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# Chemical weathering fluxes from volcanic islands and the importance of groundwater: The Hawaiian example

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## Abstract

We investigated the products and rates of chemical weathering on the Hawaiian Islands, sampling streams on Kaua'i and both streams and groundwater wells on the island of Hawai'i. Dissolved silica was used to investigate the flowpaths of water drained into streams. We found that flowpaths exert a major control on the observed chemical weathering rates. A strong link exists between the degree of landscape dissection and flowpaths of water through the landscape, with streams in undissected landscapes receiving water mainly from surface runoff and streams in highly dissected landscapes receiving a considerable fraction of their water from groundwater (springs and/or seepage). Total alkalinity in Hawaiian streams and groundwater is produced exclusively by silicate chemical weathering. We find that fluxes of total alkalinity (often called "$CO_2$ consumption rate" in the geochemical literature), from the islands are lower than those observed in basaltic regions elsewhere. Groundwater is, overall, the major transport vector for products of chemical weathering from the Hawaiian Islands. On the youngest and largest island, submarine groundwater discharge (*SGD*) transports more than an order of magnitude more solutes to the ocean than surface water and on the youngest part of the youngest island, *SGD* is the only link between the terrestrial weathering system and the ocean. These results suggest that groundwater, and particularly *SGD*, needs to be included in geochemical weathering budgets of volcanic islands.

## 1. Introduction

Recognition of the importance of weathering fluxes in volcanic terranes has led to a renewed focus on the processes that control these fluxes and how they may differ from those in continental settings. Chemical weathering fluxes from rivers draining basaltic terranes are among the highest recorded worldwide (Gislason et al., 1996; Louvat and Allègre, 1997; Dessert et al., 2003, 2009; Das et al., 2005; Pokrovsky et al., 2005, 2006; Eiríksdóttir et al., 2006; Rad et al., 2006; Schopka et al., 2011 etc.). Despite its relative accessibility, there has been little work on chemical weathering fluxes from the Hawaiian archipelago.

An early study of the chemical denudation of Hawai'i is that of Li (1988), who used stream chemistry data from the USGS to investigate chemical and physical denudation in Hawai'i. Li

(1988) found that carbonic acid is the most important weathering agent on the islands and that chemical denudation rates on all the islands are higher on the wet windward side than on the dry, leeward side of the islands. He also investigated weathering fluxes by groundwater and found them to be roughly comparable to weathering fluxes by streams. In a survey of stream weathering fluxes from basaltic terranes worldwide, Dessert et al. (2003) used available USGS stream chemistry data to estimate surface weathering fluxes from Hawai'i. They found that inferred weathering rates in Hawai'i were anomalously low relative to other basaltic terranes in broadly similar climates, but they did not consider groundwater fluxes.

Recent work has highlighted the large flux of submarine groundwater discharge (*SGD*) to the global ocean from continents (e.g. Moore, 1996; Burnett et al., 2003; Moore et al., 2008) and islands (e.g. Cardenas et al., 2010; Huang et al., 2011). In particular, it has been demonstrated that *SGD* is a very important component of the hydrological balance of volcanic islands (e.g. Kim et al., 2003). Several studies provide evidence that *SGD* is widespread in Hawai'i as well. Street et al. (2008) used multiple chemical tracers (salinity, dissolved silica and Ra-isotopes) to quantify SGD in several locations in Hawai'i, Johnson et al. (2008) used thermal infrared imagery to demonstrate the presence of large, cold freshwater plumes along the west coast of the island of Hawai'i and Peterson et al. (2009) quantified the discharge via these plumes using salinity and Ra-isotopes. *SGD* is not only an important pathway for the delivery of water from land to ocean; it also transports significant amounts of dissolved solids from weathering on land directly to the global ocean (Rad et al., 2007; Georg et al., 2009).

In this paper, we compare the magnitude of chemical weathering fluxes via surface runoff and *SGD*, and investigate the control that bedrock age, climate and degree of landscape development exert on the relative magnitude of these fluxes. Here we use data on dissolved silica (*DSi*) and total alkalinity (*TAlk*), along with constraints on hydrologic fluxes, to estimate silicate weathering fluxes and associated transfer of atmospheric $CO_2$ to the ocean. The watersheds studied here contain only silicate rocks, so the flux *TAlk* is a measure of atmospheric $CO_2$ consumption associated with silicate weathering (e.g. Dessert et al., 2003). *DSi* is unaffected by atmospheric contribution and is treated here as a record of the dissolution of primary silicate minerals. Cycling of Si by vegetation (Derry et al., 2005; Ding et al., 2005, 2008, 2009) and clay precipitation and/or dissolution (Georg et al., 2007) impact the stable isotope composition of dissolved silica but not the export flux, unless the system is out of steady state. The Si-cycle is, perhaps somewhat simplistically, treated as a steady state system in this study.

### *1.1 Study site*

The 600 km long, NW-SE trending Hawaiian archipelago lies at the edge of the tropics (19-22° N) and consists of five main islands and several smaller ones (**Figure 1**). The islands, composed exclusively of basalt, are the youngest volcanoes in the 6000 km long Hawaiian-Emperor Volcanic Chain that formed by the interaction of the Hawaiian mantle plume with the Pacific Plate. The climate is warm, with pronounced differences in rainfall between the windward (<6000 mm/yr) and leeward (100-1000 mm/yr) sides of each island. A thermal inversion layer is present at 1500-3000 m a.s.l. and above this layer, precipitation is negligible. We investigated chemical weathering fluxes via stream water and groundwater on Kaua'i and on the island of Hawai'i (**Figure 1a**). The two islands represent the extremes in age and landscape development in the Hawaiian archipelago.

The island of Hawai'i (**Figure 1b**) ranges in age from zero years on the currently active Kilauea volcano to ~700 × $10^3$ years (ka) on Kohala volcano (Dalrymple, 1971; McDougall and Swanson, 1972). The island retains considerable constructional volcanic topography, with the exception of the NE-coast of the Kohala peninsula where a large flank collapse occurred around 250 ka (Lamb et al., 2007). The leeward side of Hawai'i receives much less precipitation than the wet windward side and has no permanent streams. The lack of surface runoff results from the combination of low rainfall and the high permeability of fresh lava, which allows rapid infiltration of rainwater into the groundwater reservoir (Macdonald et al., 1983). Even when active, leeward streams typically cease to flow prior to reaching the ocean. Soil development is largely a function of precipitation, and substantial elemental loss on the oldest soils (Kohala) occurs only where mean annual precipitation (MAP) > 1100 mm/yr (Chadwick et al., 2003), with smaller losses in younger soils. Because of the combination of the orographic rain shadow and regional inversion only a small fraction of the leeward side of the island has rainfall that exceeds this value, on the upper slopes of Kohala and in south Kona where thermal convection generates slightly higher MAP (Giambelluca et al., 2011). While weathering and leaching takes place in these smaller areas, the presence of only ephemeral streams indicates that the majority of solutes exported from the weathering zone must reach the ocean via groundwater. Stream water geochemical fluxes from the leeward portions of the island of Hawai'i are therefore negligible contributors to the island wide flux.

Kaua'i (**Figure 1c**) is the oldest of the large Hawaiian Islands (the oldest dated rocks are 5.1 × $10^6$ years (Ma) old (McDougall, 1979)). Kaua'i is heavily impacted by tectonic gravitational landsliding. It is deeply eroded and retains only a small fragment of the original volcanic shield morphology in the headwaters of the Waimea Canyon. Deep valleys separated by knife-edge ridges characterize the remainder of the island, and soils are deeply weathered (Vitousek et al., 1997).The central high plateau on Kaua'i is also one of the wettest places on Earth with MAP in excess of 11000 mm/yr. Rainfall diminishes towards the coast all around the island and is the lowest on the leeward (SW) side.

As lava flows weather, their permeability decreases due to collapse of the original permeable lava structure (primary mineral dissolution, bioturbation), secondary minerals filling in empty vesicles etc. As a consequence, flowpaths of water change (Lohse and Dietrich, 2005; Jefferson et al., 2010). On young, unweathered surfaces most rainfall percolates uninterrupted to the groundwater table, and streams do not occur on the surface. This is the case on most of the leeward side of the island of Hawai'i. When incipient soil and some vegetation are present on the lava surface, some rainwater is retained on the surface. Ephemeral streams are found on the thin soils of Mauna Loa, on bedrock only a few hundred to a few thousand years old. These streams are only active for a few days every year and contribute negligibly to the overall weathering budget of the island. They are therefore omitted from this study. In contrast, perennial streams, arranged radially on the slopes of the volcano, have developed on the windward side of Mauna Kea, under heavy rainfall and on bedrock ≤30 ka old. Kohala volcano is the oldest part of the island of Hawai'i. It is the site of a large landslide that most likely accelerated valley formation on the windward side of the peninsula (Lamb et al., 2007). Thick soils mantle the high plateau, which is the remnant shield surface. Dense vegetation covers the walls and floors of the valleys that have been cut into the volcanic shield. Kaua'i is similar to the Kohala Peninsula in this respect, although millions of years separate the two islands.

Groundwater in Hawai'i is present either as a thin freshwater basal lens overlying sea water that has penetrated the lava layers, or as perched aquifers confined by dikes and/or tephra and soil layers that are much less permeable than basalt (Juvik and Juvik, 1998). Only one of the groundwater samples collected for this study is from a perched aquifer (Pahala Well, sample HI-06-59), evidenced by a water level much higher than in surrounding wells and the lowest $Cl^-$ - concentration of all wells used in this study.

## 2. Data and methods

We split the study area into four regions. The island of Hawai'i comprises three regions: Kohala (Kohala Peninsula), Hamakua-Hilo (the windward slopes of Mauna Kea) and Kilauea (the eastern flanks of Mauna Loa and Kilauea volcanoes) (see **Figure 1b,** and Figure **A1** for orientation); the island of Kaua'i is the fourth region. Water samples were collected for chemical analyses on Kaua'i and the island of Hawai'i in early 2005 and 2006, and on the island of Hawai'i in 2008 (sampling locations are shown in **Figures A1** and **A2**).

Landscape analysis was performed using ArcGIS 9 (ESRI, 2009) on a National Elevation Dataset (NED) Digital Elevation Model (DEM), obtained from the USGS seamless data warehouse (http://seamless.usgs.gov/). The DEM has a resolution of 10m.

### *2.1 Chemistry*

A total of 56 streams and tributaries were sampled, 32 on the island of Hawai'i and 24 on Kaua'i. Some streams were sampled multiple times. Given the importance of *SGD* in Hawai'i (e.g. Juvik and Juvik, 1998; Peterson et al., 2009), a total of 12 groundwater wells were also sampled on the island of Hawai'i in 2005 and 2006. Chemical data for five more groundwater wells on Maui, O'ahu and Kaua'i was obtained from the USGS online database (http://nwis.waterdata.usgs.gov/usa/nwis/qwdata). The chemical composition of stream water and groundwater is presented in **Tables A1** and **A2**, respectively.

Methods for sampling and chemical analyses are described in Schopka et al. (2011). Briefly, filtered samples were analyzed for *DSi* by molybdate blue spectrophotometry (Mortlock and Froelich, 1989). Alkalinity in samples from 2006 was determined by charge balance and in all other samples by Gran titration. Alkalinity is a measure of the capacity of a filtered water sample to neutralize strong acids and consists of the sum of titrable carbonate and non-carbonate chemical species in the sample (Rounds, 2006). Chemical analyses of our samples (not shown) show that carbonic acid is the most important anion contributing to alkalinity in our samples, and given the pH (< 8.5), $TAlk \approx [HCO_3^-]$. Other contributions to the titrated alkalinity were minor or negligible (e.g. organic anions, borates, etc.). All samples were measured for major an- and cations. These data are the subject of a paper in preparation and will not be discussed here. We do note, however, that we corrected all data for atmospheric (stream data) and seawater (groundwater) inputs, using Cl- as a tracer and X/Cl-ratios of seawater, $X = \{Na^+, K^+, Ca^{2+}, Mg^{2+}\}$. The results indicate that seawater contamination of our groundwater samples is <10% in all cases. Consequently the impact on alkalinity fluxes is also < 10%, and probably much less for *DSi* since coastal seawater has very low silica concentrations relative to Hawaiian groundwater.

## *2.2 Hydrology*

Long-term stream discharge data (defined here as five years or more of continuous data), collected by the USGS (http://waterdata.usgs.gov/nwis/dv/?referred_module=sw), are available for 27% (15 out of 56) of the streams sampled. Stream discharge in the remaining watersheds was estimated by a geospatial statistical technique (kriging) applied to runoff from neighboring streams (Schopka, 2011). This allows us to estimate total stream discharge across an entire region even if only a subset of streams in that region were gauged. The kriging technique has advantages compared to simple linear interpolation or extrapolation, including more robust estimates in data-sparse regions and improved estimates of uncertainties (e.g. Nielsen and Wendroth, 2003). Yearly mean stream discharge was used to calculate the annual export of chemical weathering products from each watershed studied.

*SGD* fluxes from the Hawaiian Islands are poorly quantified, having been modeled in a few discrete locations only (Johnson et al., 2008; Knee et al., 2008; Street et al., 2008; Peterson et al., 2009), but none of these efforts have targeted the total *SGD* flux from an entire island or the archipelago as a whole. The USGS has performed whole-island water budget studies for all the major Hawaiian Islands except for the island of Hawai'i, where the water budget has been described in several regional studies (performed by the USGS, the State of Hawai'i and private companies), which together cover the entire island. We used these studies to assess the magnitude of *SGD* from Kaua'i and the island of Hawai'i (see **Figure A3**). Importantly, the results of these water-budget studies are in general agreement with the results of the more recent studies that directly measure or model. SGD.

Most of these studies (and all the ones cited in this paper) treat groundwater recharge (*G*) as the residual in the water balance equation:

$$G = P - DR - AE - \Delta SS \qquad \text{(eq. 1)}$$

where $P$ = precipitation, $DR$ = direct runoff, $AE$ = actual evapotranspiration and $\Delta SS$ = changes in soil moisture storage (e.g. Shade, 1995). *G*, in the sense employed in the cited water budget studies, can be discharged into rivers and streams (termed "base flow" (*BF*)), or directly into the ocean as *SGD. DR* is, in this formulation, the fraction of stream flow that derives from overland flow. *G*, as reported in the USGS reports, is therefore not equivalent to *SGD*, but rather represents the sum of *SGD* and *BF*:

$$G = SGD + BF \qquad \text{(eq. 2)}$$

Introducing the term "stream discharge", *Q*, we define:

$$Q = BF + DR \qquad \text{(eq. 3)}$$

Assuming $\Delta SS = 0$ when $t > 1$ yr, and re-casting equation 1, we get:

$$SGD = P - Q - AE \qquad \text{(eq. 4)}$$

$Q$ was kriged over the study area (see above and Schopka, 2011). The total kriged $Q$ on Kaua'i is a minimum value (the kriging surface does not extend over the entire coastal zone of the island) and the calculated *SGD* from Kaua'i is therefore a maximum value. On the island of Hawai'i, data from Oki (2004) show that *BF* is a minor (~6%) component of groundwater recharge; we therefore consider the *DR*-values from the water budgets representative of $Q$ on the island of Hawai'i. The results from the water budget studies cited and our calculation of *SGD* are reported in **Table 1**.

## *2.3 Uncertainties*

We seek to estimate the total weathering fluxes delivered to the oceans by surface stream runoff and groundwater. The surface runoff is composed of many streams, and those are constrained either by direct observation or by geostatistical estimation. For the streams with more than five years of observations, we simply calculated the mean annual discharge ($Q_{mean}$) and standard deviation ($\sigma_Q$) based on daily observations, expressed as the coefficient of variation:

$$CV_Q(\%) = \sigma_Q / Q_{mean} \times 100 \qquad \text{(eq. 5)}$$

For the modeled streams, the kriging variance measures the spatial variability of the input variable but is not a measure of the reliability of the kriging estimate (Nielsen and Wendroth, 2003). To provide a conservative estimate of the variance in the modeled streams we propagated the variance on the measured input variable with the kriging variance using standard error propagation methods (Bevington and Robinson, 2002).

In order to estimate the overall uncertainty on the stream discharge from each island we propagated the uncertainties associated with the summation. The standard form for error propagation for a sum of the fluxes $f = a_1Q_1 + a_2Q_2$ ... (where $a_1$ and $a_2$ are well-defined constants but $Q_1$ and $Q_2$ have standard deviations $\sigma_1$ and $\sigma_2$) is

$$\sigma^2 = \sum_i a_i^2 \sigma_i^2 + \sum_i a_i COV_{ij} a_j \qquad \text{(eq. 6)}$$

The terms in covariance matrix ***COV*** can be expressed as $cov_{ij} = \rho_{ij}\sigma_i\sigma_j$, where $\rho_{ij}$ are the pairwise correlation coefficients. Let $a_i = 1$. Then the variance for the summed stream discharge flux depends on the correlation coefficients between rivers as well as their standard deviations:

$$\sigma_f^2 = \sum_i \sigma_i^2 + \sum_i \sum_j \rho_{ij}\sigma_i\sigma_j \qquad \text{(eq. 7)}$$

The correlation coefficient matrix ***R*** is symmetric about the diagonal (i.e. $\rho_{ij} = \rho_{ji}$, and $\rho_{ii} = 1$). Then equation 7 can be expressed in matrix form:

$$\sigma_f^2 == S \cdot R \cdot S^T \qquad \text{(eq. 8)}$$

where ***S*** is the vector of $\rho_{ij}$ values. A degree of correlation in stream discharge time series in a region is expected because they all tend to respond similarly to a common forcing (i.e. rainfall events). The covariance structure has a significant impact on the estimated uncertainty. The gauged streams in the study area do not have the same record lengths or sampling intervals, but there are enough overlapping data to estimate the degree of correlation. Values for $\rho_{ij}$ are typically 0.6 to 0.9. The modeled streams are by definition strongly correlated with the others, a function of the kriging technique. Because of the data limitations we cannot compute ***R*** directly but its terms can be estimated. We consider both a mean $\rho_{ij} = 0.8$ (but assume normally distributed variation about this mean), and the limiting cases of either no or perfect correlation of all stream discharges ($\rho_{ij} = 0$ or 1).

For Kaua'i, the propagated coefficient of variation ($CV_f$) for stream discharge is 36% (n = 32). The limiting cases ($\rho_{ij} = 0$ or 1) yield $CV_f$ = 10% and 40%, respectively. For the island of Hawai'i $CV_f$ for stream discharge is 38% ($n$ = 42). The limiting cases ($\rho_{ij} = 0$ or 1) yield $CV_f$ = 14% and 43%, respectively.

Uncertainty on *SGD* estimates is poorly constrained; none of the reports cited here deal with uncertainty explicitly. In her study of the water budget of Moloka'i, Shade (1997) arrived at two different values for *G* using two methods for calculating the water budget - one method allocated excess soil-moisture to *G* before *AE* while the other allocated excess soil moisture first to *AE* and then the *G*. We use the difference between the two *G* estimates (~35%) as our measure of uncertainty on the *G*-values, and by extension *SGD*-values, from the Hawaiian Islands. Two further studies validate this approach: Oki (2002) performed a rigorous error analysis on his revised assessment of the water budget of the Hawi aquifer on the Kohala Peninsula and found that *G* could be estimated with as little as 21% error. This low uncertainty is achieved using daily water budgeting, which dramatically improves the model's ability to correctly estimate soil moisture storage and actual evapotranspiration compared to the monthly or even yearly budgeting used in the other reports. We interpret this as the lower limit on the error with which *G* can be estimated in Hawai'i. Giambelluca et al. (1996) found that errors on estimates of *G* on land under cultivation on O'ahu are 49-58%, which we consider the upper limit on the errors of estimates of *G* in Hawai'i.

Reproduciblity on our *DSi* measurements and alkalinity measurements are generally less than 2% and 15% respectively (Schopka et al., 2011). These uncertainties were propagated with the hydrologic uncertainties when estimating the geochemical fluxes and uncertainties.

## 3. Results

### *3.1. Water fluxes*

Fluxes of water via *SGD* and *Q* are presented in **Table 1**. The ratio *SGD/Q* describes the relative importance of submarine groundwater discharge and total stream discharge in delivering water from land to the ocean.

Considering the whole of the island of Hawai'i, *SGD* is nearly four times larger than stream discharge, accounting for 79% of the total water flux from the island. *SGD/Q* in the aquifers of Kilauea and Mauna Loa volcanoes (**Figure A3)** approaches infinity, since nearly no stream discharge is observed in those areas (Takasaki, 1993), while in the Onomea aquifer just north of Hilo, the ratio is <1 due to extremely heavy precipitation.

The USGS water budget report for Kaua'i treats the island as a single aquifer and shows that around 84% of the total water discharge from the island leaves via streams, with *SGD* accounting for 16% of the total water flux.

### *3.2. Water chemistry*

Our data show that there is a clear difference between groundwater and surface water in terms of chemistry (**Figure 2**); groundwater has significantly higher concentrations of both *TAlk* (95% confidence interval (C.I.) for the mean is 1328-2162 µmol/L in groundwater vs. 307-477 µmol/L for streams) (**Figure 2a**) and *DSi* (95% C.I. for the mean is 802-973 µmol/L in groundwater vs. 220-316 µmol/L in stream water) (**Figure 2b**).

We calculate a recharge-weighted average concentration for *TAlk* and *DSi* in groundwater, assuming that the chemistry of the sampled wells is representative for the aquifer in which it is located (**Table 2**). Groundwater in the Kilauea region is significantly more dilute with respect to both *DSi* and *TAlk* than groundwater elsewhere (*DSi*: Kilauea = 697 ± 46 µmol/L (mean ± 1 s.e.); elsewhere: 928 ± 79 µmol/L. *TAlk*: Kilauea = 718 ± 159 µmol/L; elsewhere: 1913 ± 275 µmol/L.) The Kilauea aquifers have extremely high groundwater recharge rates, and ~45% of all groundwater recharge that occurs in the archipelago flows through them (**Table 1**). We therefore use a separate recharge-weighted average *TAlk* and *DSi* for the Kilauea region (see above) for flux calculations.

### *3.3. Chemical fluxes*

We compare total chemical weathering fluxes from the surface and subsurface (**Table 2, Figure 3**) by calculating $R_{sub/sur} = F_{T,gw} / F_{T,sw}$ , where $F_T$ = total flux, *gw* = groundwater and *sw* = surface water. This ratio indicates the relative importance of *SGD* and *Q* in delivering products of chemical weathering to the ocean.

We calculate $R_{sub/sur}$ for the island of Hawai'i as a whole using total island-wide chemical fluxes via *SGD* and total surface weathering fluxes from the Hamakua-Hilo and Kohala regions. Since we did not sample all streams on the island, the resulting $R_{sub/sur}$ is a maximum value (we sampled most streams in Hamakua-Hilo and around 40% of the runoff-active area on Kohala, see **Figure A1**). $R_{sub/sur}$ for *TAlk* is 14 ± 8, and $R_{sub/sur}$ for *DSi* is 16 ± 6 on the island of Hawai'i.

$R_{sub/sur}$ on Kaua'i and in individual regions on the island of Hawai'i is calculated using area-normalized subsurface fluxes ($F_{T,gw}/Area$) and the arithmetic average of area-normalized weathering fluxes from the streams in each region (see **Table A1**). On Kaua'i, an average of ~30% of solutes comes from subsurface weathering ($^{-15\%}/_{+11\%}$ for *TAlk*, $^{-6\%}/_{+4\%}$ for *DSi*). In the runoff-active parts of the island of Hawai'i, groundwater is a larger vector for chemical fluxes than on Kaua'i, where $R_{sub/sur}$ is as low as ~0.4. On average, ~60% ($^{-20\%}/_{+10\%}$) of *TAlk*-fluxes from Hamakua-Hilo and Kohala, and ~50% ($^{-10\%}/_{+7\%}$) of *DSi*-fluxes from these same regions, come from subsurface weathering. This percentage increases to ~94% ($^{-7\%}/_{+3\%}$ for *TAlk*, $^{-3\%}/_{+2\%}$ for *DSi*) for the island of Hawai'i as a whole.

## 4. Discussion

### *4.1 Water chemistry and chemical fluxes*

We attribute the higher concentrations of both *TAlk* and *DSi* in groundwater to two factors: 1) Soils in Hawai'i are rapidly depleted of primary minerals during weathering (Vitousek et al., 1997) while groundwaters may contact a much larger reservoir of fresh minerals, and 2) longer residence time ($\tau$) of water in the subsurface than in the surface environment. For example, a groundwater $\tau$ of $\leq$35 years in the Kilauea East Rift Zone was reported by Scholl et al. (1996), while a much shorter $\tau$ of $\leq$20 days has been reported for water in streams on O'ahu and the island of Hawai'i (Fagan and Mackenzie, 2007; Paquay et al., 2007). The relatively dilute character of the groundwater in Kilauea is most likely a consequence of the very high flux of water through the aquifers.

We make the simplifying assumption that the weathering system in Hawai'i is in steady state. All sampled streams are undersaturated with respect to amorphous Si and calcite. Our groundwater samples are all but one undersaturated with calcite and all are undersaturated with amorphous Si. The undersaturation indicates that Si and alkalinity are not being removed from the water to any great extent. Based on previous work on silica in Hawaiian streams (Mortlock and Frohlich, 1987; Derry et al., 2005), *DSi* varies by about a factor of two even when stream discharge varies by one to two orders of magnitude, and the correlation between *DSi* and stream discharge is very weak. Consequently hydrologic variability is the strongest control and also the largest source of uncertainty in our flux estimates. While we do not have long term *DSi* or *TAlk* data (and this would clearly be desirable), longer time series are unlikely to substantially modify the estimated fluxes.

We find that groundwater chemical fluxes are an important component of chemical weathering budgets on the Hawaiian Islands. Groundwater transports anywhere from 30% (Kaua'i) to 95% (island of Hawai'i) of the total flux of chemical weathering products from the islands. In other words, chemical weathering fluxes transported to the oceans via groundwater are up to an order of magnitude larger than via surface water.

Rad et al. (2007) also estimated the chemical weathering flux carried as groundwater discharge from two islands in the Lesser Antilles volcanic arc and the hotspot Reunion Island. They used stream discharge data and island-wide estimates of evapo-transpiration to estimate ground water infiltration. They also used limited data from geothermal springs and wells to estimate the compositon of groundwaters. Silica and bicarbonate (calculated by charge difference) in subsurface samples from Guadeloupe and Martinique are higher than reported here from Hawai'i, consistent with the hydrothermal temperatures of the sampled fluids in the Antilles samples. Silica data are not available from Reunion, but $HCO_3^-$ concentrations reported in two aquifer samples are similar to values from Hawai'i.

There is little evidence that most Hawaiian groundwater is impacted by hydrothermal activity. For example, *SGD* from the island of Hawai'i has a temperature of ~19-21°C (Johnson et al., 2008; Peterson et al., 2009), and Conrad et al. (1997) showed that groundwater in deep drill holes on the east flank of Kilauea volcano is the same temperature from sea level down to ~500 m below sea level - ~20-25°C. The results from Rad et al. (2007) are therefore not directly comparable with our work. Conrad et al. (1997) do report much higher temperatures deeper in the drillholes, but our sampling did not tap any of this water. Local geothermal sources are known from the NE Rift zone of Kilauea but we did not sample these waters. Such sources probably enhance the silica and bicarbonate fluxes delivered to the oceans in SGD but the island-wide impact is probably modest.

Rad et al. (2007) found that groundwater fluxes accounted for 45 to 70% of the total $HCO_3^-$ fluxes from the three studied islands, and 65 – 95% of cation fluxes. For the two islands for which Rad et al. (2007) report dissolved silica values, 45 – 80% of the silica flux was via groundwater. No uncertainties were calculated, but given the reconaissance nature of the sampling and water balance data they are probably large. Overall, the data of Rad et al. (2007) are consistent with the results from Hawai'i althought yielding a slightly smaller contribution from subsurface alteration. All the data imply that weathering fluxes delivered by groundwater significantly exceed stream (surface) water discharges and are the main pathway for the delivery of weathering solutes to the ocean from young volcanic islands. The new data in this study demonstrate that this conclusion holds even in the absence of high temperature water rock interaction.

Dessert et al. (2003) investigated chemical weathering fluxes from Hawaiian streams and calculated the mean $CO_2$ consumption rate (essentially equivalent to *TAlk* in this paper) in Hawai'i as $0.66 \times 10^6$ mol/km$^2$/yr. This is on the low end of $CO_2$-fluxes from basaltic regions worldwide (Dessert et al., 2003). They did not include groundwater fluxes in their study and our results are therefore not directly comparable to theirs. However, we did calculate the arithmetic average of area-normalized $F_{TAlk}$ (the $CO_2$ consumption rate) from stream discharge in individual watersheds (**Table A1**). On Kaua'i, $F_{TAlk} = 0.59 \times 10^6$ mol/km$^2$/yr and on the island of Hawai'i, $F_{TAlk} = 0.88 \times 10^6$ mol/km$^2$/yr, comparable to the value for Hawai'i previously reported by Dessert et al. (2003). They noted that $CO_2$ consumption in Hawaiian surface waters was lower than predicted from correlations with either runoff or temperature applied to other basaltic regions (Bluth and Kump, 1994; Dessert et al., 2003). Consideration of the large *SGD* flux eliminates the apparent discrepancy between $CO_2$ consumption rates in Hawai'i and those from other basaltic regions. However, estimates of the *SGD* contribution to the overall chemical weathering flux are not available from most other locations, and it is likely that inclusion of groundwater data would increase the total chemical weathering flux estimates for at least some of the basalt provinces summarized by Dessert et al. (2003). The observation that Hawaiian weathering fluxes including *SGD* fall on the global trends for other regions that do not include groundwater may be fortuitous, or may suggest that the importance of groundwater in Hawai'i is greater than some other places. Different age surfaces and different eruptive styles may impact the extent to which groundwater is an important carrier of weathering solutes from volcanic islands, in addition to climate variables.

The very large fluxes of weathering solutes delivered to the oceans via *SGD* have implications not only for the overall chemical weathering fluxes from volcanic islands but also for the role of volcanic island weathering in ocean chemical budgets. Weathering rates of volcanic islands are high as measured in stream fluxes (Louvat and Allègre, 1997; Dessert et al., 2003; Rad et al., 2007; Schopka et al., 2011), but the results of this study and of Rad et al. (2007) imply weathering rates derived only from stream fluxes will substantially underestimate the total $CO_2$ consumption in these settings. Groundwater geochemical fluxes range from being roughly equal to the stream fluxes on Kaua'i and O'ahu (Table 2 and Li, 1988) to more than an order of magnitude greater on Hawai'i (Table 2).

## *4.2. Groundwater chemical fluxes and geomorphology*

The Hawaiian Islands exhibit a striking landscape evolutionary sequence, and aspects of this are well-illustrated on the island of Hawai'i (**Figure 4**). Roughly, the windward side of the island of Hawai'i can be divided into three geomorphic sectors. All have developed under similar trade wind dominated conditions with high rainfall, although there have been glacial-interglacial climate variations (Hotchkiss et al., 2000). The constructional shield volcano surfaces of Kilauea (<4 ka) and Mauna Loa (<30 ka) are practically un-eroded (**Figure 4a**). Streams are ephemeral, even in regions of high rainfall (> 4000 mm/yr). Further NW, on older Mauna Kea surfaces (50-120 ka, Sherrod et al., 2008) an incised drainage pattern develops, although with low order branching (**Figure 4b**). Finally, on Kohala volcano deeply incised amphitheater - headed canyons dissect the windward escarpment (**Figure 4c**). The Kohala escarpment was initiated by the Pololu slump, a giant landslide constrained to have occurred between 385 and 173 ka, and possibly between 250 and 230 ka (Lamb et al., 2007). The escarpment would have been considerably higher relative to sea level at the time, given continual subsidence of the northern part of the island of ca. 2.6 mm/yr (Ludwig et al., 1991).

To investigate the extent of landscape maturity in our study regions, we extracted topographic profiles approximately parallel to the coast, along the somewhat continuous low-relief volcanic surface that has been locally incised by multiple streams. Profile "a" in **Figure 4** is from the flanks of Kilauea and Mauna Loa volcanoes. Profile "b" is from Mauna Kea (Hamakua-Hilo region) and the last profile, profile "c", is from Kohala (**Figure 4**). These profiles were created by visually estimating the location of the 200- and 500 m a.s.l. contours of the inferred pre-incision surface and plotting the present-day elevation along these pre-incision contours. We chose the 200- and 500 m a.s.l. contours because comparing the two illustrates the striking differences in the degree of incision in the different regions, as explained below.

The constructional shield volcano surface of Kilauea and Mauna Loa shows little incision (**Figure 4a**). The deepest channels observed are 10-20m deep and we cannot tell from the elevation dataset alone if these are original features in the lava surface or if some fluvial erosion has occurred. The 200 m a.s.l. profile has not undergone significantly more erosion than the 500 m a.s.l. profile. The older Mauna Kea surface is in general considerably more incised than Mauna Loa (**Figure 4b**). At the elevations shown in **Figure 4b**, streams are carved into bedrock of 64-300 kyr (2011). Erosion has removed up to ~150 m of lava (e.g. Laupaho'eho'e Stream) along the paleo-200 m a.s.l. contour and a maximum of 100 m of lava along the paleo-500 m a.s.l. contour. This is significantly more erosion than on Kilauea/Mauna Loa, but much less than in parts of Kohala (**Figure 4c**), where the transition to a highly dissected valley-and-ridge landscape is already well under way on the windward side of the peninsula. Streams in the N section of the profile drain the 120-260 kyr Hawi Volcanics, while the S part of the profile is underlain by the 260-500 kyr Pololu Volcanics (Sherrod et al., 2008). The degree of erosion seen in **Figure 4b** and the N section of **Figure 4c** is similar, which is not surprising given the similar substrate ages in these two regions. Incision has proceeded significantly further in the older Pololu Volcanics of **Figure 4c,** carving the streambed both deeper and further upstream than in profiles "a" and "b". Along the section of coast truncated by the giant Pololu slump it is not uncommon for streams to have incised almost down to sea level along the paleo-500 m a.s.l. contour. Some of these valleys, most notably Pololu and Waipi'o Valleys were cut deeper during periods of Pleistocene low sea level stands and have since been filled with alluvial sediments as base levels rose (see Lamb et al., 2007 and references therein).

The dramatic differences in present stream dissection and topography suggest different water routing pathways in the three regions. We can use the silica content of stream water to gain some insight into the sources of stream water in different geomorphic settings. Streams with different geomorphic characteristics exhibit differences in the concentration and downstream evolution of *DSi* along the stream profile (**Figure 5**).

A representative stream profile from the Hamakua-Hilo region (Nanue Stream) on the windward slope of Mauna Kea hardly differs from the little eroded constructive volcanic landscape of the volcano (**Figure 5a**). The measured $[Si]_{sw}$ of streams along the Hamakua-Hilo coast (Mauna Kea volcanics) is on the order of 100-200 μmol/L. This is on the lower end of Si-concentrations in surface water and much lower than any measured groundwater sample, suggesting that groundwater contributes very little to stream discharge in the region, even when incision is 100 – 150 m. A different picture emerges along the Kohala escarpment (**Figure 5b**), where the upper reaches of the Wailoa River and its tributaries drain gently sloping headwaters before plunging into the deeply dissected Waipi'o valley. In the headwater region, $[Si]_{sw}$ is generally very low (~50-150 μmol/L) but it rises abruptly to ~700 μmol/L when the streams enter the deep valley. This pattern is even more pronounced in the deeply incised Waimea Canyon on Kaua'i (**Figure 5c, 1d**). Before it enters the canyon, the Waimea River drains the Alaka'i Swamp, a highly weathered high plateau, where the river has low $[Si]_{sw}$ of ~ 10-100 μmol/L. The tributaries entering the main trunk stream from the east drain this swamp and also have low $[Si]_{sw}$, whereas ephemeral streams that originate near a knife-edge ridge on the west wall of the canyon generally have higher $[Si]_{sw}$ of ~ 500-600 μmol/L.

Assuming that Si behaves conservatively and using the weighted average [Si] of groundwater (928±79 μmol/L, Section 3.2) and the measured $[Si]_{sw}$ of both tributaries and the trunk streams downstream, a simple mixing model reveals that groundwater contributes 15-50% of the water volume in the Wailoa River and ~30% of the water volume of the Waimea River. We assume that the groundwater enters the streams both in discreet springs (e.g. "Tributary A" on Kaua'i) as well as via diffusive flow through the streambed. The downstream abrupt increase in silica below the major nick points in the Kohala and Waimea canyons indicates that groundwater is an important contributor to stream discharge in deeply incised valleys.

Jefferson et al. (2010) investigated the drainage development of a basaltic chronosequence in the Oregon Cascades, paying special attention to the partitioning of water among different flowpaths and how this partitioning evolves over time. There are some clear parallels between their observations and ours, although a direct comparison is not straightforward because of a lack of comparable metrics in the two studies – Jefferson et al. (2010) use hydrographs as a proxy for flowpaths whereas in this study, element concentrations are used to infer about flowpaths. Jefferson and her co-workers (2010) found drainage density ($km/km^2$) to be an excellent indicator of drainage development, showing a clear increase with age in their studied watersheds. No such trend was observed in our dataset. The constant drainage density we calculated for the Hawaiian watersheds is most likely a methodological issue – it is difficult to ascertain the exact contributing area to a watershed in the extremely porous rocks of Mauna Kea and Kohala, and the definition of channel length is subject to similar considerations (Schopka, 2011). We therefore developed alternate methods (incision along paleo-contours) to define the degree of drainage development in our study sites, as described above.

In the youngest landscapes on Hawai'i, all precipitation that does not evapotranspire goes to groundwater recharge and discharges as *SGD*. There is no permanent surface drainage or well-developed drainage network on the young Kilauea or Mauna Loa substrates, although a few channels are active during heavy precipitation events. In the Oregon Cascades young volcanic surfaces are drained by spring-fed streams whose discharge is relatively insensitive to rainfall events (Jefferson et al., 2010). In the Cascades, the hydrograph becomes flashier as streams age, the drainage network develops and surface flow takes over from baseflow as the main contributor to stream discharge. In Hawai'i, the older age of the Mauna Kea surface on the windward side of the island leads to the development of stream channels but with only low order branching. Streams in the Hamakua-Hilo region of Hawai'i are flashy and fed by surface runoff and shallow groundwater, similar to their counterparts in the Cascades. There is little chemical evidence of a deep, high silica groundwater source in streams from this intermediate stage of landscape development. In the deeply incised canyons from windward Kohala (island of Hawai'i) and Waimea Canyon, Kaua'i, the deep groundwater source is clearly evident in the stream water chemistry.

The decrease in $R_{sub/sur}$ with bedrock age (island of Hawai'i < 700 kyr, Kaua'i ~ 5 Myr) (**Figure 3**) is coupled with a general decrease in the proportion of rainfall that discharges as *SGD* (43% on the island of Hawai'i, 7% on Kaua'i, see **Table 1**). As mixing models of ground- and surface water show, this hydrological shift is accompanied by an increased contribution of groundwater to discharge in streams draining deeply incised valleys and canyons. For the purposes of geochemical budgets and weathering studies, this result implies that in these deep valleys, weathering reactions proceeding in the groundwater reservoir contribute solutes that may be erroneously reported as the products of weathering in soils and saprolite, i.e., in the surface environment. In fact, and assuming that our mixing models are valid, over 90% of *DSi* in the Waimea River on Kaua'i and up to 75% of *DSi* in Wailoa River on the Island of Hawai'i comes from groundwater. Counting groundwater-derived solutes with subsurface fluxes would increase $R_{sub/sur}$ in both these regions. A similar result was found by Calmels et al. (2011) in a steep, rapidly eroding watershed in Taiwan.

Our results show that groundwater is a major pathway for the transport of chemical weathering products from the Hawaiian Islands to the ocean. The importance of groundwater fluxes evolves with time and the geomorphic evolution of the islands. On the geologically young island of Hawai'i, groundwater discharge of weathering products to the oceans is around 15 times greater than stream fluxes. On the older island of Kaua'i, direct groundwater discharge of weathering solutes still contributes more than half of the total weathering flux to the oceans. Groundwater is an essential component of the weathering system during the entire life span of a volcanic island as observed in Hawai'i. In very young volcanic systems where the high hydraulic conductivity precludes surface runoff, groundwater is the only link between the weathering system and the ocean. As the landscape matures, surface runoff is generated and stream channel incision occurs. During this initial stage of landscape development, streams remain relatively dilute. Stream solutes are derived from the weathering of regolith, with negligible contributions from deep groundwater. A large fraction of precipitation continues to feed groundwater recharge and most of that recharge discharges directly into the ocean. Chemical weathering fluxes via surface water are nonetheless higher than at other stages in the landscape evolutionary sequence due to reactive nature of the regolith minerals. As the landscape continues to evolve, stream channels incise down to the level of the groundwater table and groundwater becomes an important component of stream discharge. Deeply incised streams have much higher concentrations of weathering solutes than at earlier stages. Groundwater "captured" by stream incision into the water table is often the largest source of weathering solutes to stream discharge.

## 5. Conclusions:

In this study we have shown that direct submarine groundwater discharge (SGD) is a major pathway for weathering solutes from Hawai'i to the oceans. Weathering in soils and regolith consumes $CO_2$ and delivers solutes to Hawaiian stream, but subsurface weathering by groundwater is much more important, by a factor of approximately fifteen on the island of Hawai'i. We obtain consistent results using either dissolved silica (*DSi*) or alkalinity (*TAlk*). The total $CO_2$ consumption from stream water analysis and surface water budgets are $965 \times 10^6$ mol/yr on Kaua'i and $618 \times 10^6$ mol/yr on the island of Hawai'i. These values are comparable to those obtained by Dessert et al. (2003). However, using estimates of groundwater recharge based on water balance modeling and the chemistry of a suite of wells, we estimate that the total $CO_2$ consumption from surface runoff and SGD combined are near $1475 \times 10^6$ mol/yr on Kaua'i and $9292 \times 10^6$ mol/yr on Hawai'i.

Large groundwater fluxes are characteristic of young volcanic landscapes in humid settings. Comparison with other examples suggests that groundwater is commonly a major vector of weathering products to the oceans in volcanic islands, and that weathering fluxes from volcanic terranes can be severely underestimated if direct groundwater discharge to the oceans is not accounted for.

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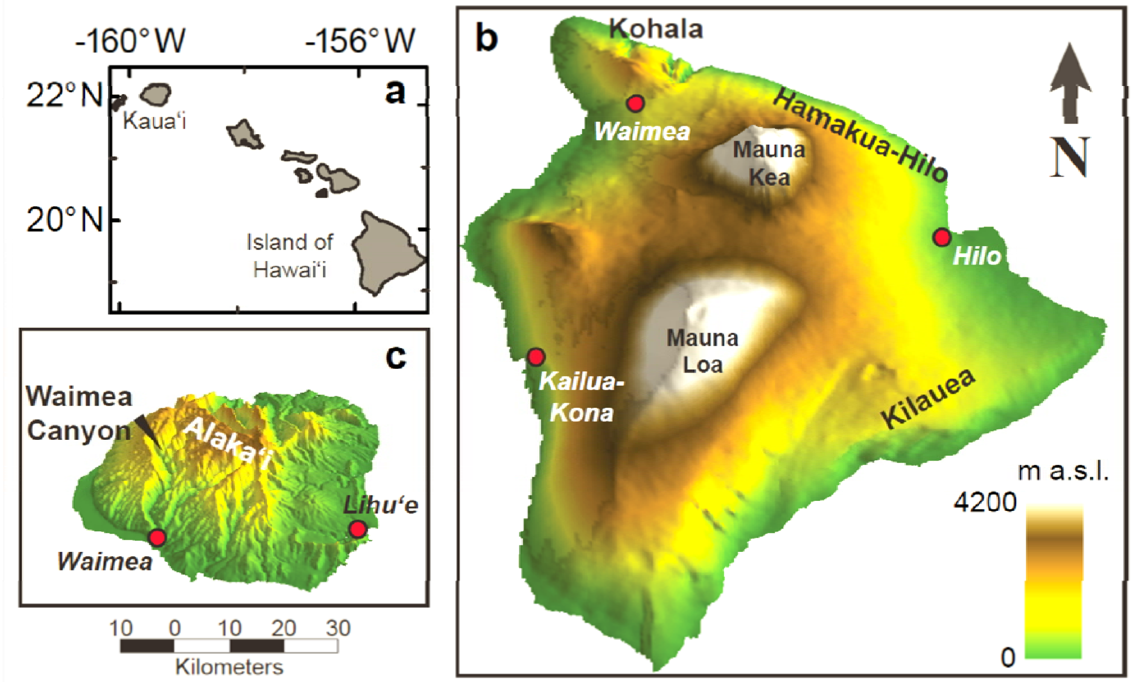


**Figure 1:** Overview of the study area. a) The Hawaiian Archipelago. Kaua'i and the island of Hawai'i are the oldest and youngest, respectively, of the islands and lie in the NW and SE extreme of the archipelago. Shaded relief maps of the island of Hawai'i (b) and Kaua'i (c) illustrate the striking difference in topography of the two islands. Place names in regular bold font indicate locations and regional division discussed in text, place names in italics indicate main towns. The elevation scale bar applies to both islands.

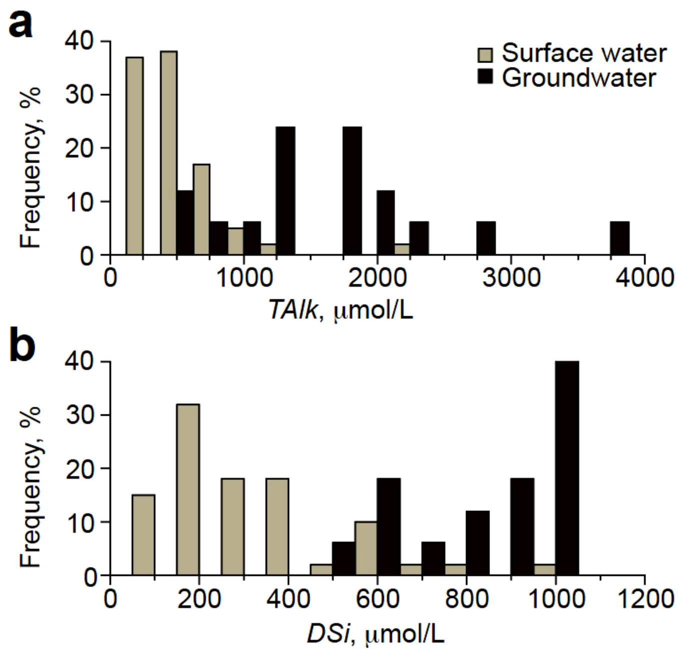


**Figure 2:** Comparison of solute concentrations in groundwater and surface water. Both alkalinity (TAlk) and dissolved silica (DSi) are consistently higher in groundwater than in surface water. a) Alkalinity, b) Dissolved silica. The data plotted in this figure are from this study and the USGS, see Table A2.

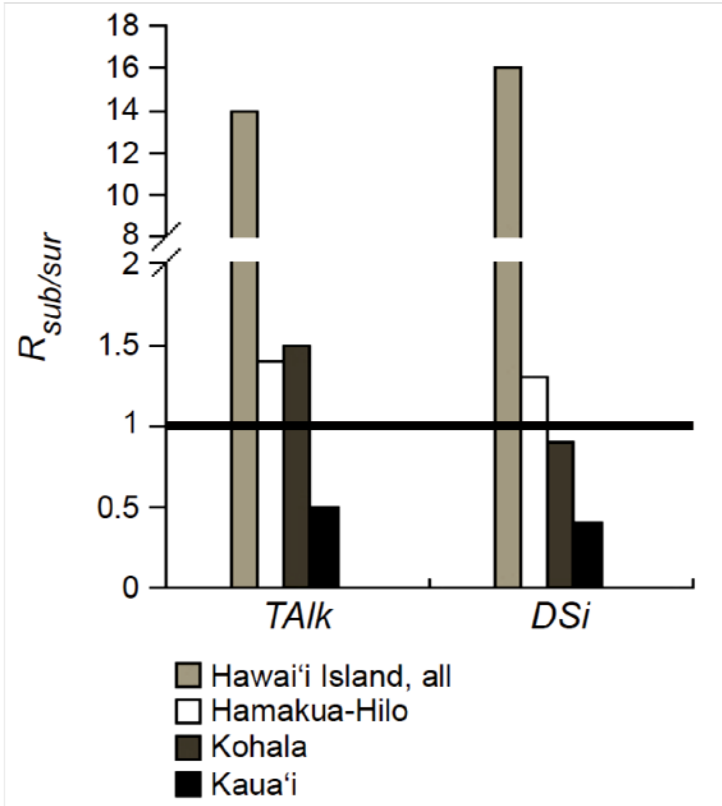


**Figure 3:** Ratios of subsurface to surface chemical fluxes ($R_{sub/sur}$), by region. The y-scale is broken for clarity. For reference, $R_{sub/sur} = 1$ is displayed with a heavy black line. $R_{sub/sur}$ diminishes rapidly as the bedrock through which the groundwater percolates ages and permeability is reduced. In Hamakua-Hilo and Kohala, groundwater contributes more to the overall flux than does surface water., In contrast, stream flow is more important for solute fluxes than groundwater is on Kaua'i.

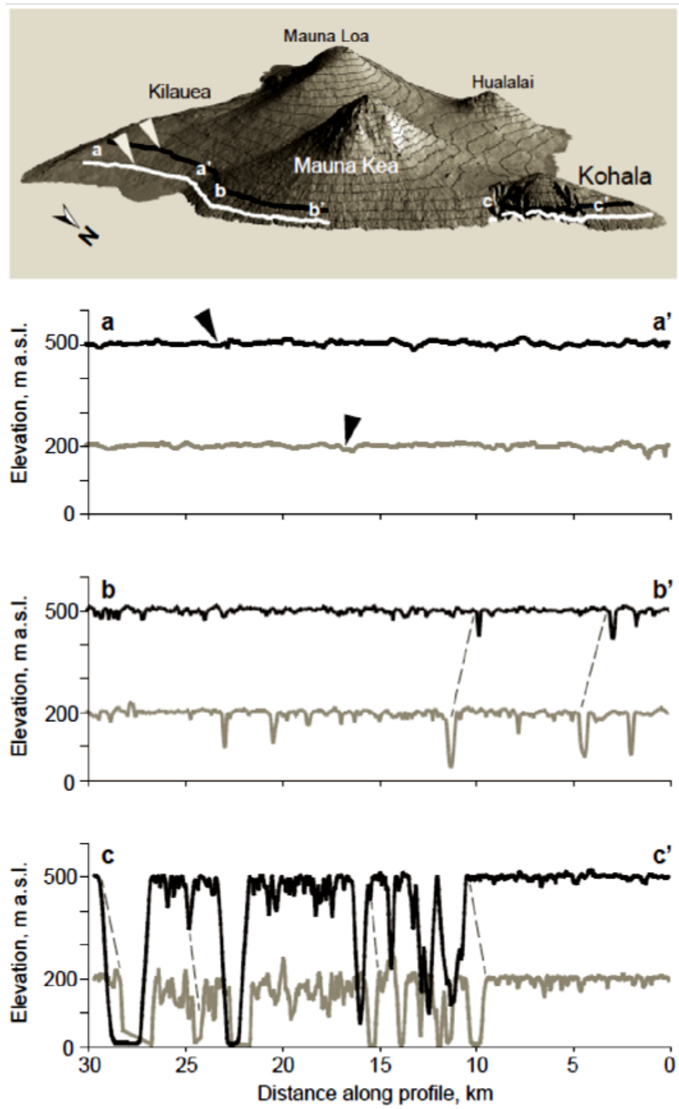


**Figure 4:** Profiles through inferred paleo-contours at present-day 500 and 200 m a.s.l. illustrate the difference in the degree of erosion in the three study regions on the island of Hawai'i. The top panel shows a shaded relief map of the island of Hawai'i with 250-m contour intervals. The lines on the shaded relief map in the top panel show the approximate location of the present-day 500 (black) and 200 m a.s.l. (white) contours. We extracted topographic profiles (a-a', b-b' and c-c') approximately parallel to the coast, along the somewhat continuous low-relief volcanic surface that has been locally incised by multiple streams. Due to the curvature of the volcanoes, streams do not always line up exactly in the contour profiles. For clarity, the gray dashed lines connect selected stream valleys. Kilauea Volcano is heavily impacted by tectonic gravitational landsliding on the seaward side. Reconstructing the original topography of the edifice in such regions is not straightforward and would furthermore target tectonic processes rather than erosion. The seaward flank of Kilauea was therefore omitted from the reconstruction. The same goes for Kaua'i, where the landscape is indeed heavily eroded but also affected by large-scale faulting and gravitational collapse (e.g. Holcomb et al., 1997; Reiners et al., 1999).

a-a') The Kilauea region is underlain in the south by lavas of Kilauea Volcano (<4 kyr) and in the north by lavas of Mauna Loa (<30 kyr, most surface lavas are <7 kyr). The white arrows in the overview map and the profile indicate the boundary between the two volcanoes. Erosion is very minor in this region.

b-b') The slopes of Mauna Kea (64-300 kyr) are significantly more incised than both Kilauea and Mauna Loa. Valleys reach a depth of ~100 m along the 500 m contour and nearly 150 m along the 200 m contour. Large areas between valleys are still little incised.

c-c') The deep valleys in the southern (left) part of the profile on Kohala are eroded into substrate of 260-500 kyr. In the northern (right) part of the profile, the substrate is of roughly the same age as in b), and the degree of erosion is very similar to the erosion in that profile.

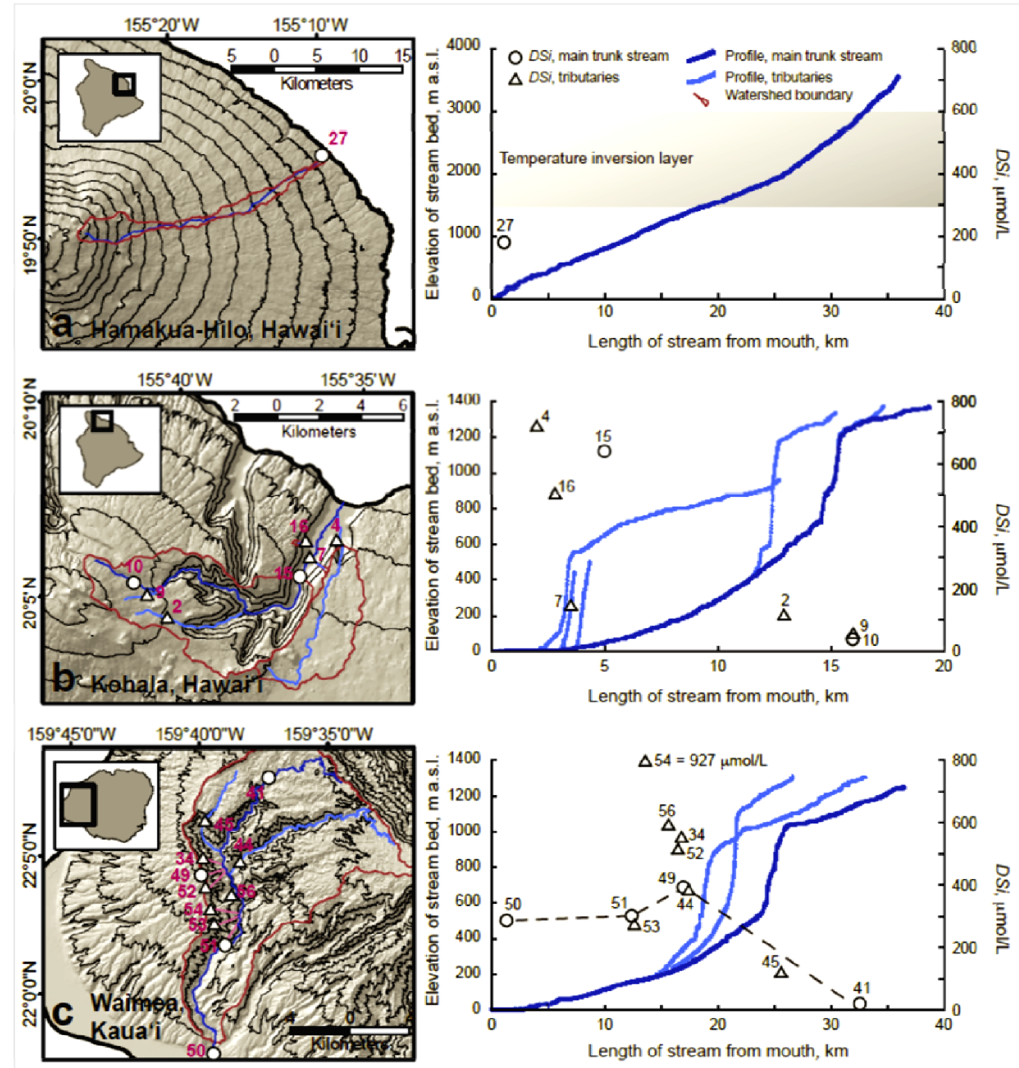


**Figure 5:** Stream profiles and *DSi* of stream samples. Note the double y-axis, with elevation in m a.s.l. on the left axis and *DSi* in µmol/L on the right axis.

a) Stream erosion along the Hamakua-Hilo coastline has not modified the original shield surface to any significant extent. The stream is defined in the DEM to near the summit of Mauna Kea at 4000 m a.s.l. However, the atmospheric inversion layer at between 1500-3000 m a.s.l. blocks stransport of moisture to high elevations, such that hardly any runoff is generated above 1500 m a.s.l.

b) In the Waipi'o Valley on Kohala Peninsula, erosion has formed a steep-sided valley with very steep headwalls leading up to a high plateau with a deeply weathered but little eroded surface, partly covered by a swamp. The *DSi* of the main trunk increases dramatically downstream.

c) The Waimea River originates in the Alaka'i Swamp and plunges into the Waimea Canyon. Numerous tributaries enter the Waimea River, both from the Alaka'i Swamp to the east of the canyon and along the west wall of the canyon. Just like in Waipi'o Valley, the *DSi* of the stream waters increases sharply once the river has entered the canyon. The dashed line connects samples taken along the main trunk of the stream and thus shows how the *DSi* of the main trunk changes along the length of the stream.

**Table 1**. Annual water budgets for the Hawaiian Islands

| Island | Age[1] (Myr) | *P* | *DR* | *Q*[2] | *AE* | *G* | *SGD*[2] | *SGD/Q* | *G/DR* | Area | Sources[3] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $10^6$ m$^3$/yr | | | | | | | | km$^2$ | |
| Kaua'i | 5.1 | 3761 | 1600 | 2111 | 1260 | 901 | 390 ± 137 | 0.18 | 0.56 | 1432 | a |
| O'ahu | 2.5-3 | 2733 | 424 | n.a. | 1214 | 1095 | n.a. | n.a. | 2.58 | 1542 | c |
| Moloka'i | 1.5 | 774 | 125 | n.a. | 385 | 264 | n.a. | n.a. | 2.11 | 675 | b |
| Maui | 1 | 4021 | 1110 | n.a. | 1395 | 1517 | n.a. | n.a. | 1.37 | 1888 | d, e |
| Island of Hawai'i, total | 0.45 | 18087 | 2045 | 2045 | 8343 | 7729 | 7729 ± 2705 | 3.78 | 3.78 | 10456 | f, g, h, i |

1: Representative ages of shield-building rocks. Sources: (McDougall, 1979) (Kaua'i); (McDougall, 1964) (O'ahu, Moloka'i and Maui); (McDougall and Swanson, 1972) (island of Hawai'i)
2: On Kaua'i, this value is calculated from kriged surface discharge. On the island of Hawai'i, $Q \approx DR$. Where no information on either *Q* or *SGD* exists (indicated with "n.a."), we report *G*/*DR* instead, in a separate column.
3: a, (Shade, 1995a); b, (Shade, 1997); c, (Shade and Nichols, 1996); d, (Shade, 1999); e, (Engott and Vana, 2007); f, (State of Hawaii, 1990); g, (Takasaki, 1993); h, (Shade, 1995b); i, (Waimea Water Services, Inc., 2004).

**Table 2**. Fluxes of *TAlk* and *DSi* via surface water and submarine groundwater discharge (Kaua'i, island of Hawai'i) and groundwater (other Hawaiian islands). See text for explanation of calculations. Errors given are ± 1 standard deviation.

| Region | *TAlk* | *DSi* | *SGD*[2] | Area | $F_{TAlk}$ | $F_{DSi}$ | $F_{TAlk}$ | $F_{DSi}$ | $R_{sub/sur}$, *TAlk* | $R_{sub/sur}$, *DSi* |
|---|---|---|---|---|---|---|---|---|---|---|
| | Groundwater[1] | | | | Groundwater | | Surface water | | | |
| | µmol/L, mean ± 1 s.e. | | $10^6$ $m^3$/yr | $km^2$ | $10^6$ mol/yr | | | | | |
| **Kaua'i** | 1913 ± 275 | 928 ± 79 | 390 ± 137 | 1437 | 510 ± 186 | 271 ± 96 | 965[3] ± 394 | 642[3] ± 244 | 0.5 ± 0.3[#] | 0.4 ± 0.1[#] |
| **Island of Hawai'i** | | | | | | | | | | |
| Hamakua-Hilo | | | 961 ± 336 | 910 | 1752 ± 638 | 929 ± 328 | 475 ±194 | 271 ± 103 | **1.4** ± 0.8[#] | **1.3** ± 0.5[#] |
| Kohala | | | 366 ± 128 | 706 | 667 ± 243 | 354 ± 125 | 143 ± 58 | 111 ± 42 | **1.5** ± 0.8[#] | 0.9 ± 0.3[#] |
| Kilauea[4] | 718 ± 159 | 697 ± 46 | 4901 ± 1715 | 3750 | 3519 ± 1281 | 3416 ± 1208 | 0 | 0 | | |
| Rest of island[4] | 1913 ± 275 | 928 ± 79 | 1501 ± 525 | 5090 | 2736 ± 996 | 1450 ±513 | 0 | 0 | | |
| Total | | | 7729 ± 2705 | 10456 | 8674 ± 3157 | 6149 ± 2174 | 618 ± 252 | 382 ± 145 | **14** ± 8[##] | **16** ± 6[##] |
| **Other islands** | | | | | | | | | | |
| O'ahu | | | 1095 | 1542 | 1996 | 1058 | n.a.[5] | n.a. | n.a. | n.a. |
| Moloka'i | | | 264 | 675 | 482 | 256 | n.a. | n.a. | n.a. | n.a. |
| Maui | | | 1517 | 1888 | 2764 | 1466 | n.a. | n.a. | n.a. | n.a. |

1: *SGD*-weighted average concentration of *TAlk* and *DSi*. Groundwater in the Kilauea region of the island of Hawai'i is significantly more dilute than groundwater elsewhere on the islands and we therefore calculate a separate *SGD*-weighted concentrations for that region. See Section 3.2 for further discussion.
2: *SGD* on Kaua'i and the island of Hawai'i, otherwise *G*.
3: Arithmetic average of area-normalized fluxes from studied watersheds multiplied by area of island.
4: Surface discharge is approximately zero for these regions (Schopka, 2011).
5: n.a. = data not available.
#: $R_{sub/sur}$ on Kaua'i and in individual regions on the island of Hawai'i is calculated using area-normalized subsurface fluxes ($F_{T,gw}/Area$) and the arithmetic average of area-normalized weathering fluxes from the streams in each region (see Table A1). See Section 3.3 for further discussion.
##: $R_{sub/sur}$ for the island of Hawai'i as a whole is calculated using total island-wide chemical fluxes via *SGD* and total surface weathering fluxes from the Hamakua-Hilo and Kohala regions. Since we did not sample all streams on the island, the resulting $R_{sub/sur}$ is a maximum value. See Section 3.3 for further discussion.

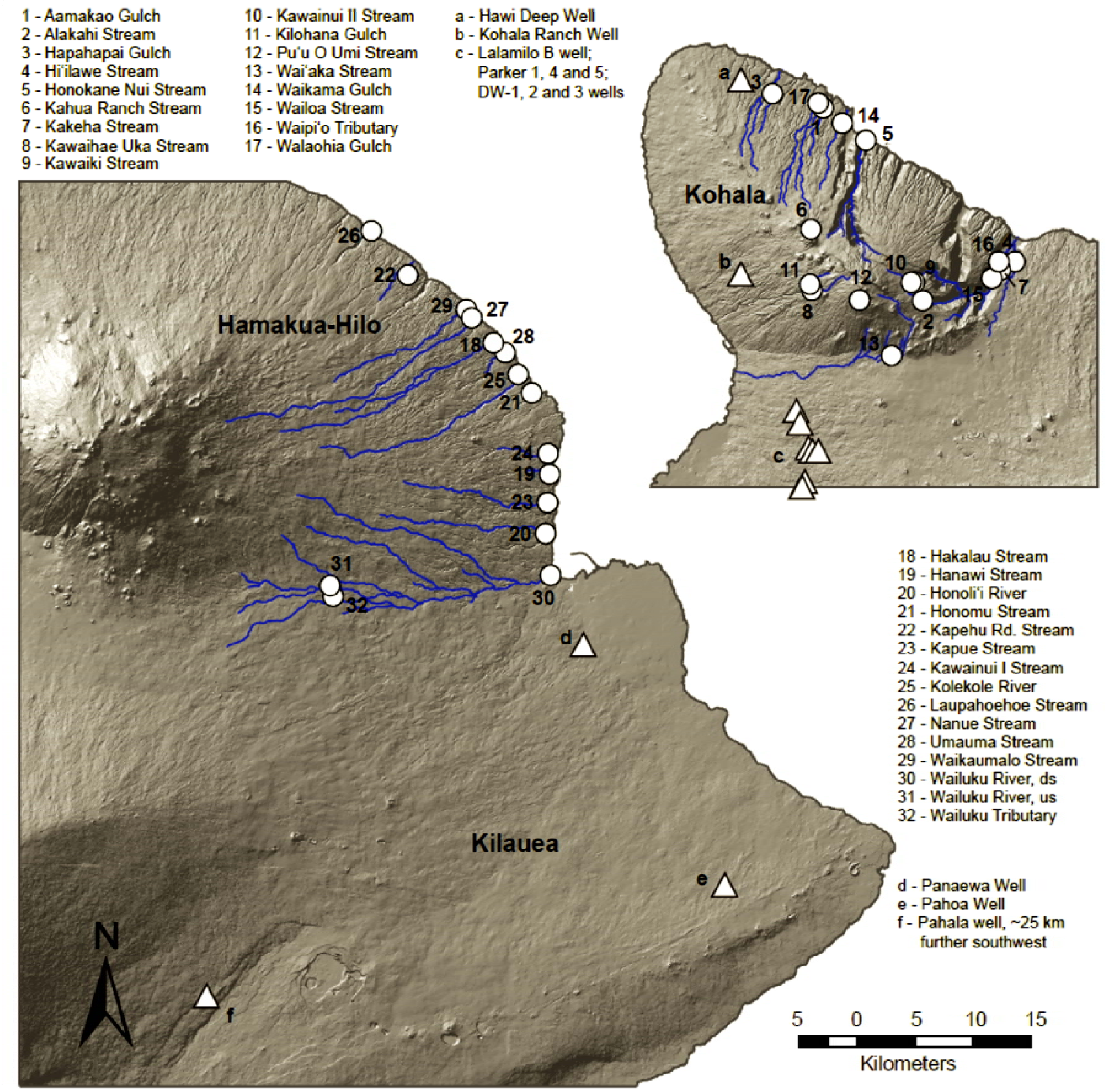


**Figure A.1:** Sample locations on the island of Hawai'i and names of regions used in the text. Circles denote stream sampling locations and triangles denote groundwater wells. Wells for which groundwater chemistry data was obtained in the USGS database are not shown. The channels of the streams we sampled are shown in blue. The base map is a shaded relief based on the USGS NED dataset with 10m resolution.

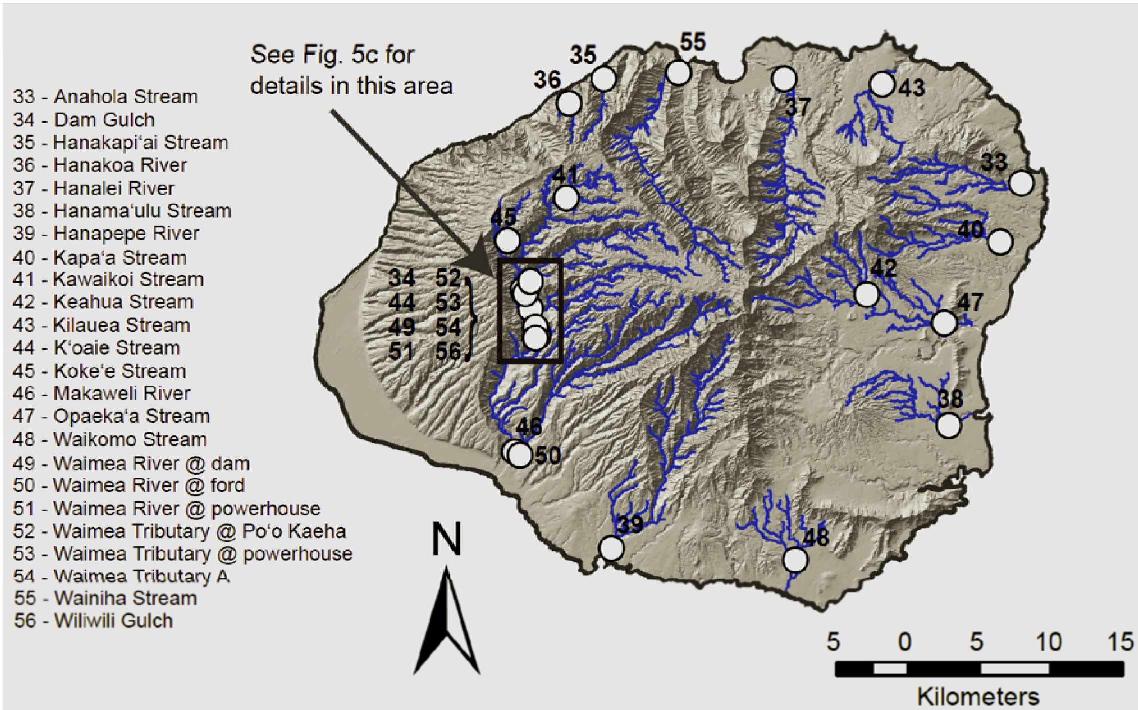


**Figure A.2:** Sample locations on Kaua'i. The channels of the streams we sampled are shown in blue. The base map is a shaded relief based on the USGS NED dataset with 10m resolution.

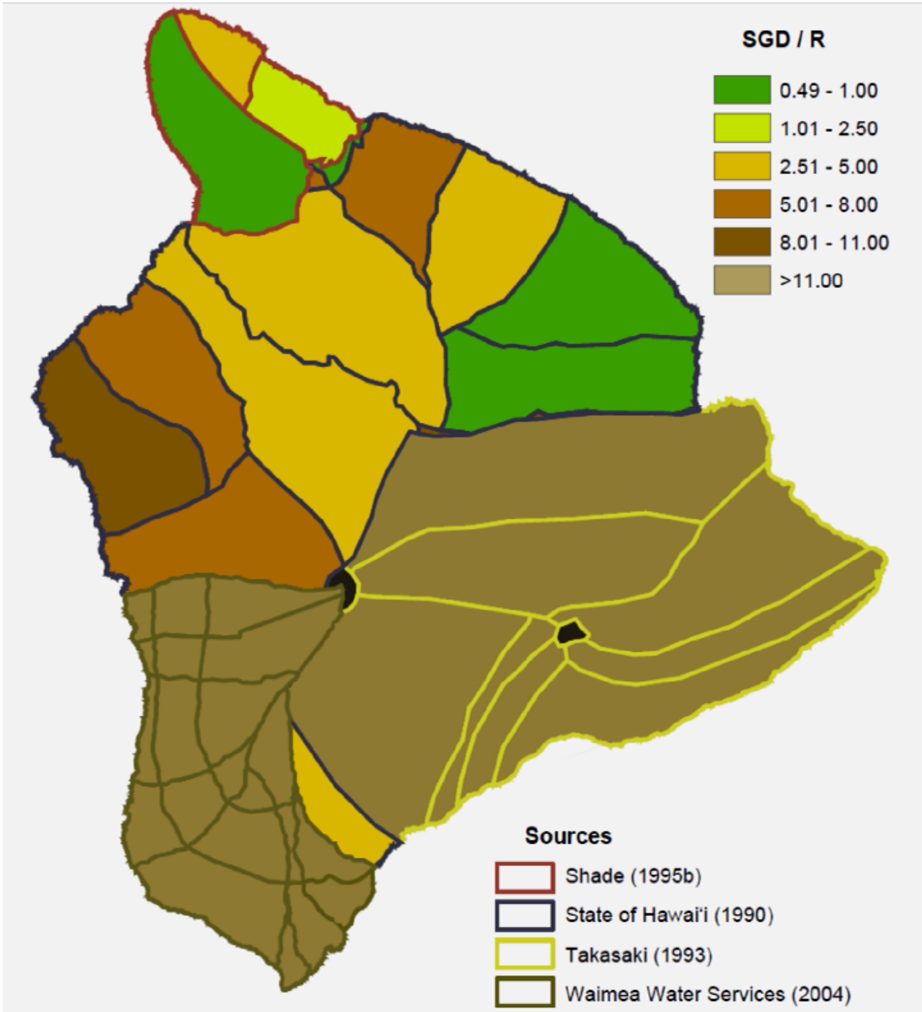


**Figure A.3:** *SGD*/*R* in individual aquifers on the island of Hawai'i (fill color of aquifer), and source of hydrological information for each aquifer (outline of aquifer). *R* exceeds *SGD* in three aquifers on the island; two in Hamakua-Hilo (where rainfall is the highest on the island and surface runoff therefore high in spite of the porous rocks) and one on Kohala, where rainfall is so scarce that hardly any groundwater recharge occurs.

Table A1. Concentrations and fluxes of alkalinity and dissolved silica in streams sampled for this study.

| River name | Area | Runoff | Sample ID | Date | Q | T | pH | Si | Alk (as $HCO_3^-$) | Si | Alk (as $HCO_3^-$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $km^2$ | mm/yr | | | $m^3$/sec | °C | | µmol/L | µeq/L | $10^6$ mol/$km^2$/yr | $10^6$ eq/$km^2$/yr |
| **Big Island** | | | | | | | | | | | |
| **Hamakua-Hilo** | | | | | | | | | | | |
| Hakalau Stream | | | HI-05-41 | 5/5/05 | n.a. | 25.0 | 7.73 | 297 | 593 | | |
| Hakalau Stream | | | HI-06-50 | 4/9/06 | n.a. | 19.5 | 8.06 | 129 | 278 | | |
| Hakalau Stream | | | HI-08-09 | 1/16/08 | n.a. | 18.6 | 7.49 | 276 | 484 | | |
| *Hakalau Stream* | 22.4 | 5236 | *3 samples* | | | *21.0* | *7.76* | *234* | *451* | 1.22 | 2.36 |
| Hanawi Stream | 10.8 | 5138 | HI-05-38 | 5/5/05 | n.a. | 23.4 | 8.07 | 280 | 558 | 1.44 | 2.87 |
| Honoli'i River | | | HI-05-36 | 5/5/05 | 0.4 | 23.4 | 7.78 | 271 | 682 | | |
| Honoli'i River | | | HI-06-16 | 3/19/06 | 39.6 | n.a. | 7.49 | 56 | 90 | | |
| Honoli'i River | | | HI-08-02 | 1/15/08 | 0.5 | 19.3 | 7.51 | 304 | 579 | | |
| *Honoli'i River* | 36.7 | 3172 | *3 samples* | | | *21* | *7.49* | *61* | *101* | 0.19 | 0.32 |
| Honomu Stream | | | HI-05-40 | 5/5/05 | n.a. | 22.4 | 7.91 | 349 | 776 | | |
| Honomu Stream | | | HI-06-07 | 3/17/06 | n.a. | 27.0 | 7.24 | 272 | 262 | | |
| *Honomu Stream* | 4.16 | 5801 | *2 samples* | | | *25* | *7.58* | *311* | *519* | 1.80 | 3.01 |
| Kapehu Rd. Stream | | | HI-06-52 | 4/9/06 | n.a. | 20.3 | 7.57 | 522 | 1175 | | |
| Kapehu Rd. Stream | | | HI-08-06 | 1/16/08 | n.a. | 20.3 | 7.19 | 556 | 1160 | | |
| *Kapehu Rd. Stream* | 1.98 | 2615 | *2 samples* | | | *20* | *7.38* | *539* | *1168* | 1.41 | 3.05 |
| Kapue Stream | | | HI-05-37 | 5/5/05 | n.a. | 23.5 | 8.05 | 234 | 543 | | |
| Kapue Stream | | | HI-06-51 | 4/9/06 | n.a. | 20.3 | 7.57 | 108 | 226 | | |
| Kapue Stream | | | HI-08-03 | 1/15/08 | n.a. | 19.2 | 7.5 | 251 | 473 | | |
| *Kapue Stream* | 24.3 | 3331 | *3 samples* | | | *21* | *7.71* | *198* | *414* | 0.66 | 1.38 |
| Kawainui I Stream | | | HI-05-39 | 5/5/05 | n.a. | 24.8 | 7.95 | 233 | 387 | | |
| Kawainui I Stream | | | HI-06-14 | 3/19/06 | n.a. | 19.2 | 6.82 | 44 | 85 | | |
| Kawainui I Stream | | | HI-08-04 | 1/15/08 | n.a. | 19.1 | 7.37 | 237 | 358 | | |
| *Kawainui I Stream* | 21.9 | 4953 | *3 samples* | | | *21* | *7.38* | *172* | *277* | 0.85 | 1.37 |
| Kolekole River | | | HI-05-01 | 3/30/05 | n.a. | 20.1 | 6.6 | 57 | -96 | | |
| Kolekole River | | | HI-05-35 | 5/4/05 | n.a. | 24.1 | 7.43 | 271 | 562 | | |
| Kolekole River | | | HI-06-13 | 3/19/06 | n.a. | 18.9 | 6.86 | 55 | 70 | | |

Table A1. (continued)

| River name | Area | Runoff | Sample ID | Date | Q | T | pH | Si | Alk (as $HCO_3^-$) | Si | Alk (as $HCO_3^-$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $km^2$ | mm/yr | | | $m^3$/sec | °C | | µmol/L | µeq/L | $10^6$ mol/$km^2$/yr | $10^6$ eq/$km^2$/yr |
| Kolekole River | | | HI-08-05 | 1/15/08 | n.a. | 18.4 | 7.46 | 280 | 537 | | |
| *Kolekole River* | 53.8 | 3104 | *4 samples* | | | *20* | *7.09* | *166* | *268* | 0.51 | 0.83 |
| Laupahoehoe Stream | 12.2 | 1449 | HI-06-11 | 3/19/06 | n.a. | 19.8 | 7.25 | 88 | 239 | 0.13 | 0.35 |
| Nanue Stream | | | HI-05-43 | 5/5/05 | n.a. | 24.1 | 7.4 | 270 | 523 | | |
| Nanue Stream | | | HI-06-12 | 3/19/06 | n.a. | 18.6 | 6.59 | 37 | 117 | | |
| Nanue Stream | | | HI-08-08 | 1/16/08 | n.a. | 17.9 | 7.47 | 278 | 472 | | |
| *Nanue Stream* | 37.5 | 1793 | *3 samples* | | | *20.2* | *7.15* | *195* | *371* | 0.35 | 0.66 |
| Umauma Stream | | | HI-05-42 | 5/5/05 | n.a. | 25.5 | 8.26 | 280 | 606 | | |
| Umauma Stream | | | HI-06-06 | 3/17/06 | n.a. | 26.0 | 7.52 | 161 | 159 | | |
| Umauma Stream | | | HI-08-10 | 1/16/08 | n.a. | 19.3 | 7.78 | 285 | 529 | | |
| *Umauma Stream* | 54.2 | 2458 | *3 samples* | | | *23.6* | *7.85* | *242* | *431* | 0.60 | 1.06 |
| Waikaumalo Stream | | | HI-05-44 | 5/5/05 | n.a. | 23.6 | 7.06 | 339 | 617 | | |
| Waikaumalo Stream | | | HI-06-05 | 3/17/06 | n.a. | 26.5 | 7.07 | 209 | 168 | | |
| Waikaumalo Stream | | | HI-08-07 | 1/16/08 | n.a. | 18.3 | 7.51 | 347 | 529 | | |
| *Waikaumalo Stream* | 35.5 | 2373 | *3 samples* | | | *22.8* | *7.21* | *298* | *438* | 0.71 | 1.04 |
| Wailuku River, ds | | | HI-05-02 | 3/30/05 | n.a. | 19.9 | 7.2 | 75 | 196 | | |
| Wailuku River, ds | | | HI-05-33 | 5/4/05 | n.a. | 22.9 | 7.99 | 252 | 457 | | |
| Wailuku River, ds | | | HI-06-15 | 3/19/06 | n.a. | n.a. | 6.79 | 64 | 56 | | |
| Wailuku River, ds | | | HI-08-01 | 1/15/08 | n.a. | 20.2 | 7.7 | 301 | 468 | | |
| *Wailuku River, ds* | 638 | 688 | *4 samples* | | | *21.0* | *7.42* | *173* | *294* | 0.12 | 0.20 |
| Wailuku River, us | 343 | 79 | HI-06-47 | 4/6/06 | n.a. | 15.7 | 7.65 | 135 | 182 | 0.01 | 0.01 |
| Wailuku Tributary | 24.3 | 79 | HI-06-46 | 4/6/06 | n.a. | 17.0 | 7.74 | 178 | 219 | 0.01 | 0.02 |
| **Kohala** | | | | | | | | | | | |
| Aamakao Gulch | | | HI-05-23 | 4/28/05 | n.a. | 22.3 | 7.89 | 331 | 381 | | |
| Aamakao Gulch | | | HI-06-04 | 3/16/06 | n.a. | 28.0 | 7.75 | 283 | 369 | | |
| Aamakao Gulch | | | HI-08-23 | 1/21/08 | n.a. | 19.5 | 7.31 | 327 | 485 | | |
| *Aamakao Gulch* | 12.5 | 1535 | *3 samples* | | | *23.3* | *7.65* | *314* | *412* | 0.48 | 0.63 |
| Alakahi Stream | 2.17 | 3292 | HI-08-11 | 1/17/08 | 0.01 | 14.4 | 6.06 | 106 | 115 | 0.35 | 0.38 |

Table A1. (continued)

| River name | Area | Runoff | Sample ID | Date | Q | T | pH | Si | Alk (as $HCO_3^-$) | Si | Alk (as $HCO_3^-$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $km^2$ | mm/yr | | | $m^3$/sec | °C | | μmol/L | μeq/L | $10^6$ mol/$km^2$/yr | $10^6$ eq/$km^2$/yr |
| Hapahapai Gulch | 3.86 | 651 | HI-05-24 | 4/28/05 | n.a. | 23.1 | 7.87 | 402 | 563 | 0.26 | 0.37 |
| Hi'ilawe Stream | | | HI-06-42 | 4/1/06 | n.a. | n.a. | 7.54 | 718 | 975 | | |
| Hi'ilawe Stream | | | HI-08-15 | 1/18/08 | n.a. | 20.6 | 8.16 | 771 | 925 | | |
| *Hi'ilawe Stream* | 16.2 | 1661 | *2 samples* | | | *20.6* | *7.85* | *744* | *950* | 1.24 | 1.58 |
| Honokane Nui Stream | 26.1 | 2316 | HI-08-21 | 1/20/08 | n.a. | 20.0 | 7.49 | 572 | 705 | 1.32 | 1.63 |
| Kahua Ranch stream | 0.37 | 1969 | HI-05-03 | 4/8/05 | n.a. | n.a. | 7.00 | 145 | 143 | 0.29 | 0.28 |
| Kakeha Stream | 0.07 | 1826 | HI-08-16 | 1/18/08 | n.a. | 19.3 | 6.48 | 142 | 132 | 0.26 | 0.24 |
| Kawaihae Uka Stream | | | HI-06-01 | 3/16/06 | n.a. | 23.5 | 6.68 | 16 | 35 | | |
| Kawaihae Uka Stream | | | HI-08-24 | 1/21/08 | n.a. | 15.7 | 5.11 | 54 | -3 | | |
| *Kawaihae Uka Stream* | 4.57 | 2853 | *2 samples* | | | *20* | *5.90* | *35* | *16* | 0.10 | 0.05 |
| Kawaiki Stream | 1.24 | 2688 | HI-08-13 | 1/17/08 | n.a. | 13.2 | 5.32 | 48 | 0 | 0.13 | 0.00 |
| Kawainui II Stream | 3.99 | 3403 | HI-08-14 | 1/17/08 | 0.05 | 13.0 | 4.79 | 49 | 0 | 0.17 | 0.00 |
| Kilohana Gulch | | | HI-05-05 | 4/11/05 | n.a. | n.a. | 7 | 67 | 17 | | |
| Kilohana Gulch | | | HI-06-02 | 3/16/06 | n.a. | 24.5 | 6.52 | 61 | 69 | | |
| *Kilohana Gulch* | 2.30 | 3128 | *2 samples* | | | *25* | *6.76* | *64* | *43* | 0.20 | 0.13 |
| Pu'u O Umi Stream | 0.15 | 2535 | HI-06-49 | 4/7/06 | n.a. | 12.5 | 4.53 | 24 | 55 | 0.06 | 0.14 |
| Wai'aka Stream | | | HI-05-04 | 4/11/05 | n.a. | n.a. | 7 | 62 | 21 | | |
| Wai'aka Stream | | | HI-05-28 | 5/2/05 | n.a. | 23.7 | 6.45 | 107 | 140 | | |
| Wai'aka Stream | | | HI-06-40 | 3/28/06 | n.a. | n.a. | 6.49 | 68 | 110 | | |
| Wai'aka Stream | | | HI-06-41 | 3/28/06 | n.a. | 21.2 | 6.51 | 72 | 116 | | |
| Wai'aka Stream | | | HI-06-45 | 4/5/06 | n.a. | 20.0 | 6.4 | 86 | 163 | | |
| Wai'aka Stream | | | HI-08-19 | 1/19/08 | n.a. | 15.4 | 6.08 | 108 | 48 | | |
| Wai'aka Stream | | | HI-08-20 | 1/19/08 | n.a. | 19.1 | 5.86 | 107 | 44 | | |
| *Wai'aka Stream* | 1.95 | 4580 | *7 samples* | | | *19.9* | *6.40* | *87* | *92* | 0.40 | 0.42 |
| Waikama Gulch | 6.65 | 1695 | HI-08-22 | 1/21/08 | n.a. | 19.0 | 7.20 | 318 | 239 | 0.54 | 0.41 |
| Wailoa Stream | | | HI-06-43 | 4/2/06 | n.a. | n.a. | 7.96 | 641 | 970 | | |
| Wailoa Stream | | | HI-08-17 | 1/18/08 | n.a. | 20.5 | 8.09 | 575 | 724 | | |
| *Wailoa Stream* | 37.4 | 1781 | *2 samples* | | | *20.5* | *8.03* | *608* | *847* | 1.08 | 1.51 |

Table A1. (continued)

| River name | Area | Runoff | Sample ID | Date | Q | T | pH | Si | Alk (as $HCO_3^-$) | Si | Alk (as $HCO_3^-$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $km^2$ | mm/yr | | | $m^3$/sec | °C | | μmol/L | μeq/L | $10^6$ mol/$km^2$/yr | $10^6$ eq/$km^2$/yr |
| Waipi'o Tributary | 0.07 | 2007 | HI-08-18 | 1/18/08 | n.a. | 20.3 | 7.78 | 508 | 698 | 1.02 | 1.40 |
| Walaohia Gulch | 12.4 | 1094 | HI-06-03 | 3/16/06 | n.a. | 27.0 | 7.35 | 281 | 370 | 0.31 | 0.40 |
| **Kaua'i** | | | | | | | | | | | |
| Anahola Stream | 23.9 | 1438 | HI-06-23 | 3/22/06 | n.a. | n.a. | 7.11 | 157 | 164 | 0.23 | 0.24 |
| Dam Gulch | 0.10 | 417 | HI-06-33 | 3/25/06 | n.a. | n.a. | 7.66 | 554 | 390 | 0.23 | 0.16 |
| Hanakapi'ai Stream | | | TA-2 | 1/1/01 | n.a. | 19.0 | | 401 | 629 | | |
| Hanakapi'ai Stream | | | HI-05-21 | 4/24/05 | n.a. | 18.4 | 7.93 | 381 | 696 | | |
| Hanakapi'ai Stream | | | HI-06-19 | 3/21/06 | n.a. | 23.0 | 7.18 | 321 | 322 | | |
| *Hanakapi'ai Stream* | 9.55 | 1597 | *3 samples* | | | *20.1* | *7.56* | *368* | *549* | 0.59 | 0.88 |
| Hanakoa River | 4.38 | 1142 | HI-05-20 | 4/24/05 | n.a. | 18.4 | 7.50 | 392 | 620 | 0.45 | 0.71 |
| Hanalei River | | | HI-05-19 | 4/22/05 | 3.3 | 23.8 | 7.56 | 243 | 816 | | |
| Hanalei River | | | HI-06-21 | 3/22/06 | 11.4 | n.a. | 7.07 | 198 | 264 | | |
| *Hanalei River* | 54.3 | 3455 | *2 samples* | | | *23.8* | *7.18* | *208* | *387* | 0.72 | 1.34 |
| Hanama'ulu Stream | | | HI-05-17 | 4/22/05 | n.a. | 23.5 | 7.56 | 225 | 670 | | |
| Hanama'ulu Stream | | | HI-06-25 | 3/22/06 | n.a. | n.a. | 7.23 | 139 | 196 | | |
| *Hanama'ulu Stream* | 25.6 | 1348 | *2 samples* | | | *23.5* | *7.40* | *182* | *433* | 0.25 | 0.58 |
| Hanapepe River | 69.2 | 1575 | HI-06-27 | 3/23/06 | n.a. | 21.4 | 7.34 | 262 | 448 | 0.41 | 0.70 |
| Kapa'a Stream | 36.2 | 1634 | HI-06-18 | 3/20/06 | n.a. | 22.0 | 7.09 | 193 | 293 | 0.32 | 0.48 |
| Kawaikoi Stream | | | HI-06-39 | 3/26/06 | 3.3 | n.a. | 6.5 | 19 | 74 | | |
| Kawaikoi Stream | | | TA-5 | 1/2/01 | 0.4 | 15.0 | | 35 | 41 | | |
| *Kawaikoi Stream* | 10.6 | 2795 | *2 samples* | | *3.31* | *15* | *5.81* | *21* | *71* | 0.06 | 0.20 |
| Keahua Stream | 9.25 | 3046 | HI-06-17 | 3/20/06 | n.a. | 21.3 | 7.35 | 214 | 206 | 0.65 | 0.63 |
| Kilauea Stream | 23.0 | 2956 | HI-06-22 | 3/22/06 | n.a. | n.a. | 7.21 | 142 | 158 | 0.42 | 0.47 |
| Koai'e Stream | 29.3 | 2094 | HI-05-07 | 4/20/05 | n.a. | 22.3 | 8.44 | 381 | 612 | 0.80 | 1.28 |
| Koke'e Stream | | | TA-4 | 1/2/01 | n.a. | 16.0 | | 276 | 409 | | |
| Koke'e Stream | | | HI-05-10 | 4/21/05 | n.a. | 18.6 | 7.09 | 149 | 197 | | |

Table A1. (continued)

| River name | Area | Runoff | Sample ID | Date | Q | T | pH | Si | Alk (as $HCO_3^-$) | Si | Alk (as $HCO_3^-$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $km^2$ | mm/yr | | | $m^3$/sec | °C | | µmol/L | µeq/L | $10^6$ mol/$km^2$/yr | $10^6$ eq/$km^2$/yr |
| Koke'e Stream | | | HI-06-38 | 3/26/06 | n.a. | n.a. | 0 | 85 | 301 | | |
| *Koke'e Stream* | 4.91 | 1376 | *3 samples* | | | *17* | *3.55* | *170* | *302* | 0.23 | 0.42 |
| Makaweli River | | | HI-05-14 | 4/21/05 | n.a. | 25.2 | 7.73 | 406 | 1151 | | |
| Makaweli River | | | HI-06-30 | 3/24/06 | n.a. | n.a. | 7.61 | 356 | 537 | | |
| *Makaweli River* | 68.7 | 2166 | *2 samples* | | | *25.2* | *7.67* | *381* | *844* | 0.83 | 1.83 |
| Opaeka'a Stream | 13.3 | 1687 | HI-06-26 | 3/23/06 | n.a. | 21.9 | 6.95 | 121 | 150 | 0.20 | 0.25 |
| Waikomo Stream | 11.5 | 138 | HI-06-29 | 3/23/06 | n.a. | 23.4 | 6.91 | 118 | 143 | 0.02 | 0.02 |
| Waimea River @ dam | | | HI-05-06 | 4/20/05 | n.a. | 22.3 | 8.81 | 461 | 739 | | |
| Waimea River @ dam | | | HI-06-32 | 3/25/06 | n.a. | n.a. | 7.13 | 321 | 257 | | |
| *Waimea River @ dam* | 52.7 | 906 | *2 samples* | | | *22.3* | *7.97* | *391* | *498* | 0.35 | 0.45 |
| Waimea River @ ford | | | HI-05-12 | 4/21/05 | n.a. | 24.6 | 8.23 | 307 | 900 | | |
| Waimea River @ ford | | | HI-06-28 | 3/23/06 | n.a. | 21.9 | 7.07 | 265 | 215 | | |
| *Waimea River @ ford* | 151 | 647 | *2 samples* | | | *23.3* | *7.65* | *286* | *558* | 0.19 | 0.36 |
| Waimea River @ powerhouse | | | HI-05-08 | 4/20/05 | n.a. | 24.1 | 8.76 | 322 | 646 | | |
| Waimea River @ powerhouse | | | HI-06-35 | 3/25/06 | n.a. | n.a. | 7.38 | 280 | 268 | | |
| *Waimea River @ powerhouse* | 113 | 614 | *2 samples* | | | *24.1* | *8.07* | *301* | *457* | 0.18 | 0.28 |
| Waimea Tributary @ Po'o Kaeha | 0.45 | 1278 | HI-06-34 | 3/25/06 | n.a. | n.a. | 7.00 | 517 | 296 | 0.66 | 0.38 |
| Waimea Tributary @ powerhouse | 1.01 | 378 | HI-06-36 | 3/25/06 | n.a. | n.a. | 7.48 | 276 | 250 | 0.10 | 0.09 |
| Waimea Tributary A | | | HI-05-09 | 4/20/05 | n.a. | 21.3 | 7.77 | 1053 | 2422 | | |
| Waimea Tributary A | | | HI-06-37 | 3/25/06 | n.a. | n.a. | 7.87 | 801 | 1721 | | |
| *Waimea Tributary A* | 0.23 | 499 | *2 samples* | | | *21.3* | *7.82* | *927* | *2071* | 0.46 | 1.03 |
| Wainiha Stream | 58.3 | 3641 | HI-06-20 | 3/21/06 | n.a. | n.a. | 7.16 | 330 | 313 | 1.20 | 1.14 |
| Wiliwili Gulch | 2.66 | 408 | HI-06-31 | 3/25/06 | n.a. | n.a. | 7.81 | 593 | 499 | 0.24 | 0.20 |

Table A2. Chemical composition of groundwater wells on the Hawaiian Islands used in this study.

| Well name | Island | USGS Site # | Sample ID | Date | T | pH | Si | Alk |
|---|---|---|---|---|---|---|---|---|
| | | | | | °C | | µmol/L | µeq/L |
| Hawi deep well 1 | Island of Hawai‘i | n.a. | HI-05-27 | 05/2005 | 28.5 | 8.04 | 796 | 1421 |
| Lalamilo well B | Island of Hawai‘i | n.a. | HI-05-25 | 05/2005 | 26.3 | 8.07 | 1001 | 1854 |
| Parker well 1 | Island of Hawai‘i | n.a. | HI-05-26 | 05/2005 | 26.6 | 8.08 | 993 | 1970 |
| Kohala Ranch Well 1 | Island of Hawai‘i | n.a. | HI-05-29 | 05/2005 | 21.4 | 7.86 | 916 | 1275 |
| Pahoa 1 | Island of Hawai‘i | n.a. | HI-06-58 | 04/2006 | 24.1 | 7.76 | 837 | 859 |
| Panaewa 1 | Island of Hawai‘i | n.a. | HI-06-57 | 04/2006 | 21.0 | 7.51 | 612 | 639 |
| Pahala Well | Island of Hawai‘i | n.a. | HI-06-59 | 04/2006 | 20.2 | 8.13 | 678 | 659 |
| DW-2 | Island of Hawai‘i | n.a. | HI-05-47 | 05/2005 | 29 | 7.90 | 1016 | 2105 |
| DW-3 | Island of Hawai‘i | n.a. | HI-05-48 | 05/2005 | 28.7 | 7.99 | 935 | 2361 |
| Parker 4 | Island of Hawai‘i | n.a. | HI-05-49 | 05/2005 | 27 | 7.65 | 1028 | 1974 |
| DW-1 | Island of Hawai‘i | n.a. | HI-05-50 | 05/2005 | 27.1 | 7.50 | 1010 | 1998 |
| Parker 5 | Island of Hawai‘i | n.a. | HI-05-51 | 05/2005 | 27.2 | 7.50 | 1022 | 2023 |
| 2-5921-01 Kalepa Ridge W-10 | Kauai | 215958159214301 | USGS | | n.a. | 7.68 | 1079 | 2762 |
| 6-5130-02 Waikapu 2 | Maui | 205154156303801 | USGS | | n.a. | 8.10 | 566 | 3868 |
| 6-5430-05 Waiehu Deep Monitor Well* | Maui | 205405156305401 | USGS | | n.a. | 8.20 | 658 | 1449 |
| 3-2300-18 Waipahu Deep Monitor Well** | Oahu | 212340158001901 | USGS | | n.a. | 7.20 | 891 | 1393 |
| 3-2901-07 Schofield Shaft | Oahu | 212927158014801 | USGS | | n.a. | 6.90 | 1049 | 1049 |

n.a. = Data not available
* = Average of two samples, least contaminated by sea water (sea water intrudes the aquifer at high tide)
** = One of two available samples, the other one is contaminated by sea water