

Prepared in cooperation with the Hawai'i Commission on Water Resource Management and the National Park Service

## Water-Chemistry Data Collected in and near Kaloko-Honokōhau National Historical Park, Hawai'i, 2012–2014



Open-File Report 2014–1173

COVER

Kaloko Cut ocean location in Kaloko-Honokōhau National Historical Park. Photograph by Fred Tillman.

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By Fred D Tillman, Delwyn S. Oki, and Adam G. Johnson

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Open-File Report 2014–1173

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## Conversion Factors

Inch/Pound to SI

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
Area		
acre	4,047	square meter (m <sup>2</sup> )
acre	0.004047	square kilometer (km <sup>2</sup> )

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:  
 $^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$

Vertical coordinate information is referenced to local mean sea level.

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S}/\text{cm}$  at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ( $\mu\text{g}/\text{L}$ ).



# Water-Chemistry Data Collected in and near Kaloko-Honokōhau National Historical Park, Hawai‘i, 2012–2014

By Fred D Tillman, Delwyn S. Oki, and Adam G. Johnson

## Abstract

Kaloko-Honokōhau National Historical Park (KAHO) on western Hawai‘i was established in 1978 to preserve, interpret, and perpetuate traditional Native Hawaiian culture and activities, including the preservation of a variety of culturally and ecologically significant water resources that are vital to this mission. KAHO water bodies provide habitat for 1 threatened, 11 endangered, and 3 candidate threatened or endangered species. These habitats are sustained by, and in the case of ‘Aimakapā Fishpond and the anchialine pools, entirely dependent on, groundwater from the Keauhou aquifer system. Development of inland impounded groundwater in the Keauhou aquifer system may affect the coastal freshwater-lens system on which KAHO depends, if the inland impounded-groundwater and coastal freshwater-lens systems are hydrologically connected. This report documents water-chemistry results from a U.S. Geological Survey study that collected and analyzed water samples from 2012 to 2014 from 25 sites in and near KAHO to investigate potential geochemical indicators in water that might indicate the presence or absence of a hydrologic connection between the inland impounded-groundwater and coastal freshwater-lens systems in the area. Samples were collected under high-tide and low-tide conditions for KAHO sites, and in dry-season and wet-season conditions for all sites. Samples were collected from two ocean sites, two fishponds, three anchialine pools, and three monitoring wells within KAHO. Two additional nearshore wells were sampled on property adjacent to and north of KAHO. Additional samples from the freshwater-lens system were collected from six inland wells located upslope from KAHO, including three production wells. Seven production wells in the inland impounded-groundwater system also were sampled. Water samples were analyzed for major ions, selected trace elements, rare-earth elements, strontium-isotope ratio, and stable isotopes of water. Precipitation samples from five sites were collected roughly along a transect upslope from KAHO. All precipitation samples were analyzed for stable isotopes of water and some precipitation samples were analyzed for rare-earth and selected trace elements.

## Introduction

The Kona area of western Hawai‘i is rapidly being developed and the quality of coastal groundwater in

Kaloko-Honokōhau National Historical Park (KAHO; fig. 1) may be affected by activities associated with this development. Since 1970, western Hawai‘i has experienced a population increase of about 83 percent and the fastest economic growth on Hawai‘i Island. Kona has been described as the “ground zero” of urban growth in western Hawai‘i (Gomes, 2010). Stakeholders in the area include the National Park Service, the Hawai‘i State Commission on Water Resource Management, the Hawai‘i County Department of Water Supply, and land developers, among others. At issue among stakeholders is whether urban development over, or withdrawals of freshwater from, the inland impounded-groundwater system will adversely affect the coastal freshwater-lens system, which itself supplies municipal, agricultural, and industrial water uses and sustains aquatic resources. Inland impounded groundwater (water levels of tens to hundreds of feet above sea level) exists adjacent to and inland from the coastal freshwater-lens system (water levels of a few feet above sea level), and is created by a low-permeability subsurface geologic feature of uncertain origin that separates the inland impounded-groundwater and coastal freshwater-lens systems (fig. 2). Previous studies and interpretations have assumed that the inland impounded-groundwater and coastal freshwater-lens systems are hydrologically connected (Oki and others, 1999). However, recently available information from deep wells could be interpreted to suggest that the inland impounded-groundwater system may be hydrologically disconnected from the coastal freshwater-lens system. In addition, a low-permeability feature confines groundwater beneath the coastal lens and forms a coastal confined-groundwater system. Currently, the extent of the hydrologic connection between the inland impounded and freshwater-lens systems is uncertain (fig. 2). From 2012 to 2014, a U.S. Geological Survey (USGS) study collected and analyzed water samples in and near KAHO to investigate potential geochemical indicators in water that might indicate the presence or absence of hydrologic connection between the inland impounded and coastal freshwater-lens systems in the area.

## Purpose and Scope

The purpose of this report is to document the sampling and processing procedures, laboratory methods, analytical results, and quality-assurance measures of water and precipitation

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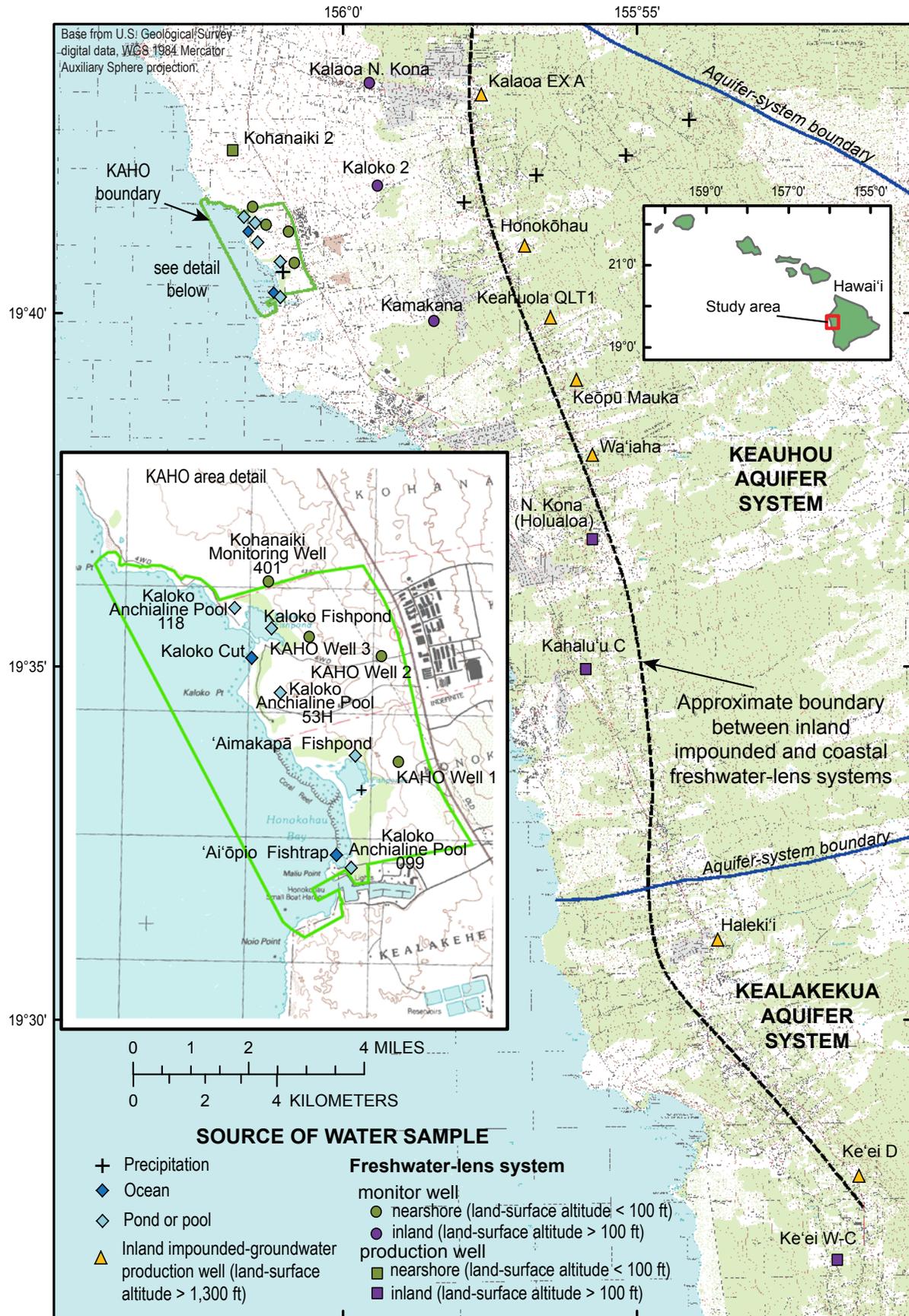
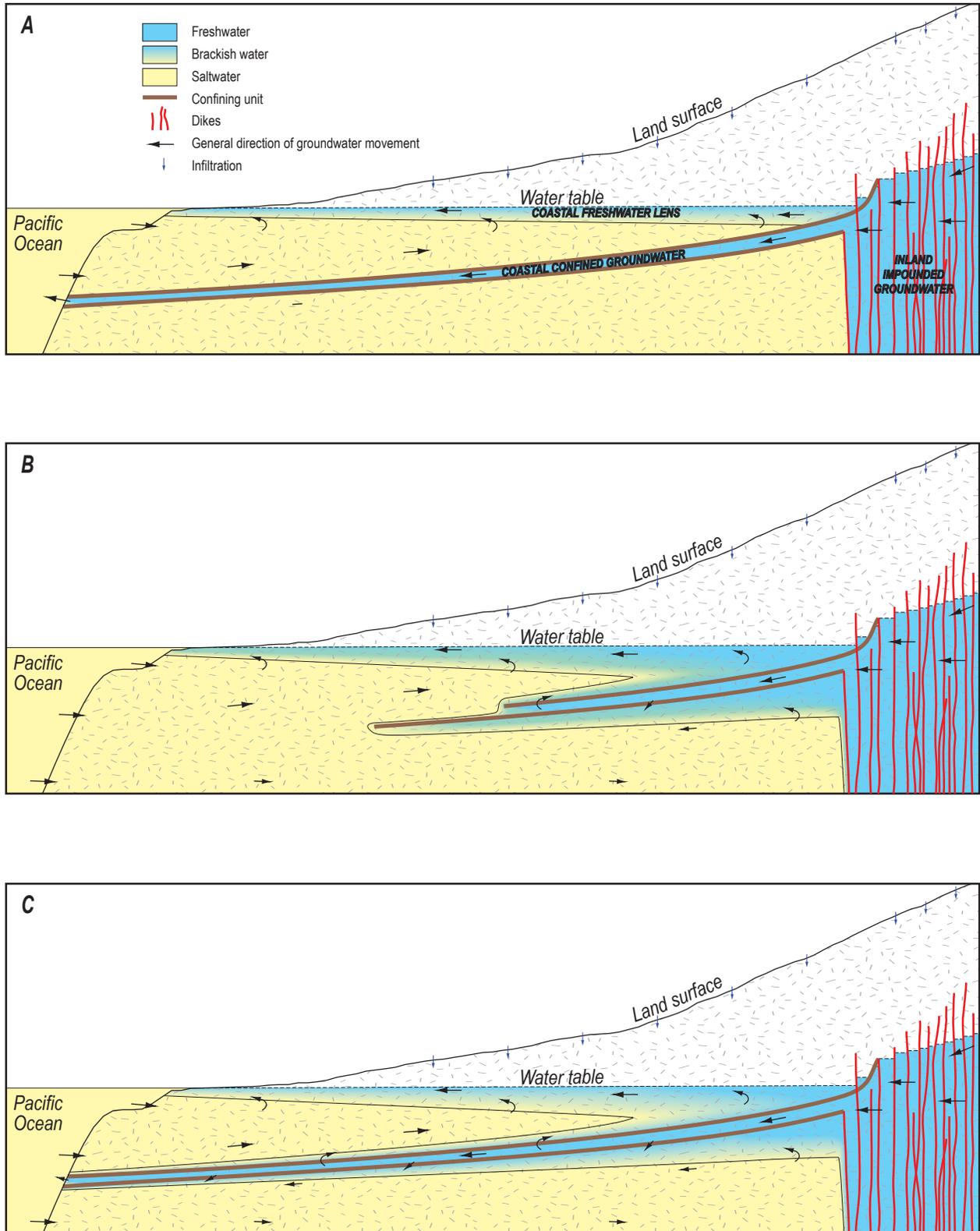


Figure 1. Location of water-chemistry sampling sites in and near Kaloko-Honokōhau National Historical Park, Hawai'i, 2012–2014.



**Figure 2.** Three conceptual models of interconnection among groundwater bodies in the study area. A) the freshwater lens system is completely separated from the other groundwater bodies by impermeable rock, B) all discharge from the inland impounded system ultimately contributes to the recharge of the freshwater lens system, and C) some discharge from the inland impounded system contributes to the recharge of the freshwater lens system and the remainder goes directly to the ocean at depth beneath the freshwater lens system.

samples collected in the KAHO area by USGS from 2012 to 2014.

## Description of Study Area

Much of the western (Kona) part of the island of Hawai‘i is formed by volcanic rocks from Hualālai and Mauna Loa Volcanoes (Stearns and Macdonald, 1946). The Keauhou aquifer system surrounding KAHO is bounded on the northeast by the Northwest Rift Zone of Hualālai Volcano, on the southeast by the approximate surface contact between volcanic rocks from Hualālai and Mauna Loa, and on the west by the coast (fig. 1). Thus, the Keauhou aquifer system mainly is formed by volcanic rocks from Hualālai. Within the Keauhou aquifer system, land-surface altitudes range from 0 ft at the coast to 8,271 ft near a volcanic vent within the Northwest Rift Zone of Hualālai. Kaloko-Honokōhau National Historical Park lies on the western flank of Hualālai below an altitude of approximately 80 ft. The Keauhou aquifer system contains three main groundwater bodies: (1) a coastal freshwater-lens system, which supplies KAHO with groundwater, (2) a coastal confined-groundwater system beneath the coastal lens, and (3) an inland impounded-groundwater body with high water levels inland from the coastal lens (fig. 2).

Mean annual air temperatures range from approximately 77 °F near the coast (Arguez and others, 2011) to less than 59 °F at higher altitudes (Nullet and Sanderson, 1993). Mean annual rainfall for the period 1978 to 2007 in the study area was less than 15 in. at the coast, between 15 and 25 in. within KAHO, and between approximately 40 and 65 in. in a band from 1,000 to 3,000 ft altitude, and generally less than 41 in. above an altitude of 3,400 ft (Giambelluca and others, 2013).

KAHO was established in 1978 to preserve, interpret, and perpetuate traditional Native Hawaiian culture and activities. KAHO contains a variety of culturally and ecologically significant water resources that are vital to this mission. The water in KAHO is considered a cultural resource, as it made possible the settlement of this arid region by Native Hawaiians (Honokōhau Study Advisory Commission, 1974). KAHO contains (1) two large ancient Hawaiian fishponds, the 15-acre ‘Aimakapā Fishpond and the 11-acre Kaloko Fishpond (fig. 1; Kikuchi and Belshe, unpublished data, 1971; Kikuchi, 1976); (2) more than 180 known anchialine pools, which are small brackish coastal pools that lack a surface connection to the ocean but are hydrologically connected to groundwater and the ocean through a permeable aquifer (Holthius, 1973; Brock and Kam, 1997); and (3) 627 acres of marine waters that support coral reefs, marine turtles, fishes, invertebrates, and marine mammals (Gibbs and others, 2007). These water bodies provide habitat for 1 threatened, 11 endangered, and 3 candidate threatened or endangered species. These habitats are sustained by, and in the case of ‘Aimakapā Fishpond and the anchialine pools, entirely dependent on, groundwater. The anchialine pools may have been an important source of drinking

water for pre-industrial Native Hawaiians (Cordy and others, 1991) particularly during dry periods. KAHO contains about 25 percent of the estimated 700 anchialine pools in Hawai‘i (Mitchell and others, 2005) and these pools support rare endemic species (some of which may not be described) and candidate species. The wetlands and fishponds are important breeding and foraging habitat for the endangered Hawaiian coot (*Fulica americana alai*) and the Hawaiian stilt (*Himantopus mexicanus knudseni*) (Morin, 1994).

The coastal freshwater-lens system within KAHO is composed of brackish water overlying saltwater in a highly permeable volcanic-rock aquifer (Oki and others, 1999). Water levels in the coastal freshwater-lens system are substantially affected by ocean tides and ocean level. The brackish water is formed by seaward-flowing fresh groundwater mixing with underlying saltwater from the ocean. Brackish water flowing through KAHO ultimately discharges to the coastal fishponds and anchialine pools in KAHO or to the ocean. The freshwater component of groundwater in KAHO is derived from infiltration of rainfall over the coastal freshwater-lens system and possibly from discharge from the underlying coastal confined-groundwater system or the inland impounded-groundwater body with high water levels. A recent study involving baseline groundwater-quality sampling by USGS in and near KAHO indicates possible nutrient enrichment and pharmaceuticals that may be related to wastewater sources (Hunt, in press), but the study did not directly address potential contamination associated with future development over the inland impounded-groundwater system nor the hydrologic connection between the inland-impounded and coastal-groundwater systems.

## Water-Chemistry Sites

In this report, if the top of a well casing is below a land-surface altitude of 100 ft then the well is considered a nearshore well and if the top of the well casing is above a land-surface altitude of 100 ft then the well is considered an inland well. Groundwater samples were collected from the coastal freshwater-lens system and the inland impounded-groundwater body and no water samples were collected from the coastal confined-groundwater system that underlies the coastal freshwater-lens system. Samples collected from all nearshore wells are from the freshwater-lens system and samples collected from inland wells are from the freshwater-lens system (land-surface altitude below 1,200 ft) or the inland impounded-groundwater body (land-surface altitude above 1,300 ft). In 2012 and 2013, water samples were collected in KAHO from two ocean locations (‘Ai‘ōpio Fishtrap and Kaloko Cut), two fishponds (‘Aimakapā and Kaloko), three anchialine pools (Anchialine Pool 099, Anchialine Pool 53H, and Anchialine Pool 118), and three shallow monitoring wells (KAHO Wells 1, 2, and 3)(fig. 1, table 1). Additionally, one monitoring well (Kohanaiki monitoring well 401) and one production well (Kohanaiki 2) at a development adjacent to and just north of KAHO were sampled. Other samples from

the coastal freshwater-lens system in the Keauhou aquifer system were collected from five inland wells upslope from the coast, including three monitoring wells (Kalaoa N. Kona, Kaloko 2, and Kamakana) and two production wells (N. Kona [Holualoa], Kahalu'u C) upslope from the coast (fig. 1). Five production wells (Kalaoa EX A, Honokōhau, Keahuola QLT 1, Keōpū Mauka, and Wai'aha) in the Keauhou aquifer system that are developed in the inland impounded-groundwater system also were sampled. Production wells south of the Keauhou aquifer system that were sampled include two in the inland impounded-groundwater system (Haleki'i and Ke'ei D) and one in the coastal freshwater-lens system (Ke'ei W-C). Finally, precipitation samples, composited over several-month periods in 2012–14, were collected from five locations, roughly along a transect upslope from KAHO.

## Sampling and Field Methods

Water samples were collected from ocean, pond, anchialine-pool, and monitoring- and production-well locations in June 2012 and March 2013. The June 2012 sampling was chosen to represent wet-season conditions and the March 2013 sampling dry-season conditions. KAHO sites were sampled during both high-tide ( $\geq 1$  ft above mean sea level) and low-tide ( $\leq 1$  ft below mean sea level) conditions during June 2012. The wet/dry season and high/low tide comparisons were performed to evaluate if these conditions had an effect on water-chemistry results. Precipitation samples were composited over several month periods beginning in September 2012 through March 2014.

### Sampling Methods

Water samples were collected and processed using standard USGS field and laboratory protocols (U.S. Geological Survey, variously dated). Ocean samples at 'Ai'ōpio Fishtrap and Kaloko Cut were collected by dipping a pre-cleaned 4-liter polyethylene bottle below the ocean surface after first rinsing the bottle three times with ocean water. Similarly, pond samples at 'Aimakapā and Kaloko Fishponds, and pool samples at Anchialine Pool 099, Anchialine Pool 53H, and Anchialine Pool 118 also were collected in pre-cleaned 4-liter bottles after on-site rinsing. Ocean, pool, and pond samples were all transported to KAHO park headquarters for filtration and preservation processing. Monitoring wells in KAHO (KAHO Wells 1, 2, and 3) were purged using a battery powered submersible pump for at least three well volumes and until stable field parameters (temperature, specific conductance, pH) were recorded. Samples from KAHO monitoring wells were processed on site directly from the pump outflow. All production wells were equipped with pumps (Kalaoa EX A, Honokōhau, Keahuola QLT 1, Keōpū Mauka, Wai'aha, Haleki'i, Ke'ei D, Kohanaiki 2, N. Kona [Holualoa], Kahalu'u C, and Ke'ei W-C) and were sampled from the pump discharge line (before any collection in

tanks or treatment) after stable field parameters were recorded and were also processed onsite.

All monitoring wells outside of KAHO (Kalaoa N. Kona, Kaloko 2, Kamakana, Kohanaiki monitoring well 401) were sampled using bailers without purging. Samples were not purged because the depth to water in most of the monitoring wells exceeded 500 ft, which made bailing difficult, and the volume of water required made purging impractical. Not purging the monitoring wells listed above also permitted the collection of depth-discrete samples at two of the wells. During June 2012, bailed samples were collected using 1.6 by 36 in. disposable polyethylene bailers with a ball-check valve. During March 2013, bailed samples were collected using 2.5L Hydrasleeve disposable bag samplers (<http://www.hydrasleeve.com>). Pre-cleaned 4-liter bottles were filled from multiple bailer sample collections, and were transported to KAHO headquarters for processing. For Kohanaiki monitoring well 401 and the Kamakana well, where samples were collected at two depths, the uppermost sample was collected first.

Precipitation samples were collected from cumulative precipitation collectors stationed at altitudes between approximately 5 and 4,610 ft, roughly along a transect upslope from KAHO (fig. 1). Each precipitation collector was a 5-gallon high-density polyethylene bucket with a 4.8-in. diameter funnel set into an O-ring sealed bucket lid. Collectors contained 0.7 in. of mineral oil to prevent evaporation of accumulated water that was sampled at intervals of 5 to 7 months.

### Field-Parameter Analyses

Analysis of sample pH, temperature, and specific conductance was performed in the field for samples from most sites as time and equipment performance allowed (table 2). Sample pH, temperature, and specific conductance were measured on unfiltered samples by handheld multi-meters. Total alkalinity and alkalinity speciation (bicarbonate, carbonate, and hydroxide concentrations) were determined using the inflection-point titration method on filtered samples.

### Quality-Assurance Measures

Equipment blanks were collected during the 2012 and 2013 sampling events using a portable submersible pump. These equipment blanks were collected by sampling certified blank water from a glass cylinder through the pump and tubing system, and processing the sample in the same manner as other environmental samples. The equipment blank samples were analyzed for major ions and selected trace elements. Additionally, duplicate samples were collected, processed, and analyzed in 2012 and 2013 from the KAHO Well 3 monitoring well. Duplicate samples were analyzed for major ions and selected trace elements for the 2012 and 2013 samples, plus stable and strontium isotopes for the 2013 duplicate sample.

Ion charge balances were computed for all water samples with major ion analytical results. Sample results with greater than  $\pm 5$  percent difference between the charge balance of cations and anions were assumed to be affected by laboratory interference. Trace-element results for samples that were analyzed by multiple laboratories were also compared for consistency.

## Water-Chemistry Analyses

Water samples from ocean, pond, anchialine-pool, and well sites were analyzed for several constituents including major ions, selected trace elements, strontium-isotope ratio ( $\text{Sr}^{87/86}$ ), stable isotopes of water (ratio of oxygen-18 to oxygen-16 [ $\delta^{18}\text{O}$ ] and the ratio of hydrogen-2 to hydrogen-1 [ $\delta\text{D}$ ]) and rare-earth elements. Not all samples were analyzed for all constituents, as described below. All precipitation samples were analyzed for stable isotopes of water and some precipitation samples were analyzed for rare-earth and selected trace elements.

The USGS National Water Quality Laboratory (NWQL) in Denver, Colo. analyzed all 2012–13 water samples, with the exception of the 2012 Kamakana well sample, for major ions and selected trace elements using methods described in Fishman (1993), Fishman and Friedman (1989), Garbarino (1999), and Garbarino and others (2006). An ion and trace-element sample was not collected from the Kamakana well in 2012 because of insufficient sample volume from several unsuccessful bailer collection attempts. The major ions analyzed by NWQL include bromide, calcium, chloride, fluoride, magnesium, potassium, sodium, and sulfate. The selected trace elements analyzed include arsenic, boron, chromium, iron, lithium, manganese, molybdenum, selenium, silica, strontium, uranium, and vanadium. The USGS Reston Stable Isotope Laboratory (RSIL) in Reston, Va. performed analyses of stable isotopes of water ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) following methods by Révész and Coplen (2008a,b) on all samples, including precipitation samples. The Anchialine Pool 099 sample collected in 2012 during low-tide conditions was not submitted for stable-isotope analysis because of insufficient sample volume. Strontium isotope ratio analyses were performed at the U.S. Geological Survey Metal and Metalloid Isotope Laboratory in Menlo Park, Calif. using methods described by Bullen and others (1996). Strontium-isotope ratio analyses were not part of the original scope of this project, but six samples were analyzed for strontium-isotope ratio from the 2012 sampling event to determine if useful information might be gained from these analyses. The six samples analyzed for strontium-isotope ratio in 2012 were roughly along a transect upslope from KAHO and include an ocean sample from Kaloko Cut; coastal freshwater-lens samples from the nearshore monitoring wells KAHO Well 2 and Kohanaiki monitoring well 401, and the inland monitoring well Kaloko 2; and inland impounded-groundwater samples from Kalaoa EX A and Honokōhau (fig. 1). Strontium-isotope ratio analyses were performed on 2013 samples from all sites. Likewise, rare-earth element analyses were not originally

part of the scope of this geochemical investigation, but it was thought that these analyses might differentiate groundwater in contact with shield-stage tholeiitic basalt at higher altitudes from groundwater in contact with postshield-stage alkalic basalt at lower altitudes. Rare-earth element analyses were performed on samples from most 2013 sampling-event sites by the USGS Trace-Element Research Laboratory in Boulder, Colo. using methods described in Garbarino and Taylor (1996) and Shabani and others (1992). Rare-earth elements included in the analyses were cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lutetium, neodymium, praseodymium, samarium, terbium, thulium, and ytterbium. In addition to the rare-earth element analyses, the USGS Trace-Element Research Laboratory also provided results for the trace elements aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, cesium, chromium, cobalt, copper, lead, lithium, manganese, molybdenum, nickel, phosphorus, rhenium, rubidium, selenium, strontium, tellurium, thallium, thorium, uranium, vanadium, yttrium, zinc, and zirconium.

## Quality-Assurance Results

Portable submersible-pump equipment blank samples contained non-detectable or trace-level concentrations ( $<1$  percent of lowest result from other sites sampled with the pump) for all constituents analyzed, with two exceptions (tables 3–5). The arsenic concentration of 0.15 micrograms per liter ( $\mu\text{g/L}$ ) in the 2012 equipment blank is 27 percent of the 0.55  $\mu\text{g/L}$  found in the 2012 KAHO Well 2 sample. Manganese concentrations of 0.23 and 0.22  $\mu\text{g/L}$  in the 2012 and 2013 equipment blanks, respectively, are 51 and 49 percent, respectively of the 0.45  $\mu\text{g/L}$  result from the 2012 KAHO Well 3 sample. The small but detectable concentrations of arsenic and manganese may be a result of contributions from the submersible pump and (or) from contamination in sample processing or analysis. Sample results for manganese and arsenic, particularly for samples that were collected using the portable submersible pump (KAHO Well 1, 2, and 3), should be interpreted with the consideration that a very small amount ( $<0.25$   $\mu\text{g/L}$ ) of contamination might be present.

Analyses of major ion and alkalinity results revealed 10 samples analyzed by NWQL with cation/anion charge balance differences (computed as the charge difference divided by the sum) of greater than 10 percent and another 5 samples with differences from 5 to 8 percent. The 10 high charge imbalance samples are all from 2013 sampling and include samples from 'Aimakapā Fishpond (high tide), Anchialine Pool 53H (both low and high tide), KAHO Well 2, KAHO Well 3 (sample and duplicate sample), Kohanaiki monitoring well 401 (top sample), Kohanaiki 2 well, Kamakana well (top sample), and the Kalaoa N. Kona well (shaded red in table 3). All 10 samples have a negative percentage difference in charge balance, meaning that one or more anion results are too high or that one or more cation results are too low. The five samples with major ion charge imbalances between

5 and 8 percent were all from 2012 sampling and include samples from ‘Ai‘ōpio Fishtrap (high tide), Kaloko Fishpond (both low and high tide samples), KAHO Well 3 (high tide), and the Wai‘aha production well (shaded orange in table 3). Because information on sample chloride concentration is important for many of the interpretative analyses performed on these samples (for example, percentage ocean water in a sample), a determination of the acceptability of the chloride results from poor ion charge balance samples was made by comparing chloride results with strontium results for these samples. Strontium concentrations vary linearly with chloride concentrations in samples with ion charge balance differences less than 5 percent (fig. 3). For this procedure, a linear regression was performed between chloride and strontium concentration for all data with ion charge balance differences less than 5 percent (55 samples; fig. 3). Next, upper and lower confidence intervals were constructed on the slope of the regression to qualitatively include nearly all variability in the data ( $p=1E-25$ ). From this analysis, it was determined that all chloride concentrations from samples with ion charge imbalances between 5 and 8 percent, and 7 of the 10 samples with greater than 10 percent ion charge imbalance, are within the confidence intervals and by this criterion are acceptable (fig. 3, table 3).

Bromide concentrations from two samples, one from Kaloko Cut (0.652 mg/L) and one from Kaloko Anchialine Pool 099 (0.106 mg/L), were about 2 orders of magnitude less than bromide concentrations from other samples at the same sites (table 3). Although the results were verified by NWQL, laboratory comments for both results state “lots of interference on peak, value is suspect.”

Analyses of selected trace elements were available from both NWQL and the Trace-Element Research Laboratory for some of the samples collected in 2013 (tables 4 and 6). Manganese concentrations from the Trace-Element Research Laboratory were systematically lower than concentrations from NWQL by almost a factor of 10 for many of the nearshore coastal groundwater samples (table 4). Chromium concentrations from KAHO Well 1 and Kohanaiki monitoring well 401 were higher from the Trace-Element Research Laboratory (86 percent and 165 percent higher than the mean value, respectively; table 4). Seventy percent of the remaining 148 comparable trace-element concentrations from the two laboratories were within 10 percent of the mean value of the two results (table 4).

For the 2012 KAHO Well 3 duplicate samples, the mean absolute concentration difference relative to the original sample was 5 percent for all major ion and NWQL trace elements analyzed (tables 2–4). A notable exception was the 32 percent difference relative to the original sample in manganese concentration between the two samples (0.66 and 0.45  $\mu\text{g/L}$ ). Ion charge balance issues described above prevented a meaningful comparison of major ion results from the 2013 duplicate samples at KAHO Well 3. Mean absolute concentration difference relative to the original sample for NWQL trace elements was less than 7 percent for 2013

duplicate KAHO Well 3 samples. Duplicate sample analyses of stable and strontium isotopes from KAHO Well 3 in 2013 resulted in concentrations within 6.5 percent of original sample values (table 6).

## Water-Chemistry Results

The specific conductance of water samples ranged from about 50,000 microsiemens per centimeter ( $\mu\text{S/cm}$ ) in ocean-water samples to less than 150  $\mu\text{S/cm}$  in inland impounded-groundwater samples from some production wells (table 2). Sample alkalinity was composed mostly of bicarbonate for all samples (table 2). Major ion concentrations were dominated by sodium and chloride at all sites (table 3), with high-tide ocean-sample concentrations of about 11,000 mg/L and 20,000 mg/L, respectively, and inland impounded-groundwater samples as low as 13.4 mg/L and 4.7 mg/L, respectively. The ocean-water fraction of each sample is estimated on the basis of sample chloride concentration and end-member chloride concentrations from (1) high-tide Kaloko Cut ocean samples and (2) inland impounded-groundwater production wells in the Keauhou aquifer system (table 3). Low-tide ocean samples from both ‘Ai‘ōpio Fishtrap and Kaloko Cut locations contain from 30 to 46 percent freshwater (table 3). Samples from Kaloko Fishpond, which has a direct surface connection to the ocean, had 47–71 percent ocean-water chloride concentration, whereas samples from ‘Aimakapā Fishpond, which does not connect by surface flow to the ocean, had 32–37 percent ocean-water chloride concentrations (table 3). Samples from three KAHO anchialine pools had about 26 percent ocean-water chloride concentration (pool 53H) to about 45 percent ocean-water chloride concentration (pool 099; table 3). Bailed samples from Kohanaiki monitoring well 401 indicate fresher water near the top of the water column in the well (about 25 percent ocean-water chloride concentration) relative to near the bottom of the well (about 70 percent ocean-water chloride concentration; table 3). Similarly, a deep sample from the Kamakana inland coastal groundwater monitoring well had about 86 percent ocean-water chloride concentration (table 3). Samples from all production wells (with the exception of Kohanaiki 2) in both the coastal freshwater-lens and inland impounded-groundwater systems had less than 1 percent ocean-water chloride concentration (table 3).

Arsenic, uranium, and vanadium were detected in water samples from all sites (excluding precipitation sites) at concentrations above reporting limits (table 4). Strontium, boron, and lithium concentrations appear relatively high in ocean-water samples, and then progressively decrease in less saline samples (table 4). Conversely, silica concentrations are low in high-tide ocean-water samples, and increase in higher-percentage freshwater samples (table 4). Concentrations were below reporting limits, or below the concentration in the KAHO Well 2 blank sample, for nearly all rare-earth elements analyzed for most sites, with

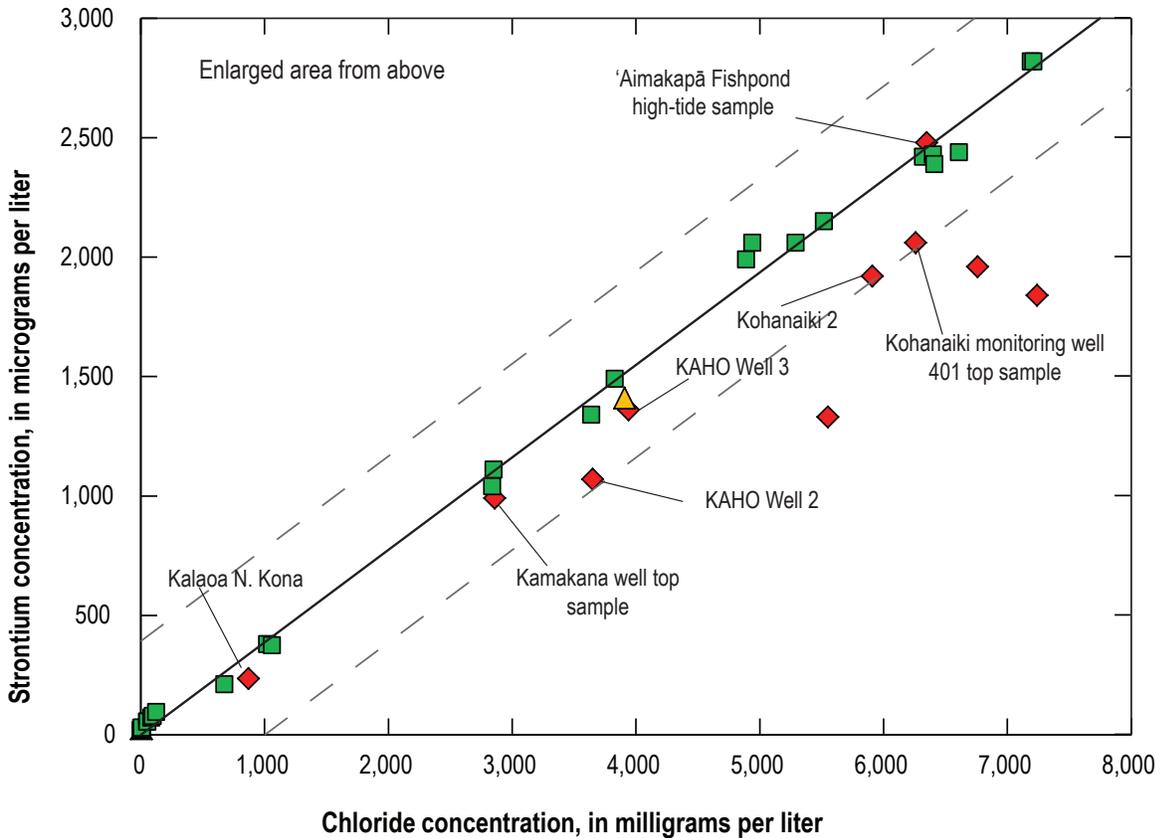
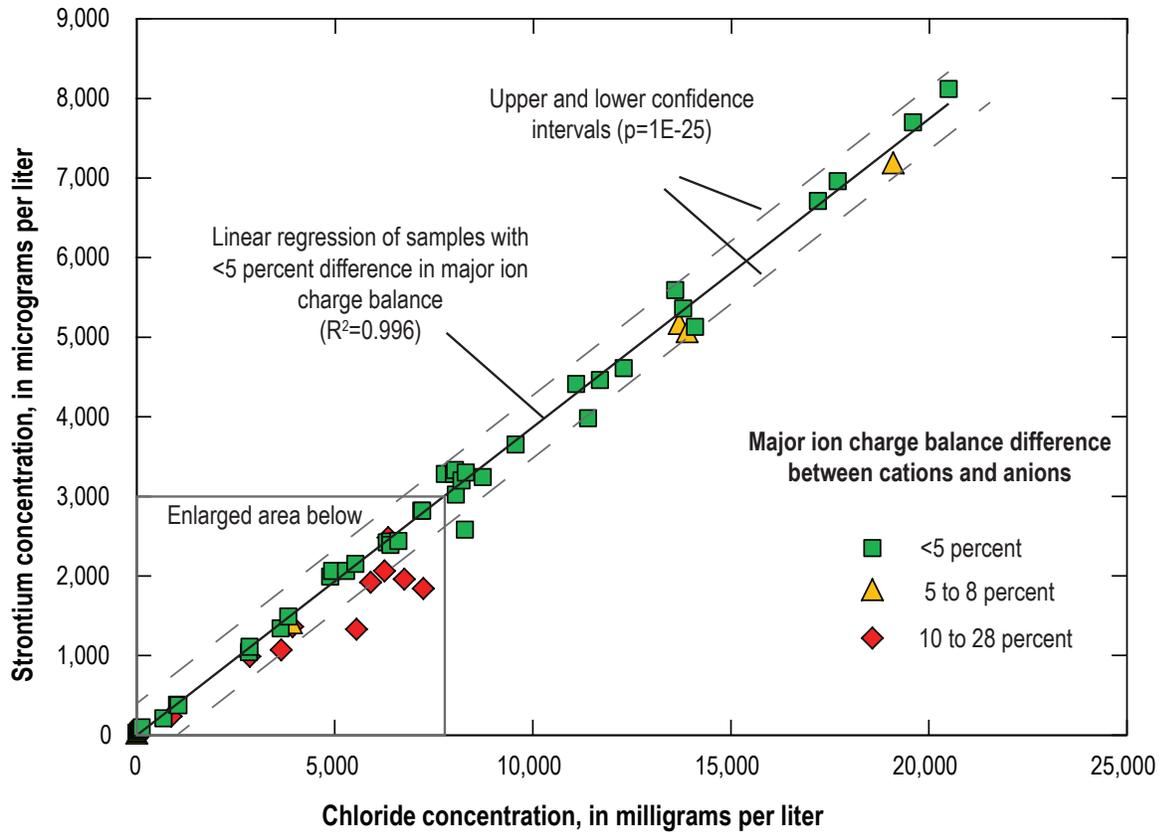
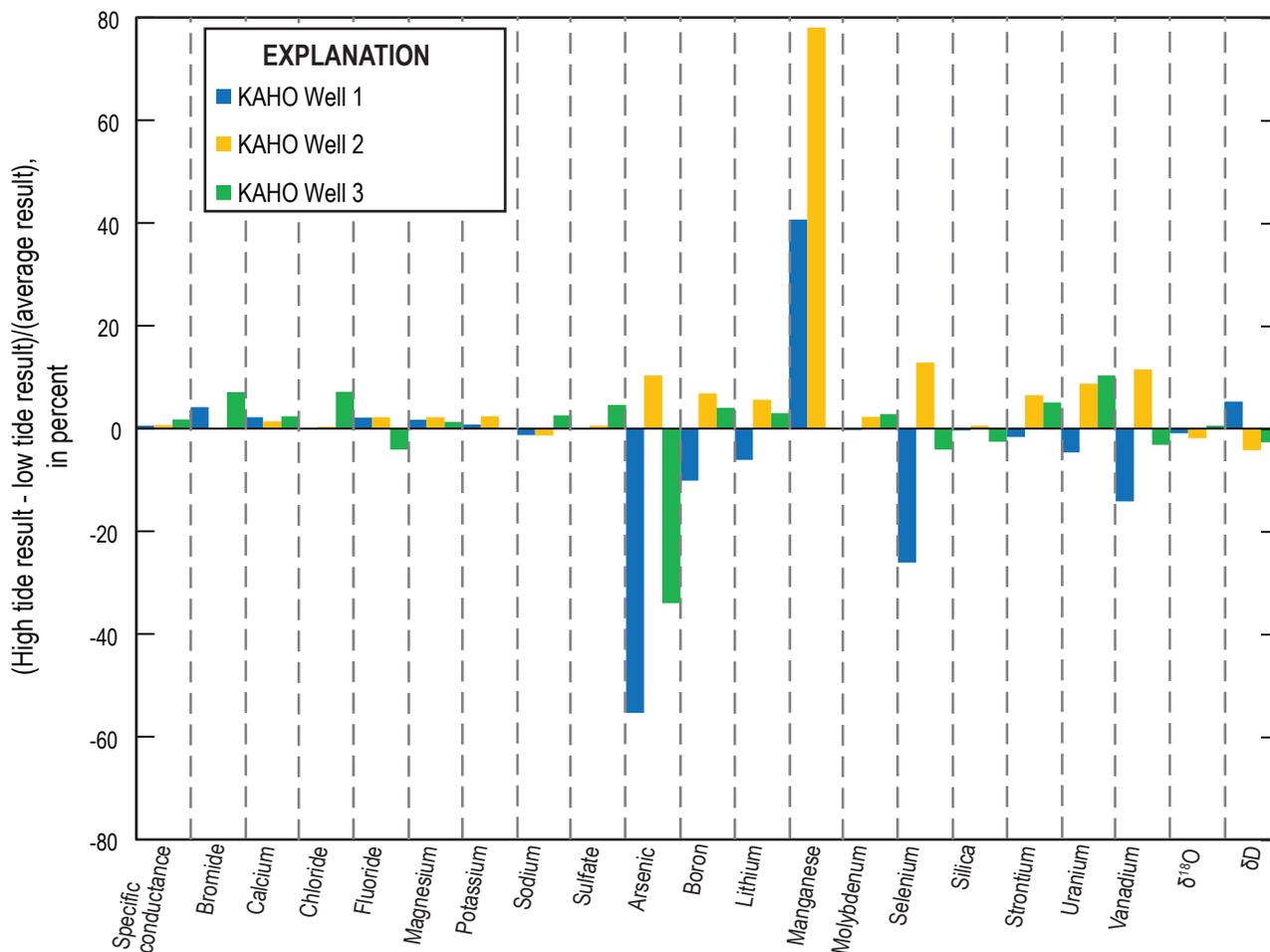


Figure 3. Relation of sample chloride concentration to strontium concentration used to evaluate samples with poor ion charge balances.



**Figure 4.** Difference between high-tide and low-tide sample concentrations at three KAHO monitoring wells sampled in 2012. Comparison for chromium and iron not shown, owing to numerous non-detect values (see tables 3–6 for all results).

the exception of the lighter elements cerium, lanthanum, and praseodymium (table 5). Ocean-water, pond, and anchialine-pool samples are enriched in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in comparison to inland impounded-groundwater samples (table 6). Strontium-isotope ratios are higher in ocean-water samples and generally decrease with decreasing ocean-water fraction (table 6).

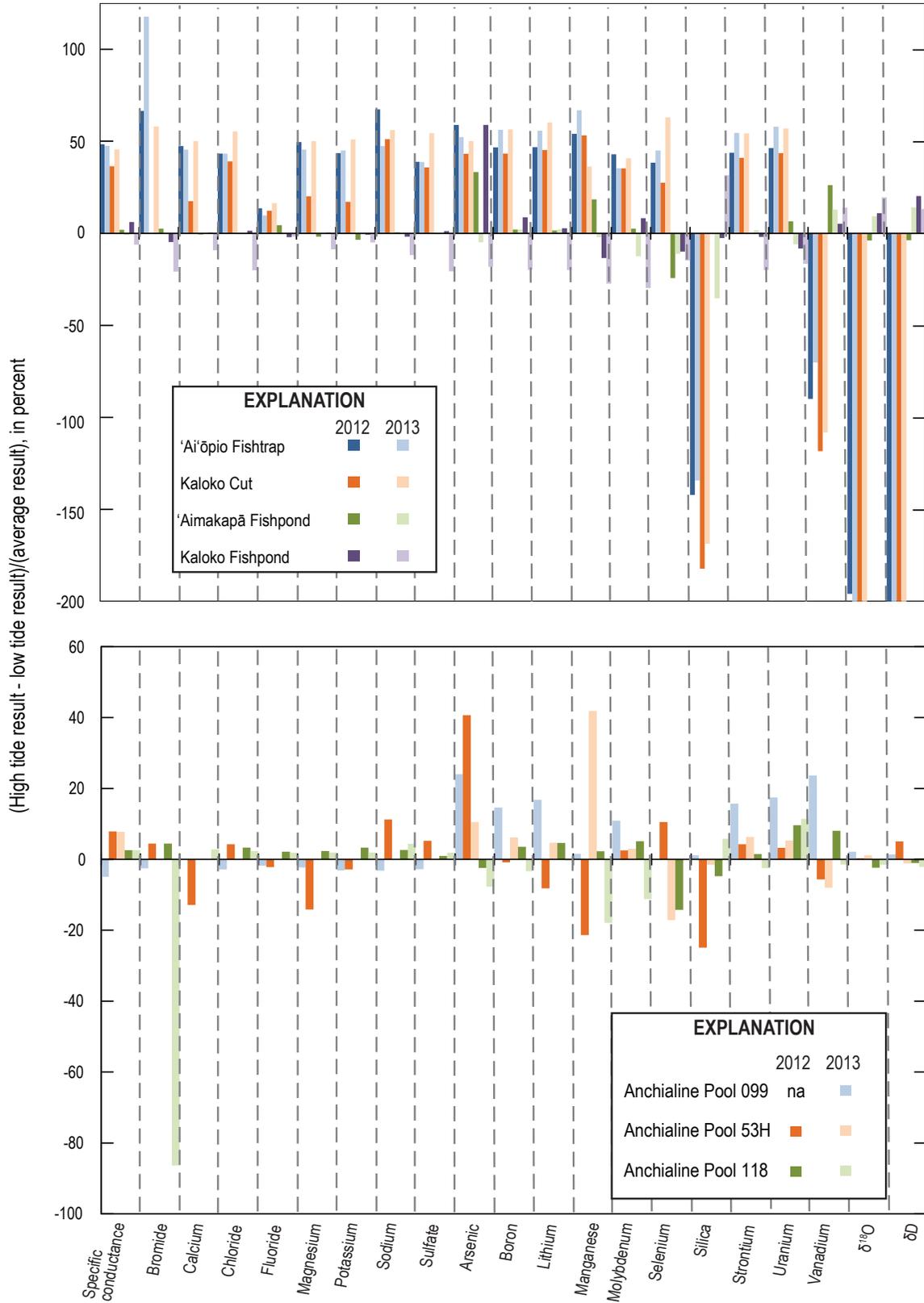
Constituent concentrations in samples from ocean, pond, and pool sites in KAHO were more variable for more constituents than in samples from wells between high-tide and low-tide sampling (tables 3, 4, and 6; figs. 4 and 5). Tide-coordinated sampling for ocean, pond, and pool sites was performed in both 2012 and 2013. Tide-coordinated sampling was discontinued for 2013 for well sites because the tidal variability in concentrations was generally less than about 10 percent, although exceptions include: (1) arsenic at KAHO Well 1 (0.68 and 1.2  $\mu\text{g/L}$ ) and KAHO Well 3 (0.66 and 0.93  $\mu\text{g/L}$ ); (2) chromium at KAHO Well 2 (1.4 and 0.75  $\mu\text{g/L}$ ) and KAHO Well 3 (0.66 and 1.3  $\mu\text{g/L}$ ); and (3) manganese at KAHO Well 1 (2.13 and 1.41  $\mu\text{g/L}$ )

and KAHO Well 2 (1.39 and 0.61  $\mu\text{g/L}$ ) (tables 3 and 4; fig. 4).

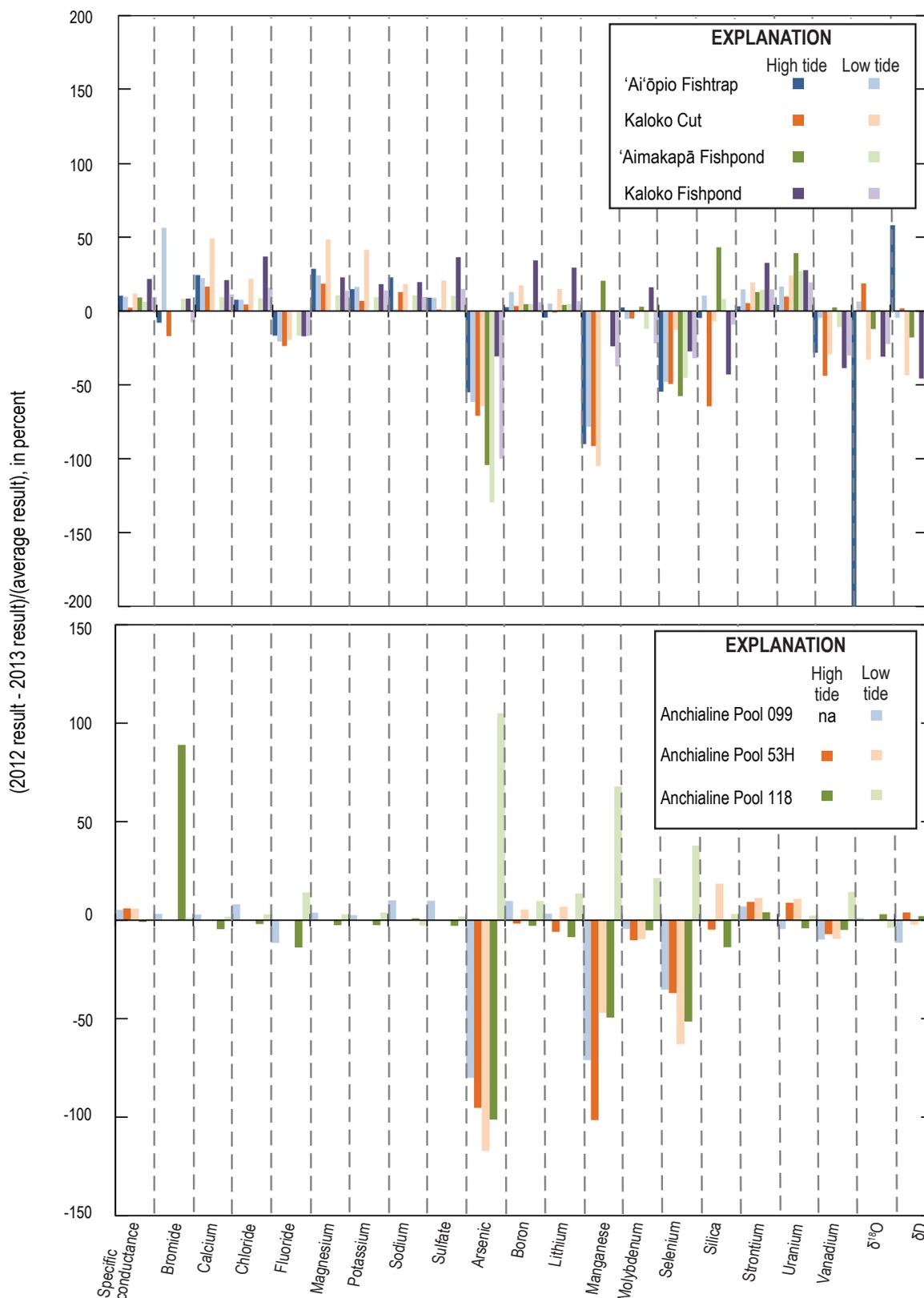
A similar magnitude difference is seen between 2012 (wet season) and 2013 (dry season) sample results for ocean and KAHO fishpond samples as for high-tide/low-tide comparisons for these sites. Anchialine-pool samples indicate a somewhat higher difference for wet/dry season comparison than high-tide/low-tide comparison (tables 3, 4, and 6; fig. 6). Seasonal differences in concentrations in samples from both nearshore and inland coastal groundwater wells in the Keauhou aquifer system (fig. 7) are greater than in samples from production wells in coastal and inland impounded-groundwater of the Kealakekua aquifer system (fig. 8).

## Summary

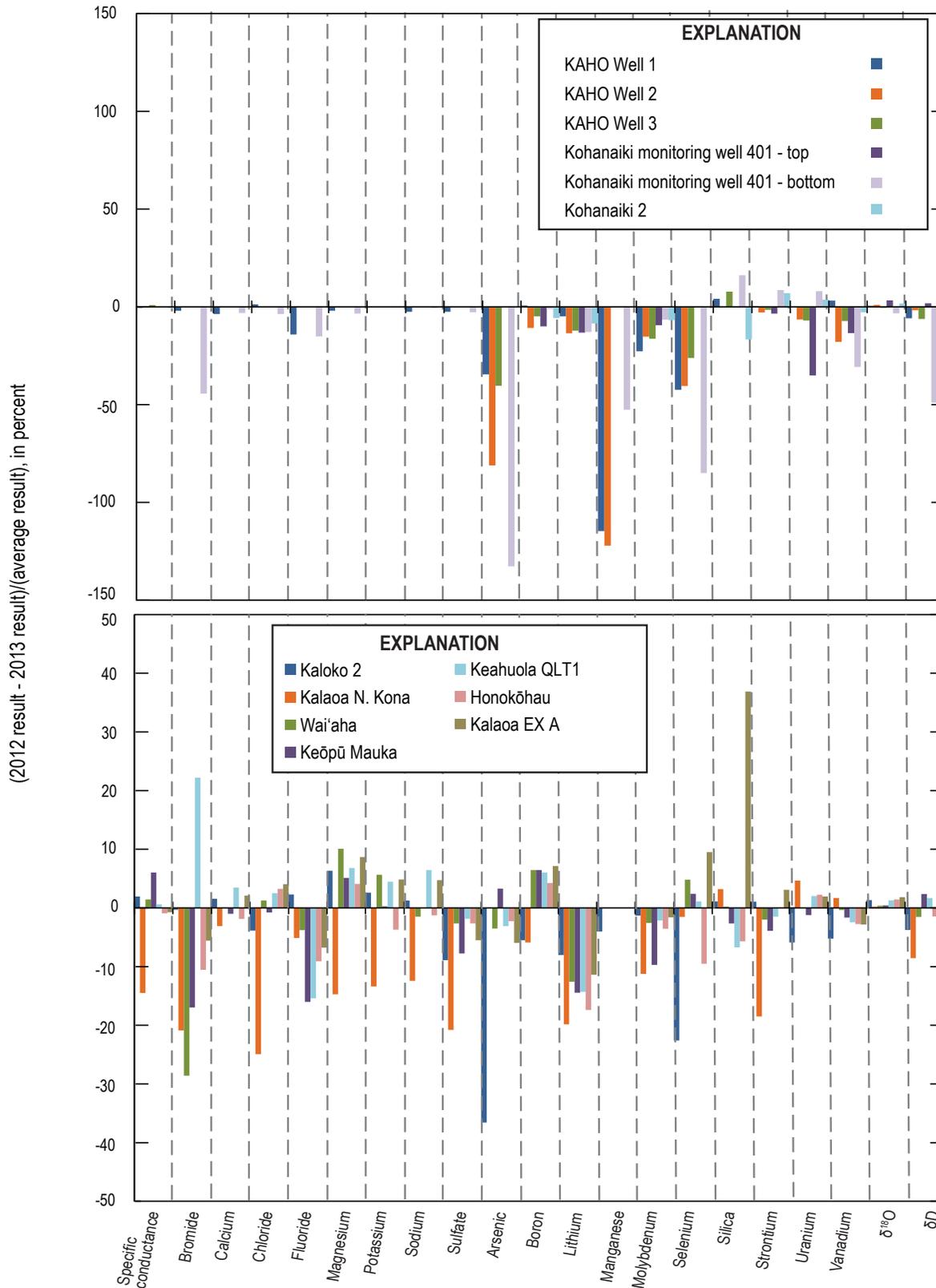
From 2012 to 2014, this study collected and analyzed water samples from 25 sites in and near KAHO to provide data that might elucidate the degree of hydrologic connection



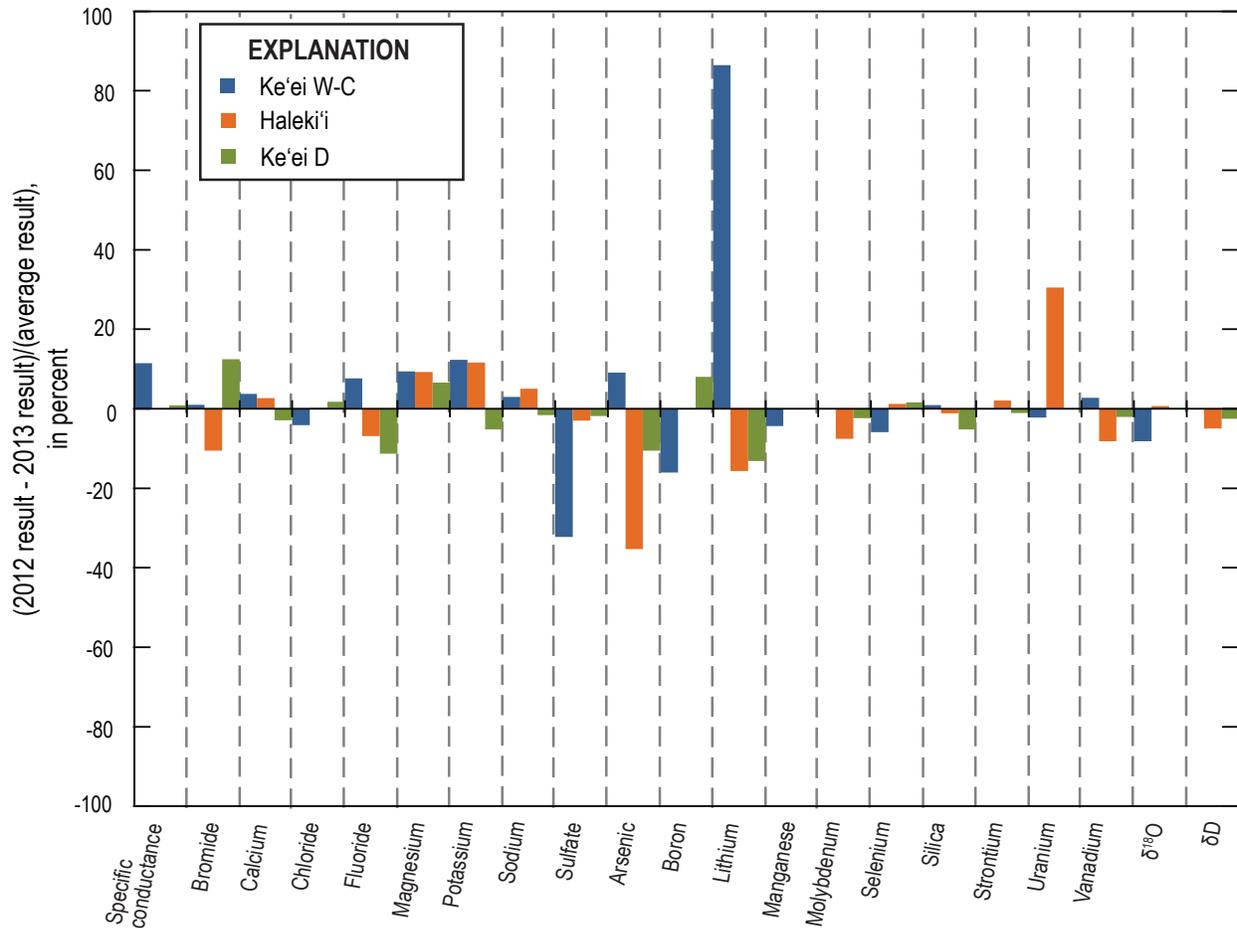
**Figure 5.** Difference between high-tide and low-tide sample concentrations at KAHO ocean and fishpond sites (upper panel) and anchialine-pool sites (lower panel). The differences of most stable isotope samples in upper panel extend beyond -200 percent. Comparison for chromium and iron not shown, owing to numerous non-detect values (see tables 3–4, and 6 for all results). Major ion comparisons not available for 2013 'Aimakapā Fishpond and Anchialine Pool 53H samples.



**Figure 6.** Difference between June 2012 (wet season) and March 2013 (dry season) sample concentrations for ocean and pond samples (upper panel) and anchialine-pool samples (lower panel). Difference of 'Ai'ōpio Fishtrap  $\delta^{18}\text{O}$  result in upper panel extends beyond -200 percent. Comparison for chromium and iron not shown, owing to numerous non-detect values (see tables 3–4, and 6 for all results). Major ion comparisons not available for 'Aimakapā Fishpond and Anchialine Pool 53H samples.



**Figure 7.** Difference between June 2012 (wet season) and March 2013 (dry season) sample concentrations for nearshore coastal groundwater wells (upper panel), and inland coastal groundwater wells (Kaloko 2 and Kalaoa N. Kona) and inland impounded-groundwater wells (lower panel) in the Keauhou aquifer system. Comparison for chromium and iron not shown, owing to numerous non-detect values (see tables 3–6 for all results). Major ion comparisons not available for KAHO Well 2, KAHO Well 3, Kohanaiki monitoring well 401 – top, and Kohanaiki 2.



**Figure 8.** Difference between June 2012 (wet season) and March 2013 (dry season) sample concentrations for production wells in the Kealakekua aquifer system. Comparison for chromium and iron not shown, owing to numerous non-detect values (see tables 3–6 for all results).

between the inland impounded and coastal groundwater systems in the area. Samples were collected under high-tide and low-tide conditions for KAHO sites, and in wet- and dry-season conditions for most sites. Water samples were analyzed for major ions, selected trace elements, strontium-isotope ratio, stable isotopes of water, and rare-earth elements. Precipitation samples from five sites were collected roughly along a transect upslope from KAHO. All precipitation samples were analyzed for stable isotopes of water and some precipitation samples were analyzed for selected trace elements and rare-earth elements.

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