Controls on the $\delta^{13}C_{\text{DIC}}$ and alkalinity budget of a flashy subtropical stream (Manoa River, Hawaii)

Benjamin Hagedorn $^{a, *}$, Aly I. El-Kadi $^{b, c}$, Robert B. Whittier $^{d}$

$^{a}$ Department of Geological Sciences, California State University, Long Beach, CA 90840, USA
$^{b}$ Department of Geology and Geophysics, School of Ocean and Earth Sciences and Technology, University of Hawaii at Manoa, Honolulu, HI 96822, USA
$^{c}$ Water Resources Research Center, University of Hawaii at Manoa, Honolulu, HI 96822, USA
$^{d}$ State of Hawaii, Department of Health, Honolulu, HI 96822, USA

A R T I C L E   I N F O

Article history:
Received 29 March 2016
Received in revised form 13 July 2016
Accepted 19 July 2016
Available online 20 July 2016

Keywords:
DIC
Hawaii
Streamflow
Carbon isotope
Volcanic island
Urban land cover

A B S T R A C T

Hawaiian streams are flashy in nature because watersheds are small and steep and receive intense and unevenly distributed rainfall. As a result, stream chemistry is characterized by considerable spatiotemporal variability. To examine how rainfall and streamflow affect the solute content of the Manoa River in Hawaii, time-series geochemical data collected during 17 sampling campaigns in spring-fall of 2010 were evaluated in a coupled $\delta^{13}C_{\text{DIC}}$/major ion inversion model. Spatially, the stream is characterized by a distinct shift from a low HCO$_3^-$ (43 mg/L), low pCO$_2$ (3760 ppmv) and heavy $\delta^{13}C_{\text{DIC}}$ ($-6.5\%$) fingerprint in the upper reaches to a high HCO$_3^-$ (91 mg/L), high pCO$_2$ (8961 ppmv) and light $\delta^{13}C_{\text{DIC}}$ ($-11.7\%$) signature in the lowlands. These trends are attributed to (1) progressive weathering of exposed aluminosilicates, and (2) downstream enrichment in CO$_2$ from organic matter decay in the soil zone. Solute (i.e., nitrate) yields from nitric acid weathering are generally low (<1% of TDS), even in the developed lowlands, where runoff of nitrate-enriched urban effluent has historically been documented. Data furthermore indicate a significant positive correlation between $\delta^{13}C_{\text{DIC}}$ and rainfall rates in the mid-stream section of the river which is consistent with an atmospheric CO$_2$ dilution effect during high rainfall events. This dilution effect needs to be accounted for to reliably describe the role of volcanic island river systems in global assessments of silicate weathering and CO$_2$ degassing.

1. Introduction

Current trends in climate change and their potential impacts on resource sustainability have sparked numerous efforts to understand the natural carbon cycle, and to discern how it may shift under scenarios of climate and land use change (Regnier et al., 2013; Reichstein et al., 2013). Rivers play a crucial role in the carbon cycle because they act as both sources and sinks of atmospheric CO$_2$. Chemical weathering of carbonate and silicate minerals by H$_2$CO$_3$ and the subsequent transport of HCO$_3^-$ to the oceans consumes atmospheric CO$_2$ on time-scales of greater than 10$^3$ years (Berner et al., 1983; Garrels and Mackenzie, 1974). Decay of organic matter, in turn, can cause a release of CO$_2$ to the atmosphere (CO$_2$ degassing) if river water pCO$_2$ levels exceed that of the surrounding atmosphere (Cole and Caraco, 2001). Unlike the CO$_2$ consumption by chemical weathering, CO$_2$ degassing acts on current environmental time scales of hours to days and global estimates derived upon data of the world’s largest watersheds suggest that CO$_2$ degassing (1.8 × 10$^{15}$ gC/yr) (Raymond et al., 2013) largely exceeds CO$_2$ consumption by combined silicate and carbonate weathering (2.4 × 10$^{14}$ gC/yr) (Hartmann et al., 2009).

Despite these global scale assessments, there is an ongoing debate on how CO$_2$ consumption and degassing may respond to spatial and temporal changes in hydrologic variables (i.e., rainfall and runoff). Several studies argued that increased runoff, such as during floods, favors CO$_2$ consumption and CO$_2$ degassing because it increases the intensity of weathering (Gaillardet et al., 1999; Hartmann et al., 2009), and because of the soil CO$_2$ input to streams from enhanced net primary production in wet soils (Bianchi et al., 2013; Butman and Raymond, 2011). Others however, noted more complex relationships and non-linear correlations between weathering fluxes and runoff (Gaillardet et al., 1999; Moosdorf et al., 2011) which indicates that cationic load dilution can become important when flow rates are high. Furthermore, 

* Corresponding author. Tel.: +1 562 985 4198.
E-mail address: Klaus.Hagedorn@csulb.edu (B. Hagedorn).
et al. (2007) and Hagedorn and Cartwright (2010) observed a shift towards reduced CO2 degassing during high flow events due to atmospheric dilution, particularly in areas with thin soils and along losing stream segments where the inflow of groundwater (i.e., baseflow) is insignificant. The fact that river water pCO2 patterns generally exhibit no significant correlations with streamflow (e.g., Abril et al., 2000; Neal et al., 1998; Teodoro et al., 2009, etc.) highlights the complex hydrologic controls on stream CO2 dynamics.

One aspect that has received little attention in riverine carbon cycling studies and that may help further assessing the roles of hydrologic variables on stream CO2 patterns is the role of the acid source on the river alkalinity budget (Galy and France-Lanord, 1999; Spence and Telmer, 2005). In general, hydration of atmospheric or soil-derived CO2 will generate H2CO3 that will dissociate via carbonate and silicate weathering to generate HCO3 with distinct δ13C fingerprints (Telmer and Veizer, 1999).

One processes that can alter these fingerprints is carbonate weathering by other acids, such as sulfuric acid from oxidation of accessory sulfides (Galy and France-Lanord, 1999; Ryu and Jacobsen, 2012) and acid mine drainage (Fonyuy and Atekwana, 2008), or nitric acid from nitrification of leaf litter (Berthelin et al., 1985) or anthropogenic ammonium (Barnes and Raymond, 2009; Brunet et al., 2011; Perrier et al., 2008). In addition, in-situ processes such as photosynthesis, respiration, methanogenesis, rapid CO2 degassing and/or atmospheric equilibration can also impact the stream HCO3 and δ13C signatures (Amiotte-Suchet et al., 1999; Barth et al., 1998; Brunet et al., 2006; Doctor et al., 2008; Polsenaere and Abril, 2012; van Geldern et al., 2015; Venkiteswaran et al., 2014). Only in settings where the relative importance of each of these particular processes is well constrained is it possible to trace the different CO2 sources (i.e., biologic vs. atmospheric), which, in turn, allows evaluating whether atmospheric dilution is occurring or not.

In this study, we present time-series geochemical data to trace CO2 sources in a river system of Hawaii. Hawaiian watersheds serve as valuable proxies for carbon cycling processes in tropical volcanic island settings as they are characterized by a warm and humid climate and thick and productive soils that generate high amounts of CO2 (Chimner, 2004; Raich, 1998). In addition, the erodible lithologies of such settings have yielded among the highest weathering yields recorded (Goldsmith et al., 2010). Accordingly, Hawaiian streams rank high globally in CO2 consumption and CO2 degassing rates (Hartmann et al., 2009; Raymond et al., 2013). What makes Hawaiian watersheds unique, however, is their steep topographic gradient and their remarkable variability in rainfall, streamflow and land cover (Giambelluca et al., 2013; Lau and Mink, 2006) which has been shown to cause pronounced temporal variability in geochemical parameters (pH, Electrical Conductivity) (Augustijn et al., 2011; Tomlinson and De Carlo, 2003). Using a coupled δ13C/δ15N major ion inversion model based on time-series data obtained during 17 sampling campaigns in 2010, we trace the various acids (carbonic biologic vs. carbonic atmospheric vs. sulfuric vs. nitric) that can generate stream alkalinity and evaluate how the system shifts in response to short-term changes in hydrology.

2. Local physiographic setting

The Manoa Watershed (13.1 km²) comprises a deeply eroded valley along the southwestern flanks of the extinct Koolau volcano on southeastern Oahu, Hawaii (Fig. 1). Elevations range from 914 m above sea level to sea level, with nearly 90% of the elevation drop occurring in the first 1–2 km from the ridge crest. The climate is subtropical-humid with year-round warm temperatures (22–27 °C) (Lau and Mink, 2006) and abundant rainfall that varies from 750 mm/yr in the lowlands to more than 3500 mm/yr in the uplands (Giambelluca et al., 2013).

The Manoa River and its tributaries drain mainly Pliocene to Pleistocene tholeiitic basalts and associated tuffs of the Koolau Volcanics in the upper reaches, and undifferentiated Holocene al-luvium in the lowlands (Deenik and McClellan, 2007; Sherrod et al., 2007). Minor outcrops of Pleistocene alkalic vent deposits generated during a period of rejuvenated-stage volcanism (i.e., the Honolulu Volcanics; Fig. 1) are located in the upper portion and western ridge line of the watershed (Hunt, 1996; Sherrod et al., 2007).

Streamflow in the Manoa River is characterized as highly variable (i.e., "flashy"); Tomlinson and De Carlo (2003) due to the steep topography, low soil infiltration capacities and high rainfall frequencies (Lau and Mink, 2006). This is particularly the case in the uplands (e.g., Waihi tributary; Fig. 1) where runoff, based on USGS data, between 1950 and 2015 ranged from 5.46 × 10⁷ m³ to 0.19 m³/d. For this area, Tomlinson and De Carlo (2003) reported rainfall frequencies as high as 76 mm in 1 h (recurrence interval of one year) and changes in stream flow and turbidity values by factors of 60 and 30, respectively, in just a few minutes. A streamflow range exceeding one order of magnitude was also observed in the lowlands at Kanewai Field (Fig. 1) during our 4-months sampling time frame (Fig. 2a).

Unlike other Hawaiian streams that receive large portions of their streamflow from leaking of perched, diked-impounded groundwater (Lau and Mink, 2006), streamflow in the upper Manoa River is driven mainly by year-round orographic rainfall (Sahoo et al., 2006). This is supported by daily streamflow data (10/01/2011–12/31/2014) reported for the upstream Waihi tributary USGS gaging station 2385 (Fig. 2b; see Fig. 1 for gaging station location). The data exhibit a steep flow duration curve (FDC) and a low Q90/Q50 ratio of 33% which is consistent with a "losing" stream setting (Smakhtin, 2001) characterized by highly variable flow. However, baseflow input, as implied by flatter FDCs (Fig. 2b) and Q90/Q50 ratios >50%, becomes more significant in the eastern tributaries such as the Waiakea Kua (USGS gaging station 2405), where more dikes are present (Fig. 1), and along the downstream sections at Woodlawn Drive and Kanewai Field (USGS gaging stations 2416 and 2425, respectively).

Land use/land cover ranges from pristine rain forests in the upper valley (55–60%) to developed residential lands (40–45%) in the lowlands (Fig. 1). The total population of the Manoa Watershed is 18,537 with a population density of 1353 persons/km² (see: http://www.city-data.com/neighborhood/Manoa-Honolulu-HI.html). Urban development in the lowlands has led to the modification of the natural streambeds by low permeability concrete channels and stormwater drainage systems. This development has impacted the water quality as evidenced by past detections of dissolved pollutants such as herbicides, insecticides, volatile organic compounds, metals and nitrate (Anthony et al., 2004; De Carlo et al., 2004).

3. Materials and methods

3.1. Water and soil sampling

Water samples from 3 stream locations (upstream, mid-stream and lowland) were collected during 17 sampling campaigns between March and July 2010 (Fig. 1). All samples were collected during broad daylight between 10 pm and 2 pm for consistency purposes and to normalize the data from cyclical trends associated with diel biochemical processes (Nimick et al., 2011). The 4 months sampling period covers the seasonal change from the annual dry to wet season (Lau and Mink, 2006). Sampling locations were selected...
Fig. 1. Study area in southeastern Oahu with stream and soil sampling sites, and rainfall and stream gaging locations. Rainfall data from Giambelluca et al. (1986) and geologic features from Sherrod et al. (2007).
to (1) represent the transition from the undeveloped forested uplands to the more developed (and urbanized) lowlands, (2) cover the natural stream segments and not the concrete stormwater drainage systems, and (3) be located in close proximity to local weather and streamflow gaging stations (Fig. 1), so that hydrologic controls on the stream chemistry could be assessed. No streamflow data were available for the up- and mid-stream sampling locations at the time of sampling so rainfall data from the Manoa Lyon Arboretum weather station (WRGC, 2011) were used as a cursory proxy. Despite the associated uncertainty, we consider this a reasonable approach because of (1) the close proximity of the up- and mid-stream sampling locations and the weather station (i.e., 0.5 km and 1.15 km, respectively), and (2) the strong positive correlation ($r = 0.74$; $p < 0.005$; relationship not shown) between rainfall and available streamflow data (for the time period 2012–2015) from the Waihi tributary which is located about 700 m downstream of the weather station. The fact that rainfall correlates with Waihi streamflow suggests a similar if not stronger correlation with streamflow at the upstream and mid-stream sampling locations, as they are both located upstream of the Waihi gage and should therefore exhibit a more direct response to fluctuations in rainfall. For the lowland sampling location, we used streamflow data from the USGS 2425 Kanewai Field station as a hydrologic proxy as it is located 10 m from the sampling site.

Soil samples were collected throughout the watershed to establish a $^{6}{^{13}}$C endmember signature for particulate organic carbon (POC) from the C3 vegetation that can be flushed into the stream (Fig. 1). Soils were collected on gently sloping, low relief positions in close proximity (about 10–50 m) to the Manoa stream channel. Samples 1 and 3 comprise leaf litter collected directly from the humus-rich forest floor (i.e., O-) horizon with C concentrations of 388 g C/kg soil and 362 g C/kg soil, respectively. Sample 2 is a mineral/humus mixture (88.3 g C/kg soil) excavated at a depth of about 12 cm.

3.2. Geochemical analyses

All water samples were filtered through 0.45 µm membrane filters immediately after collection, acidified (with 1% HNO$_3$) for cation analysis and stored in HDPE bottles free of air below 4 °C. All soil samples were dried in pre-combusted aluminum weigh boats at 60 °C for 24 h and homogenized in an agate grinder. Water pH, temperature and dissolved oxygen (DO) were measured in the field using portable Hach probes with precision levels of ±1%. Alkalinity was determined in the field via Gran titration using Hach titrator kits with a precision level of ±5%. PCO$_2$ values were calculated following the approach by Clark and Fritz (1997) using measured alkalinitities, pH and the temperature-dependent Henry’s Law constant $K_{\text{CO}_2}$.

Major ions and stable isotope measurements were carried out at the University of Hawaii’s School of Ocean and Earth Sciences and Technology and Water Resources Research Center. Major ions were analyzed using a Dionex DX-120 ion chromatograph with a precision of ±10% based on repeat analyses. Charge balance errors (CBE) were within the acceptable range of ±5% (mean and median values of 1.67% and 1.79%, respectively). The slight CBEs in some instances likely reflect slight compositional differences given that bicarbonate concentrations were measured via gran titration in the field, while major ion concentrations were measured on a separately collected sample via ion chromatography. Dissolved organic carbon (DOC) was measured on a Shimadzu TOC-V analyzer at a precision level of 3%. Isotopic analyses of $^{3}{^{13}}$C of DIC were carried out immediately after sample collection by a continuous-flow gas-ratio mass spectrometer (ThermoFinnigan MAT252) coupled with the Gas Bench II peripheral. $^{3}{^{13}}$C values of DIC were measured following Torres et al. (2005) in samples that had been acidified with phosphoric acid at room temperature after He gas flushing. $^{3}{^{13}}$C of POC of the soil samples was determined using a Carla Erba NC2500 Elemental Analyzer interfaced with a ThermoFinnigan MAT Delta S mass spectrometer. Standardization of all $^{3}{^{13}}$C used a range of international and internal standards and values are expressed relative to PDB. Precision (1σ) is ±0.1% for DIC and ±0.2% for POC. Appendix A lists the geochemistry of all analyzed samples.

3.3. Geochemical modeling

3.3.1. Characterization of chemical weathering pathways

To quantify the role of various acids on the stream alkalinity and $^{13}$C budget, the main weathering (and acid dissociation) pathways were first identified based on major ion data. In pristine areas, rainfall in equilibrium with atmospheric CO$_2$ that infiltrates the soil zone to reach a stream will become progressively enriched in H$_2$CO$_3$ from CO$_2$ released from decaying organic matter (Eq. (1)). The degree of that enrichment depends on the residence time of water in soils, temperature and the composition and thickness of the soil zone. Carbonic acid silicate weathering (Eq. (2)) and carbonic acid carbonate weathering (Eq. (3)) transform the H$_2$CO$_3$ into HCO$_3^-$ with the latter additionally contributing HCO$_3^-$ from the CO$_2$ of the mineral phase.

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$$

$$\text{H}_2\text{CO}_3 + \text{Ca}(\text{aq}) \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

$$\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{HCO}_3^-$$
2H₂CO₃ + CaSiO₃ + H₂O → 2HCO₃⁻ + Ca²⁺ + H₄SiO₄
(2)
H₂CO₃ + CaCO₃ → 2HCO₃⁻ + Ca²⁺
(3)

In light of the global accumulation of reactive nitrogen from changes in land use (e.g., agricultural) practices and the expanding supply of ammonium due to the Haber Bosch process (Erismann et al., 2008; Galloway et al., 2004), solute yields from nitric acid carbonate dissolution (Eqs. (4) and (5)) should also be considered relevant in human impacted watersheds:

\[ \text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ \]  
(4)
\[ \text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \]  
(5)

Although measured nitrate levels in the Manoa River are consistently below EPA’s maximum contaminant level (MCL) of 10 mg/L (EPA, 2014), there is a downstream increase from a mean value of 0.02 mg/L in the upper reaches to 0.44 mg/L in the lowland sections which is likely related to inflow of septic effluent. Given this trend, we included nitric acid weathering (Eq. (5)) as the anthropogenic weathering pathway (Brunet et al., 2011) in the riverine alkalinity and ¹³C budget.

Carbonate weathering by sulfuric acid derived from oxidation of accessory sulfides can also contribute HCO₃⁻. However, volcanic lithologies on Oahu are generally depleted in reduced S (Jackson et al., 1999; Sherrod et al., 2007). In addition, measured stream SO₄²⁻ contents (Appendix A) are similar to, and in some instances even less than, reported SO₄²⁻ contents of rainfall on Oahu (2.30 mg/L) (Swain, 1973) and on the Big Island (reported weighted averages of between 0.85 mg/L and 3.46 mg/L) (Eriksson, 1957; Harding and Miller, 1982; NADP, 2014). These observations are consistent with an atmospheric sulfate origin in the water samples. Accordingly, only carbonic and nitric acid weathering are considered to impact the Manoa River.

3.3.2. Alkalinity budget modeling

The HCO₃⁻ contributions from mineral weathering by carbonic and nitric acid can be modeled using δ¹³C values, which vary with the source of carbonic acid (atmospheric vs. soil-derived) and lithology (silicate vs. carbonate), and the nitrate proportion XNO₃ (ratio of [NO₃⁻] over the sum of [NO₃⁻] + [HCO₃⁻]) which varies with the relative proportion of carbonic vs. nitric acid. The applied methodology follows the approaches outlined by Galy and France-Lanord (1999) and Spence and Telmer (2005) and can be expressed by the following equations:

\[ [\text{HCO}_3^-]_{\text{sw}} = [\text{HCO}_3^-]_{\text{atm}} + [\text{HCO}_3^-]_{\text{soil}} + [\text{HCO}_3^-]_{\text{carb}} \]  
(6)
\[ \delta^{13}\text{C}_{\text{sw}} = (\delta^{13}\text{C}_{\text{atm}} \delta^{13}\text{C}_{\text{soil}} \delta^{13}\text{C}_{\text{carb}})/[\text{HCO}_3^-]_{\text{sw}} \]  
(7)
\[ \text{XNO}_3 = [\text{NO}_3^-]_{\text{intr}}/[\text{NO}_3^-]_{\text{sw}} + [\text{HCO}_3^-]_{\text{sw}} \]  
(8)

\[ [\text{HCO}_3^-]_{\text{atm}}, [\text{HCO}_3^-]_{\text{soil}}, \text{and } [\text{HCO}_3^-]_{\text{carb}} \] are the measured HCO₃⁻ values in stream water and the estimated HCO₃⁻ contributions from silicate weathering by atmosphere-derived H₂CO₃, silicate weathering by soil-derived H₂CO₃ and carbonate weathering by combined nitric and carbonic acid, respectively. \δ^{13}\text{C}_{\text{sw}} and \δ^{13}\text{C}_{\text{atm}} correspond to the measured δ¹³C value in the stream sample and that of the individual HCO₃⁻ (i) sources in Eq. (6). [NO₃⁻]_{\text{intr}} and [NO₃⁻]_{\text{sw}} refer to the estimated nitrate concentrations from nitrification of NH₄ and the measured NO₃ concentration in the stream water, respectively. XNO₃ is expressed as an equivalent ratio ranging from 0% for pure carbonic acid weathering to 100% for pure nitric acid weathering. To model the alkalinity budget, major ion and isotope data are combined by solving equations (1) through (8) simultaneously for various proportions of silicate vs. carbonate weathering and nitric acid vs. carbonic acid weathering. Because no direct measurements of the δ¹³C values are available in this study, they are estimated based on the following approaches.

For \δ¹³\text{C}_{\text{carb}}, Quade et al.’s (2013) δ¹³C value for caliche deposits on basaltic units near Kona on the Big Island of Hawaii (−0.17 ± 1.83‰) is chosen as a proxy. \δ¹³\text{C}_{\text{atm}} (0 ± 0.5‰) is estimated using an atmospheric CO₂ δ¹³C end-member of −8.3‰, mean air temperature (22.2 °C ± 1.4 °C) recorded at the local weather station during the sampling period (WRCC, 2011), as well as temperature dependent fractionation factors for the conversion of CO₂ to HCO₃⁻ (Myrtinyt et al., 2012, 2015; Zhang et al., 1995). \δ¹³\text{C}_{\text{soil}} is estimated using soil organic matter δ¹³C values. However, even in an area dominated by relative uniform C3 vegetation, these are not constant, but generally change with depth due to isotopic fractionation during decomposition of plant material and humification (Agren et al., 1996). In comparable settings on the Big Island of Hawaii, δ¹³C values increase at depths of 40 cm and below have been reported for forested soils (Osher et al., 2003). Such an enrichment trend with depth is not observed here as our δ¹³C values range from −28.3 to −30% on the surface to −29.5% at a depth of 12 cm (Appendix A). This suggests that our sampling depth profile was too shallow to accurately capture the soil δ¹³C decomposition trend. Given this and based on the results reported by Osher et al. (2003) and other studies carried out in the tropics (Martin et al., 1990; Medina et al., 1986), we estimate the δ¹³C of decomposed organic matter (−26.2 ± 0.8‰) using the measured δ¹³C of leaf litter and the reported decomposition enrichment factor of 3‰. This estimated δ¹³C value, together with Cerling et al.’s (1991) fractionation factor for diffusion of respired CO₂ (4.4‰) and Zhang et al.’s (1995) CO₂ to HCO₃⁻ conversion factor at an average stream temperature of 21.2 °C, yield a δ¹³C soil end-member of −13.6 ± 0.8‰.

The system expressed by Eqs (1)–(8) is simplified and is based on the following limiting assumptions: (1) there is no significant input of volcanic CO₂, which, on the Big Island of Hawaii, exhibits an enriched δ¹³C of >4‰ (Hilton et al., 1997), (2) all measured NO₃⁻ is derived from nitrification of locally-derived NH₄ (Berthelin et al., 1985; Brunet et al., 2011), (3) there is no δ¹³C fractionation by CO₂ degassing and/or atmospheric equilibration which has been shown to be important in larger river systems with typically longer water residence times (van Geldern et al., 2015; Wachniew, 2006) and (4) there is no significant DIC or NO₃ fractionation from diel biological activity (in stream photosynthesis, respiration and methanogenesis) (de Montety et al., 2011; Nimick et al., 2011). This is implied by the fact that all samples were collected during the same time of the day throughout the sampling period and because the Manoa River exhibits hydrological characteristics (a short water residence time in the order of hours instead of days, variable streamflow, high topographic drive, low submerged macrophyte content and shading from sunlight by dense canopy) that are not amenable to pronounced in stream processing of nutrients. The consistently high DO levels of ≥ 8 mg/L (Appendix A) and the lack of correlation (r < 0.1; p > 0.5; relationships not shown) between stream pCO₂ and DO and between stream δ¹³CDOC and DOC are consistent with this hypothesis.

4. Results and discussion

4.1. Carbonate vs. silicate rock weathering

Despite the reported mineralogical differences between the tholeiitic Koolau Basalts and the alkaline Honolulu Volcanics, the local volcanic lithologies exhibit similar Ca/Na and Mg/Na ratios...
that are higher than those of stream samples and local rainfall (Fig. 3). This is likely related to the abundance of Mg-olivine as a primary component in the Honolulu Volcanics and as a phenocryst phase in the Koolau Volcanics (Jackson et al., 1999). This, together with the fact that stream ratios show a low variability in Ca/Na and Mg/Na ratios (Ca/Na = 0.28 ± 0.1 and Mg/Na = 0.46 ± 0.07) suggests that the effect of lithological differences on the stream major ion chemistries is relatively small compared to streams draining more diverse lithological settings (see, e.g., Hagedorn and Whittier, 2015).

Many previous studies highlighted the importance of secondary carbonate weathering in silicate-dominated watersheds. However, these results stem from (1) more arid settings with longer water residence times and/or (2) watersheds with significant baseflow contribution to streamflow (Barth et al., 2003; Hagedorn and Whittier, 2015). Measured data reported here are not consistent with secondary carbonate weathering as a major process as it would significantly raise Ca/Na and Mg/Na ratios (Gaillardet et al., 1999) which is not observed. A lack of macroscopic secondary calcite (e.g., fracture filling or grain coating) deposits in the field and the undersaturation of river samples with respect to calcite or dolomite (Appendix A) further support this hypothesis.

4.2. Carbonic vs. nitric acid weathering

A system where [HCO₃]₀ is negligible and where variable mixtures of soil-derived carbonic acid and nitrification-derived nitric acid weather variable proportions of carbonates and silicic acids is illustrated in Fig. 4. The data suggest only a minor contribution (< 2%) of nitric acid weathering (i.e., HNO₃ dissociation), particularly in the upper reaches, where XNO₃ < 0.1%. However, all stream samples show a remarkable δ¹³C enrichment relative to the soil CO₂ source which, according to Fig. 4, implies a significant solute contribution from carbonate weathering. This is most evident for the upstream samples where δ¹³C values are > -7.3‰. However, the importance of secondary calcite weathering in the watershed is not supported by field observations and major ion data (Fig 3.). The apparent δ¹³C enrichment of stream samples relative to a soil CO₂ source thus requires an alternate explanation.

![Fig. 3. Ca/Na vs. Mg/Na ratios in Manoa River waters (n = 48), Oahu rainfall (n = 4; data from Swain, 1973), Koolau basalt (n = 164; data from Sherrod et al., 2007) and the Honolulu Volcanics (n = 141; data from Sherrod et al., 2007). Error bars represent one standard deviation from mean values. The carbonate weathering solute source field is taken from Gaillardet et al. (1999).](image)

![Fig. 4. Relationship between δ¹³C in Manoa River waters modeled after Eqns (1)–(6) (see text for explanation of input parameters). Lines describe modeled trends for variable mixtures of silicate vs. carbonate lithology composition, and nitric vs. carbonic acid weathering.](image)

4.3. CO₂ degassing

One potential mechanism to enrich stream δ¹³C values relative to the soil CO₂ source is rapid degassing of CO₂ which can cause kinetic isotopic fractionation via HCO₃-dehydration (Doctor et al., 2008). Measuring and modeling the effect of CO₂ degassing from streams is challenging (Cole and Caraco, 2001; Polsenaere and Abril, 2012) for several reasons, including (1) the complex nature of turbulent flow and the related challenge of selecting appropriate gas-water exchange coefficients (Generex and Hemond, 1992; Jeffery et al., 2009), (2) uncertainty in identifying representative soil CO₂ concentration input values as these vary with climate, season and soil depth (Brook et al., 1983; Medina et al., 1986; Rightmire, 1978), (4) issues regarding the selection of an appropriate soil CO₂ input value given the rather large range of δ¹³C values in settings covered by diverse vegetation and soils (Medina et al., 1986; Townsend et al., 1995), (5) the fact that the degree of δ¹³C fractionation from diffusion of respired soil CO₂ is strongly controlled by the soil water content (Davidson, 1995) which can be highly variable in tropical soils (Lawrence and Hornberger, 2007; Nullet et al., 1990), (6) the challenge of selecting a representative δ¹³C in rivers affected by δ¹³C fractionation via diel cycles of in-stream biological activity (de Montety et al., 2011), and (7) the pH-dependency of δ¹³C enrichment induced by degassing which has been shown, in experimental studies, to range from 1‰ at a pH of 2 (Zhang et al., 1995) to 14.7‰ at a pH of 8.2 (Marlier and O'Leary, 1984). These factors prohibit a reliable quantitative assessment of CO₂ degassing in the Manoa River, however, some qualitative conclusions can still be derived from the available data.

The spatial trends typically attributed to CO₂ degassing - downstream decreases in pCO₂ and increases in δ¹³C (e.g., Doctor et al., 2008; Zavadlav et al., 2013; van Geldern et al., 2015) - are reversed in the Manoa River, where pCO₂ increases from a mean value of 3760 ppmv (upstream) to 8961 ppmv (lowland), and δ¹³C decreases from a mean value of −6.5‰ (upstream) to −11.7‰ (lowland) (Fig. 5). One explanation for the Manoa trend could be that unlike in other, larger river systems, where topographic gradients are flatter and degassing is mainly controlled by the air-water pCO₂ gradient, the CO₂ degassing pattern in the Manoa River is more controlled by the changes of the flow regime. In the steep upper reaches, where streamflow is turbulent (as evidenced by the cascades of the nearby Manoa Falls waterfall), the
The role of atmosphere-derived CO₂ on the stream alkalinity is commonly considered negligible (Galy and France-Lanord, 1999; Khadka et al., 2014), particularly in tropical/subtropical humid settings characterized by thick and productive soils with high pH. Nevertheless, studies carried out in high-relief Hawaiian streams attributed significant short-term fluctuations in stream Total Dissolved Solids, Total Suspended Solids, Electrical Conductivity and pH to influxes of “dilute” rainwater (Augustin et al., 2011; De Carlo et al., 2004; Tomlinson and De Carlo, 2003). We assessed the potential role of this “dilute” rainwater on the stream alkalinity budget by setting up the system, described by Eqs (1)–(8), for substrate weathered by variable mixtures of soil-derived and atmosphere-derived H₂CO₃ and nitrification-derived HNO₃. This system is shown in Fig. 6. To express uncertainty in the substrate minerology (primary silicate vs. secondary carbonate), we assumed a silicate content of 90–100% which corresponds to a [HCO₃]marine contribution of 0–10% to [HCO₃]low (Eq. (6)). The effects of this compositional range on modeled stream δ¹³C and XNO₃ are illustrated in the error bars in Fig. 6.

The resulting model allows us to reconstruct the hydrochemical evolution of stream water via two characteristic trend lines. The first (carbonic acid weathering) depicts the expected δ¹³C and XNO₃ trend from rainfall to upstream stream water due to pure carbonic acid weathering. The theoretical XNO₃ of rainfall (10%) is calculated based on weighted average geochemical data (pH = 5.27, NO₃ = 0.12 mg/L) from the Mauna Loa National Atmospheric Depositional Program station (NAPD, 2014), recorded mean temperature (22.2 °C) at the Mauna Lyon Arboetum weather station (WRC, 2011), and an atmospheric pCO₂ of 380 ppm with the T dependent KCO₂ and K₅ constants (Clark and Fritz, 1997). In this trend line, the relative HCO₃ contribution of soil-derived H₂CO₃ dissociation increases with residence time of water in the soil zone from 0% (rainfall end-member) to about 50% (mean upstream river end-member). No nitrification-derived nitric acid weathering is considered to affect the stream waters in this scenario. XNO₃ will decrease from 10% to <0.1% in the upstream samples due to HCO₃ input from progressive carbonic acid weathering.

The second trend line (carbonic acid + nitric acid weathering) depicts the δ¹³C and XNO₃ trend from upstream to lowland river waters. In this scenario, nitrification-derived HNO₃ does affect the stream chemistry, albeit at low degrees (XNO₃ < 2%). Furthermore, the relative HCO₃ contribution from biologic (i.e., soil-derived) H₂CO₃ dissociation increases to 75–100% in the mid-stream and lowland waters suggesting that it is at the transition between the mid-stream and lowland flow regime where the river equilibrates with soil CO₂. However, the overall scatter in δ¹³C, XNO₃ and pCO₂ data (Figs. 5 and 6) suggest that this transition may shift in space and time potentially as a result of the dynamic flow characteristics of the stream and the effects of in-stream biological activity not accounted for in this study.

### 4.4. Biologic vs. atmospheric carbonic acid weathering

The effect of cavitation at the air-water interface could potentially outweigh that of the air-water pCO₂ gradient in less turbulently flowing lowland waters. As such, CO₂ degassing in the Manoa River likely continues downstream, but its relative effect on the stream pCO₂ and δ¹³C signature could decrease as the degree of flow turbulence decreases (the stream channel becomes wider as the slope becomes flatter) and as increasing components of soil-derived H₂CO₃ are flushed in via interflow or surface runoff.

One problem with the CO₂ degassing hypothesis, however, is the rather large δ¹³C discrepancy between the δ¹³C values of the upstream samples (~6‰ to ~7‰) and that of the theoretical soil water δ¹³C end-member (Fig. 4). Doctor et al. (2008), based on field data obtained in a forested, silicate-dominated tributary with pH values similar to those in the Manoa River, noted a distinct δ¹³C enrichment factor of about 2.4‰ per natural log unit decrease in excess pCO₂. Similar isotopic enrichment has been observed in field settings elsewhere (Khadka et al., 2014; van Geldern et al., 2015; Zavadil et al., 2013). Considering this factor appropriate for the Manoa River and assuming carbonate weathering to be negligible, measured δ¹³C data would indicate a rather extreme degree of CO₂ degassing of >88% in the upstream samples. Such a CO₂ loss should be manifested by a significant increase in pH or carbonate mineral supersaturation which is not observed (Appendix A). Given this, we do not consider degassing as a major process in the upper reaches, although it may very well explain the slight 1–1.5‰ δ¹³C enrichment of the lowland stream samples compared to the estimated soil water δ¹³C (Fig. 4).

### 4.5. Hydrologic controls on stream alkalinity and δ¹³C

There still remains debate on the specific effects of hydrologic...
variables (i.e., rainfall and streamflow) on stream alkalinity and δ^{13}C. We attempted to assess the effects of these variables in the Manoa Watershed by comparing time-series major ion and δ^{13}C values to trends in concurrently measured rainfall and streamflow data.

There is no correlation between rainfall or streamflow and pCO₂, HCO₃, DIC, and DOC values (r < 0.36; p > 0.2) at any stream sampling location which underscores the complex controls on riverine carbon transport (Schulte et al., 2011). The positive correlation between streamflow and NO₃ in the lowland samples (Fig. 7a) is attributed to surface runoff input of anthropogenic NO₃ (i.e., septic effluent) in the lowlands. The specific controls on NO₃ formation in the undeveloped upstream and mid-stream locations are not clear as there is no correlation between rainfall and NO₃ for any of these sampling locations (r < 0.34; p > 0.2). The large scatter in the measured data could simply reflect the variable NO₃ content in precipitation which, at the Mauna Loa station on Hawaii’s Big Island, has fluctuated between 0.01 and 0.84 mg/L (mean value: 0.12 mg/L) over the time period 1980–1993 (NADP, 2014). More concentration and isotope data of NO₃ of river water and rainfall collected in the Manoa Watershed could allow a more refined assessment of NO₃ sources (natural vs. anthropogenic) in the system.

There is also no correlation between rainfall and δ^{13}C_{DIC} at the upstream location (r = 0.05; p = 0.85) and streamflow and δ^{13}C_{DIC} at the lowland location (r = 0.18; p = 0.50). For the mid-stream samples, however, there is a significant positive correlation between rainfall and δ^{13}C_{DIC} (Fig. 7b). The spatial discrepancy in correlation coefficients could have many causes. In the case of the upstream samples, which were collected more than 1 km away from the weather station, it is possible that the applied rainfall data are simply not representative for local streamflow variability. It could also be that the relative effect of rainfall or streamflow on stream δ^{13}C signatures in the upstream and lowland region is lower than that of the variability of the δ^{13}C signature of soil POC. More soil POC data from this region could potentially confirm this hypothesis. In any case, the narrow range in upstream and lowland δ^{13}C_{DIC} implies that processes are consistent throughout the 4 month sampling period and that changes in streamflow do not exert significant effects on the stream δ^{13}C_{DIC} signature.

As discussed earlier, we attribute the δ^{13}C_{DIC} depletion from the upstream to the lowland sampling locations to varying degrees of H₂CO₃ enrichment by soil CO₂. This enrichment appears to simply shift from low (about 50%) in the upstream region to high (>75%) in the lowland region (Figs. 5 and 6) without any significant influences by short-term changes in rainfall and, by implication, streamflow. It could be that at the humid upstream location, where time scales of storm hydrographs are on the order of hours (Tomlinson and De Carlo, 2003) and where the flow contribution from baseflow is minor, stream water residence times are consistently short. As a result, water will retain a large and consistent component of the atmospheric δ^{13}C_{DIC} signature. Towards the lowlands, however, where net rainfall decreases by 390% (Giambelluca et al., 2013) and where baseflow input exceeds 50% (Fig. 2b), the water residence time will be consistently long enough for CO₂ inputs of biological CO₂ by soil water and groundwater. Mid-stream samples, on the other hand, can be seen to represent some sort of transitional regime where short-term variations in rainfall rate (and likely also streamflow) exert a much stronger effect on stream water residence time and H₂CO₃ enrichment. In this instance, increased rainfall appears to counteract enrichment of soil-derived CO₂ and favor the input of atmosphere-derived CO₂ which would decrease the stream’s potential to (1) degas CO₂ and (2) generate HCO₃ and consume CO₂ via weathering. Given these factors, it is possible that average CO₂ consumption and CO₂ degassing values for volcanic island drainages, particularly if determined based on grab sampling data from single spot locations at the river mouths, may be biased high. However, new streamflow information for the up- and mid-stream sampling locations and a more refined (and higher resolution) chemical dataset could certainly provide more information on the geochemical response of the system to sudden changes in flow conditions. These data could also lead to a better understanding of the potential roles of CO₂ degassing, and DOC oxidation on δ^{13}C_{DIC} fractionation. In addition, new datasets on short-lived radioactive isotopes (e.g., ²²⁴Rn) may help evaluating the controls of water residence time and groundwater-surface water interaction on the streamwater alkalinity and δ^{13}C_{DIC} budget.

5. Conclusions and implications

Hawaiian watersheds are small, steep and characterized by rain events that are short in duration and intense. These patterns are reflected in highly variable streamflow and complex stream chemistries with pronounced temporal and spatial variations. Ionic and δ^{13}C_{DIC} analyses suggest that chemical weathering of exposed aluminosilicates by carbonic acid controls the solute loads of the Manoa River and that the contribution from nitric acid dissociation to these loads is generally low (i.e., XNO₃ < 2%), even in the developed and densely populated lowlands.

Unlike many other streams on tropical islands that are dominated by soil-derived H₂CO₃ dissociation and thus high CO₂ degassing and high CO₂ consumption rates, data from the Manoa River in Hawaii indicate a significant atmospheric H₂CO₃ dilution effect particularly in the remote upper reaches, where rainfall rates exceed 3500 mm/yr (Giambelluca et al., 2013) and where topographic gradients can exceed 100% (Lau and Mink, 2006). Towards the lowlands, the proportion of biologic H₂CO₃ (and hence the

![Fig. 7](image-url) Relationship between NO₃ and streamflow (a) in the developed lowland section of the Manoa River, and δ^{13}C_{DIC} and precipitation (b) in the undeveloped mid-stream section.
potential to degas CO₂ and generate alkalinity) increases dramatically as a result of increased water residence time in soils and increased baseflow input of groundwater. In-between the upper reaches and lowlands, stream waters exhibit more variable δ¹³C-DIC values as the relative dominance of atmosphere vs. biologic H₂CO₃ appears to shift with changes in hydrology. Because the role of high standing volcanic islands in riverine carbon transport greatly exceeds their percentage of global extent (Goldsmith et al., 2010; Lyons et al., 2002), the documented variability in stream water H₂CO₃ source should be taken into account in spatiotemporal extrapolations of riverine CO₂ transport in high-rainfall/high-relief watersheds.

Acknowledgements

The authors thank J. Lichwa and E. Gier for their help with the geochemical analysis and S. De Nola and K. Mitchell for their collection of field data. We furthermore thank A. Mair for his valuable inputs on the local hydrology and J.A.C. Barth and an anonymous reviewer for their valuable revision comments. This work was supported by the State of Hawai’i Water Resources Research Center (grant number: 94682).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2016.07.008.

References

EPA, 2008. Environmental Protection Agency - National Primary Drinking Water Regulations. [water.epa.gov/drink/contaminants].
Lawrence, J.E., Hornberger, G.M., 2007. Soil moisture variability across climate