Investigation of geochemical indicators to evaluate the connection between inland and coastal groundwater systems near Kaloko-Honokōhau National Historical Park, Hawai'i

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Abstract
Kaloko-Honokōhau National Historical Park (KAHO) is a coastal sanctuary on the western side of the Island of Hawai‘i that 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 and water-related habitat for species that have been declared as threatened or endangered by the U.S. Fish and Wildlife Service, or are candidate threatened or endangered species. These habitats are dependent on coastal unconfined groundwater in a freshwater-lens system. The coastal unconfined-groundwater system is recharged by local infiltration of rainfall but also may receive recharge from an inland groundwater system containing groundwater impounded to high altitudes. The area inland of and near KAHO is being rapidly urbanized and increased groundwater withdrawals from the inland impounded-groundwater system may affect habitat and water quality in KAHO, depending on the extent of connection between the coastal unconfined groundwater and inland impounded-groundwater. An investigation of the geochemistry of surface-water and groundwater samples in and near KAHO was performed to evaluate the presence or absence of a connection between the coastal unconfined groundwater and inland impounded-groundwater. Analyses of major ions, selected trace elements, rare-earth elements, and strontium-isotope ratio results from ocean, fishpond, anchialine pool, and groundwater samples were consistent with a linear mixing process between the inland impounded and coastal unconfined-groundwater systems. Stable isotopes of water in many samples from the coastal unconfined-groundwater system require an aggregate recharge altitude that is substantially higher than the boundary between the coastal unconfined and inland impounded systems, a further indication of a hydrologic connection between the two systems. The stable isotope composition of the freshwater component of water samples from KAHO indicates that about 25–70% of the freshwater is derived from the inland impounded system.

1. Introduction
Understanding the hydrologic connection among groundwater systems is critical for developing sustainable groundwater-management strategies. For cases in which groundwater systems are hydrologically disconnected, withdrawals from one groundwater system will not affect the other. For cases in which two groundwater systems are hydrologically connected, withdrawals from one groundwater system will affect the other. Where hydrogeologic information is insufficient to establish the degree of connection between adjacent groundwater systems, geochemical indicators can be used to evaluate the connection (for example, see Baillie et al., 2007; Wahi et al., 2008; Manning, 2009; Musgrove et al., 2010; Gardner and Kirby, 2011).

In the western part of the Island of Hawai‘i, the groundwater-flow system consists of three main groundwater systems: (1) a coastal unconfined-groundwater system in the form of a freshwater-lens system (FWL system), (2) a coastal confined-groundwater system (CC system) beneath the coastal freshwater-lens system, and (3) an inland impounded-groundwater system with high water levels (HL system) (Fig. 1; Oki et al., 1999). The geologic structures that form the CC and HL systems are poorly understood but are recognized due to salinity and hydraulic-head

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Fig. 1. Location of study area and water-chemistry sampling sites in and near Kaloko-Honokōhau National Historical Park (KAHO), 2012–2014. Rift zones shown in inset map modified from Langenheim and Clague (1987).
differences relative to the FWL system. The FWL system is separated from the CC system by a zone of high salinity groundwater (Supplemental Fig. 1). The FWL system is separated from the HL system by low-permeability rocks that may be related to volcanic dikes, low-permeability lava flows, or faults (Oki et al., 1999). Groundwater levels in the FWL system are less than a meter above mean sea level, whereas groundwater levels in the HL system exceed 10 m above mean sea level. The surface expression of the boundary between FWL and HL systems is near an altitude of about 460 m and ranges from more than 7 to less than 2.5 km from the coast (Fig. 1). Limited data indicate that the hydraulic head in the CC system likely is greater than 7 m above mean sea level.

The FWL system is recharged by a mixture of local infiltration of rainfall, possible outflow from the HL system (investigated in this study), and other minor sources including excess irrigation water, leachate from septic tanks and cesspools, wastewater discharges, and water pipeline leaks. From a daily water-budget model, total recharge originating from the land surface overlying the FWL system, exclusive of 0.066 m³/s wastewater discharge into a seepage pit about 1.1 km inland from Honokōhau Harbor, is estimated at about 0.086 m³/s per km of aquifer width, equivalent to 400 mm/yr averaged over the area near KAHO (Engott, 2011). Total irrigation, septic leachate, and pipeline leakage is estimated to be about 0.015 m³/s per km (Engott, 2011), representing about 17% of the FWL-system recharge exclusive of the seepage-pit discharge. Because of evapotranspiration, the recharge associated with irrigation, septic leachate, and pipeline leakage may contain groundwater from the HL system. Thus, the FWL system may receive a component of freshwater indirectly from the HL system through these sources, although the overall contribution from the HL system through these indirect sources is expected to be less than 17%. The FWL system also may receive recharge in the form of seaward discharge directly from the HL system or upward discharge from the CC system. On the basis of hydraulic head and geographic considerations, the CC system receives its recharge from the HL system. Three scenarios for the interconnection among groundwater bodies are considered: (1) the FWL system receives recharge only from local infiltration of rainfall and is completely separated from the other groundwater bodies by impermeable rock, with all of the discharge from the HL system going directly to the ocean at depth beneath the FWL system (Fig. 2a); (2) the FWL system is partially separated from the other groundwater bodies by low-permeability rock, with all of the discharge from the HL system contributing ultimately to the recharge of the FWL system (Fig. 2b); and (3) the FWL system is partially separated from the other groundwater bodies by low-permeability rock, with some of the discharge from the HL system contributing to the recharge of the FWL system and the remainder going directly to the ocean at depth beneath the FWL system (Fig. 2c). In scenario 1, groundwater withdrawals from the CC system and the HL system will not affect water levels and salinity in the FWL system, whereas in scenarios 2 and 3 they will. All groundwater that is not withdrawn from wells in the three groundwater bodies ultimately discharges to the ocean or nearshore areas. In this study, geochemical indicators are used to evaluate the hydrologic connection between the FWL system and the HL system in the western part of the Island of Hawai‘i. Understanding the connection is critical for developing an effective resource-management strategy for the area.

### 1.1. Study area

The study area is the Keaʻauhou aquifer system (State of Hawai‘i, 2014), formed mainly by volcanic rocks from Hualālai Volcano, in the western part of the Island of Hawai‘i. The study area contains the coastal Kaloko–Honokōhau National Historical Park (KAHO) (Fig. 1), which includes water-related habitat for species that have been declared as threatened or endangered by the U.S. Fish and Wildlife Service, or are candidate threatened or endangered species, including the shrimp Metabetaeus lohena and Palaemonella burnsii. These habitats are dependent on FWL-system groundwater. The area inland of and near KAHO is being rapidly urbanized, with population in the 96740 zip code that includes KAHO increasing by 33% from 2000 to 2010 (http://factfinder2.census.gov/pages/face/nav/ jsp/pages/community_facts.xhtml). This area has been characterized as “ground zero” for urban growth in the western area of the Island of Hawai‘i (Honolulu Star Advertiser, October 17, 2010, p. D1 and D8). Withdrawals from West Hawai‘i wells of about 20,000 m³/day in 1980 increased to about 128,700 m³/day by 2006 (http://hi.water.usgs.gov/recent/westhawaii/pump.html) and projected water demand for full build-out conditions exceeds the State’s sustainable-yield estimate (Fukunaga and Associates, 2010), although projected water demand is being updated. Increased groundwater withdrawals from the HL system may affect habitat and water quality in KAHO, depending on the extent of connection between the FWL and HL systems.

Within the study area, land-surface altitudes range from 0 m at the coast to about 2500 m near the northwest rift zone of Hualālai. KAHO lies below an altitude of 25 m. Mean annual air temperatures range from about 25 ºC near the coast (Arguez et al., 2011) to less than 15 ºC at higher altitudes (Nullet and Sanderson, 1993). Rainfall is affected by topography and ocean-land temperature and pressure gradients related to heating of the west-facing slopes of Hualālai and Mauna Loa Volcanoes. In the Kona area of western Hawai‘i, heating of the land surface during the day generates sea breezes that may converge with the trade winds diverted around the high volcanoes, producing a zone of convergence on west-facing slopes (Giambelluca et al., 1986). The sea breezes bring moisture-laden air from offshore to the mountain slopes, commonly resulting in rainfall in the afternoon hours. In the Kona area, rainfall is greater during the summer months (May through October), characterized by more intense heating and persistent trade winds, than during the winter months (November through April). This seasonal pattern of rainfall in the study area differs from other areas in Hawai‘i (particularly dry areas), which have greater rainfall during the winter months. Mean annual rainfall for the period 1978–2007 in the study area was less than 380 mm at the coast near the northwestern boundary, between 380 and 635 mm within KAHO, between about 1020 and 1650 mm in a band from 300 to 900 m altitude, and generally less than 1020 mm above an altitude of 1050 m (Giambelluca et al., 2013). Mean annual rainfall ranges from less than 380 to about 1270 mm over most of the FWL system. Groundwater recharge in the study area (Engott, 2011) generally reflects the pattern of rainfall and fog, with lowest mean annual recharge (less than 300 mm) near the coast and at altitudes above 1050 m, and highest mean annual recharge (400–900 mm) between altitudes of 300 and 900 m.

KAHO contains two large ancient Hawaiian fishponds (Kaloko Fishpond in the north and ‘Aimakapā Fishpond in the south) with large associated wetlands, more than 180 known anchialine pools, and 254 hectares of marine waters. Kaloko Fishpond is separated from the ocean by a rock seawall and ‘Aimakapā is separated from the ocean by a sand beach berm. Brackish groundwater discharges to both fishponds. The anchialine pools are rare brackish-water ecosystems that lack a surface connection to the ocean and are hydrologically connected to groundwater and the ocean through a permeable aquifer. The water surface exposed in anchialine pools represents the surface expression of the groundwater table and moves up and down in response to ocean tides.
2. Methods and approach

2.1. Sampling and laboratory methods

In June 2012 and March 2013, water samples were collected from 25 sites within and near KAHO in order to investigate potential geochemical indicators of the degree, or absence, of connection between the freshwater-lens (FWL) system and the inland impounded-groundwater system with high water levels (HL system) in the area. No samples were collected from the coastal unconfined-groundwater system (CC system). Samples from KAHO sites were collected under both high-tide and low-tide conditions, and samples from all sites were collected during wet-season and dry-season periods, in order to address potential tidal or seasonal variability. Detailed site information, including well depths and diameters, is described in Tillman et al. (2014). Water samples were collected from two ocean sites, two fishponds, three anchialine pools, and three monitoring wells in the FWL system within KAHO (Fig. 1). Two additional nearshore coastal wells in the FWL system, one a monitoring well and one a production well, were sampled on property adjacent to KAHO. Samples were collected from five wells in the FWL system upslope from KAHO including three monitoring wells and two production wells. Five production wells in the HL system also were sampled. Additionally, three wells (one inland production well in the FWL system and two production wells in the HL system) in the Kealakekua aquifer system, adjacent to and south of the Keauhou system, were sampled (Fig. 1). The Kealakekua system is south of the Keauhou system that is the primary focus of this investigation, but is thought to be analogous to the Keauhou system in that inland groundwater is impounded by an undefined geologic formation and the degree of connection between the HL and coastal FWL systems is unknown. Precipitation samples also were composited over several month periods beginning in September of 2012 through March 2014 from sites at five altitudes (Fig. 1).

Sampling, sample processing, analytical procedures, and quality-assurance measures are described in detail in Tillman et al. (2014) and are summarized briefly here. Water samples from
ocean, fishpond, and anchialine-pool locations were collected directly into 60-mL glass bottles for stable-isotope analyses. For all other analyses, samples from these locations were collected into clean 4-L polyethylene bottles and processed at KAHO headquarters. KAHO monitoring wells were purged using a battery powered Fultz™ submersible pump for at least three well volumes until stable field parameters were recorded, and samples from these wells were processed on site directly from the pump outflow. All monitoring wells outside of KAHO were sampled using disposable polyethylene bailers or Hydrasleeve™ disposable bag samplers without purging. Clean 4-liter bottles were filled from multiple bailer or bag-sample collections, and were transported to KAHO headquarters for processing. For Kohanaiki monitoring well 401 and the Kamakama well, where samples were collected at two depths, the uppermost sample was collected first. Discrete-depth samples from Kohanaiki monitoring well 401 and the Kamakama well were collected with bailers and bag samplers because a pump would induce borehole flow in these deep monitoring wells having long slotted casings. All production wells were equipped with pumps and were sampled directly from the pump discharge line and processed onsite. Precipitation samples were collected from cumulative precipitation collectors stationed at altitudes between about 1.5 and 1405 m, roughly along a transect upslope from KAHO (fig. 1). Each precipitation collector was a 19-L high-density polyethylene bucket with a 12.3-cm diameter funnel set into an O-ring sealed bucket lid. Collectors contained 1.8 cm of mineral oil to prevent evaporation of accumulated water that was sampled at intervals of 5–7 months.

Water samples were analyzed for major ions, selected trace elements, rare-earth elements, strontium-isotope ratio, and stable isotopes of water. Major-ion and selected trace-element analyses were performed by the USGS National Water Quality Laboratory (NWQL) in Denver, CO using inductively coupled plasma-mass spectrometry (ICP-MS) or ion chromatography (IC) methods described in Fishman (1993), Fishman and Friedman (1989), Garbarino (1999), and Garbarino et al. (2006). The USGS Trace-Element Research Laboratory in Boulder, CO performed rare-earth element analyses using ICP-MS methods described in Garbarino and Taylor (1996) and Shabani et al. (1992). Reporting limits were 0.06 mg/L or less for major ions, 18 μg/L or less for selected trace elements, and 0.0006 μg/L or less for rare-earth elements. Strontium isotope ratio analyses were performed at the USGS Metal and Metalloid Isotope Laboratory in Menlo Park, CA using ICP-MS methods described by Bullen et al. (1996), and were reported to 0.00001 units. Stable isotopes of water were analyzed by the USGS Reston Stable Isotope Laboratory following methods by Révész and Coplen (2008a,b), and were reported to 0.01 units. Not all analyses were available for all water samples (see Tillman et al., 2014). All precipitation samples were analyzed for stable isotopes of water and one set of precipitation samples was further analyzed for selected trace elements and rare-earth elements.

2.2. Approach

Major ions, selected trace elements, rare-earth elements, strontium-isotope ratio, and stable isotopes of water were investigated as possible geochemical indicators of the degree of connection between the FWL and HL groundwater systems.

2.2.1. Major ions and trace elements

The relative ion composition of the major ions bromide, calcium, chloride, fluoride, magnesium, potassium, sodium, sulfate, and alkalinity (carbonate and bicarbonate) was used to evaluate the type of water represented in samples and to determine if samples from different systems would group together based on their compositions. Major ions and selected trace elements of arsenic, boron, chromium, lithium, manganese, molybdenum, selenium, silica, strontium, uranium, and vanadium are plotted against chloride to investigate potential mixing relations between HL groundwater and ocean water. Chloride is used to represent ocean water in these mixing analyses because freshwater contains near zero chloride concentration, ocean water contains about 20,000 mg/L chloride, and volcanic rocks in which the aquifers are located are not a source of chloride (Visher and Mink, 1964).

2.2.2. Ocean-water fraction

Because chloride concentration is an indicator of saltwater derived from the ocean, the ocean-water fraction of samples was determined using a chloride-mixing model (Clark and Fritz, 1997):

\[ f_{ow} = (C_{sample} - C_{fw}) / (C_{low} - C_{fw}) \]

where \( f_{ow} \) is the ocean-water fraction of the sample, \( C_{sample} \) is the chloride concentration of the sample, and \( C_{fw} \) and \( C_{low} \) are the end-member chloride concentrations for fresh groundwater and ocean water, respectively. The choices of end-member values for Eq. (1) are important as they affect the determination of ocean-water fraction and later the determination of the isotopic composition of the freshwater component of samples. Mean values are used for end members in the mixing model, but the possible effect of uncertainty in these means is addressed by bounding ocean-water-fraction estimates with calculations made using maximum and minimum end-member values.

2.2.3. Rare-earth elements

The rare-earth elements (REEs) are comprised of the 14 elements of the lanthanide series and yttrium (the geochemical twin of holmium with similar behavior). The abundance of the REEs in the earth’s crust are about the same as those of tin, lead, and cobalt, so they are not actually rare but are best referred to as dispersed, because they are spread thinly throughout the major phases of the lithosphere (Haskin and Frey, 1966). For this study, REEs were investigated to determine if unique geochemical signatures could be determined for the HL and FWL systems.

2.2.4. Strontium-isotope ratio

Isotopes of the radiogenic element strontium have been used to understand earth-surface processes, ecosystem processes, and chemical weathering (for example, see Banner, 2004; Capo et al., 1998; Chadwick et al., 2005; Blum and Erel, 2003; Stewart et al., 2001) as well as to understand groundwater sources, evolution, and mixing (for example, see Musgrove and Banner, 1993; Jørgensen et al., 2008; Mazor et al., 1985; Hogan and Blum, 2003; Hogan et al., 2000; Woods et al., 2000). Unlike the stable-isotope ratio of a mixture of water, the strontium-isotope ratio of a mixture is dependent on both the isotopic ratios of the mixing waters and the number of strontium atoms in each of the mixing waters. A mixture of two components having different concentrations of strontium and different \( ^{87} \text{Sr}/^{86} \text{Sr} \) ratios can be related by

\[ \frac{^{87} \text{Sr}}{^{86} \text{Sr}} = \frac{\text{Sr}_{A} \text{Sr}_{B} \left( \frac{^{87} \text{Sr}}{^{86} \text{Sr}} \right)_{B} - \left( \frac{^{87} \text{Sr}}{^{86} \text{Sr}} \right)_{A} + \frac{\text{Sr}_{A} \left( \frac{^{87} \text{Sr}}{^{86} \text{Sr}} \right)_{B} - \left( \frac{^{87} \text{Sr}}{^{86} \text{Sr}} \right)_{A}}{\text{Sr}_{A} - \text{Sr}_{B}}}{\text{Sr}_{M} (\text{Sr}_{A} - \text{Sr}_{B})} \]

where subscripts M, A, and B denote the mixture, end member A, and end member B, respectively. \( ^{87} \text{Sr}/^{86} \text{Sr} \) is the strontium-isotope ratio and Sr is strontium concentration (Faure, 1986). This hyperbolic-mixing equation in coordinates of \( ^{87} \text{Sr}/^{86} \text{Sr} \)M and SrM can be transformed into a straight-line equation by plotting \( ^{87} \text{Sr}/^{86} \text{Sr} \) against 1/Sr, which allows the fraction of each end member in samples to be estimated.
2.2.5. Stable isotopes of water

Stable-isotope compositions of surface-water and groundwater samples in the KAHO area were analyzed in two related ways. First, the isotopic concentration of the freshwater component from each sample was determined from a mixing model between ocean water and fresh groundwater, and a minimum aggregate altitude of recharge was estimated for these freshwater components. Second, a ternary mixing model was developed with end members of ocean water, HL-system groundwater, and coastal precipitation to determine if the isotopic composition of water samples could be explained by only coastal precipitation and ocean water, or if other input is required.

2.2.5.1. Recharge altitude analysis. For the recharge altitude analysis, estimates of the isotopic composition of the freshwater component of each sample were needed. A mixing model was used to correct isotopic composition of water samples for ocean-water content in order to focus on the fresh groundwater component (Scholl et al., 1996):

\[
\delta_{\text{cw}} = \left( \delta_{\text{sample}} - \delta_{\text{ow}} \right) / \left( 1 - \delta_{\text{ow}} \right)
\]

where \(\delta_{\text{cw}}\) is the isotopic composition (either \(\delta^{18}O\) or \(\delta D\)) of the fresh groundwater component of the sample, \(\delta_{\text{sample}}\) is the unadjusted isotopic composition of the water sample, \(\delta_{\text{ow}}\) is the ocean-water fraction of the sample, and \(\delta_{\text{ow}}\) is the isotopic composition of ocean water. The appropriate isotopic composition of ocean water to use in Eq. (3) is uncertain because the ocean-water component of a sample is derived from an unknown depth in the ocean and the isotopic composition of ocean water is depth dependent. Thus, a range of isotopic compositions of ocean water derived from different depths is considered to capture this uncertainty.

To estimate the aggregate recharge altitude of the fresh groundwater component of the sample, information on the isotopic composition of precipitation and the relation of \(\delta^{18}O\) in precipitation to land-surface altitude is required. Limited precipitation data collected during the lifespan of this project precluded the development of a reliable, independent local meteoric water line (LMWL) or a regression between altitude and volume-weighted average \(\delta^{18}O\) with which to interpret water-isotope data. A LMWL developed on Hawai’i by Scholl et al. (1996 and 2002) and Fackrell and Glenn (2014) relations and are bounded between the isotopic composition of precipitation at sea level and at 550 m, a conservative maximum land-surface altitude overlying the FWL system in the area. The HL-system groundwater end-member range is defined by the most depleted and most enriched samples collected during this study. A sample composition plotting within the triangle formed by the three end members indicates that the sample is made up of a mixture of the three end members. A sample composition plotting along a side of the triangle indicates that the sample is made up of a mixture of the two end members forming the triangle side.

For the quantitative representation, the relative contributions of the end members can be shown on a ternary plot after computing the relative fractions of each end member in the mixed sample. The relative fractions are computed by solving a system of three equations with three unknowns:

\[
\begin{align*}
C_1 \delta^{18}O f_1 + C_2 \delta^{18}O f_2 + C_3 \delta^{18}O f_3 &= C_{\text{cw}}^{18}O \\
C_1 \delta D f_1 + C_2 \delta D f_2 + C_3 \delta D f_3 &= C_{\text{cw}} D \\
f_1 + f_2 + f_3 &= 1
\end{align*}
\]

where \(C_{\text{cw}}^{18}O\) and \(C_{\text{cw}} D\) are the compositions of the stable isotopes of water, \(f\) is the relative fraction of the end member, subscripts 1, 2, and 3 refer to the three end members, and subscript \(s\) refers to the sample. For the ternary plot, only samples from pools and wells in and near KAHO, the main area of interest, are considered. The inland HL-system groundwater end member was based on the average isotopic composition of the samples from Kalaoa EX A and Honokōhau, which are located upgradient of KAHO. Because of uncertainty in applicable end-member isotopic compositions for ocean water and coastal precipitation, ranges of isotopic compositions were considered for the ternary plot. Ocean-water end members used in the model were from the most depleted deep-ocean sample and the most enriched near-shore ocean sample. Coastal precipitation end members included average compositions for both 225 m (mid-altitude of the FWL system) and 550 m (conservative maximum altitude of the FWL system) from the Scholl et al. (1996 and 2002) and Fackrell and Glenn (2014) relations.

3. Results and discussion

3.1. Major ions and trace elements

Piper diagrams of major-ion results demonstrate that the major-ion composition of water samples from the sites form three main groups (Fig. 4). Samples from the ocean, KAHO ponds and...
pools, nearshore freshwater-lens (FWL) system wells, and inland FWL-system monitoring wells are all strongly sodium-chloride type waters, with >77% sodium and >88% chloride composition for all samples. The anionic composition of samples from the inland impounded-groundwater system with high water levels (HL system) is dominated by bicarbonate alkalinity, with 65–76% of anions from bicarbonate. Cation composition of the HL-system samples is still strongly influenced by sodium (53–59%), but indicates a greater contribution from both magnesium (18–30%) and calcium (17–26%) than most of the FWL-system samples. Major-ion composition of water from FWL-system production wells could be explained by mixing between HL-system groundwater and FWL-system coastal groundwater, as the composition generally falls along a mixing line between these two end members. This explanation, however, is not conclusive. Because both the HL and FWL systems are most likely in similar basalt material, the composition of the freshwater component of the inland FWL-system production-well samples may be very similar to HL-system groundwater, without necessarily being from the HL system. All fresh groundwater is from infiltrating precipitation through alkalic basalt at the ground surface, although saltwater in the FWL system and fresh groundwater in the HL system also may flow through tholeiitic basalt.

When plotted against chloride concentration, ion concentrations of bromide, calcium, magnesium, potassium, sodium, sulfate, and alkalinity all follow binary mixing lines between inland production well samples (either from the HL or FWL systems) with chloride concentrations less than 125 mg/L and ocean samples with chloride concentrations 11,100–20,500 mg/L (Fig. 5). As previously discussed, chloride concentration is an indicator of saltwater derived from the ocean. Thus, these major ions suggest a linear-mixing process between freshwater derived from precipitation and saltwater derived from the ocean. Lack of substantial deviation from the mixing line may indicate that little water–rock interaction is taking place along the flow path from higher to lower altitudes, or if water–rock interactions are affecting ion concentrations, the effect is small and masked by the effect of mixing with saltwater derived from the ocean. Fluoride concentrations are less than 0.7 mg/L in all samples, although slight increases in fluoride concentrations can be seen with increases in chloride concentrations. Fluoride and alkalinity concentrations in the HL system are more similar to other FWL concentrations than the other major ions, and the concentrations are more variable, possibly reflecting (1) the presence of a low-permeability barrier that separates the FWL and HL systems and restricts mixing between freshwater and saltwater in the HL system, (and) or (2) variable weathering rates, rock chemistry, or groundwater ages in the HL system. The bottom sample from the inland FWL-system Kamakana monitoring well (chloride concentration of 17,200 mg/L) has an ionic composition similar to the ocean samples (uppermost inland monitoring well symbol plotted in Fig. 5).

Sample concentrations of the trace elements boron, lithium, molybdenum, silica, strontium, uranium, and vanadium may be explained at least partly by the mixing of fresh groundwater and saltwater (Fig. 6). Arsenic and selenium have greater scatter in the data, but both appear to increase with increasing chloride concentration (Supplemental Fig. 2). Chromium and manganese, both relatively low in concentration in most samples, do not appear to be related only to mixing (Supplemental Fig. 2).

Results from major-ion and most trace-element analyses indicate that mixing of HL-system groundwater with saltwater derived from the ocean could produce the results seen in most FWL-system samples. An alternate explanation that cannot be ruled out by these data, however, is that water similar in ionic and trace-element composition to HL-system groundwater, but exclusively from local recharge, mixes with saltwater from the ocean to produce FWL-system groundwater compositions. The major-ion and trace-element data are not sufficient to conclude that HL-system groundwater discharges to the FWL system, although FWL-system sample results are consistent with this explanation.

3.2. Ocean-water fraction

Ion and trace-element sample concentrations indicate that, at most sites, sample water chemistry appears to be a function of the amount of saltwater derived from the ocean in the sample. Using chloride concentration as an indicator of ocean-water contribution to the sample, a simple chloride-mixing model (Clark and Fritz, 1997) was used to calculate the ocean-water fraction of water samples. For the fresh groundwater chloride concentration...
end member, data from the five production wells in the HL system of the Keauhou aquifer system (Fig. 1) were used (low = 4.8 mg/L, mean = 6.4 mg/L, high = 9.0 mg/L). The ocean-water chloride end member was defined from high-tide samples from the Kaloko Cut ocean location (Fig. 1; low = 19,600 mg/L; mean = 20,050 mg/L; high = 20,500 mg/L). Resulting ocean-water fraction for

Fig. 5. Relation of major-ion concentration to chloride concentration in water samples collected in and near KAHO. See Fig. 1 for sample locations.

SOURCE OF WATER SAMPLE

- Coastal unconfined groundwater (FWL)
- Pond and pool locations
- Inland impounded groundwater (HL)
- Monitor well
- Nearshore
- Inland
- Production well

end member, data from the five production wells in the HL system of the Keauhou aquifer system (Fig. 1) were used (low = 4.8 mg/L, mean = 6.4 mg/L, high = 9.0 mg/L). The ocean-water chloride end member was defined from high-tide samples from the Kaloko Cut ocean location (Fig. 1; low = 19,600 mg/L; mean = 20,050 mg/L; high = 20,500 mg/L). Resulting ocean-water fraction for
3.3. Rare-earth elements

Results from the 2013 sampling indicate most REE concentrations were below reporting limits or below the concentration measured in blank water. Only the lighter REEs of cerium, lanthanum, praseodymium, and yttrium were present in detectable concentrations in samples from nearshore FWL-system wells, inland FWL-system wells, and HL-system wells (Tillman et al., 2014). The relations of the detectable rare-earth elements to chloride concentration in 2013 groundwater and ocean samples are presented in Fig. 6. Chloride concentration was not available for the ocean sample that was analyzed for REEs, but strontium concentration was available. A chloride concentration from the same site, under the same sampling conditions earlier in the year, and with almost the same strontium concentration (7602 μg/L for the REE ocean sample; 7700 μg/L for the earlier sample) was used for the ocean REE sample. Similar patterns in sample concentrations of cerium (Ce), lanthanum (La), praseodymium (Pr), and yttrium (Y) are seen (Fig. 6), with lower concentrations in most groundwater samples nearly as high as or higher than ocean concentrations. REE concentrations in the single ocean sample (concentrations about 0.006 μg/L for Ce and La, 0.0014 μg/L or less for Pr, and 0.03 μg/L or less for Y) and higher concentrations in the single ocean sample (concentrations about 0.10 μg/L or more for Ce and La, 0.005 μg/L or more for Pr, and 0.15 μg/L or more for Y). Anomalies include both the top and bottom samples from the Kohanaiki monitoring well 401 well and the Kamakana well bottom sample, which have REE concentrations nearly as high as or higher than ocean concentrations. REE concentrations in Kohanaiki monitoring well 401 may be affected by groundwater recharge from nearby golf-course irrigation, which is pumped from the brackish FWL system. Focusing on the majority of groundwater samples with lower concentrations (enlarged areas on the right of Fig. 6), REE concentrations are low and vary somewhat in samples from HL-system wells, and generally increase with increasing chloride concentration (and thus saltwater composition). With the exceptions noted above, REE results for most samples are generally consistent with evidence of a linear mixing process seen in results from major ions and trace elements.

SOURCE OF WATER SAMPLE

- Ocean
- Pond or pool
- Inland impounded groundwater (HL)
- Production well
- Coastal unconfined groundwater (FWL)
- Nearshore
- Inland

Fig. 6. Relation of selected trace-element concentrations and rare-earth element concentrations to chloride concentration in water samples collected in and near KAHO. Only samples with concentrations greater than reporting limits are shown. See Fig. 1 for sample locations. Other trace-element results available in Supplemental Fig. 2.
3.4. Strontium isotopes

To evaluate the possible connection between the HL and FWL systems, strontium isotope mixing (Eq. (2)) was investigated. Average $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr values from Kaloko Cut high-tide ocean samples were used for the ocean-water end member (end member A in Eq. (2)). Two groundwater end members (end member B in Eq. (2)) were investigated to bound sample results: one, the average $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr values from the five HL-system production wells in the Keauhou aquifer system and the second, the $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr values from the N. Kona (Holualoa) production well in the FWL-system (strontium-isotope results were unavailable for the Kahalu’u C FWL production well). The $^{87}\text{Sr}/^{86}\text{Sr}$ end member of 0.70914 (standard deviation = 0.00013) from Kaloko Cut is similar to the reported modern ocean-water ratio of about 0.7092 (Faure, 1986; Woods et al., 2000; Jørgensen et al., 2008) and the HL-system groundwater end member of 0.70394 (standard deviation = 0.00013) is slightly higher than reported values of 0.70373 for Hualalai tholeiitic shield-stage basalt (Yamasaki et al., 2009) and 0.70358 for Hualalai postshield-stage basalt (Hanano et al., 2010). Fig. 7 demonstrates the necessity of including Sr concentration in the analysis of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio data. As an example, the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of HL-system production wells of about 0.7039 appears to indicate quite different water than what is sampled at the N. Kona (Holualoa) FWL-system production well, with an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70602. As Fig. 7 indicates, however, a mixture of less than 0.3% of ocean water with samples from HL-system production wells in the Keauhou aquifer system would result in the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as the N. Kona (Holualoa) sample, through addition of higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio water coupled with substantially higher Sr-concentration water. Water samples from wells in the HL system (Haleki’i and Ke’ei D) and the inland part of the FWL system (Ke’ei W-C) in the adjacent Kealakekua aquifer system have less Sr, but the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, as water from wells in the HL system and inland part of the FWL system (N. Kona [Holualoa]) in the Keauhou aquifer system, respectively (Fig. 7). Most samples of FWL-system groundwater and KAHO surface water fall near one of the two mixing lines (Fig. 7). An exception is the 2013 top sample from Kohanaiki monitoring well 401, which has a higher Sr concentration of 2060 μg/L than would be expected from an

Fig. 7. Relation between sample strontium-isotope ratio and 1/strontium concentration and mixing lines between HL-system groundwater/ocean water and FWL-system groundwater/ocean water. See Fig. 1 for sample locations.
3.5. Stable isotopes of water

Stable isotopes of water, $\delta^{18}O$ and $\delta^D$, from production wells in the HL system are depleted relative to most other samples from FWL-system groundwater with a few exceptions (Fig. 8). Two inland FWL-system wells, the Kalaoa N. Kona well (3% ocean-water fraction) and the Kahalu’u C production well (0.4% ocean-water fraction), and the nearshore FWL-system well Kohanaki 2 (24–30% ocean-water fraction) are as depleted as HL-system production wells Ke‘pi’ Mauka, Wai‘aha, and Keahuluana QLT1 (Fig. 8). Samples from the ocean, KAHO fishponds and anchialine pools, most nearshore FWL-system wells, and the bottom sample from the Kamakana inland FWL-system well depart from the Scholl et al. (2002) LMWL (Fig. 8), probably owing to mixing with ocean water and possible evaporation. Generally, more deviation from the Scholl et al. (2002) LMWL is seen in samples with a higher fraction of ocean water (Fig. 8).

3.5.1. Freshwater isotopic composition and aggregate recharge altitude

Determination of the isotopic composition of the freshwater component in a sample requires an estimate of the isotopic composition of the ocean-water component (Eq. (3)). The source of the ocean-water component in groundwater samples is controlled by the saltwater circulation system in the aquifer and mixing between terrestrial- and ocean-derived waters. Because of uncertainty in the source depth of ocean water in the groundwater samples, two end members for ocean-water isotopic composition were considered, each bounded by minimum and maximum values. Kaloko Cut high-tide ocean samples were used to represent a shallow ocean source end member (low, mean, high $\delta^{18}O = 0.34, 0.37, 0.41$; $\delta^D = 5.2, 5.25, 5.3$). Deep ocean-water samples (>650 m) collected by NELHA (Keith Olson, 2014, written commun.) off the coast north of KAHO were used to represent a deep ocean source end member (low, mean, high $\delta^{18}O = -0.13, -0.012, 0.08$; $\delta^D = -0.6, -0.06, 0.3$).

All samples with an ocean-water component were corrected towards depleted freshwater isotopic composition to some degree, with samples composed of a greater ocean-water fraction corrected the most (Fig. 9). Most of the freshwater components of the samples fall along one or more of the LMWLs used for this study, suggesting little enrichment of $\delta^{18}O$ in these samples from evapotranspiration effects on precipitation before it becomes aquifer recharge (Hsieh et al., 1998). Exceptions are noted in surface-water samples from ‘Aimakapā Fishpond and high-salinity groundwater samples from near the bottoms of the Kohanaki monitoring well 401 nearshore FWL-system well and the Kamakana inland FWL-system well (Fig. 9). The use of deep-ocean samples in place of near-shore samples for the ocean-water isotopic composition end member results in little change to corrected freshwater
compositions for most inland groundwater-well samples, with the exception of the bottom Kamakana well sample. The bottom Kamakana well sample has an ocean-water fraction of 86%, resulting in a large difference in corrected freshwater isotopic compositions and associated error bars (Fig. 9).

Groundwater integrates precipitation that falls at a range of altitudes. Regressions between land-surface altitude and volume-weighted average $\delta^{18}O$ of precipitation from Scholl et al. (1996, 2002), and Fackrell and Glenn (2014) provide insight into likely aggregate recharge altitudes of the freshwater isotopic compositions in the water samples. The aggregate recharge altitude for the freshwater isotopic composition of all coastal-groundwater and surface-water samples, with the exception of 'Aimakapā Fishpond and the bottom Kamakana well sample, is at least in the range of 700–1200 m (depending on which regression is used), and mainly greater than 1300 m (Fig. 9). These high aggregate recharge altitudes, well above the maximum land-surface altitude of 400–500 m of the FWL system, and a lack of substantial surface runoff from higher altitudes to lower altitudes, require a connection between HL and FWL systems in the area.

3.5.2. Ternary mixing model

A three-component (ternary) mixing model was developed to explain the isotopic composition of water samples collected in the KAHO study area in terms of ocean water, coastal precipitation, and HL-system groundwater components. A range of end members is presented and used to bound the contribution of each component to the isotopic composition of the water samples. Fig. 8 indicates that most water samples in and near KAHO are comprised of some combination of ocean water, coastal precipitation, and

![Diagram of Stable Isotopes of Water, $\delta^{18}O$ and $\delta^D$, from Surface-Water and Groundwater Samples in and near KAHO with at least 10% Freshwater, Adjusted for Ocean-Water Content. Range of Precipitation Altitudes for Equivalent $\delta^{18}O$ from Scholl et al. (1996 and 2002), and Fackrell and Glenn (2014) Provided for Comparison. Meteoric Water Lines are from Hawai‘i (Scholl et al., 1996 – Blue Line; Fackrell and Glenn, 2014 – Orange Line), Maui (Scholl et al., 2002 – Green Line); and the Global Meteoric Water Line (Craig, 1961 – Black Line). Error Bars Reflect the Combined Uncertainty Associated with End Members for Chloride Content and Stable Isotope Composition. (For Interpretation of the References to Color in This Figure Legend, the Reader is Referred to the Web Version of This Article.)

Fig. 9. Stable isotopes of water, $\delta^{18}O$ and $\delta^D$, from surface-water and groundwater samples in and near KAHO with at least 10% freshwater, adjusted for ocean-water content. Range of precipitation altitudes for equivalent $\delta^{18}O$ from Scholl et al. (1996 and 2002), and Fackrell and Glenn (2014) provided for comparison. Meteoric water lines are from Hawai‘i (Scholl et al., 1996 – blue line; Fackrell and Glenn, 2014 – orange line), Maui (Scholl et al., 2002 – green line); and the global meteoric water line (Craig, 1961 – black line). Error bars reflect the combined uncertainty associated with end members for chloride content and stable isotope composition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
HL-system groundwater end members. Water from the inland FWL-system wells Kalaoa N. Kona, Kahalu’u C, N. Kona (Houlaoloa), and Kaloko 2 appear to fall along a mixing line of HL-system groundwater and coastal precipitation, suggesting these samples are primarily a mixture of these two end members (Fig. 8). Water from most KAHO ponds and anchialine pools, and nearshore FWL-system wells appear to fall along a mixing line of one or more HL-system groundwater end members and an ocean-water end member. Although little evidence was seen of isotopic enrichment in sample freshwater components of Fig. 9, it is possible that water in KAHO fishponds, with δ18O values greater than −2.3, are actually mixtures of evaporation-enriched coastal precipitation and ocean water. Similarly, stable isotopes from KAHO anchialine pools might also be explained by a mixture of evaporation-enriched coastal precipitation from the most depleted coastal precipitation end member and ocean water. However, the isotopic composition of FWL-system samples from the nearshore KAHO Well 3, Kohanaki monitoring well 401 top, and Kohanaki 2 wells; the inland Kahalu’u C production well; and the inland Kalaoa N. Kona monitoring well are all depleted relative to even the most depleted coastal precipitation end member (Fig. 8). It is thus likely that these samples must contain a mixture that includes a more isotopically depleted source than coastal precipitation – further evidence of a connection between HL and FWL systems.

The ternary mixing model was used to quantitatively estimate the contribution of ocean water, coastal precipitation, and HL-system groundwater to FWL-system samples for anchialine-pool and groundwater sites in KAHO and for the inland FWL-system groundwater end members and an ocean-water end member. For the analysis. Within KAHO, most results indicate that samples for the coastal precipitation end member, 225-m (δ18O = −2.87 and δD = −9.49) and 550-m (δ18O = −3.38 and δD = −13.63) precipitation compositions were considered; and for the HL-system groundwater end member, the average composition from Kaloa EX A and Honokōhau samples was used (δ18O = −41.45 and δD = −6.71). Isotopic compositions for multiple samples from the same sites were averaged. High tide and low tide samples from anchialine pools, and top and bottom samples from both Kohanaki monitoring well 401 and Kamakana well, were averaged separately. A ternary mixing model (Eqs. (4)–(6)) was used to estimate the fraction contribution to samples from all combinations of the three end members, with the exception of samples from Kohanaki 2, Kamakana well – bottom sample, and Kaloko 2. The average isotopic composition of each of these three samples fell outside the triangle between possible end-member compositions. A binary mixing model between the two closest end members to the sample (Fig. 8) was used to estimate contributions to these samples. Modeling of δ18O and δD compositions was done separately for the binary cases, with an average result used for the fraction contribution.

The results of the mixing analysis (Fig. 10) indicate a wide range of possible end-member contributions to water samples in and near KAHO: 0–92% for ocean water; 0–90% for coastal precipitation; and 0–73% for HL-system groundwater. The wide range of values is attributed at least partly to the range of end-member values selected for the analysis. Within KAHO, most results indicate that samples from pools and wells contain about 5–50% ocean water; 5–80% coastal precipitation; and 20–50% HL-system groundwater. The freshwater component of the samples consists of contributions from coastal precipitation and HL-system groundwater. Within KAHO,
the freshwater component of water samples consists of 15–93% HL-system groundwater, with most values falling in the range of 25–70% (Fig. 10). For most samples, the ocean-water fraction estimated from stable isotopes was within 0.06 fractional units of the ocean-water fraction estimated from chloride concentrations, although in a few cases the two values differed by more than 0.1 units.

Results of the mixing analysis may be affected by a number of factors, including (1) possible isotopic enrichment of recharge in the coastal area caused by fractionation associated with evaporation of rainfall; (2) possible isotopic enrichment of anehialine-pool samples caused by evaporation; and (3) local irrigation. The end-member isotope values used for coastal precipitation may not account for possible enrichment of recharge associated with evaporation, and this would lead to underestimation of the contribution from the HL-system. Likewise, evaporation from anehialine pools would tend to move the isotopic signature of samples away from the HL-system end member, also leading to underestimation of the contribution from the HL-system. Irrigation, septic leachate, and pipeline leakage is estimated to contribute less than 17% of the recharge from sources overlying the FWL-system. The source of water for irrigation, septic leachate, and pipeline leakage may be the HL system. The golf course and landscaped areas in the Kohala development immediately north of KAHO receive irri-

gation water derived from the FWL-system. One of the wells used to provide irrigation water for this development is Kohala 2, and the freshwater component of the pumped water from Kohala 2 is estimated to be derived almost entirely from the HL system (Fig. 10). The water from Kohala 2 undergoes reverse-osmosis treatment, which reduces the salinity of the source water but does not cause fractionation of O, H, or Sr isotopes (Kloppmann et al., 2008). Subsurface injection of the reverse-osmosis waste may affect the major ion and trace-element chemistry of water samples from nearby wells as the waste gets entrained and mixed in the saltwater circulation system in the FWL-system. However, the fact that the freshwater component of water pumped by Kohala 2 is derived almost entirely from the HL-system would indicate that the HL and FWL systems are in hydrologic connection, in spite of some of the complicating factors related to irrigation and waste disposal.

4. Summary and conclusions

Major ions, selected trace elements, rare-earth elements, strontium-isotope ratio, and stable isotopes of water samples collected in and near Kaloko-Honokōhau National Historical Park in the western area of the Island of Hawai‘i were investigated for evidence of hydrologic connection between HL-system groundwater and FWL-system groundwater in the area. Understanding the presence or absence of a hydrologic connection is critical for developing an effective groundwater-management strategy for the area, which is experiencing a substantial increase in development of groundwater resources. Water samples were collected from sites within and near KAHO including two ocean sites, two fishponds, three anehialine pools, eleven wells in the FWL-system, and seven production wells in the HL-system. Samples from KAHO sites were collected under both high-tide and low-tide conditions, and samples from all sites were collected during both wet-season and dry-season time periods. Results of major-ion, trace-element, and rare-earth-element water chemistry for most FWL-system samples are consistent with mixing between ocean water and freshwater that is chemically similar to HL-system groundwater. It cannot be concluded from these data, however, that the source of freshwater in these FWL-system samples is from the HL-system and not from coastal groundwater recharge derived from local precipitation that results in freshwater similar to HL-system groundwater. Strontium-isotope analyses also reveal that some coastal groundwater sites are potentially a mix of HL-system groundwater and ocean water, but are also not conclu-
sive with respect to the source of freshwater. Taken separately, the different lines of geochemical evidence presented in this study, with the exception of the stable isotopes of water, are consistent with some degree of connection between the HL-system and the FWL-system, but are not sufficient to prove such a connection. Analyses of stable isotopes of water, however, strongly suggest high-altitude recharge is the source of at least part of the freshwater in many FWL-system groundwater samples, requiring a hydrologic connection between the HL and FWL-systems. While the exact nature of the connection between the HL and FWL systems is not known, interpretation of the stable-isotope data is consistent with the major-ion, trace-element, and rare-earth data and, taken together, supports the overall conclusion of a hydrologic connection between the two systems (i.e., Fig. 2b or c). The freshwater component of water samples from KAHO indicates that about 25–70% of the freshwater is derived from the HL-system. The results of this study have implications for the management of groundwater in the KAHO area. Evidence supporting the conclusion that the HL and FWL groundwater systems are connected might lead efforts to protect the FWL groundwater system from HL-system pumping effects.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2014.10.003.

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