear correlation with salinity, although more sites deviated from the conservative mixing line.  $\text{PO}_4^{3-}$  concentrations in inland freshwater wells and one T8 beach pit fell below the mixing line, whereas those in samples collected from mid-harbor springs at T9, one anchialine pool located between T8 and T9, a different beach pit at T8, and the T10 beach pit fell above it. The relationship between salinity and Si concentration in groundwater samples was highly linear, with no samples falling significantly above or below the conservative mixing line.

No relationship between salinity and  $\text{NH}_4^+$  concentrations in groundwater samples was observed.

When the anomalous samples mentioned above were excluded from linear regressions between nutrient concentrations and salinity in groundwater samples, the predicted nutrient concentrations at open ocean salinity (35.7; Peterson et al. 2009) were consistent with nutrient concentrations measured in offshore samples (Table 3). Nutrient concentrations at open ocean salinity predicted based on linear regressions between salinity and nutrient concentrations at each coastal ocean transect were also similar to measured offshore concentrations, although these predicted concentrations varied somewhat by site.

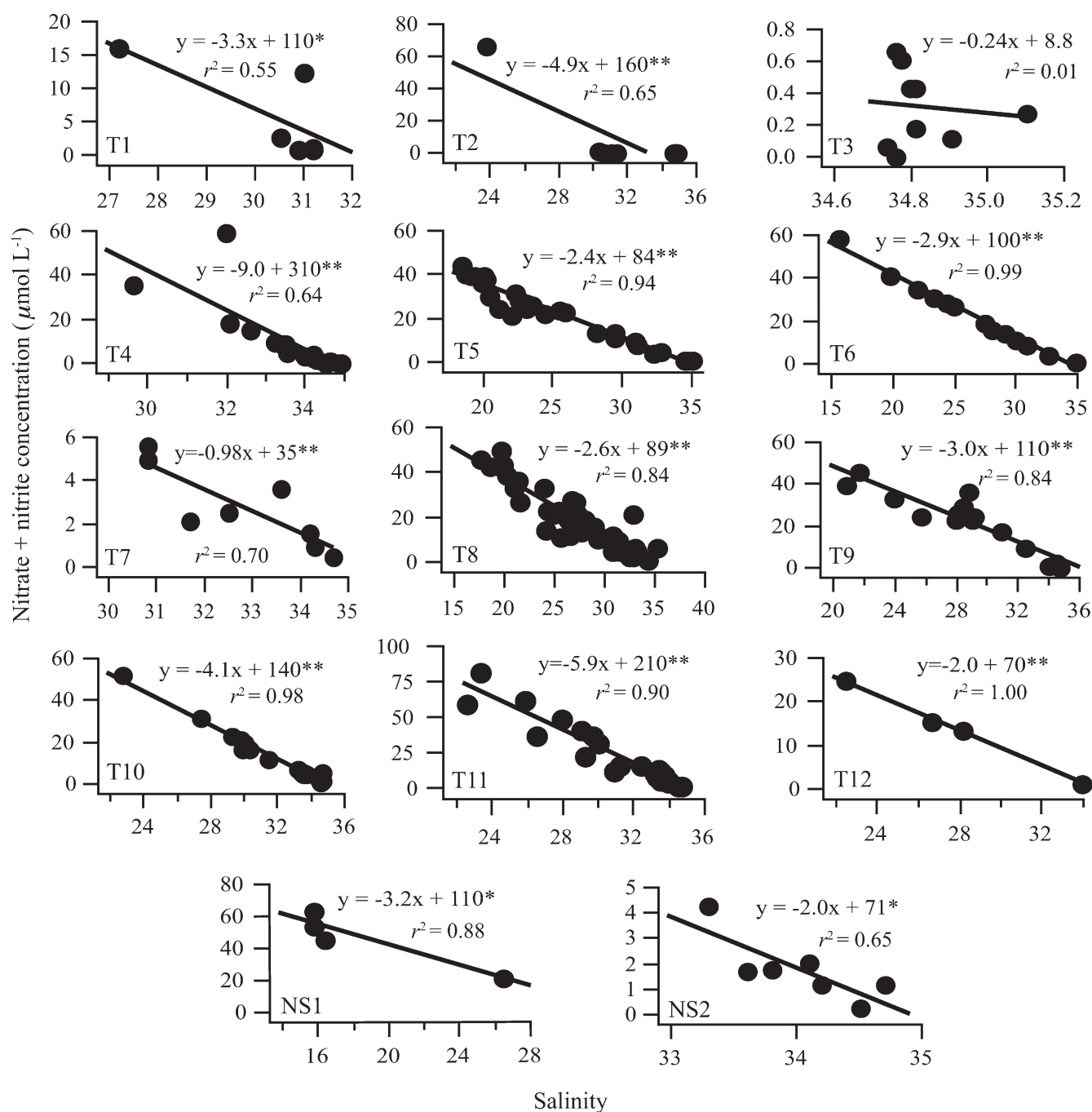


Fig. 6. Relation between salinity and combined nitrate and nitrite (N + N) concentration at coastal ocean sites. Phosphate and silica concentrations (not shown) showed a similar pattern, but with less variability among sites (Table 6). The equation for the line of best fit is presented on each panel. Two asterisks indicate a regression with  $p < 0.01$ , one asterisk indicates  $0.01 < p < 0.05$ , and no asterisks indicate  $p > 0.05$ .

We note that the groundwater nutrient–salinity relationships described above (Fig. 7) are based on all groundwater samples, from all sites, pooled together. This pooling was possible because the relationship between salinity and nutrient concentrations in groundwater was consistent across most sites. Salinities and nutrient concentrations of groundwater samples that could be collected at each site were generally consistent with the inverse linear relation-

ships between salinity and nutrient concentrations observed in coastal ocean samples collected at the same location.

*Estimation of nutrient concentrations in the fresh SGD component*—The concentrations of N + N,  $\text{PO}_4^{3-}$ , Si, and  $\text{NH}_4^+$  in the fresh SGD component (i.e., the portion of discharging groundwater that originated as fresh groundwater, rather than as seawater entrained in the coastal

Table 4. Mean concentrations of nitrate and nitrite (N + N), phosphate ( $\text{PO}_4^{3-}$ ), silica (Si), and ammonium ( $\text{NH}_4^+$ ) in pit or spring samples representing discharging groundwater at each site, and nutrient concentrations inferred for the fresh submarine groundwater discharge (SGD) component at each site based on nutrient–salinity relations in coastal ocean samples. The numbers of groundwater and coastal ocean samples collected at each site are given in Tables 1 and 3. The 95% confidence intervals for nutrient concentrations in inland freshwater wells (salinity < 1) are included for comparison.†

| Site                              | $C_{\text{gw}}$ (average concentration in pit and/or spring samples, $\mu\text{mol L}^{-1}$ ) |                    |     |                 | $C_{\text{f}}$ (inferred concentration in fresh SGD component, $\mu\text{mol L}^{-1}$ ) |                    |         |                 |
|-----------------------------------|-----------------------------------------------------------------------------------------------|--------------------|-----|-----------------|-----------------------------------------------------------------------------------------|--------------------|---------|-----------------|
|                                   | N+N                                                                                           | $\text{PO}_4^{3-}$ | Si  | $\text{NH}_4^+$ | N+N                                                                                     | $\text{PO}_4^{3-}$ | Si      | $\text{NH}_4^+$ |
| T1                                | 12                                                                                            | 0.7                | 81  | 0.35            | 110*                                                                                    | 2.1*               | 1400*   | 0.2             |
| T2                                | 7.1                                                                                           | 1.0                | 27  | 0.00            | 160**                                                                                   | 7.9**              | 980**   | 1.4             |
| T3                                | 1.4                                                                                           | 0.7                | 14  | 0.57            | 9                                                                                       | 0.0                | 250*    | 5.9             |
| T4                                | 9.3                                                                                           | 0.7                | 24  | 3.7             | 310**                                                                                   | 6.2**              | 1600**  | —               |
| NS1                               | —                                                                                             | —                  | —   | —               | 110*                                                                                    | 5.0**              | 890*    | —               |
| T5                                | 53                                                                                            | 2.7                | 500 | 0.27            | 84**                                                                                    | 5.0**              | 930**   | 1.2             |
| T6                                | —                                                                                             | —                  | —   | —               | 99**                                                                                    | 4.4**              | 850**   | 1.7*            |
| T7                                | —                                                                                             | —                  | —   | —               | 34**                                                                                    | 7.9**              | 860**   | 3.7*            |
| T8                                | 36                                                                                            | 2.3                | 240 | 0.67            | 89**                                                                                    | 2.7**              | 840**   | 2.0**           |
| T9‡                               | 43                                                                                            | 3.8                | 350 | 0.66            | 110**                                                                                   | 7.2**              | 910**   | 0.6             |
| T10                               | 46                                                                                            | 2.2                | 280 | 0.82            | 140**                                                                                   | 4.2**              | 820**   | —               |
| NS2                               | —                                                                                             | —                  | —   | —               | 70*                                                                                     | 4.0**              | 730**   | 4.0*            |
| T11                               | 170                                                                                           | 3.8                | 590 | 0.39            | 210**                                                                                   | 5.8**              | 900**   | 1.3             |
| T12                               | —                                                                                             | —                  | —   | —               | 70**                                                                                    | 4.8**              | 890**   | 1.8             |
| FP1                               | 0.5                                                                                           | 0.4                | 23  | —               | 64**                                                                                    | 3.8**              | 770**   | 1.9**           |
| FP2                               | —                                                                                             | —                  | —   | —               | 630*                                                                                    | 41*                | 500     | 7.2             |
| Inland freshwater wells ( $n=8$ ) | —                                                                                             | —                  | —   | —               | 60–83                                                                                   | 3.9–4.3            | 660–920 | 0.1–0.5         |

† — indicates either that no data are available, or that the y-intercept of the nutrient–salinity regression was negative, suggesting that fresh SGD was not a nutrient source. In the fresh SGD section of the table, no asterisk indicates  $p > 0.05$  (not statistically significant) for regression between salinity and nutrient concentration.

‡ Two data points corresponding to a high-salinity, high-Ra, high- $\text{PO}_4^{3-}$  mid-harbor spring (see Fig. 5) were removed from the regression between salinity and  $\text{PO}_4^{3-}$  at T9.

\* Regression between salinity and nutrient concentration with  $0.01 < p < 0.05$ ; \*\* regression between salinity and nutrient concentration with  $p < 0.01$ .

aquifer) were inferred by extrapolating significant ( $p < 0.01$ ) linear relations between salinity and the concentrations of these nutrients in seawater at each coastal ocean site to zero salinity. Coastal ocean samples, rather than groundwater (beach pit, spring, well, and anchialine pool) samples, were used to infer fresh SGD component nutrient concentrations because only a few groundwater samples, generally spanning a narrow salinity range, could be collected at each site (Table 1; see Web Appendix). Some coastal ocean sites (T5, T7, T8, T9, and T11) were sampled during more than one trip, but no significant differences in the resulting linear regressions between salinity and nutrient concentrations in the coastal ocean were observed among trips, so data from all trips were pooled together for each site.

A limitation of this method is that salinities along coastal ocean transects typically ranged from 15 to 35, and at some sites (T1, T3, T4, T7, NS2) the range was much narrower. Extrapolating relationships observed in high-salinity samples to zero salinity may not be valid in all cases. However, the observation of linear nutrient–salinity relationships in groundwater as well as coastal ocean samples suggests that the assumption of conservative nutrient behavior in groundwater is reasonable.

Nutrient concentrations inferred for the fresh SGD component varied considerably among coastal ocean sites, and were often higher than concentrations measured in

inland freshwater wells (Table 4). N + N concentrations inferred for the fresh SGD component ranged from 34  $\mu\text{mol L}^{-1}$  at T7 (Aimakapa Beach) to 310  $\mu\text{mol L}^{-1}$  at T4 (Ka'upulehu), whereas  $\text{PO}_4^{3-}$  concentrations inferred from statistically significant ( $p < 0.01$ ) linear regressions ranged from 2.7  $\mu\text{mol L}^{-1}$  at T8 (Honokohau Beach) to 7.9  $\mu\text{mol L}^{-1}$  at T2 (Puako) and inferred Si concentrations ranged from 730  $\mu\text{mol L}^{-1}$  at NS2 (Kealahou Bay) to 1600  $\mu\text{mol L}^{-1}$  at T4. The inferred  $\text{NH}_4^+$  concentration in the fresh SGD component at T8, the only site where a significant ( $p < 0.01$ ) linear relationship between salinity and  $\text{NH}_4^+$  concentration was observed, was 2.0  $\mu\text{mol L}^{-1}$ , higher than concentrations in inland freshwater wells (Table 4).

Inverse linear relations between salinity and concentrations of N + N,  $\text{PO}_4^{3-}$ , and Si in fishpond FP1 suggested that the fresh component of groundwater discharging into this fishpond was similar, in terms of nutrient concentrations, to the fresh component of groundwater discharging at coastal ocean sites (Table 4). Additionally, a significant inverse correlation was observed between salinity and  $\text{NH}_4^+$  concentration at FP1, with an inferred fresh SGD component concentration of 1.9  $\mu\text{mol L}^{-1}$ . No significant linear relations were observed between nutrient concentrations and salinity in fishpond FP2, which had a very narrow salinity range (95% CI = 12.0–12.3; see Table 3; see Web Appendix).

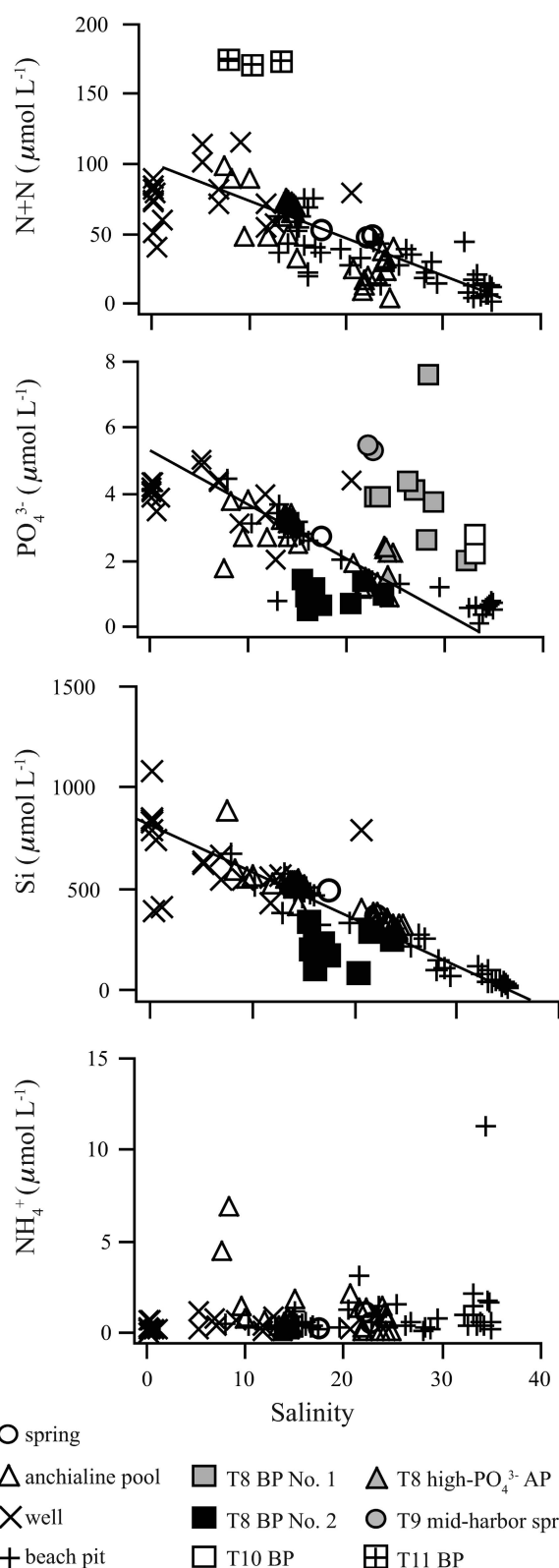


Fig. 7. Relations between salinity and nitrate + nitrite ( $N + N$ ), phosphate ( $PO_4^{3-}$ ), silica ( $Si$ ), and ammonium ( $NH_4^+$ ) in groundwater samples, including springs, anchialine pools (AP), wells, and beach pits (BP). The conservative mixing line is shown in black. All sites are represented by a generic symbol corresponding to sample type (left column of legend), except

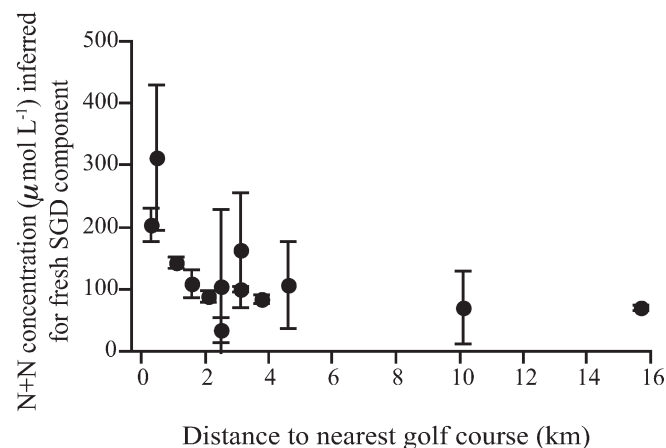


Fig. 8. Relation between proximity to a golf course and combined nitrate and nitrite ( $N + N$ ) concentration inferred for the fresh SGD component at nearshore sites. Error bars represent the 95% confidence interval for the y-intercept of the regression between salinity and  $N + N$  concentration at each site.

**Land use and land cover**—Land use and population density varied among coastal ocean study sites. Although all analyses were conducted at both the 5-km and watershed scales, no significant correlations between land use and groundwater nutrient concentrations were observed at the watershed scale, so only 5-km scale results are presented (Table 2). Three significant correlations between land use at the 5-km radius scale and nutrient concentrations inferred for the fresh SGD component were observed: a negative correlation between population density and  $Si$ , a positive correlation between bare land and  $N + N$ , and a positive correlation between bare land and  $Si$ . No correlation between kiawe tree prevalence and fresh SGD component  $N + N$  concentration was observed. Additionally, a nonparametric Spearman test indicated that sites closer to golf courses had higher  $N + N$  concentrations in the fresh SGD component (Spearman  $\rho = -0.68$ ;  $p = 0.02$ ;  $df = 11$ ; Fig. 8). However, because only two sampling sites (T4 and T11) were located within 1 km of a golf course, and a considerable degree of uncertainty was associated with the estimate of  $N + N$  concentration in the fresh SGD component at T4 (Fig. 8), these results should be interpreted with caution. Further research should focus on clarifying the relationship between golf courses and groundwater  $N + N$  concentrations in this area.

**Temporal variability in salinity,  $Ra$  isotope activity, and nutrient concentrations**—In coastal ocean samples, salinity was an average of 16% lower at low tide than at high tide ( $p < 0.01$ ,  $df = 24$ ), and  $^{224}Ra$  activity was an average of 52% higher ( $p < 0.05$ ,  $df = 24$ ). Low tide concentrations of  $N + N$ ,  $PO_4^{3-}$ , and  $Si$  were 82%, 130%, and 102% higher

←

when a site deviated significantly from the mixing line for a particular nutrient, in which case it was assigned a unique symbol (middle and right columns of legend).

( $p < 0.01$ ,  $df = 24$ ), respectively, than high tide concentrations at coastal ocean sites. Beach pits and fishponds did not display significant tidal differences in any water quality parameter. Coastal ocean  $^{223}\text{Ra}$  activity was 77% higher and  $^{224}\text{Ra}$  activity was 88% higher ( $p < 0.05$ ,  $df = 12$ ) in December 2003 than in November 2005. Concentrations of  $\text{N} + \text{N}$  and  $\text{NH}_4^+$  in coastal ocean water were 39% and 66% higher ( $p < 0.05$ ,  $df = 8$ ), respectively, in April 2006 than in December 2003. No significant difference in salinity,  $\text{PO}_4^{3-}$ , or Si concentration was observed between any pair of trips.

## Discussion

*The Kona coast subterranean estuary*—Although it is useful to consider the fresh SGD component separately because of the strong correlations between salinity and nutrients, the available evidence suggests that pure fresh SGD is rare on the Kona coast. Rather, our data are consistent with a broad mixing zone between fresh, high-nutrient groundwater and saline, low-nutrient seawater in the Kona coastal aquifer and adjacent nearshore waters. Depressed salinity, indicating freshwater from SGD, can be detected over a kilometer offshore at T9 (Fig. 2), and a monitoring well in Kaloko-Honokohau National Historical Park located a kilometer inland had a salinity of 5.3. Thus, at least at some locations, the mixing zone extends a kilometer or more in either direction from the shoreline.

Salinities and Ra activities of pit and spring samples collected close to the shoreline, which represent discharging groundwater, suggested that most SGD occurs as a brackish, high-Ra mixture of fresh groundwater and recirculated seawater. At a few sites (T1, T11, and NS2), Street et al. (2008) documented low-salinity, low-Ra SGD, which likely occurs via preferred flow paths such as fractures or lava tubes that bypass the aquifer mixing zone, and which may contribute freshwater (but little or no Ra) at some sites.

Assuming that SGD occurs as a brackish, high-Ra mixture of fresh groundwater and recirculated seawater, the brackish flux (calculated based on excess nearshore  $^{224}\text{Ra}$  activity) would be equivalent to the total flux, and the fresh flux (calculated based on salinity) would be fully included within it. However, if a separate, low-Ra, low-salinity SGD source is also present, the fresh flux would only partially overlap with the brackish flux, and the total would be greater than the brackish flux but less than the sum of the brackish and fresh fluxes.

*SGD-related fluxes of water and nutrients to the coastal ocean*—Brackish and fresh SGD fluxes into the coastal ocean at each site were estimated using a mass-balance approach or box model. The nearshore box was defined as the volume of water at each coastal site where groundwater presence (depressed salinity or enhanced  $^{224}\text{Ra}$  activity compared to offshore values) was apparent. The open ocean salinity value of 35.7 reported by Peterson et al. (2009) and the average  $^{224}\text{Ra}$  activity of offshore samples collected in this study (13 mBq [100 L] $^{-1}$ ) were used as offshore values. If salinity or  $^{224}\text{Ra}$  activity did not

reach the offshore value at any transect point, the entire transect length was used as the box length.

The depth of each box was defined as the average water depth along the coastal ocean transect (typically 1 m) at beaches, or as 1 m in bays and harbors. A 1-m depth was chosen because only surface water was sampled in this study and because previous research in Honokohau Harbor (Bienfang 1980; Johnson et al. 2008) showed that most brackish, high-nutrient water was confined to a surface layer approximately 1 m thick. More recent, high-resolution depth profiles of salinity ( $S$ ) and temperature at T5 and T9 (E. E. Grossman unpubl. data) have indicated that the SGD plume at these sites is typically between 1 and 2.5 m thick. Thus, our estimates, which were calculated using a 1-m depth, are conservative.

For bays and Honokohau Harbor (T9, T10, and T11), the width of the box was defined as the width of the bay or harbor mouth, and the total flux was divided by the box width to yield the shoreline-normalized flux ( $\text{L m}^{-1} \text{ min}^{-1}$ ). For beaches (T1, T4–8, T12), no explicit assumptions about box width were made, and fluxes were calculated directly per meter of shoreline.

The brackish SGD flux into the nearshore box at each coastal ocean site was calculated as

$$\text{SGD} = \frac{(\text{Ra}_{\text{ns}} - \text{Ra}_{\text{os}}) \times V_{\text{box}}}{\text{Ra}_{\text{gw}} \times T_r \times L_s} \quad (2)$$

where SGD is the brackish SGD flux ( $\text{L m}^{-1} \text{ min}^{-1}$ );  $\text{Ra}_{\text{ns}}$ ,  $\text{Ra}_{\text{os}}$ , and  $\text{Ra}_{\text{gw}}$  are the  $^{224}\text{Ra}$  activities of nearshore water, offshore seawater, and groundwater, respectively, in mBq (100 L) $^{-1}$ ;  $V_{\text{box}}$  is the volume of the nearshore box (L);  $T_r$  is the residence time within the nearshore box (min); and  $L_s$  is the length of shoreline at the nearshore site (m). The flux of the fresh SGD component was calculated in the same manner, except that the term  $(\text{Ra}_{\text{ns}} - \text{Ra}_{\text{os}})/\text{Ra}_{\text{gw}}$  was replaced by  $(S_o - S_{\text{ns}})/S_o$ , representing the freshwater fraction in the nearshore box, where  $S_o$  is open ocean salinity (35.7), and  $S_{\text{ns}}$  is the salinity within the nearshore box.

The upper and lower bounds on residence times used at most sites were 6 and 65 h, with the lower bound based on current meter measurements at a subset of sites (E. E. Grossman unpubl. data) and the upper bound determined by the sensitivity of the Ra AR. At T9, we used a range of 12–18 h from literature values (Gallagher 1980; Peterson et al. 2009), and at T10, we used a literature value of 38 h (Peterson et al. 2009). Although our data were insufficient to generate precise residence times for most sites, it is likely that residence times at open coastline sites (T3, T4, T6, T7) are much closer to 6 h than to 65 h, putting SGD fluxes at these sites closer to the upper end of the reported range.

The average salinity and excess  $^{224}\text{Ra}$  activity within each nearshore box was estimated from plots of salinity or  $^{224}\text{Ra}$  activity vs. distance from shore (Figs. 2, 5). The salinity or  $^{224}\text{Ra}$  activity within each linear segment of the plot was calculated, each of these values was weighted by the proportion of the box length represented by the linear segment, and the weighted average was calculated. No SGD fluxes were calculated for T2 because offshore gradients in salinity and  $^{224}\text{Ra}$  activity were not observed.

Table 5. Parameters and results for brackish and fresh submarine groundwater discharge (SGD) fluxes calculated using the mass-balance approach.  $L_t$  is the transect length (m),  $S_{\text{box}}$  and  $Ra_x$  are the weighted average salinity and excess  $^{224}\text{Ra}$  activity ( $\text{mBq [100 L}^{-1}\text{]}$ ) along each transect, and  $S_{\text{gw}}$  and  $Ra_{\text{gw}}$  are the average salinity and  $^{224}\text{Ra}$  activity in discharging groundwater. Brackish fluxes could be calculated only at sites where discharging groundwater could be sampled and had a higher  $^{224}\text{Ra}$  activity than coastal ocean water. No consistent gradients in salinity or  $^{224}\text{Ra}$  activity with distance offshore were observed at T2, making it impossible to calculate SGD fluxes using our approach.

| Site | $L_t$ | $S_{\text{box}}$ | $S_{\text{gw}}$ | $Ra_{\text{gw}}$ | $Ra_x$ | Residence time range (h) | Brackish SGD flux ( $\text{L m}^{-1} \text{min}^{-1}$ ) | Fresh SGD flux ( $\text{L m}^{-1} \text{min}^{-1}$ ) |
|------|-------|------------------|-----------------|------------------|--------|--------------------------|---------------------------------------------------------|------------------------------------------------------|
| T1   | 500   | 31.0             | 32.2            | 200              | 36     | 6–65                     | 20–300                                                  | 20–200                                               |
| T3   | 300   | 34.8             | 35.0            | 160              | 14     | 6–65                     | 3–30                                                    | 2–20                                                 |
| T4   | 150   | 33.9             | 34.7            | 88               | 24     | 6–65                     | 10–100                                                  | 2–20                                                 |
| T5   | 70    | 28.9             | 17.6            | 620              | 300    | 6–65                     | 9–90                                                    | 3–40                                                 |
| T6   | 200   | 31.6             | —               | —                | 79     | 6–65                     | —                                                       | 6–60                                                 |
| T7   | 500   | 33.4             | —               | —                | 67     | 6–65                     | —                                                       | 8–90                                                 |
| T8   | 220   | 31.1             | 23.3            | 210              | 240    | 6–65                     | —                                                       | 7–80                                                 |
| T9   | 2059  | 31.8             | 22.1            | 450              | 210    | 12–18                    | 890–1300                                                | 210–310                                              |
| T10  | 600   | 33.8             | 22.1            | 120              | 53     | 38                       | 120                                                     | 14                                                   |
| T11  | 1000  | 33.6             | 11.2            | 35               | 29     | 6–65                     | 100–1000                                                | 7–80                                                 |
| T12  | 100   | 30.2             | —               | —                | 41     | 6–65                     | —                                                       | 4–40                                                 |

The average  $^{224}\text{Ra}$  activity of all beach pit and spring samples at each coastal ocean site was used as an estimate of the  $^{224}\text{Ra}$  activity of discharging brackish groundwater. The salinity of this brackish SGD varied from 11.2 at T11 to 35.0 at T3 (Table 5). No pit or spring samples could be collected at T6, T7, or T12. Thus, brackish SGD fluxes could not be calculated at these sites because we had no input value for groundwater  $^{224}\text{Ra}$  activity. At T8, the average  $^{224}\text{Ra}$  activity in beach pit samples was lower than that of coastal ocean samples, so the brackish SGD flux could not be calculated. However, because the salinity of the fresh groundwater component was, by definition, zero, fluxes of the fresh SGD component could be calculated at transect sites regardless of whether groundwater sampling was possible or whether pits were representative of brackish SGD.

Brackish SGD fluxes (Table 5) ranged from 3–30  $\text{L m}^{-1} \text{min}^{-1}$  at T3 (Kekaha Kai State Park) to 890–1300  $\text{L m}^{-1} \text{min}^{-1}$  at T9 (Honokohau Harbor), similar to brackish fluxes reported for the leeward coasts of Maui and Moloka'i (Street et al. 2008), and Kahana Bay, O'ahu (Garrison et al. 2003), but greater than those estimated for the north shore of Kaua'i (Knee et al. 2008).

Our brackish SGD estimate for T9 (890–1300  $\text{L m}^{-1} \text{min}^{-1}$ ) is considerably higher than the total SGD estimate of Peterson et al. (2009; 83  $\text{L m}^{-1} \text{min}^{-1}$ ) for the same site, a discrepancy that may result from the fact that Peterson et al. (2009) included only SGD occurring within 10 m of the inner harbor spring, whereas we included any SGD present in the  $\sim 1000\text{-m}$ -long harbor, which has springs along the length of its walls (E. E. Grossman unpubl. data). Our brackish SGD estimate for T10 (120  $\text{L m}^{-1} \text{min}^{-1}$ ) was slightly higher than that of Peterson et al. (2009; 70  $\text{L m}^{-1} \text{min}^{-1}$ ). We note that we divided published fluxes (Johnson et al. 2008; Peterson et al. 2009) that were not shore-normalized by shoreline length or bay mouth width for the purpose of comparison.

Fluxes of the fresh SGD component ranged from 2–20  $\text{L m}^{-1} \text{min}^{-1}$  at T3 (Kekaha Kai State Park) and T4

(Ka'upulehu) to 210–310  $\text{L m}^{-1} \text{min}^{-1}$  at T9 (Honokohau Harbor), consistent with previous estimates of fresh SGD along the entire Kona coast by Kay et al. (1977; 6–19  $\text{L m}^{-1} \text{min}^{-1}$ ) and Oki (1999; 8  $\text{L m}^{-1} \text{min}^{-1}$ ). Our fresh SGD estimate for T9 also agrees well with a previous estimate of 190  $\text{L m}^{-1} \text{min}^{-1}$  for the same site by Gallagher (1980), although it is considerably higher than more recent estimates of 93  $\text{L m}^{-1} \text{min}^{-1}$  by Johnson et al. (2008) and 60  $\text{L m}^{-1} \text{min}^{-1}$  by Peterson et al. (2009). However, our fresh SGD component flux for T10 (14  $\text{L m}^{-1} \text{min}^{-1}$ , respectively) is somewhat lower than that of Peterson et al. (2009; 41  $\text{L m}^{-1} \text{min}^{-1}$ ). In this study, brackish SGD fluxes were higher than fresh fluxes at all sites where both could be calculated (Table 5), suggesting a significant recirculated seawater component of the total SGD flux at many sites.

Brackish SGD-related nutrient fluxes were calculated by multiplying the brackish SGD flux by the average nutrient concentrations in pit and/or spring samples representing discharging groundwater at each site. Nutrient fluxes associated with the fresh SGD component were calculated by multiplying inferred fresh SGD component nutrient concentrations by the flux of the fresh SGD component, and were calculated only when the linear relationship between salinity and nutrient concentration in nearshore waters at a coastal ocean site was statistically significant ( $p < 0.05$ ). At T9, two data points apparently associated with one or more high-salinity, high- $Ra$ , high- $\text{PO}_4^{3-}$  mid-harbor springs (Fig. 5) were removed from the regression between  $\text{PO}_4^{3-}$  and salinity in order to calculate the  $\text{PO}_4^{3-}$  flux from fresh SGD into the harbor. Several such springs have been noted previously (E. E. Grossman unpubl. data), and two were sampled in this study (Fig. 7; see Web Appendix).

N + N fluxes from brackish SGD ranged from 0.01–0.1  $\text{mol d}^{-1} \text{m}^{-1}$  at T3 (Kekaha Kai State Park) to 30–300  $\text{mol d}^{-1} \text{m}^{-1}$  at T11 (Keauhou Bay), whereas N + N fluxes from the fresh SGD component ranged from 0.4–5  $\text{mol d}^{-1} \text{m}^{-1}$  at T5, T7, and T12 (Kaloko Beach, Aimakapa Beach, and City of Refuge) to 30–50  $\text{mol d}^{-1} \text{m}^{-1}$  at T9 (Honokohau Harbor). Brackish SGD-related  $\text{PO}_4^{3-}$

fluxes ranged from 0–0.03 mol d<sup>-1</sup> m<sup>-1</sup> at T3 to 5–7 mol d<sup>-1</sup> m<sup>-1</sup> at T9, whereas those from the fresh SGD component ranged from 0.02–0.2 mol d<sup>-1</sup> m<sup>-1</sup> at T4 (Ka'upulehu) to 2–3 mol d<sup>-1</sup> m<sup>-1</sup> at T9. Brackish SGD-related Si fluxes ranged from 0.05–0.6 mol d<sup>-1</sup> m<sup>-1</sup> at T3 to 400–700 mol d<sup>-1</sup> m<sup>-1</sup> at T9, whereas those from the fresh SGD component ranged from 4–50 mol d<sup>-1</sup> m<sup>-1</sup> at T4 to 300–400 mol d<sup>-1</sup> m<sup>-1</sup> at T9 (Table 6). Brackish SGD-related NH<sub>4</sub><sup>+</sup> fluxes ranged from 0–0.03 mol d<sup>-1</sup> m<sup>-1</sup> at T3 to 0.8–1 mol d<sup>-1</sup> m<sup>-1</sup> at T9. The fresh SGD-related NH<sub>4</sub><sup>+</sup> flux at T8 (Honokohau Beach), the only site where such a flux could be calculated, was 0.02–0.2 mol d<sup>-1</sup> m<sup>-1</sup>.

At all sites except T1 (Spencer Beach Park) and T4, nutrient fluxes associated with brackish SGD were higher than those associated with fresh SGD, which is consistent with fresh SGD being a component of the total brackish flux. The results at T1 and T4 suggest a distinct, low-salinity, low-Ra, high-nutrient groundwater source at these sites. At T5 and T9, nutrient inputs from the fresh SGD component were almost as large as those from brackish SGD, suggesting that fresh groundwater was the dominant nutrient source to the coastal ocean at these sites. In contrast, at T8 and T11 brackish SGD-related nutrient fluxes were considerably larger than those from fresh water, suggesting significant nutrient inputs from recirculated seawater.

The SGD-related nutrient fluxes presented in this study are considerably higher than those that have been estimated for most other locations, including sites in Hawaii. They are several orders of magnitude higher than those presented for the north shore of Kaua'i (Knee et al. 2008), and they are also generally higher than total dissolved nitrogen, phosphorus, and Si fluxes calculated for Kahana Bay, O'ahu (1.30, 0.07, and 0.78 mol d<sup>-1</sup> m<sup>-1</sup>; Garrison et al. 2003), a much more developed location. Fresh SGD-related N + N, PO<sub>4</sub><sup>3-</sup>, and Si fluxes estimated for T11 (Keauhou Bay; Table 6) are comparable to those previously reported for the same site (1.7, 0.09, and 17 mol d<sup>-1</sup> m<sup>-1</sup>, respectively) by Dollar and Atkinson (1992). Additionally, recirculated seawater-related nutrient inputs (calculated as brackish less fresh nutrient fluxes) at this site, which were not considered previously, are 7, 4, and 4 times greater than fresh SGD-related inputs of N + N, PO<sub>4</sub><sup>3-</sup>, and Si, respectively (Table 6). These high nutrient inputs from recirculated seawater may indicate natural or anthropogenic nutrient sources very close to shore, where groundwater is already brackish. They also underscore the importance of recirculated seawater in coastal nutrient budgets at some sites.

*Spatial and temporal distribution of SGD*—Because of uncertainty surrounding specific coastal ocean residence times at each site, fresh and brackish SGD fluxes calculated for most sites should be viewed as estimates. Despite this, clear differences among sites were observed. T9 (Honokohau Harbor) almost always had the highest fluxes of water and nutrients, whereas fluxes at T3 (Kekaha Kai State Park) and T4 (Ka'upulehu) were low. Even before Honokohau Harbor was created in 1970, this part of the coastline was known to be a site of high SGD, and creating

Table 6. Estimated fluxes of combined nitrate and nitrite (N + N), phosphate (PO<sub>4</sub><sup>3-</sup>), silica (Si), and ammonium (NH<sub>4</sub><sup>+</sup>), in moles per day per meter of shoreline, from fresh and brackish submarine groundwater discharge (SGD) at coastal ocean sites. The ranges represent the uncertainty in magnitude of fresh or brackish SGD fluxes (Table 5).

| Site |          | N+N flux | PO <sub>4</sub> <sup>3-</sup> flux | Si flux  | NH <sub>4</sub> <sup>+</sup> flux |
|------|----------|----------|------------------------------------|----------|-----------------------------------|
| T1   | Fresh    | 3–30     | 0.05–0.6                           | 30–400   | —                                 |
|      | Brackish | 0.4–4    | 0.02–0.3                           | 3–30     | 0.01–0.1                          |
| T3   | Fresh    | —        | —                                  | —        | —                                 |
|      | Brackish | 0.01–0.1 | 0–0.03                             | 0.05–0.6 | 0–0.03                            |
| T4   | Fresh    | 0.9–9    | 0.02–0.2                           | 4–50     | —                                 |
|      | Brackish | 0.1–2    | 0.01–0.1                           | 0.4–4    | 0.06–0.6                          |
| T5   | Fresh    | 0.4–5    | 0.02–0.3                           | 5–50     | —                                 |
|      | Brackish | 0.7–7    | 0.03–0.4                           | 6–70     | 0–0.04                            |
| T6   | Fresh    | 0.8–9    | 0.04–0.4                           | 7–80     | —                                 |
|      | Brackish | —        | —                                  | —        | —                                 |
| T7   | Fresh    | 0.4–4    | 0.09–1                             | 10–100   | —                                 |
|      | Brackish | —        | —                                  | —        | —                                 |
| T8   | Fresh    | 0.9–10   | 0.04–0.4                           | 9–100    | 0.02–0.2                          |
|      | Brackish | —        | —                                  | —        | —                                 |
| T9   | Fresh    | 30–50    | 2–3                                | 300–400  | —                                 |
|      | Brackish | 60–80    | 5–7                                | 400–700  | 0.8–1                             |
| T10  | Fresh    | 3        | 0.09                               | 20       | —                                 |
|      | Brackish | 8        | 0.4                                | 50       | 0.1                               |
| T11  | Fresh    | 2–20     | 0.06–0.7                           | 10–100   | —                                 |
|      | Brackish | 30–300   | 0.6–6                              | 90–1000  | 0.06–0.6                          |
| T12  | Fresh    | 0.4–4    | 0.03–0.3                           | 5–50     | —                                 |
|      | Brackish | —        | —                                  | —        | —                                 |

the harbor, including blasting out bedrock and “unplugging” lava tubes, likely increased the already substantial flow (Bienfang 1980). The calculated proportions of the fresh and recirculated seawater SGD components were not the same at all sites. For example, T1 had high fresh SGD and relatively little recirculated seawater, whereas SGD at T8 and T11 contained a greater proportion of recirculated seawater.

Greater amounts of both brackish SGD and the fresh SGD component were present in the nearshore zone at low tide compared to high tide, an effect that has been noted in many previous studies (Garrison et al. 2003; Boehm et al. 2004; Robinson et al. 2007), and that may result from greater SGD at low tide, landward migration of the mixing zone at high tide, or greater dilution with inflowing seawater at high tide. Fresh and brackish SGD on the Kona coast may also vary with the spring–neap tidal cycle (de Sieyes et al. 2008), although we did not investigate this. Significant variations in coastal ocean salinity, Ra activity, and nutrient concentrations occurred among seasons and/or years. These differences may result from seasonal or interannual variations in groundwater recharge and discharge, groundwater quality, or coastal circulation. Based on our data alone, it is not possible to distinguish between these explanations.

*Nutrient behavior in the subterranean estuary and coastal ocean*—In contrast to previous work showing biogeochemical transformations of nutrients, particularly nitrogen, within the subterranean estuary (Talbot et al.

2003; Tesoriero et al. 2005; Kroeger and Charette 2008), the behavior of  $N + N$ ,  $PO_4^{3-}$ , and Si in groundwater samples on the Kona coast appeared to generally be conservative. Johnson et al. (2008) observed that nutrient concentrations in coastal wells and ponds near T9 (Honokohau Harbor), T10 (Kailua Bay), and NS2 (Kealakekua Bay) deviated significantly from the conservative mixing trend they reported for coastal waters. Although we obtained similar results for T9 and T10, our data set as a whole suggests that at other Kona coast locations, conservative mixing between high-nutrient fresh groundwater and low-nutrient seawater occurs within the coastal aquifer along a broad salinity gradient (Fig. 7).

The conservative behavior we observed may result from several characteristics of the coastal aquifer in this area. The nutrient enrichment we observed in fresh groundwater most likely originates in rainy, vegetated upland areas with more mature soils. This high-nutrient groundwater then flows quickly through the coastal aquifer because of its relatively steep hydraulic gradient and high hydraulic conductivity (Oki 1999). The arid coastal zone, where soil is usually poorly developed or absent, may be less likely to alter groundwater nutrient concentrations (Crews et al. 1995), and the rapid rate of groundwater flow allows relatively little time for biogeochemical transformations to occur. Additionally, the coastal aquifer's young basalt may be less favorable for such transformations than more weathered sands and soils (Vitousek and Farrington 1997). More work should be done to confirm and explain these nutrient–salinity relationships in Kona coastal groundwater.

Fresh groundwater concentrations of  $PO_4^{3-}$  and  $N + N$  inferred based on coastal ocean nutrient–salinity relationships were higher than concentrations measured in inland freshwater wells, suggesting that some nutrient additions to fresh groundwater occur within 2 km of the coastline (Fig. 7). These additions may result from anthropogenic inputs or natural processes, such as microbial mineralization of organic nitrogen and nitrification, near the coast. However, because the hydrologic connection between the inland freshwater wells included in this study and the coastal unconfined aquifer in the vicinity of the study sites is not well understood, it is also possible that the inland freshwater wells tap a distinct, lower-nutrient freshwater aquifer.

Compared to those in groundwater samples (Fig. 7), relations between salinity and concentrations of  $N + N$ ,  $PO_4^{3-}$ , and Si in the coastal ocean were more linear, with less scatter about the conservative mixing line (Fig. 6; Table 4). This observation of highly conservative nutrient behavior in the coastal ocean is consistent with previous work in Honokohau Harbor (Bienfang 1980) and Honokohau, Kailua, and Kealakekua Bays (Johnson et al. 2008; Parsons et al. 2008; Street et al. 2008). Bienfang and Johnson (1980) cited rapid flushing rates, a highly stratified nutricline, and heavy grazing as explanations for the combination of high nutrient concentrations and low phytoplankton abundance they observed in Honokohau Harbor (T9). Nutrient concentrations in Honokohau Harbor and Kealakekua Bay (NS2) have increased in recent decades, and although these inputs may have affected

local coral reefs (Parsons et al. 2008), the conservative behavior of macronutrients has not changed over time. This study shows that conservative nutrient behavior in the coastal ocean is spatially pervasive on the Kona coast. The dissipation of coastal ocean nutrient concentrations by physical, rather than biological, processes may modulate the effects of potential future increases in nutrient inputs. However, it is also possible that if nutrient inputs were to increase greatly in the future, physical processes would no longer suffice to dissipate them.

*Relation of land use and land cover to groundwater nutrient concentrations*—The correlations between land use and fresh groundwater nutrient concentrations observed in this study—a negative correlation between population density and Si, positive correlations between bare land and both Si and  $N + N$ , and a positive correlation between proximity to a golf course and  $N + N$ —may reflect the relatively undeveloped status of the Kona coast. The higher concentrations of  $N + N$  and Si in the fresh SGD component at sites with more bare land may be related to the biogeochemical properties of the relatively young, barren basalt flows that make up most bare land in this area. The negative correlation between population density and Si concentration in the fresh SGD component may be related to the lower incidence of impervious surfaces that prevent infiltration of rainfall, such as rooftops, roads, and parking lots, in areas with low population density. Alternatively, irrigation in more densely populated areas may dilute natural groundwater Si concentrations. To the best of our knowledge, no studies have documented higher groundwater nutrient concentrations in conjunction with low population density or bare land; thus, these results should be confirmed and explored further.

The high  $N + N$  concentrations inferred for the fresh SGD component at sites close to golf courses (Fig. 8) likely result from fertilizer and treated wastewater applications. In contrast to  $N + N$ ,  $PO_4^{3-}$  sorbs readily to aquifer materials (Wong et al. 1998), which may explain why concentrations of that nutrient in the fresh SGD component were not significantly higher at sites near golf courses, even though fertilizer and wastewater contain high concentrations of both nutrients (Wong et al. 1998; Table 3). Although previous work by Dollar and Atkinson (1992) suggested that golf courses contribute nutrients to Kona coast groundwater, this is the first study to show statistically that sites near golf courses have higher  $N + N$  concentrations in the fresh component of discharging groundwater. Because of the relatively low prevalence of farmland and houses in Kona at present, fertilizers applied to golf courses may represent an unusually large proportion of the total anthropogenic nitrogen load in this area. However, fresh SGD-related  $N + N$  fluxes were generally not higher at sites near golf courses, despite higher concentrations in the fresh SGD component, because these sites did not have particularly high fresh SGD fluxes (Tables 5, 6). This finding illustrates the importance of understanding both the magnitude and the nutrient concentration of SGD in order to evaluate its potential effects on coastal systems.

The lack of positive correlation between nutrient concentrations in the fresh SGD component and urban development, population density, or agriculture on the Kona coast is surprising, given that such correlations have been found elsewhere (Nolan 2001; Choi et al. 2007). One explanation is that development in this area is not extensive enough to noticeably affect water quality. Population densities within 5 km of our study sites ranged from  $< 1$  to  $186 \text{ km}^{-2}$ , compared to  $4000 \text{ km}^{-2}$  in Honolulu, Hawaii's capital and largest city. The intensity of agricultural and industrial land use is also lower on the Kona coast than in many other areas where studies have been conducted. However, the present lack of significant correlations between urban or agricultural land use and groundwater nutrient concentrations should not be taken to mean that more intense development in the future will not lead to groundwater quality impairment. Rather, it simply suggests that land use at its present intensity on the Kona coast (with the possible exception of golf courses) is not the major control on groundwater nutrient concentrations at most sites. It is also possible that other variables, such as differences in aquifer substrate, rainfall, topography, weather, and vegetation obscure the land-use effect.

*Potential effects of SGD-derived nutrient subsidies on coral reefs*—Numerous studies have shown relations between high nutrient concentrations in the coastal ocean and adverse effects on coral reefs, such as decreased coral abundance and diversity, increased coral mortality, and increased macroalgal growth (for reviews, see McCook 1999; Fabricius 2005). A recent study focusing on T9 and NS2 (Parsons et al. 2008) found that high  $\text{N} + \text{N}$  concentrations were correlated with higher percentages of dead coral cover and that concentrations of  $\text{N} + \text{N}$  at both sites had increased over the past 30–40 yr. Additionally, long-term monitoring at T2 has documented a 5–18% decrease in coral cover since 1982 (Friedlander et al. 2008). Large discharges of nutrient-rich SGD are common on the Kona coast, and rapid population growth and development have occurred throughout the region, so it is likely that increases in nutrient concentrations and decreases in coral cover have occurred at other coastal ocean sites besides T2, T9, and NS2 and will continue to occur in the future.

This study illustrates that SGD delivers large subsidies of  $\text{N} + \text{N}$ ,  $\text{PO}_4^{3-}$ , and Si to the coastal ocean at many locations on the Kona coast, confirming the results of previous studies (Dollar and Atkinson 1992; Johnson et al. 2008; Street et al. 2008). Furthermore, it extends these results to a larger number of sites and characterizes how the chemical composition and magnitude of SGD fluxes in this area vary in space and time.

Our data from sites around Honokohau Harbor were consistent with the findings of Johnson et al. (2008), suggesting that treated wastewater injections are associated with high groundwater  $\text{PO}_4^{3-}$  concentrations there. We also showed that  $\text{N} + \text{N}$  concentrations in the fresh SGD component were higher at locations near golf courses, suggesting an anthropogenic source of a portion of SGD-derived nitrogen subsidies.

Because spatial heterogeneity in SGD is high, local SGD fluxes should be considered in land use decisions, especially those regarding development projects likely to add nutrients or other pollutants to the coastal aquifer. Moreover, because fresh SGD and recirculated seawater fluxes are not always related in terms of quantity or quality, it is important to consider how each affects the nutrient budgets of a given site or the coastline as a whole.

Finally, the conservative behavior of macronutrients in groundwater and the coastal ocean has important implications for how this system will respond to possible future nutrient additions. The generally conservative behavior of nutrients in the subsurface suggests that biogeochemical processes within the aquifer may not mitigate nutrient additions to groundwater in the coastal aquifer. Future research should focus on understanding why so little biological nutrient uptake is occurring in the coastal ocean: rapid advection, stratification, and limitation of phytoplankton by micronutrients such as trace metals (Reuter and Petersen 1987; Downs et al. 2008) are all possibilities. Current conditions of nutrient delivery and coastal circulation appear to insulate Kona's coral reefs from negative effects of nutrient addition, such as increased growth of macroalgae and phytoplankton. What remains unknown is the level of nutrients that the system can handle and how impending development will influence groundwater and nutrient fluxes to the coast and the health of Kona's reefs.

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