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

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ABSTRACT

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 $\delta^{13}C_{DIC}$/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 $\delta^{13}C_{DIC}$ (−6.5‰) fingerprint in the upper reaches to a high HCO_3 (91 mg/L), high pCO_2 (8961 ppmv) and light $\delta^{13}C_{DIC}$ (−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 $\delta^{13}C_{DIC}$ 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_2CO_3 and the subsequent transport of HCO_3 to the oceans *consumes* atmospheric CO_2 on time-scales of greater than 10^5 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, Yao

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et al. (2007) and Hagedorn and Cartwright (2010) observed a shift towards reduced CO_2 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 pCO_2 patterns generally exhibit no significant correlations with streamflow (e.g., Abril et al., 2000; Neal et al., 1998; Teodoru et al., 2009, etc.) highlights the complex hydrologic controls on stream CO_2 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 CO_2 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 CO_2 will generate H_2CO_3 that will dissociate via carbonate and silicate weathering to generate HCO_3 with distinct $\delta^{13}C$ 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 Jacobson, 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; Perrin et al., 2008). In addition, in-situ processes such as photosynthesis, respiration, methanogenesis, rapid CO_2 degassing and/or atmospheric equilibration can also impact the stream HCO_3 and $\delta^{13}C$ signatures (Amiotte-Suchet et al., 1999; Barth et al., 1998; Brunet et al., 2009; 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 CO_2 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 CO_2 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 CO_2 (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 CO_2 consumption and CO_2 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 $\delta^{13}C_{DIC}$/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 km^2) 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 alluvium 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 ridgeline 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 5.46×10^{-5} m/d to 0.19 m/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 many 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 Q_{90}/Q_{50} 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 Q_{90}/Q_{50} ratios >50%, becomes more significant in the eastern tributaries such as the Waiakeakua (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/km^2 (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