Chlorofluorocarbon apparent ages of groundwaters from west Hawaii, USA

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SUMMARY

The volcanic coastal aquifers of west Hawaii supply drinking water to the area’s residents and nutrient-rich groundwater discharge to the nearby oligotrophic coastal waters. Despite the societal and ecological importance of the water in these aquifers, very little is known about the ages and recharge areas of the groundwater. We therefore determined aquifer recharge areas and groundwater residence times by sampling 18 locations for the oxygen and hydrogen isotopic composition of groundwater and chlorofluorocarbon (CFC) apparent groundwater ages. We sampled water supply wells, coastal wells, and coastal ponds. We applied a $\delta^{18}O$/altitude gradient and well-established lapse rates to find that groundwater recharge predominantly occurs in the area’s maximum rainfall zone. Furthermore, the isotopic data suggest that fog drip contributes to aquifer recharge. A single-water source model yielded recharge years ranging from the mid-1960s to mid-1980s for ten samples (56% of samples). Alternatively, a simple binary mixing model, with one water source recharging before 1940 and the other after 1940, indicated that 14 samples (78% of samples) contained young water that recharged the aquifer between the mid-1970s and mid-1980s. We also find that CFCs can be used to distinguish between water originating from different aquifers in the area.

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1. Introduction

Large volcanic islands located in humid tropical regions have unique characteristics that promote groundwater recharge and flow. These islands typically have high elevations and receive large volumes of rainfall annually. Their basaltic aquifer materials are often fractured, contributing to high permeability. Furthermore, younger islands typically exhibit immature landscapes with poorly developed drainage systems, making infiltration rates extremely high. Combined, these factors make the potential for high volumes of groundwater flow possible and likely. People living in such settings therefore depend either on rain catchment systems or groundwater for their water supply. Hawaii island is one location where these characteristics are exemplified, making groundwater one of Hawaii’s most important natural resources (Oki et al., 1999a).

Despite the prolific groundwater resources on the island of Hawaii, little is known about aquifer geometries, aquifer recharge areas, groundwater residence times, and groundwater flow paths in the region. This study is therefore primarily aimed at answering two hydrologic questions: (1) Where are the recharge areas for west Hawaii fractured basal aquifers? and (2) What are the residence times for water in these aquifers? To address these questions, we present an integrated approach that uses oxygen and hydrogen isotopes of water, $\delta^{18}O$/altitude gradients, and lapse rates to determine that groundwater mainly recharges from a zone of maximum precipitation on west Hawaii. We demonstrate below how apparent groundwater ages from CFCs can be established for the area’s fairly pristine aquifers and that these groundwaters are relatively young. We further show that CFCs can distinguish groundwater in the basal aquifer from groundwater in high-level aquifers, which may help constrain the extent of high-level aquifers.

Oxygen and hydrogen isotopes are proven tracers for establishing recharge areas in locations with rapid elevation changes like the Hawaiian Islands. The progressive removal of heavier water isotopes in orographic precipitation is known as the altitude effect. This effect causes the stable oxygen and hydrogen isotopic compositions of precipitation to become relatively depleted in $^{18}O$ and $^2H$ with increasing elevations in a predictable and measurable manner (Ingraham, 1998). Recharge altitudes and approximate recharge...
areas of groundwater samples can therefore be established from $\delta^{18}$O/altitude gradients in such settings (Scholl et al., 1996).

Anthropogenic activities related to industrial, commercial, and household applications prompted manufacture and release of CFCs into the atmosphere beginning in the 1930s (CFC-11 and CFC-12) and 1940s (CFC-113; Plummer and Busenberg, 2000, 2006a; Happell et al., 2006). CFCs were banned in the United States in 1995 (Cook et al., 2003) to curtail their deleterious effects on Earth’s ozone layer. CFCs are generally stable under oxic conditions and are water soluble, so they have been imbibed into Earth’s hydrologic cycle through precipitation, infiltration, and groundwater recharge. CFC incorporation into the hydrologic cycle has closely followed CFC production and release, making CFCs excellent tracers and age determination tools for water younger than ~60 years (Plummer and Busenberg, 2000). CFC data have provided important information about residence times and groundwater flow paths at numerous research sites (e.g. Happell et al., 2006; Plummer et al., 2000; Darling et al., 2010) and have been used more recently by Koh et al. (2012) and Ako et al. (2013) in volcanic settings.

The data in this study will provide an important base-line from which to evaluate how changing climatological patterns, land-use practices, urbanization, and groundwater withdrawal rates impact the quantity and quality of west Hawaii groundwater. Our study also enhances the current understanding of fractured basalt rock aquifers, particularly in coastal settings.

2. Materials and methods

2.1. Subsurface geology and groundwater occurrence of West Hawaii

Hawaii Island is composed of numerous lava flows with variable thicknesses and compositions. Permeability is heterogeneous, but high overall (Stearns and MacDonald, 1946). Aa lava clinker zones, voids between lava flow contacts, cooling joints normal to flow surfaces, and lava tube contribute to the aquifer’s high permeability (Stearns and MacDonald, 1946). Fractures in the rocks and the aforementioned characteristics facilitate rapid groundwater transport through the area’s unsaturated zones and aquifers (Oki et al., 1999b).

All Hawaiian volcanoes contain low permeability and low hydraulic conductivity dike complexes, which are typically associated with rift zones (Takasaki and Mink, 1985). The northwest rift zone of Hualalai Volcano bisects the study area (Fig. 1). The rift zone consists of a 1.9–4.0 km wide and 21.1 km long subaerial portion as well as a submarine portion (not shown; Oki, 1999; Finders et al., 2013). Oki (1999) considered the rift zone a groundwater divide and no-flow boundary. We also adopt this interpretation. Dikes are thought to be most abundant within central rift zones (Takasaki and Mink, 1985). The northwest rift zone of Hualalai Volcano bisects the study area (Fig. 1). The rift zone consists of a 1.9–4.0 km wide and 21.1 km long subaerial portion as well as a submarine portion (not shown; Oki, 1999; Finders et al., 2013). Oki (1999) considered the rift zone a groundwater divide and no-flow boundary. We also adopt this interpretation. Dikes are thought to be most abundant within central rift zones (Takasaki and Mink, 1985). The northwest rift zone of Hualalai Volcano bisects the study area (Fig. 1). The rift zone consists of a 1.9–4.0 km wide and 21.1 km long subaerial portion as well as a submarine portion (not shown; Oki, 1999; Finders et al., 2013). Oki (1999) considered the rift zone a groundwater divide and no-flow boundary. We also adopt this interpretation. Dikes are thought to be most abundant within central rift zones (Takasaki and Mink, 1985). The northwest rift zone of Hualalai Volcano bisects the study area (Fig. 1). The rift zone consists of a 1.9–4.0 km wide and 21.1 km long subaerial portion as well as a submarine portion (not shown; Oki, 1999; Finders et al., 2013). Oki (1999) considered the rift zone a groundwater divide and no-flow boundary. We also adopt this interpretation. Dikes are thought to be most abundant within central rift zones (Takasaki and Mink, 1985). The northwest rift zone of Hualalai Volcano bisects the study area (Fig. 1). The rift zone consists of a 1.9–4.0 km wide and 21.1 km long subaerial portion as well as a submarine portion (not shown; Oki, 1999; Finders et al., 2013). Oki (1999) considered the rift zone a groundwater divide and no-flow boundary. We also adopt this interpretation. Dikes are thought to be most abundant within central rift zones (Takasaki and Mink, 1985). The northwest rift zone of Hualalai Volcano bisects the study area (Fig. 1). The rift zone consists of a 1.9–4.0 km wide and 21.1 km long subaerial portion as well as a submarine portion (not shown; Oki, 1999; Finders et al., 2013). Oki (1999) considered the rift zone a groundwater divide and no-flow boundary. We also adopt this interpretation. Dikes are thought to be most abundant within central rift zones (Takasaki and Mink, 1985). The northwest rift zone of Hualalai Volcano bisects the study area (Fig. 1). The rift zone consists of a 1.9–4.0 km wide and 21.1 km long subaerial portion as well as a submarine portion (not shown; Oki, 1999; Finders et al., 2013). Oki (1999) considered the rift zone a groundwater divide and no-flow boundary. We also adopt this interpretation. Dikes are thought to be most abundant within central rift zones (Takasaki and Mink, 1985). The northwest rift zone of Hualalai Volcano bisects the study area (Fig. 1). The rift zone consists of a 1.9–4.0 km wide and 21.1 km long subaerial portion as well as a submarine portion (not shown; Oki, 1999; Finders et al., 2013). Oki (1999) considered the rift zone a groundwater divide and no-flow boundary. We also adopt this interpretation. Dikes are thought to be most abundant within central rift zones (Takasaki and Mink, 1985).

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2.2. Climate of West Hawaii

Coastal areas of west Hawaii experience little variation in seasonal air temperature (mean annual temperature = 23.7°C). Near the coast, high temperatures vary between 26 and 29°C and low temperatures approach 21°C and 18°C (Nullet and Sanderson, 1993). The tallest topographic feature in the immediate area is Hualalai Volcano (2521 m). Hualalai’s summit has a mean annual air temperature of 10.6°C. In west Hawaii, east-flowing sea breezes converge daily with approximately west-flowing northeast trade winds. The trade winds pass between Mauna Kea and Mauna Loa (Fig. 1 inset), or the freshwater, forming a transitional area within the aquifer that is composed of brackish water. Regardless of composition, water in this aquifer is locally called basin water (Fig. 2). This aquifer generally has water levels <3 m above MSL (Oki et al., 1999b). At the shoreline, this water leaves the aquifer as fresh to saline groundwater discharge depending on the discharge location.
blow over Mauna Loa’s upper slopes, resulting in afternoon rainfall over the ocean that drifts toward the shore at night (Schroeder, 1993).

A fog belt (Fig. 1) typically exists between 975 and 2255 m (County of Hawaii, 2003), but never extends lower than 760 m (Juvik and Ekern, 1978). The fog belt forms when trade winds ascend Hualalai Volcano, causing mountain-hugging clouds (Giambelluca and Sanderson, 1993). The maximum elevation of the fog belt is often limited by the base of a trade wind inversion layer (Giambelluca and Schroeder, 1998). This layer prevents formation of large raindrops, resulting in high ratios of fog to rain (0.31–0.69), especially near the base of the inversion layer (Juvik and Ekern, 1978; Engott, 2011). Some fog contributes to aquifer recharge (Giambelluca and Sanderson, 1993; Engott, 2011).

2.3. Sample collection

We collected water samples between 28 July and 2 August 2008 from 18 locations (Table 1) along west Hawaii. We sampled water from nine Hawaii Department of Water Supply drinking water wells (supply wells), five brackish coastal ponds and wells, three coastal monitoring wells, and water flowing through a lava tube submerged at the bottom of Kailua Bay (Fig. 1). All wells were purged before sample collection. We collected samples using existing pumps installed in three basal and six high-level supply wells. Basal wells extended no greater than 15 m below MSL. Open intervals in the wells ranged from 2 to 137 m in thickness. The three monitoring wells reached no greater than 5 m below MSL and were sampled using a portable stainless-steel Fultz Pump equipped with polyethylene tubing. Coastal well and pond samples were obtained using a peristaltic pump (Geopump by Geotech, Denver, CO) equipped with Viton tubing (Barnant MasterFlex, Thermo Scientific). These samples were acquired by placing the end of the tubing as close as possible to spring vents or the bottom of the well or pond. Temperature and salinity measurements were taken at the time of sample collection using a multiparameter meter (YSI Inc. model 63, Yellow Springs, OH) accurate to within ±1% for both temperature and salinity. Geographic position was determined using a hand-held GPS receiver (Garmin eTrex, Olathe, KS) with better than 15 m accuracy.

2.4. Oxygen and hydrogen isotopic analysis of water

Samples for oxygen and hydrogen isotopic analysis of water were collected in 20 mL glass vials (MicroLiter Analytical Supplies, Inc. #20-2300). Vials were filled from the bottom up and sealed underwater with a rubber septum (MicroLiter Analytical Supplies, Inc. #20-0025) and aluminum crimp-top seal (MicroLiter Analytical Supplies, Inc. #20-0000A). At least three volumes of water flowed through each vial prior to sealing. Samples were analyzed at the University of Utah Stable Isotope Ratio Facility for Environmental Research (SIRFER). All oxygen and hydrogen isotope data are expressed in ‰ notation relative to Vienna Standard Mean Ocean Water (VSMOW) on a normalized scale in which δ¹⁸O of standard light Arctic precipitation (SLAP) water is −428‰ and δ¹⁸O of SLAP water is −55.5‰.

2.5. Establishing recharge elevation

Recharge elevations were calculated using two different methods. The first method involved matching the δ¹⁸O value of each water sample to the δ¹⁸O value of precipitation from the East Maui rain-shadow δ¹⁸O/altitude gradient from Scholl et al. (2002):

\[ \delta^{18}O = -0.00123m - 4.42 \]  \hspace{1cm} (1)

where \( \delta^{18}O \) is the ratio of \(^{18}O/^{16}O \) of water and \( m \) is the calculated recharge elevation. The second method assumed that the \( \delta^{18}O \) value...
of each water sample was integrated to reflect recharge to some distance upslope of the sample location. For this calculation we used the following equation from Scholl et al. (1996):

$$\delta^{18}O_{\text{sample}} = \frac{\sum_{n=1}^{n} (\delta^{18}O/n)(R/n)}{\sum_{n=1}^{n} R/n}$$  \hspace{1cm} (2)

where $\delta^{18}O$ is the isotopic value of precipitation for elevation interval $n$ (obtained from Eq. (1)) and $R/n$ is the estimated recharge volume for elevation interval $n$. We used 50 m elevation intervals and derived recharge volumes from Engott (2011).

We used salinity to correct the $\delta^{18}O$ value of brackish samples for seawater content by mass balance. For this correction, we assumed brackish coastal wells and ponds were a mixture of fresh meteoric water (salinity = 0) and seawater (salinity = 35 and $\delta^{18}O = +0.2\%$ relative to SMOW; Epstein and Mayeda, 1953).

2.6. Establishing recharge temperature

We used the recharge altitude calculated from Eq. (1) to derive a recharge temperature based on well-established lapse rates for the Hawaiian Islands (Nullet and Sanderson, 1993). Below an elevation of 1100 m, we used a lapse rate of:

$$7.3 \degree C/1000 \text{m}$$  \hspace{1cm} (3)

while above an elevation of 1100 m, we used a lapse rate of:

$$4.1 \degree C/1000 \text{m}$$  \hspace{1cm} (4)

We assumed 0 m elevation corresponded to 23.7 $\degree C$ (mean annual air temperature of coastal west Hawaii).

2.7. Chlorofluorocarbon analysis of water

Samples for CFC analysis were collected in 125 ml boston round glass bottles (Wheaton #217112) in triplicate. Bottles were filled from the bottom up, and at least three volumes of water overflowed each bottle before it was sealed under water using an aluminum foil–lined screw cap (Scientific Specialties #A69522). Caps were then double sealed using electrical tape and bottles were stored upside-down until analysis. Samples were analyzed at the University of Miami Rosenstiel School of Marine and Atmospheric Science (RSMAS) using purge-and-trap gas chromatography with electron capture detection (Bullister and Weiss, 1983; Happell et al., 1996) approximately one month after sample collection. CFC concentrations are reported on the Scripps Institution of Oceanography 1998 (SIO 1998) absolute calibration scale (Pinn et al., 2000). The detection limit for CFC-12 and CFC-113 was 0.010 pmol/kg and the limit for CFC-11 was 0.005 pmol/kg. Reported precision for all three CFCs was 2% or less. However, a recent inter-laboratory comparison experiment by Labasque et al. (2014) has shown that analytical and standardization procedures can impact the reported precision of CFC analyses.

All CFC ages are apparent ages, but we use the term age for brevity, where age indicates the time elapsed since isolation of recharged water from the atmosphere. Results are also expressed

### Table 1

<table>
<thead>
<tr>
<th>Name</th>
<th>Latitude (N)</th>
<th>Longitude (W)</th>
<th>Date Sampled</th>
<th>Sam. Temp. (°C)</th>
<th>Sam. Elev. (m)</th>
<th>Sal. (‰)</th>
<th>Recharge Temp. (°C)</th>
<th>Recharge Elev. (m)</th>
<th>Integrated Recharge Elev. (m)</th>
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</thead>
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<td>Hind Well</td>
<td>19°51’14.5”</td>
<td>155°55’23.2”</td>
<td>7/28/2008</td>
<td>22.0</td>
<td>3</td>
<td>1.9</td>
<td>11.2</td>
<td>2382</td>
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<td>155°55’38.3”</td>
<td>7/29/2008</td>
<td>24.7</td>
<td>3</td>
<td>1.9</td>
<td>11.6</td>
<td>2285</td>
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<tr>
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<td>7/29/2008</td>
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<td>548</td>
<td>0.1</td>
<td>14.3</td>
<td>1610</td>
<td>3900</td>
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<tr>
<td>Hololaila4</td>
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<td>21.7</td>
<td>342</td>
<td>0.3</td>
<td>23.7(17.3)</td>
<td>-195/975</td>
<td>900</td>
<td></td>
</tr>
<tr>
<td>Hualalai4</td>
<td>4258-03</td>
<td>7/29/2008</td>
<td>21.7</td>
<td>513</td>
<td>0.1</td>
<td>11.7</td>
<td>2252</td>
<td>N/A</td>
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<tr>
<td>KAHO 1*</td>
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<td>8/01/2008</td>
<td>20.0</td>
<td>7</td>
<td>5.2</td>
<td>22.6(17.3)</td>
<td>163/975</td>
<td>300–1200</td>
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<tr>
<td>KAHO 2*</td>
<td>4161-02</td>
<td>8/01/2008</td>
<td>22.9</td>
<td>17</td>
<td>4.7</td>
<td>23.7(17.3)</td>
<td>-276/975</td>
<td>900</td>
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<tr>
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<td>10.2</td>
<td>23.1(17.3)</td>
<td>98/975</td>
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<td>155°59’42.7”</td>
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<td>762</td>
<td>0.2</td>
<td>19.0(17.3)</td>
<td>715/975</td>
<td>1800–1950</td>
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<td>155°57’43.2”</td>
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<td>2</td>
<td>5.5</td>
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<td>7/30/2008</td>
<td>22.4</td>
<td>8</td>
<td>7.3</td>
<td>23.7(17.3)</td>
<td>-813/975</td>
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</tbody>
</table>
as recharge years. The recharge year refers to the year when the water was isolated from the atmosphere and reached the aquifer.

2.8. Establishing chlorofluorocarbon apparent ages

Individual concentrations of CFC-11, CFC-12, and CFC-113 were used to derive groundwater ages using well-established formulas and standard techniques described by Plummer et al. (2006c). Briefly, we calculated the concentration of a particular CFC, \( C_i \), dissolved in water and in equilibrium with air. This concentration is proportional to the partial pressure, \( p_i \), of the gas in the air:

\[
C_i = K_i p_i 
\]

where \( K_i \) is the Henry's Law constant for \( C_i \), \( K_i \) is dependent on the temperature of the recharging water, which we calculated using Eqs. (3) and (4). We corrected all brackish samples for the salinity dependence of \( K_i \). The \( p_i \) for \( C_i \) is defined by:

\[
p_i = x_i(P - p_{\text{H}_2\text{O}}) 
\]

where \( x_i \) is the dry air mole fraction of \( C_i \) (\( x_i \leq 1 \)), the total atmospheric pressure is \( P \), and the water vapor pressure is \( p_{\text{H}_2\text{O}} \) (Warner and Weiss, 1985; Plummer et al., 2006a). \( P \) is dependent on recharge altitude, which we calculated using Eq. (1). We then replaced the dry air mole fraction with a dry air mixing ratio, volume per volume. The dry air mixing ratio of a particular CFC was compared to the appropriate historical atmospheric mixing ratio to determine a recharge year.

CFC ages were also determined from measured concentrations of two CFCs by well-established time-dependent atmospheric CFC concentration ratios (Plummer et al., 2006b). Briefly, if a fraction \( x \) of CFC-free water mixed with a fraction \( (1-x) \) of water that contained CFCs, then the concentrations of the CFCs, for example CFC-113 and CFC-12, are established by simple mass balance rules using:

\[
[C\text{FC-113}]_{\text{mixture}} = (1-x)[C\text{FC-113}]_y 
\]

and

\[
[C\text{FC-12}]_{\text{mixture}} = (1-x)[C\text{FC-12}]_y 
\]

where \([C\text{FC-113}]_{\text{mixture}}\) and \([C\text{FC-12}]_{\text{mixture}}\) are CFC concentrations in the water, and \([C\text{FC-113}]_y\) and \([C\text{FC-12}]_y\) are concentrations of the fraction of water containing CFCs. The apparent age of the younger water with CFCs is described by:

\[
[C\text{FC-113}]_{\text{mixture}}/[C\text{FC-12}]_{\text{mixture}} = [C\text{FC-113}]_y/[C\text{FC-12}]_y 
\]

Once this calculation is complete, a mixing ratio is calculated by:

\[
[C\text{FC-113}]_{\text{mixture}}/[C\text{FC-113}]_y = [C\text{FC-12}]_{\text{mixture}}/[C\text{FC-12}]_y 
\]

A similar process can be followed for CFC-113/11 and CFC-11/12 ratios.

3. Results and discussion

3.1. Oxygen and hydrogen isotopes and recharge elevation determination

Correct use of \( \delta^{18}O/\delta^{2}H \) vs. altitude gradients requires a calibrated local meteoric water line (LMWL). Unfortunately, a LMWL is not established for west Hawaii. Trade wind microclimates in the Hawaiian Islands, however, exert strong influences on \( \delta^{18}O/\delta^{2}H \) vs. altitude gradients (Scholl et al., 2002). Microclimates follow predictable and similar patterns within and between the islands (Scholl et al., 2002). Additionally, the rate of change in temperature with elevation from similar facing slopes of west Hawaii and west Maui should be comparable. These relationships are exemplified in Fig. 3, which shows our samples plotting on or slightly below the LMWL established by Scholl et al. (2002) for the East Maui rain-shadow microclimate. The slight enrichment in \( \delta^{18}O \) relative to the LMWL was 0.10 ± 0.11‰ (\( n = 11 \)) for the supply wells. Evaporation trends were not apparent in salinity-corrected data (Table A.1). Salinity-corrected data are similar to other Hawaiian Island studies (Scholl et al., 1996, 2002). Non-salinity corrected data are also provided (Table A.1).

We used salinity-corrected \( \delta^{18}O \) values (Table A.1) and Eq. (1) to calculate approximate recharge elevations for the samples (Table 1). This slight \( \delta^{18}O \) enrichment in our samples relative to the East Maui LMWL yielded an uncertainty of up to ±89 m (\( n = 11 \)) on the recharge elevations of the samples. We then determined approximate recharge zones (Fig. 4) by drawing straight line trajectories from each sample location normal to elevation contours (not shown). The topography upslope of the Hualalai well sample mandated a kink in the trajectory on the steepest part of Hualalai Volcano. This slope-normal method yielded recharge zones that agreed with rift zone no-flow boundaries. Furthermore, the trajectories demonstrate that most samples recharged within the maximum rainfall zone (Fig. 4), an area that receives ~2000 mm of rain annually.

Fog drips are a large component of recharge water in Hawaiian mountains (Juvin and Ekern, 1978; Scholl et al., 2002). For Hualalai Volcano, Engott (2011) estimates that the ratio of fog interception to rainfall is 0.3 above 1500 m and 0.5 above 2100 m. Fog is isotopically enriched compared to precipitation (Scholl et al., 2002). When using Eq. (1) to calculate recharge elevations, fog drip will therefore cause recharge elevations to be biased low. In some instances, this bias causes recharge elevations to plot geographically downslope from the sample locations. Approximate recharge elevations for Holualoa, KAHO 2, Kailua Lava Tube, and PUHO (Table 1), were impossibly low, plotting below sea level. Furthermore, the calculated recharge elevation of Kahaluu A was lower than the actual collection elevation (Table 1), but within the uncertainty of our elevation calculation. These results suggest...
that fog drip contributed to aquifer recharge and is isotopically detectable in these samples. Integrated recharge elevations from Eq. (2) (black dashed lines in Fig. 4) typically exceeded elevations where the oxygen isotopic value of the groundwater matched that of precipitation (Eq. (1)) by 400–800 m (Table 1). Some samples near the central part of the study area (Keahualoa QLT-1, Kahaluu Shaft, Kahaluu A, Keauhou Pond, and Halekii) had integrated recharge elevations that exceeded non-integrated elevations by 900–1500 m. These samples had integrated trajectories that extended to the lower flanks of Mauna Loa. For brevity, we will concentrate the following discussion on the non-integrated elevation results.

Water from the two southern-most basal wells and the three southern-most high-level wells recharged 1.4–4.7 km upslope of their geographic locations (Fig. 4). The three northern-most high-level wells recharged along the flanks of Hualalai Volcano, 5.3–9.4 km upslope of the collection locations. Water from the three southern-most coastal wells and ponds recharged within the main precipitation zone, 1.0–8.1 km upslope of their sampling locations. Recharge zones for the KAHO samples were within the fog belt, varying from 8.7 to 9.0 km upslope of the well sites. Water from coastal samples north of the rift zone could have recharged from the upper-most flanks of Hualalai Volcano (17.6–18.7 km upslope). The recharge trajectories of these samples fully intersected the fog belt, however; isotopic data did not indicate a fog drip component. Because fog drip biases recharge elevations low, and the recharge trajectories for these samples indicate recharge from near the summit of Hualalai Volcano, an alternative recharge zone for these samples could be the lower slopes of Mauna Kea or Mauna Loa. The data from the Hualalai and Honokohau Wells also showed no fog drip. However, their recharge trajectories traversed the fog belt. Calculated recharge elevations for these samples may also be biased low.

All KAHO samples recharged from elevations above the four high-level wells on Hualalai Volcano. Although the high-level aquifer boundaries have not been precisely located, the recharge areas of these samples suggests that their water traversed the high-level/basal aquifer boundary. A similar relationship also exists for all other coastal well and pond samples south of the rift zone, except for the sample from Keauhou Pond. These spatial relationships provide evidence that high-level water recharges the basal lens throughout the field area.

### 3.2. Recharge temperature determination

Recharging water is colder at higher elevations because atmospheric temperatures are lower (Mink, 1964). Once recharged, friction causes groundwater to warm as it flows downhill (Mink, 1964). Ten of our calculated recharge temperatures were colder than temperatures measured during sample collection (Table 1), conforming to the expected relationship. However, calculated recharge temperatures were warmer than measured temperatures for KAHO 1, KAHO 3, Cameron’s Well, and Keeei D (Table 1). This reverse relationship also held true for the four samples with impossibly low recharge elevations. Six of these eight samples were brackish. We hypothesize that these samples were cooled, at least in part, by relatively cold seawater circulating through the coastal aquifer (Fig. 2). Two freshwater samples also had temperature disparities. These samples from high-level wells were not influenced by recirculating seawater. We therefore hypothesize that our recharge elevations were either underestimated, or that these samples contained fog drip. To test the underestimated recharge elevation hypothesis, we recalculated recharge elevations using the unusually cold sample temperatures recorded during collection to determine the maximum recharge elevation based on those temperatures. This calculation resulted in elevations of 401 ± 180 m (n = 7) upslope of the sample locations. We omitted the Holualoa sample because its temperature indicated recharge downslope of the sample location. We have no explanation for this relationship. Nevertheless, 401 m exceeds the 89 m uncertainty from the δ18O data and at least partially discounts the elevation hypothesis. A likely explanation is the fog-drip contribution hypothesis given the prevalence of fog around Hualalai Volcano. We therefore assigned the lower elevation of the main fog belt (975 m; Fig. 1) as the recharge elevation with a corresponding temperature of 17.3 °C for these eight samples (Table 1). This elevation also corresponds to the maximum precipitation zone (Fig. 4).
3.3. Chlorofluorocarbons and the unsaturated zone

Proper use of CFCs for apparent age dating requires that CFC concentrations of recharging water (at the top of the water table) be in equilibrium with atmospheric concentrations when recharge occurs (Busenberg and Plummer, 1992; Plummer and Busenberg, 2000; Plummer et al., 2000; Katz et al., 2001). To achieve equilibrium, there must be fast gas exchange between air in the troposphere and the unsaturated zone. If fast exchange does not occur, groundwater ages will indicate equilibrium with old air (Plummer et al., 2006a), but not actual recharge years. Several circumstances likely facilitate fast gas exchange through the unsaturated zone in west Hawaii: (1) lava flows with high permeability, (2) complex networks of fractures and lava tubes, (3) high recharge rates, (4) barometric pumping of air, and (5) thermally induced topographic wind that drives gas transport through the unsaturated zone (Nilson et al., 1991).

3.4. The piston flow model for chlorofluorocarbons

A piston flow model is commonly used to determine groundwater ages from CFC data (e.g. Katz et al., 2001; Happell et al., 2006; Plummer and Busenberg, 2006b). We used measured concentrations of the three CFCs in water (Table A.2) to calculate equivalent atmospheric concentrations (Table A.2), which were used in the piston flow model (Table A.3). Age agreement of all three CFC compounds suggests that a sample can be modeled as one water source of uniform age. We found age agreement for Halekii and Keei D, which recharged between 1963 and 1969 and between 1971 and 1977, respectively (Fig. 5). Results from the other samples were less straightforward. For example, CFC-11 indicated more recent recharge than CFC-113 for Holualoa, Honokohau, and possibly Kalaoa A (Fig. 5). This pattern suggests contamination of the samples by CFC-11 (Plummer et al., 2006a). Furthermore, pesticides have been shown to be a source of CFC-11 contamination (Plummer et al., 2000). Farming of agricultural fields, which are common on the flanks of Hualalai Volcano, may have inadvertently caused CFC-11 contamination of the groundwater through pesticide application. If we omit the CFC-11 data for these samples, the piston flow model gave recharge years between 1961 and 1968 for Holualoa and 1953–1958 for Honokohau (Fig. 5). The age agreement for Kalaoa A was too poor for a piston flow model interpretation. Interestingly, the model can explain the age relationships for four of the six high-level wells and none of the basal wells. The relatively tight age agreement for the three CFC species in these wells (Fig. 5) suggests that the high-level water may be biased toward permeable layers of the aquifer. The complex and imprecisely known geometry of aquifer systems in the area (Oki, 1999; Tillman et al., 2014a) makes it unsurprising that the piston flow model worked for fewer than half of the water supply samples. Furthermore, these wells had large open intervals (2–137 m), which increased the likelihood of sampling numerous packets of water with varying ages.

Water in coastal wells and ponds recharged the aquifer between the 1970s and 1980s (Fig. 5). Apparent ages for KAHO 2, KAHO 3, and Keauhou Pond agreed extremely well (late 1980s for all). All KAHO samples were collected using polyethylene tubing, which has been shown to contaminate water samples with low amounts of CFC-11 and CFC-113 and trace amounts of CFC-12 (Cook et al., 2006). This tubing may have contributed noticeable amounts of CFC-11 contamination to all three samples, or the contamination may have been from another source. However, the CFC-11 and CFC-12 ages were indistinguishable for KAHO 2 and KAHO 3, indicating that CFC-11 contamination was not detectable within the precision of the analysis or was the same for both samples (Fig. 5). Of the CFC’s measured, CFC-11 is the most susceptible to microbial degradation (Burton et al., 2002). The more recent CFC-11 recharge years for Cameron’s Well and the PUHO sample suggests that these samples may have experienced CFC-11 degradation. If true, unmodified CFCs yielded recharge years that ranged from 1986 to 1988. The piston flow model was also suitable for Kailua Lava Tube if the sample was contaminated with CFC-11. If true, water from this sample recharged the aquifer between 1975 and 1979.

We evaluated the validity of piston flow model results by estimating horizontal hydraulic conductivities for the four high-level wells. We first calculated water velocity by using the average recharge year and straight-line travel distance from the recharge zone to the well head. We then multiplied water velocity by porosity and divided by hydraulic gradient to calculate horizontal conductivity according to Darcy’s law. Porosity values for Hawaiian lavas span a wide range (<0.05–0.5; Peterson and Seghal, 1974; Lau and Mink, 2006). We followed Whittier et al. (2010) and used a conservative porosity value of 0.05 in our calculations. This simplified calculation assumed uniform regional flow and no tortuosity in the flow path. We found hydraulic conductivities of 0.08 m/d for Holualoa (calculated from straight trajectory), 0.14 m/d for Honokohau, 0.07 m/d for Halekii, and 0.02 m/d for Keei D. Meyer and Souza (1995) used a numerical model to calculate horizontal hydraulic conductivities ranging from 0.003 to 0.03 m/d for dike complexes. Marginal dike zones are transitional areas between dike complexes and dike-free areas. Marginal dike zones ranged from 0.15 to 3.05 m/d (Oki, 1999). Lava flows in dike-free areas, away from rift zones, have the greatest horizontal hydraulic conductivities (152–10,330 m/d) as determined by groundwater level variations caused by ocean tides (Kanehiro and Peterson, 1977; Nance, 1991; Oki et al., 1999b). Our estimates ranged between dike complex to marginal-dike zone areas, a reasonable result given the exact locations of dike zones are unknown.

We used the same technique to estimate maximum horizontal hydraulic conductivities for the coastal well and pond samples. We found 0.48 and 0.50 m/d for KAHO 2 and KAHO 3, respectively, 0.03 m/d for Keauhou Pond, 0.29 m/d for Kailua Lava Tube, 0.28 m/d for Cameron’s Well, and 0.33 m/d for PUHO. Except for Keauhou Pond, maximum horizontal hydraulic conductivities exceeded estimates for the supply wells. These results suggest water reaching coastal wells and ponds flows through more permeable aquifers compared to supply wells.

Our samples mainly recharged from high elevations. Large over- or under-estimations (±1000 m) in recharge elevation bias the groundwater age toward older values if elevation is underestimated or younger values if elevation is overestimated. We conducted a sensitivity analysis by varying the temperature and elevation estimate ranges from 11.7 °C at 2255 m (top of fog belt) to the elevation and corresponding temperature at each sample’s geographic location (Table 1). Calculated recharge ages were accurate to within ten years.

3.5. The binary mixing model for chlorofluorocarbons

The binary mixing model has a mixture of two end-member waters, where one end-member recently recharged and the other end-member recharged in the past (Happell et al., 2006). Theoretically, the end-members can be any age (Happell et al., 2006). We assumed one end-member recharged before 1940 (free of CFCs), and the other recharged after 1940 (contains CFCs). For this model, we used ratios of CFC concentrations (CFC 113/12, CFC 113/11, and CFC 11/12) to calculate groundwater ages (Eqs. 7–10). Binary mixing models best explain the data if all three CFC ratios have similar fractions of recently recharged water (Plummer et al., 2006b).

When the CFC-113 recharge year is more recent than the CFC-11 and CFC-12 recharge years, mixing of two water sources is
qualitatively demonstrated (Plummer et al., 2006b). This relation-
ship exists for Hind Well, Bakken Pond, Holualoa, Hualalai, 
Keahualoa QLT-1, Kahaluu Shaft, Kahaluu A, Cameron’s Well, Keei 
D, and PUHO (Fig. 5), suggesting that these samples are more appro-
priately modeled by binary mixing rather than piston flow. We 
found similar fractions of recently recharged water for Holualoa,
Hualalai, Honokohau, Kahaluu Shaft, Kahaluu A, Halekii, and Keei 
D (Table A.3), further supporting use of the binary mixing model 
for these samples. These wells had young fractions of water that 
recharged between the mid-1970s and late-1980s (Fig. 6). These 
samples varied from 5% to 46% young water, with the remainder 
recharging before the atmospheric release of CFCs. The northern-
most wells (Holualoa, Hualalai, and Honokohau), which are pre-
sumptively located closer to the Hualalai rift zone, with a greater 
density of low permeability dikes, contained a larger percentage 
of old water than the southern wells. This relationship may indicate 
lower hydraulic conductivities and slower water movement 
through this area. Water from the supply wells therefore likely came 
from a part of the aquifer where flow lines of relatively old, CFC-free 
water converged with relatively young, CFC-containing water.

We modeled several coastal well and pond samples with the 
binary mixing model. The KAHO samples, Cameron’s well, and
PUHO were dominated by water that recharged from the 
mid-1980s to early-1990s with smaller fractions (7–23%) of 
CFC-free water (Fig. 6). We averaged the nine fractions of young 
water for Bakken Pond (Table A.3) and found that it contained 
~63% mid- to late-1980s water, and although less robust, Hind 
Well contained ~47% early- to mid-1980s water. These results sug-
gest that the top of the basal lens near the coast was fairly uniform 
in age. Additionally, coastal wells and ponds in proximity to each 
other have similar patterns of CFC degradation or contamination, 
suggesting that strong local land-use and/or aquifer controls influ-
ence the samples.

3.6. Travel distance and water age

Samples with longer straight-line travel distances from their 
recharge zones (Eq. (1)) to water sampling depth generally had 
greater fractions of water that recharged prior to 1940 (Fig. 7).
Supply wells were strongly correlated ($r^2 = 0.94$) between percent 
young water and straight-line travel distance. Furthermore, the 
maximum water travel distance for supply wells was shorter than 
10 km, possibly constraining sizes of high-level aquifers. Basal sup-
ply wells plotted on the same line as the high-level wells. This may 
suggest that basal water is influenced by water leakage from the 
high-level aquifers. Although less robust ($r^2 = 0.80$), the relation-
ship from coastal wells and ponds tracked fairly closely to 100% 
young water at a sampling distance of zero meters, indicating that 
coastal samples were likely dominated by local recharge. Flow 
lines of older water within the aquifer must have been close to 
the water table because none of the coastal samples contained 
100% young water.
3.7. Distinguishing water masses

Groundwater samples can be grouped by CFC compounds into distinct water masses that contain similar fractions of recently recharged water. As described in Darling et al. (2010), modern fractions of water (from the binary mixing model) were converted into percentages and plotted on a ternary diagram (Fig. 8). Water equilibrated with modern air resides at the center of the triangle. These
3.8. Precipitation patterns

Rainfall patterns in the Hawaiian Islands are influenced by El Niño-Southern Oscillation (ENSO), the Pacific Decadal Oscillation (PDO), longer-term trends from global warming, and possibly volcanic activity at Kilauea Volcano (Giambelluca et al., 2011). Since the late-1970s, the PDO has been in a positive phase, which is generally associated with decreased rainfall in the Hawaiian Islands. Furthermore, rainfall in Hawaii has slowly declined over the past 90–100 years (Giambelluca et al., 2011).

The CFC data suggest that it minimally takes ~30 years for groundwater along west Hawaii to travel from recharge to discharge areas. These travel times coupled with the overall decrease in precipitation over the past century suggest that the area's groundwater supply as well as coastal groundwater discharge may decrease over the next 30 years as water that recharged within the past ~30 years travels toward the coast.

3.9. Land-use changes and future planning

The CFC results indicate some water recharged the aquifers between the late-1970s and mid-1980s. Land-use in West Hawaii in 1976 was dominated by evergreen forestland and rangeland, with smaller amounts of agricultural land, bare exposed rock, and urban land (State of Hawaii Office of Planning, 2014). Since then, land-use has changed dramatically. For example, urbanized land cover has increased by more than 60% between 1992 and 2010 (Yale University Center for Industrial Ecology, 2014). These changes (urbanization) coupled with increased population should decrease the quantity of groundwater within the aquifers as well as the quantity reaching the coast. Furthermore, assuming status quo, we hypothesize that there will be a shift in the nutrient biogeochemistry of the groundwater over the next 30 years. Our results suggest that the current groundwater supply should be more indicative of the 1970s forest and rangeland conditions, while groundwater withdrawn in the future should show a progressive shift toward more urbanized signatures. Given the groundwater ages shown here, more research is needed to understand the consequences of how past land-use changes may influence future groundwater supplies in this region, with specific attention paid to how urbanization affects the long-term quantity and quality of the groundwater.

4. Conclusions

The results presented here suggest that many samples from west Hawaii recharge from the primary rainfall zone, an area of maximum precipitation. High-level water recharges the basal aquifer and many water samples contain an isotopically detectable fog drip signature. Fog drip along west Hawaii requires more detailed study. Furthermore, once a δ18O/altitude precipitation gradient is firmly established for the area, results from this study should be reevaluated and a follow-up study should be completed.

CFC apparent age dating was applicable in the fractured-rock aquifers of west Hawaii. Overall, groundwater in the fractured-rock aquifers of the area was best modeled using the binary mixing model, indicating that the water in the area's aquifers is a mixture of young and old water. Some water in the water supply wells recharged within the last 30 years, while the coastal well and pond samples were dominated by recent, local recharge. We found distinct and robust correlations for the percent of young water and travel distance in our samples. Such correlations may be beneficial for constraining sizes of high-level aquifers in volcanic islands. Water samples from the basal and high-level aquifers plotted on the same correlation line, suggesting that high-level water leaks into the basal aquifer. Furthermore, a ternary plot of young fractions of recharging water conveys that it is possible to differentiate between water from high-level aquifers and water from basal aquifers. It would be interesting to look for similar relationships on other volcanic islands and in settings where water from one aquifer may leak into another aquifer. The results also indicate that the Kailua lava pipe sample is from a high-level water source, despite discharging to the bottom of a bay. Numerous lava tubes and conduits conducive to groundwater flow likely exist on...
volcanic islands. It appears that CFCs could be used in such locations to determine sources of water within the conduits.

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