4-15-2013

Groundwater and Porewater as Major Sources of Alkalinity to a Fringing Coral Reef Lagoon (Muri Lagoon, Cook Islands)

Tyler Cyronak  
*Southern Cross University - Lismore, Australia*, tcyronak@nova.edu

Isaac R. Santos  
*Southern Cross University - Lismore, Australia*

Dirk V. Erler  
*Southern Cross University - Lismore, Australia*

Bradley D. Eyre  
*Southern Cross University - Lismore, Australia*

Find out more information about Nova Southeastern University and the Halmos College of Natural Sciences and Oceanography.

Follow this and additional works at: [https://nsuworks.nova.edu/occ_facarticles](https://nsuworks.nova.edu/occ_facarticles)

Part of the [Marine Biology Commons](https://nsuworks.nova.edu/marinebio), and the [Oceanography and Atmospheric Sciences and Meteorology Commons](https://nsuworks.nova.edu/oceanography)

---

NSUWorks Citation


---

This Article is brought to you for free and open access by the Department of Marine and Environmental Sciences at NSUWorks. It has been accepted for inclusion in Marine & Environmental Sciences Faculty Articles by an authorized administrator of NSUWorks. For more information, please contact nsuworks@nova.edu.
Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands)

T. Cyronak, I. R. Santos, D. V. Erler, and B. D. Eyre
Centre for Coastal Biogeochemistry, School of Environment, Science and Engineering, Southern Cross University, Lismore, New South Wales, Australia

Correspondence to: T. Cyronak (tcyonak@gmail.com)

Received: 23 October 2012 – Published in Biogeosciences Discuss.: 5 November 2012
Revised: 22 March 2013 – Accepted: 22 March 2013 – Published: 15 April 2013

Abstract. To better predict how ocean acidification will affect coral reefs, it is important to understand how biogeochemical cycles on reefs alter carbonate chemistry over various temporal and spatial scales. This study quantifies the contribution of shallow porewater exchange (as quantified from advective chamber incubations) and fresh groundwater discharge (as traced by $^{222}$Rn) to total alkalinity (TA) dynamics on a fringing coral reef lagoon along the southern Pacific island of Rarotonga over a tidal and diel cycle. Benthic alkalinity fluxes were affected by the advective circulation of water through permeable sediments, with net daily flux rates of carbonate alkalinity ranging from $-1.55$ to $7.76$ mmol m$^{-2}$ d$^{-1}$, depending on the advection rate. Submarine groundwater discharge (SGD) was a source of TA to the lagoon, with the highest flux rates measured at low tide, and an average daily TA flux of $1080$ mmol m$^{-2}$ d$^{-1}$ at the sampling site. Both sources of TA were important on a reef-wide basis, although SGD acted solely as a delivery mechanism of TA to the lagoon, while porewater advection was either a sink or source of TA dependent on the time of day. This study describes overlooked sources of TA to coral reef ecosystems that can potentially alter water column carbonate chemistry. We suggest that porewater and groundwater fluxes of TA should be taken into account in ocean acidification models in order to properly address changing carbonate chemistry within coral reef ecosystems.

1 Introduction

The recent increase in atmospheric CO$_2$ has led to an increase in oceanic $p$CO$_2$ as roughly 30% of anthropogenic CO$_2$ has been absorbed by the oceans (Feely et al., 2004; Sabine et al., 2004; Orr et al., 2005; Doney et al., 2009). Ocean acidification is the term given to this increase in oceanic $p$CO$_2$, which alters the carbonate chemistry of seawater leading to a reduction in pH at a rate of roughly $0.002$ pH yr$^{-1}$ (Feely et al., 2004; Doney et al., 2009). Ocean acidification can have drastic effects on biological processes and the biogeochemistry of marine ecosystems, with coral reefs being some of the most susceptible ecosystems (Fabry et al., 2008; De’ath et al., 2009). The biogeochemical processes occurring in coral reefs can modify the carbonate chemistry of the overlying seawater, leading to large diel variations in alkalinity, $p$CO$_2$, pH, and dissolved oxygen (DO) (Santos et al., 2011; Shamberger et al., 2011; Gray et al., 2012; Shaw et al., 2012). In order to understand how ocean acidification will affect coral reefs, it is important to understand how natural processes, which can potentially buffer or intensify changes in seawater pH, alter the carbonate chemistry of seawater within coral reef ecosystems.

As CO$_2$ dissolves in water, it is hydrolyzed to form carbonic acid in the following equilibrium reactions:

$$
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}. \quad (1)
$$

Due to the production of HCO$_3^-$ and CO$_3^{2-}$, the increase in H$^+$ ions causes a reduction in seawater pH but does not change the total alkalinity (TA) (Millero, 1979; Zeebe and Wolf-Gladrow, 2001). The TA of a solution represents the ability of the solution to absorb H$^+$ ions without an
associated reduction in the pH, and in seawater is equal to the following equation (Wolf-Gladrow et al., 2007):

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-]$$

$$+ [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] + [\text{NH}_3]$$

$$+ [\text{HS}^-] - [\text{H}^+] - [\text{H}_2\text{PO}_4^-] - [\text{HF}]$$

$$- [\text{H}_3\text{PO}_4] - [\text{HNO}_2].$$

Within the range of normal oceanic pH, and especially in oligotrophic waters, the majority of alkalinity in seawater is found in the form of dissolved inorganic carbon (DIC) as HCO$_3^-$ and CO$_3^{2-}$ (Millero, 1979; Wolf-Gladrow et al., 2007).

The dissolution and precipitation of carbonate minerals, both biotic and abiotic, can alter the water column TA within coral reef lagoons (Andersson et al., 2007; Rao et al., 2012). These changes in TA are large enough that ecosystem calcification rates have historically been measured using the alkalinity anomaly technique (Chisholm and Gattuso, 1991; Gattuso et al., 1996), which relies on measuring the change in water column TA according to the following equation:

$$\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}.$$  (3)

Because CO$_3^{2-}$ is equal to 2 TA equivalents, calcification rates are equal to half the change of TA concentrations.

TA measurements are widely used in ocean acidification research to quantify community calcification rates (Shamberger et al., 2011; Silverman et al., 2012), measure sediment precipitation and dissolution rates (Andersson et al., 2007; Cyronak et al., 2013), correct net ecosystem calcification rates (Andersson et al., 2007; Cyronak et al., 2013), and to measure reef dissolution and bioerosion (Lazar and Loya, 1991; Zundelevich et al., 2007; Manzello et al., 2008). Also, it has been suggested that alkalinity generated from sediment dissolution may act as a partial buffer against any decrease in pH associated with ocean acidification, (Kleyaps and Langdon, 2006; Morse et al., 2006), although this buffering capacity is still being debated (see Andersson and Mackenzie, 2012). The importance of TA in ocean acidification research makes it important to constrain all sources and sinks of TA within coral reef ecosystems.

The exchange of solutes between the water column and permeable carbonate sediments is driven mainly by advective processes (Precht and Huettel, 2003; Santos et al., 2012). Flow- and topography-induced porewater exchange (see Fig. 1 in Santos et al., 2012) is probably the dominant process driving porewater exchange within coral reef lagoons due to the formation of ripples and crests within permeable carbonate sediments (Precht and Huettel, 2003). This process acts on short temporal (minutes to hours) and small spatial scales (cm) to induce the exchange of porewater solutes with the overlying water column (Precht and Huettel, 2003). Pore-water advection has a stimulatory effect on biological processes occurring within the sediments (Cook and Roy, 2006; Eyré et al., 2008; Glud et al., 2008) and has also been shown to have a stimulatory effect on TA fluxes, with increasing advection rates increasing net daily TA fluxes (Rao et al., 2012; Cyronak et al., 2013). However, while coral reef community calcification rates are negatively correlated with the aragonite saturation state ($\Omega_{Ar}$) of the water column (see Fig. 6 in Shamberger et al., 2011), carbon cycling in permeable sediments cannot be easily predicted by the $\Omega_{Ar}$ of the overlying water (Cyronak et al., 2013).

Submarine groundwater discharge (SGD) has been shown to be an important component of freshwater delivery to coastal ecosystems, on the scale of 6% to 10% of surface water flow, which amounts to an estimated 10 000 L m$^{-1}$ d$^{-1}$ along the global coast (Burnett et al., 2003; Santos et al., 2012). The few studies assessing SGD rates on coral reefs describe a range from 52 to 4732 L m$^{-1}$ h$^{-1}$, and suggest that SGD can be an important source of solutes to coral reef ecosystems (Lewis, 1987; D’Elia and Wiebe, 1990; Paytan et al., 2006; Knie et al., 2010; Blanco et al., 2011). There are multiple methods to estimate SGD into coastal ecosystems including seepage meters, piezometers, natural tracers, water balance approaches, and theoretical modeling (Burnett et al., 2006). Due to its naturally high concentrations in groundwater compared to surface waters, and its unreactive nature, $^{222}\text{Rn}$ has been used as a natural tracer for groundwater in aquatic systems for decades (Cable et al., 1996; Burnett et al., 2006). Mass balance models using $^{222}\text{Rn}$ have been developed that estimate SGD fluxes into coastal ecosystems (Burnett and Dulaiova, 2003).

Groundwater concentrations of TA can be higher than oceanic waters and encompass a broad range from 90 to 23 300 µmol L$^{-1}$ (Mahlknecht et al., 2004; Rad et al., 2007; Wolf-Gladrow et al., 2004).
Moore et al., 2011; Schopka and Derry, 2012). Using radium-based SGD efflux rates, Moore et al. (2011) demonstrated that SGD is a source of alkalinity to the water column in the Wadden Sea. Therefore, groundwater exchange processes occurring on larger temporal and spatial scales than flow-induced advective exchange also have the potential to deliver TA to coral reef lagoons. In fact, Kleypas and Langdon (2006) postulated that ocean acidification may be buffered against in coral reef ecosystems through the exchange of groundwater. The ability of groundwater to act as a source of TA to coral reef lagoons is highly dependent on the exchange rates with the water column, which can have large temporal and spatial variation (Lewis, 1987; Burnett et al., 2003; Santos et al., 2012). Determining the sources and sinks of alkalinity to coral reef ecosystems from groundwater and porewater exchange mechanisms is important in constraining how increasing pCO2 will impact seawater carbonate chemistry within coral reef ecosystems.

The hypothesis of this study is that two groundwater sources will contribute TA to Muri Lagoon, a fringing coral reef lagoon in the Cook Islands. To test this hypothesis, advective, benthic incubations were used to determine the influence of porewater advection on alkalinity fluxes from permeable sediments over short temporal and spatial scales (herein referred to as porewater fluxes). Measurements of 222Rn were also undertaken to determine the input of alkalinity from larger temporal and spatial scale groundwater exchange (herein referred to as SGD or groundwater). While “porewater” and “groundwater” are technically synonymous (i.e., any water in contact with geological materials), the hydrology and oceanochemistry communities tend to refer to porewater as a shallow interstitial water and groundwater as deeper, fresher water (Burnett et al., 2003, 2006).

2 Materials and methods

2.1 Study site

Our study site was located on the island of Rarotonga, a South Pacific, volcanic island within the archipelago of the Cook Islands. Rarotonga is the largest island in the Cook Islands group (67 km2) and made up of volcanic rocks that are comprised of 42 % to 53 % SiO2 and 2 % to 14 % CaO (Waterhouse et al., 1986). Rarotonga has a rainy (November to April) and dry (May to October) season, with average annual rainfall of 1900 mm yr−1 (Thompson, 1986). Muri Lagoon is a fringing, coral reef lagoon located along the southwestern coast of Rarotonga (Fig. 1). The study site was divided into two locations within Muri Lagoon: one where the chamber incubations were performed and the second where the water column monitoring station was set up (Fig. 1). The chamber sampling site was located further (~75 m) from shore to minimize any SGD impact and because of the large area of carbonate sediments free from macrophytes. The monitoring station consisted of multiple probes and a bilge pump connected to a cinder block roughly 10 m offshore from the low tide mark. The lagoon extended ~750 m offshore to the reef crest from our monitoring station (Fig. 1). Muri Lagoon has an average depth of about 1.4 m and covers an area of 1.75 km2 (Holden, 1992). The flow in Muri Lagoon is dominated by wave setup and runs from the reef crest towards shore, and then northeast along the shore towards a channel that opens to the ocean (Holden, 1992). The tidal cycle in Muri Lagoon is semi-diurnal with an average range of 1 m. The tidal range during our sampling period was 0.4 m and was towards the end of a spring tide cycle.

Sediment in the lagoon has a hydraulic conductivity of ~17.3 m−1 d−1, which equates to a permeability of approximately 1.91 × 10−11 m2. Sediment grain size was 5.8 % >2 mm, 16.5 % between 1–2 mm, 19.4 % between 500 µm–1 mm, 30.6 % between 250 µm–500 µm, 25.0 % between 125 µm–250 µm, 2.5 % between 63 µm–125 µm, and 0.2 % <63 µm. Bulk carbonate sediments were composed of 0.5 % calcite, 0.7 % quartz, 26.3 % Mg calcite (15.5 % Mg content), and 71.9 % aragonite as determined by X-ray diffraction analysis. Visual inspection of the sediments revealed black coloration a few cm below the surface, which is typical of high sulfide concentrations.

2.2 Advective chamber sampling and porewater fluxes

Chambers identical to those described in Glud et al. (2008) and Eyre et al. (2008) were used to measure in situ benthic solute fluxes at three different advection rates. Three chambers were inserted 15 cm into the sediment and enclosed roughly 4L of overlying seawater during the incubations. Advection was induced within the chambers based on the spinning rate, in rotations per minute (RPM), of the acrylic disk within each chamber (diffusive, 40 RPM, and 60 RPM). Three stirring rates were chosen in order to investigate any effect of advection on alkalinity flux rates, similar to studies done in other coral lagoons (Glud et al., 2008; Cyronak et al., 2013). In order to maintain a homogenous distribution of solutes within the diffusive chamber, it was operated with the disk slowly spinning clockwise for one rotation, then pausing and spinning counter clockwise for one rotation and repeating (Glud et al., 2008). Incubations were run concurrently with the water column sampling, starting at 07:00 LT on 17 March 2012 and lasting for 28.5 h. Samples of 150 mL were drawn by syringe with ambient seawater allowed to replace the sample volume. The sample volume removed represented a minor percentage of the volume within the chambers (<4 %) and therefore was unlikely to greatly influence chamber solute concentrations. Flux rates from the chambers were calculated using the integral-based technique as described in Cyronak et al. (2013). Negative numbers represent a flux into the sediments, while positive numbers represent fluxes of solutes out of the sediments. In order to compare advective flux rates to 222Rn-derived SGD
flux rates, averages between the two advective stirring rates (40 and 60 RPM) were used (discussed in detail later).

2.3 Water column sampling

Discrete samples were taken every 2 h from the water column along with the monitoring of physico-chemical parameters every 5 min using a multi-probe. A Hydrolab DSSX (Hach Environmental) was deployed 0.2 m from the bottom and 10 m offshore of the low tide mark to monitor temperature (±0.5 °C), PAR (±5%), and salinity (±0.5%) every 5 min. Depth was measured using an In-Situ Inc. Aqua Troll 200. For the monitoring data, an average over 1 h (30 min before and after) was taken over half-hour intervals in order to smooth the data and better reveal any trends. Sampling of the water column started at 7:00 LT on 17 March 2012 and lasted for 28.5 h. Discrete water samples were taken using 150 mL plastic syringes and brought back to lab to measure salinity, DO, TA, δ¹³C DIC, and pH.

In order to measure ²²²Rn concentrations in the water column, a submersible bilge pump continuously pumped seawater to an onshore gas equilibration device (GED) at about 2 L min⁻¹. The GED equilibrates gas through a shower head exchanger similar to that described in Burnett et al. (2001). Air was recirculated through a closed loop from the GED into a RAD7 ²²²Rn detector in order to monitor ²²²Rn concentrations every 30 min (Burnett et al., 2001). In order to generate a groundwater endmember for ²²²Rn-derived flux calculations, a bore was dug 10 m offshore of the high tide mark and piezometers were inserted to depths of 1 m and 2.5 m. Discrete samples were taken from the 1 m piezometer at 3 separate times during the study, and one sample was taken from the 2.5 m piezometer. To measure the ²²²Rn end-member of groundwater, a peristaltic pump was used to pump water from the piezometers at 1 L min⁻¹ into the GED. The ²²²Rn concentrations were allowed to equilibrate and then measured for 1 to 4 h with the average concentration during that time used as the groundwater endmember. Gas permeable silicone tubing was only used in the pump head in order to minimize any losses of ²²²Rn. Laboratory experiments revealed no differences in concentrations when using a peristaltic pump and other pumps to feed the exchanger.

We used a non-steady-state ²²²Rn mass balance model from Burnett and Dulaiova (2003) to determine groundwater flux rates in cm³ m⁻² d⁻¹. The model incorporated sources of ²²²Rn from groundwater balanced by losses due to atmospheric evasion as a function of wind speed, mixing, and radioactive decay. The alkalinity of the mixed endmember (discussed in detail later) was multiplied by the flux rates generated by the model in order to get ²²²Rn-derived fluxes of groundwater TA into the lagoon. Both the advective TA fluxes and ²²²Rn-derived TA fluxes were calculated at the sampling locations and extrapolated along a 750 m transect to the reef crest (discussed in detail later).

2.4 Sample analysis

Both water column and benthic chamber samples were immediately brought back into the laboratory. Dissolved oxygen (±1%) was measured directly following collection using a Hach Luminescent Dissolved Oxygen (LDO®) probe. Samples for nutrients were filtered with a 0.45 µm cellulose acetate filter and frozen at −20 °C until analyzed following the methods of Eyre and Ferguson (2005) using a Lachat flow injection analysis (FIA) system. Samples for TA and pH were filtered through a 0.45 µm cellulose acetate filter and stored in an airtight container with no headspace until analysis within 4 h of sampling. pH (±0.003) was measured using a Metromoh Electrode Plus calibrated to Oakton National Bureau of Standards (NBS) standards of 4, 7, and 10. To determine TA, Gran titrations were performed using a Metromoh Titrando automatic titrator and pH electrode. Pre-standardized 0.01 mol L⁻¹ HCl was used as the titrant, which was calibrated against Dickson certified reference material (Batch 111). Alkalinity samples were run twice, and the average of the two values was used. During the study the % CV of duplicate TA measurements was 0.15%.

Samples for δ¹³C DIC (analytical error of ±0.1‰) were 0.7 µm filtered with a Whatman GF/F syringe filter, preserved using 50 µL of saturated HgCl with no head space, and stored at 4 °C. δ¹³C DIC was measured in order to separate any sources of TA and DIC in the groundwater and water column. Samples were acidified with 5% (v/v) phosphoric acid, and the resulting CO₂ was analyzed via continuous flow wet oxidation isotope ratio mass spectrometry (CF-WO-IRMS) using an Aurora 1030W total organic carbon (TOC) analyzer coupled to a Thermo Delta V Plus IRMS (Oakes et al., 2010). DIC concentrations and W_Ar were estimated with the Excel macro CO₂ System (CO2SYS) (Pierrot et al., 2006) using inputs of TA and pH and the constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987) and W_Ar. Data from Cyronak et al. (2013) showed excellent agreement between measured and calculated DIC concentrations using the same inputs into CO2SYS as this study. Carbonate alkalinity (TAC) for the chamber samples was calculated by subtracting the alkalinity, as determined in CO2SYS, contributed by B(OH)₄⁻, OH⁻ and total dissolved phosphorus (TDP) from TA.

3 Results

3.1 Advective chambers

The flux rates of TAC, DIC, DO, and H⁺ from the chambers are shown in Fig. 2. All of the rates follow a distinct diel pattern that is consistent with biological activity acting as the driver of solute fluxes from permeable sediments. Flux rates of TAC decreased throughout the day and began to increase in the late afternoon (Fig. 2a). TAC flux rates became
positive around sunset and increased until midnight, and then varied slightly for the rest of the night until becoming negative in the morning. DIC flux rates showed a similar pattern to TA$_C$ (Fig. 2b). DO and H$^+$ flux rates followed the opposite pattern of DIC and TA$_C$ fluxes (Fig. 2). DO fluxes increased throughout the morning then decreased in the late afternoon, becoming negative around sunset and levelling off during the night (Fig. 2c). H$^+$ fluxes showed the same trend as DO fluxes with slight variation in the night (Fig. 2d). Figure 3 shows the hourly flux rates of TA$_C$, DIC, and DO plotted against the average PAR values measured during the same time period as the flux. Flux rates are in mmol m$^{-2}$ h$^{-1}$.

### 3.2 Water column time series

The water column time series was conducted over two tidal cycles and one diel cycle (Fig. 4). Salinity fluctuated throughout the day, and the lowest salinities occurred during the low tides (Fig. 4a and b). DO concentrations and $\Omega_{AR}$ followed a trend that was consistent with diel variation driven by biological processes, and throughout the course of the day $\Omega_{AR}$ varied from 2.3 to 4.4 (Fig. 4e and f). In contrast, TA had a complex dynamics that was related to both diel and tidal cycles, supported by the variation in TA concentrations measured over one diel cycle and two tidal cycles (Fig. 4c). DIC concentration showed a similar trend to TA while the $\delta^{13}C$ of DIC followed the opposite trend, decreasing with any increase in [DIC] (Fig. 4d). During sampling, $^{222}$Rn concentrations in the water column varied between 7471 dpm m$^{-3}$ and 16 040 dpm m$^{-3}$, and were highest during low tides (Fig. 5).

### 3.3 Groundwater endmembers

Groundwater measured from piezometers at 1 m and 2.5 m was fresh but differed in solute composition (Table 1). The water chemistry in the three samples taken from the 1 m well did not vary much between the different sampling times, so we reported the average (see Table 1). The DIC concentrations were about twice as high in the shallower groundwater than in the deeper groundwater while $\delta^{13}C$ DIC was more enriched in the deeper groundwater. TA was 7134 µmol L$^{-1}$ in the shallow groundwater and 3989 µmol L$^{-1}$ in the deeper groundwater. However, $^{222}$Rn concentrations showed the opposite trend of the solutes, with concentrations in the deeper groundwater roughly 6 times higher than in the shallow groundwater. The pH of the shallow groundwater was lower than the deeper groundwater. We suspect that the discharging groundwater represents a mixture of these two and potentially other groundwater endmembers.

### 4 Discussion

#### 4.1 Diel cycling of TA in advective chambers

Hourly flux rates of TA$_C$, DIC, DO, and H$^+$ followed trends that were consistent with biological activity driving the fluxes of those solutes over a diel cycle (Fig. 2). During the day, flux rates of all solutes were greatest, whether negative or positive, in the afternoon at the 15:30 LT sampling point (Fig. 2). This is consistent with the availability of PAR driving rates...
of benthic photosynthesis. Photosynthesis would alter the chemistry of porewaters by taking up DIC and releasing DO into the porewaters, thereby affecting both flux rates of TA_C (by promoting carbonate precipitation) and H^+, while respiration would have the opposite effect (Cook and Røy, 2006; Cyronak et al., 2013). Efflux rates of TA_C in the morning indicate that dissolution of carbonates is still occurring until the late morning when the sediments shift to TA_C uptake. During the nighttime, the flux rates of all solutes tended to level off after the transition between light and dark (Fig. 2). This is probably due to the shift in biological activity from production to respiration and the associated changes in porewater chemistry.

Maximum hourly TA_C uptake and efflux rates were similar between all three chambers (Table 2). When compared to flux rates obtained from identical chambers in Heron Island (Australia), fluxes from the Cook Islands were generally lower (Table 2). Also uptake rates were stimulated by advection in Heron Island, whereas TA_C uptake rates in the Cook Islands were similar between the stirring rates. The exact mechanisms behind these differences are unknown, but visual inspection of the two sediments revealed less biota (e.g., calcareous algae and fauna) in the Cook Island sediments. Lower amounts of benthic fauna would decrease any biologically driven stimulatory effect of advection on benthic fluxes (Cook and Røy, 2006; Cyronak et al., 2013). In addition, the black reducing layer apparent in the Cook Island sediments was not present in Heron Island. As advection delivers oxygen to this layer, it may lower the TA concentrations in the porewaters due to sulfide oxidation (Ku et al., 1999). This is consistent with reduced benthic fluxes in the

Table 1. Measurements of solutes in the groundwater endmembers (EM), EM1 n = 3, EM2 n = 1. δ^{13}C DIC of the mixed endmember was estimated from the y-intercept of a Keeling plot. The 47 % EM1 : 53 % EM2 is the concentration calculated from the δ^{13}C DIC-estimated endmember values.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>DIC (µmol L^{-1})</th>
<th>δ^{13}C DIC</th>
<th>TA (µmol L^{-1})</th>
<th>^{222}Rn (dpm m^{-3})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater EM1</td>
<td>1</td>
<td>9381 ± 354</td>
<td>-10.1 ± 1.0</td>
<td>7134 ± 60</td>
<td>49585 ± 1743</td>
</tr>
<tr>
<td>Groundwater EM2</td>
<td>2.5</td>
<td>4251</td>
<td>-6.3</td>
<td>3989</td>
<td>294146 ± 4601</td>
</tr>
<tr>
<td>47 % EM1 : 53 % EM2</td>
<td>-</td>
<td>6661</td>
<td>-8.10</td>
<td>5467</td>
<td>179202</td>
</tr>
</tbody>
</table>

Table 2. Maximum hourly uptake and efflux rates of TA_C measured from advective benthic chambers in this study compared to a similar study on the Great Barrier Reef. Daily flux rates of TA_C are also shown.

<table>
<thead>
<tr>
<th>Location</th>
<th>Chamber</th>
<th>TA_C Efflux (mmol m^{-2} h^{-1})</th>
<th>TA_C Uptake (mmol m^{-2} h^{-1})</th>
<th>Daily TA_C Flux (mmol m^{-2} d^{-1})</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cook Islands</td>
<td>Diffusive</td>
<td>3.32</td>
<td>-4.01</td>
<td>-1.16</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>40 RPM</td>
<td>3.96</td>
<td>-4.78</td>
<td>7.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 RPM</td>
<td>3.17</td>
<td>-4.01</td>
<td>-1.55</td>
<td></td>
</tr>
<tr>
<td>Heron Island</td>
<td>Diffusive</td>
<td>5.21</td>
<td>-4.83</td>
<td>5.13</td>
<td>Cyronak et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>40 RPM</td>
<td>4.93</td>
<td>-5.65</td>
<td>8.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80 RPM</td>
<td>5.61</td>
<td>-7.36</td>
<td>8.78</td>
<td></td>
</tr>
</tbody>
</table>
a diel cycle (Schneider et al., 2009). Similar processes may be occurring in the microbiota living in the sediments, which would contribute to the observed hysteresis. Also, because DO is consumed through sulfide oxidation (Ku et al., 1999), high sulfide production and the subsequent buildup in the porewaters overnight might also lead to the observed hysteresis in flux rates. If sulfide concentrations built up overnight, DO produced in the morning would be consumed in the sediments, potentially leading to the lower oxygen efflux rates observed in the morning than the afternoon (Fig. 3).

The slope of DIC vs. TA\textsubscript{C} can be used to determine the amount of DIC that was produced due to organic or inorganic processes (Gattuso et al., 1996; Andersson and Gledhill, 2013). DIC and TA\textsubscript{C} fluxes in the chambers were tightly correlated with an $R^2$ of 0.970 (Fig. 6a). The organic to inorganic ratio of the DIC flux was 2.13 as calculated from the slope in Fig. 6a. This value is lower than those reported from water column measurements but typical of sediments, possibly due to sediment porewaters being in close contact to a non-organic source (i.e., carbonates) of DIC (Gattuso et al., 1996; Cyronak et al., 2013). TA\textsubscript{C} flux rates were well correlated with DO and DIC fluxes in the sediments (Fig. 6b and c), indicating that photosynthesis and respiration drive carbonate precipitation and dissolution. However, TA\textsubscript{C} flux rates were not as well correlated with DO fluxes (Fig. 6b) as DIC fluxes corrected for the contribution of TA due to carbonate precipitation and dissolution (Fig. 6c). This may be related to oxygen consumption by sulfides in the sediments (Ku et al., 1999). Additional investigations on the role sulfides play in alkalinity cycling in coral reef sediments are warranted.

### 4.2 Estimating a mixed groundwater endmember

When plotted against salinity, DIC concentrations in the water column showed a significant linear correlation consistent with conservative mixing between groundwater and the water column (Fig. 7). A Keeling plot, or the linear regression of $\delta^{13}$C DIC versus 1/[DIC], can be used to estimate the $\delta^{13}$C of DIC added to the system by calculating the y-intercept (Fig. 8) (Mortazavi and Chanton, 2004; Köhler et al., 2006; Hu and Burdige, 2007). The contribution of both groundwater endmembers (shallow and deep) to the water column can be estimated by using the $\delta^{13}$C of added DIC generated from the Keeling plot as the $\delta^{13}$C of the mixed endmember. The estimated contribution of the shallow and deep endmembers to the water column was 47% and 53%, respectively (Table 1). The concentrations of DIC, TA, $^{222}$Rn, and pH calculated using the above percentages were used as the endmember in subsequent mixing models, which matched well to the measured groundwater values in the bores (Table 1).

We recognize that since $^{222}$Rn concentrations were variable with depth, the groundwater endmembers could be variable over larger spatial scales (Dulaivova et al., 2008; Santos et al., 2009). A larger number of groundwater samples could be important to decrease any potential uncertainties with the groundwater endmember and better elucidate fluxes over larger spatial scales.

A two-source mixing model can be used to estimate the water column concentrations of TA based on $^{222}$Rn concentrations measured during the sampling period. $^{222}$Rn concentrations from the water column were divided by the mixed
endmember concentration (47% EM1 : 53% EM2), and a percent groundwater input was then multiplied by the endmember of TA (Table 1). When a range of endmembers was used for water column TA concentrations (2100 to 2400 µmol L$^{-1}$), which would change over the course of a day due to biological and geochemical activities (Gattuso et al., 1996; Shamberger et al., 2011), the measured concentration of TA fit within the model (Fig. 9a). A variable endmember model was also calculated based on the change in lagoonal TA concentrations over the course of a day estimated from Fig. 10. During the day, $^{222}$Rn versus TA showed a different linear slope than during the night, which is consistent with carbonate precipitation being dominant during the day and dissolution during the night (Fig. 10). The initial concentration of water column TA (i.e., in the morning) was estimated as the y-intercept from the night regression of TA vs. $^{222}$Rn (2327 mmol L$^{-1}$). Based on the difference between the y-intercepts for the night and day linear regressions (Fig. 10), an average rate of change for TA in the water column that excludes the effects of groundwater was estimated as $-20$ mmol m$^{-2}$ h$^{-1}$ during the day and 20 mmol m$^{-2}$ h$^{-1}$ at night. When the variable endmember was applied to the water column portion of the $^{222}$Rn mixing model, there was good agreement between the predicted and measured water column TA concentrations (Fig. 9b). Observed variability between the measured and predicted water column TA is probably due to diel variability in TA fluxes that are not accounted for in this model.

Because $\delta^{13}$C of DIC is depleted in the groundwater ($-6\%$ to $-10\%$) when compared to oceanic water (0% to 2%) (Williams et al., 2011), and most of the TA in the groundwater is present as DIC, sources of TA to the groundwater can be inferred. The low $\delta^{13}$C values of DIC in the groundwater are indicative of an organic source of carbon, as carbonate minerals tend to have $\delta^{13}$C values from 0% to 2% (Weber and Woodhead, 1969; Eadie and Jeffrey, 1973; Ogrinc et al., 2003). Sulfate reduction is well known to increase TA concentrations (Wolf-Gladrow et al., 2007), and may account for a portion of the high TA concentrations in Rarotonga groundwater. The uncoupling of sulfate reduction from sulfide oxidation would generate carbonate alkalinity with a depleted $\delta^{13}$C value due to the organic C source, perhaps accounting for the depleted $\delta^{13}$C DIC values found in the groundwater (Ku et al., 1999).

Because $\delta^{13}$C of DIC is depleted in the groundwater ($-6\%$ to $-10\%$) when compared to oceanic water (0% to 2%) (Williams et al., 2011), and most of the TA in the groundwater is present as DIC, sources of TA to the groundwater can be inferred. The low $\delta^{13}$C values of DIC in the groundwater are indicative of an organic source of carbon, as carbonate minerals tend to have $\delta^{13}$C values from 0% to 2% (Weber and Woodhead, 1969; Eadie and Jeffrey, 1973; Ogrinc et al., 2003). Sulfate reduction is well known to increase TA concentrations (Wolf-Gladrow et al., 2007), and may account for a portion of the high TA concentrations in Rarotonga groundwater. The uncoupling of sulfate reduction from sulfide oxidation would generate carbonate alkalinity with a depleted $\delta^{13}$C value due to the organic C source, perhaps accounting for the depleted $\delta^{13}$C DIC values found in the groundwater (Ku et al., 1999).
Fig. 7. Regression of salinity vs. [DIC] in the water column measured over the course of the study. The regression equation and $R^2$ value are displayed.

Fig. 8. Keeling plot of $\delta^{13}$C DIC vs. 1/[DIC] measured in the water column.

4.3 $^{222}$Rn-derived TA groundwater fluxes

Advection rates of groundwater into the water column were estimated using a non-steady-state $^{222}$Rn mass balance model (Burnett and Dulaiova, 2003) and the concentration of $^{222}$Rn estimated in the groundwater endmember (179 202 dpm m$^{-3}$) (Table 1). Fluxes of groundwater ranged from 0 to 46 cm d$^{-1}$ and were highest during low tides. This is consistent with steep hydraulic gradients at low tide driving fresh groundwater flow into the lagoon (Chanton et al., 2003; Kuan et al., 2012). The groundwater flux rates can be converted to an hourly basis and multiplied by the groundwater endmember concentration of TA (5467 µmol L$^{-1}$) to estimate the fluxes of TA into the water column (Fig. 11). Fluxes ranged from 0 to 46 cm d$^{-1}$ and were highest during low tides. The

average daily $^{222}$Rn-derived TA flux measured during this study was 1080 mmol m$^{-2}$ d$^{-1}$ at the sampling site. These flux rates are most likely spatially variable throughout the lagoon, with the highest flux rates found close to shore where SGD is most influential.

The $^{222}$Rn-derived TA fluxes are high when compared to other TA sources and sinks in coral reef environments (Gat吐so et al., 1998; Shamberger et al., 2011). However, the hourly flux rates agree well with flux rates that are needed to explain the observed changes in water column TA concentrations. Flux rates needed to account for the observed increases in TA concentrations during the day were as high as 103 mmol m$^{-2}$ h$^{-1}$. These values are comparable to the SGD-derived TA fluxes calculated from the $^{222}$Rn mass balance and groundwater TA concentrations, which ranged from 0 to 105 mmol m$^{-2}$ h$^{-1}$ (Fig. 11). The fact that these two independent calculations, agree well lends support to hourly and daily $^{222}$Rn-derived SGD TA fluxes. Also, TA concentrations at our study site were elevated (up to 2608 µmol L$^{-1}$;
Fig. 10. TA vs. \(^{222}\)Rn concentrations in the water column: separate regressions were made for daytime and nighttime hours. The three daylight time points taken during the second sampling day were removed from the regressions.

Fig. 11. Hourly SGD-derived flux rates of TA into the water column plotted alongside depth over the course of the study.

Fig. 12. Hourly flux rates of TA from advective sediment incubations and SGD along a 750 m transect from the study site to reef crest. 100% cover was assumed for advective sediments, and SGD was estimated as mixing 50 m offshore.

There are a number of factors that would influence the flux of TA from SGD into coastal ecosystems, one of which is the concentration of TA in the groundwater. In general TA concentrations of groundwater exhibit a large range and are probably highly dependent on local geology, but can be up to 6 times as high as oceanic TA (Table 3). The amount of TA fluxed into the lagoon is dependent on how far the groundwater mixes offshore and the location of point sources of SGD within the lagoon (Burnett et al., 2003; Burnett and Dulaiova, 2003; Schopka and Derry, 2012). Based on radium isotope ratios in Muri Lagoon, a conservative residence time of 6 days was estimated for water in the lagoon. This long residence time means TA derived from groundwater can accumulate in the lagoon, raising the water column \(\Omega_{Ar}\) above oceanic levels and potentially buffer against ocean acidification. However, groundwater may also act as a source of \(\text{CO}_2\), which would inhibit the buffering capacity of SGD-derived TA fluxes. Also, groundwater is a potential source of nutrients (Valiela et al., 1999; Burnett et al., 2003; Paytan et al., 2006), contaminants (Cohen et al., 1984; Bedient et al., 1994), and other solutes that could degrade reef health.

There are not many studies assessing the influence of SGD on alkalinity fluxes to the water column, and none in coral reef ecosystems. Moore et al. (2011) used radium isotopes to trace the fluxes of groundwater to the Wadden Sea, showing that SGD acts as an important source of TA, Mn, dissolved organic carbon (DOC), and silicate to the ocean. Other studies have measured the concentration of TA in groundwater, but do not discuss SGD fluxes of TA to open water ecosystems (see Table 3). There are multiple groundwater exchange processes besides terrestrial hydraulic gradients that could alter TA cycling in coral lagoons (Burnett et al., 2003; Santos et al., 2012). For instance, tidal pumping and saltwater intrusion occurring on a larger scale than advective process may alter microbial processes in the sediment, and subsequently the cycling of TA (Kuan et al., 2012; Santos et al., 2012). The impact of these processes on TA fluxes into coral reef lagoons merits further investigation. Also, any seasonal variability in rainfall may influence SGD flux rates over larger temporal and spatial scales.
cause advective processes follow a diel cycle and groundwa-
ter is driven by tidal cycles, longer term experiments may be
ter is driven by tidal cycles, longer term experiments may be
Table 3. Concentrations of TA (µmol L\(^{-1}\)) measured in groundwater throughout the world. * Designates concentrations measured as HCO\(_3\)\(^-\).

<table>
<thead>
<tr>
<th>TA (µmol L(^{-1}))</th>
<th>System type</th>
<th>Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2150–2949</td>
<td>Subtropical estuary</td>
<td>South Carolina, USA</td>
<td>Cai et al. (2003)</td>
</tr>
<tr>
<td>90–8920</td>
<td>Subtropical estuary</td>
<td>Kunsan, South Korea</td>
<td>Kim et al. (2004)</td>
</tr>
<tr>
<td>4020</td>
<td>Subtropical estuary</td>
<td>Southern China</td>
<td>Liu et al. (2012)</td>
</tr>
<tr>
<td>753–7026*</td>
<td>Inland mountains</td>
<td>Central Mexico</td>
<td>Mahlknecht et al. (2004)</td>
</tr>
<tr>
<td>2550–23 300</td>
<td>Tidal flat</td>
<td>Wadden Sea, Germany</td>
<td>Moore (2011)</td>
</tr>
<tr>
<td>95–2000*</td>
<td>Tropical island</td>
<td>Guadeloupe</td>
<td>Rad et al. (2007)</td>
</tr>
<tr>
<td>1400–13 000*</td>
<td>Tropical island</td>
<td>Martinique</td>
<td>Rad et al. (2007)</td>
</tr>
<tr>
<td>800–4016*</td>
<td>Tropical island</td>
<td>Réunion</td>
<td>Rad et al. (2007)</td>
</tr>
<tr>
<td>2290*</td>
<td>Coastal lagoon</td>
<td>Brazil</td>
<td>Santos et al. (2008)</td>
</tr>
<tr>
<td>1328–2162</td>
<td>Tropical island</td>
<td>Hawaiian Islands</td>
<td>Schopka and Derry (2012)</td>
</tr>
<tr>
<td>3989–7134</td>
<td>Tropical island</td>
<td>Cook Islands</td>
<td>This study</td>
</tr>
</tbody>
</table>

4.4 Upscaling porewater and groundwater fluxes

Because the flux rates of these benthic processes are variable
ter is driven by tidal cycles, longer term experiments may be

Previous studies have estimated coral reef community
calcification rates that range from 31.2 to 292.8 mmol
CaCO\(_3\) m\(^{-2}\) d\(^{-1}\) (or \(-62.4 to \(-585.6\) mmol TA m\(^{-2}\) d\(^{-1}\))
(Shamberger et al., 2011). Using that range of community
TA uptake rates along the 750 m transect reveals that pore-
water advection can add from 0.4 to 7.5 % of the TA taken
out of the water column by coral communities. SGD-derived
TA fluxes can add from 10 % to 107 % of the TA taken up
by coral communities. The community TA uptake rates of coral
lagoons are generally low compared to other reef ecosystems
(Kinsey, 1983), which means it is likely that groundwater
processes contribute towards the higher end of that range in
Muri Lagoon. This is consistent with the elevated TA con-
centrations at the study site. This previously unaccounted for
source of TA is important in changing the carbonate chem-
istry within Muri Lagoon over tidal and diel cycles.

5 Conclusions

Alkalinity concentrations in Muri Lagoon followed a pattern
which is indicative of both biological and tidal drivers influ-
encing the dynamics of water column TA over a diel cycle
(Fig. 4). Different groundwater exchange mechanisms, act-
ing on varying temporal and spatial scales, can have different
influences on water column alkalinity. Small-scale porewater
advection acted as both a source and sink of TA over the
course of a day, with net daily fluxes ranging from \(-1.55\) to
7.76 mmol m\(^{-2}\) d\(^{-1}\) depending on advection rates. Based on
the average of the 40 and 60 RPM chambers along the 750 m
transect, porewater advection was a net source of TA to the
lagoon (2.1 to 4.7 mmol m\(^{-2}\) d\(^{-1}\)). SGD fluxes were driven
by tidal processes and delivered 1080 mmol TA m\(^{-2}\) d\(^{-1}\) to
the water column at the study site. The daily SGD-derived
TA flux is high when compared to other sources and sinks
of TA. However, it is site-specific and groundwater is likely
discharged only a discrete distance from shore. Along the
750 m transect, SGD fluxed from 60 to 67 mmol TA m$^{-2}$ d$^{-1}$ to the water column. It is likely that similar advective exchanges of TA occur throughout different reef systems, while SGD is highly dependent on the specific geological, physical, and biological attributes of the land masses associated with coral reefs. It is important to constrain the variability of SGD-derived fluxes over larger temporal and spatial scales by measuring $^{222}$Rn concentrations across broad areas of coral reef environments. Assessing groundwater exchange processes occurring in coral reef ecosystems is necessary so that more detailed models predicting how ocean acidification will alter reef carbonate chemistry can be developed.

Acknowledgements. Kevin Befus, Alicia Hidden, and Douglas Tait provided valuable help during the field campaign. Matheus Carvalho skilfully ran DIC isotope samples, and Iain Alexander ran nutrient samples. This project was funded by the Australian Research Council grants (LP100200732 and DP110103638), the Australian Agency for International Development (AusAID), and the Cook Islands Ministry of Infrastructure and Planning.

Edited by: S. Bouillon

References


