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# Drivers of pCO<sub>2</sub> Variability in Two Contrasting Coral Reef Lagoons: The Influence of Submarine Groundwater Discharge

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# Global Biogeochemical Cycles

## RESEARCH ARTICLE

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### Key Points:

- Groundwater can influence  $p\text{CO}_2$  variability in coral reefs
- Submarine groundwater discharge may enhance local ocean acidification
- Measurements of net community calcification can be influenced by groundwater

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## Drivers of $p\text{CO}_2$ variability in two contrasting coral reef lagoons: The influence of submarine groundwater discharge

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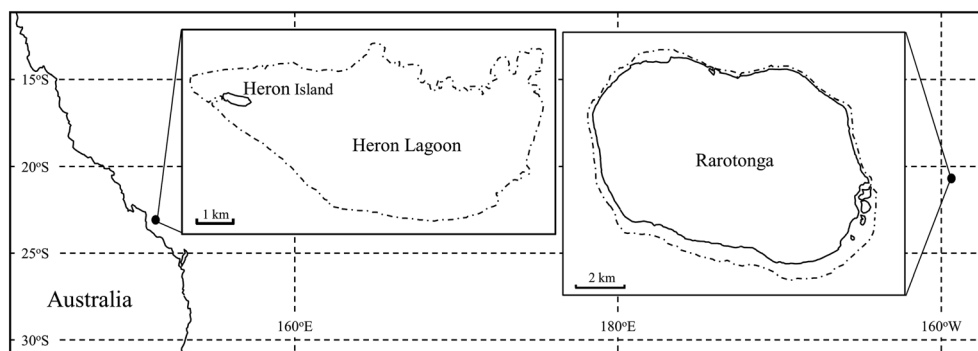
**Abstract** The impact of groundwater on  $p\text{CO}_2$  variability was assessed in two coral reef lagoons with distinct drivers of submarine groundwater discharge (SGD). Diel variability of  $p\text{CO}_2$  in the two ecosystems was explained by a combination of biological drivers and SGD inputs. In Rarotonga, a South Pacific volcanic island,  $^{222}\text{Rn}$ -derived SGD was driven primarily by a steep terrestrial hydraulic gradient, and the water column was influenced by the high  $p\text{CO}_2$  (5501  $\mu\text{atm}$ ) of the fresh groundwater. In Heron Island, a Great Barrier Reef coral cay, SGD was dominated by seawater recirculation through the sediments (i.e., tidal pumping), and  $p\text{CO}_2$  was mainly impacted through the stimulation of biological processes. The Rarotonga water column had a higher average  $p\text{CO}_2$  (549  $\mu\text{atm}$ ) than Heron Island (471  $\mu\text{atm}$ ). However,  $p\text{CO}_2$  exhibited a greater diel range in Heron Island (778  $\mu\text{atm}$ ) than in Rarotonga (507  $\mu\text{atm}$ ). The Rarotonga water column received  $29.0 \pm 8.2$  mmol free- $\text{CO}_2$   $\text{m}^{-2} \text{d}^{-1}$  from SGD, while the Heron Island water column received  $12.1 \pm 4.2$  mmol free- $\text{CO}_2$   $\text{m}^{-2} \text{d}^{-1}$ . Over the course of this study, both systems were sources of  $\text{CO}_2$  to the atmosphere with SGD-derived free- $\text{CO}_2$  most likely contributing a large portion to the air-sea  $\text{CO}_2$  flux. Studies measuring the carbon chemistry of coral reefs (e.g., metabolism and calcification rates) may need to consider the effects of groundwater inputs on water column carbonate chemistry. Local drivers of coral reef carbonate chemistry such as SGD may offer more approachable management solutions to mitigating the effects of ocean acidification on coral reefs.

## 1. Introduction

Since the industrial revolution, oceans have absorbed approximately 30% of anthropogenically produced  $\text{CO}_2$  from the atmosphere, resulting in an increase in oceanic  $p\text{CO}_2$  [Feely *et al.*, 2004]. This increase in  $p\text{CO}_2$  changes the carbonate chemistry of seawater, reducing the pH in a process termed ocean acidification (OA) [Doney *et al.*, 2009]. This increase in  $p\text{CO}_2$  has been apparent in the open ocean, but has been difficult to detect in coastal ecosystems, which can experience large  $p\text{CO}_2$  variability on diel and seasonal time scales [Kayanne *et al.*, 1995; Friedrich *et al.*, 2012; Duarte *et al.*, 2013]. High  $p\text{CO}_2$  has been shown to have deleterious effects on coral health through a reduction in calcification rates attributed to decreases in seawater pH and aragonite saturation state ( $\Omega_{\text{Ar}}$ ) [Leclercq *et al.*, 2000, 2002; Langdon *et al.*, 2003]. In order to properly address how OA is likely to affect coral reef ecosystems, a detailed understanding of  $p\text{CO}_2$  variability and its associated drivers is needed.

Previous studies have generally assessed coral reef  $p\text{CO}_2$  variability in terms of community metabolism [Drupp *et al.*, 2011; Gattuso *et al.*, 1993, 1995; Frankignoulle *et al.*, 1996], calcification [Shamberger *et al.*, 2011; Shaw *et al.*, 2012], and air-sea  $\text{CO}_2$  fluxes [Kayanne *et al.*, 1995; Bates, 2002; Massaro *et al.*, 2012] and may have overlooked important drivers of  $\text{CO}_2$  dynamics. In the early to mid-1990s, there were a number of studies that measured  $p\text{CO}_2$  variability in coral reefs, mainly attempting to assess whether reefs were a source or sink of  $\text{CO}_2$  to the atmosphere [Ware *et al.*, 1992; Kayanne *et al.*, 1995; Buddemeier, 1996]. Recent interest in OA, however, has increased the demand for high-resolution  $p\text{CO}_2$  data sets from coral reef ecosystems.

The diel variability of  $p\text{CO}_2$  in coral reefs is often attributed to their high benthic metabolic rates [Kayanne *et al.*, 1995]. Along with photosynthesis and respiration, calcification has been shown to alter the  $p\text{CO}_2$  of coral reefs, as  $\sim 0.6$  mol of  $\text{CO}_2$  are released for each mole of calcium carbonate ( $\text{CaCO}_3$ ) produced



**Figure 1.** Map showing the location of Heron Island and Rarotonga. The dotted line around each island represents the boundary of the reefal crest.

[Frankignoulle *et al.*, 1994]. In shallow coral reef lagoons and reefal flats,  $p\text{CO}_2$  can range from 77 to 1256  $\mu\text{atm}$  over a diel cycle [Gray *et al.*, 2012; Shaw *et al.*, 2012]. There is also variability in  $p\text{CO}_2$  over seasonal time scales, with lower values and narrower diel ranges usually found in the winter due to temperature effects and reduced ecosystem metabolism [Bates, 2002; Kayanne *et al.*, 2005; Gray *et al.*, 2012]. Often, net ecosystem metabolism and calcification are calculated based on changes in carbonate system parameters, which can be reflected in  $p\text{CO}_2$  values [Kinsey, 1978; Gattuso *et al.*, 1993; Shamberger *et al.*, 2011]. Therefore, any drivers that alter the carbonate chemistry of coral reefs that are not associated with metabolism and calcification could affect the measurements of net community metabolic and calcification rates.

Submarine groundwater discharge (SGD) has been shown to be an important source of freshwater and dissolved materials to coastal ecosystems [Burnett *et al.*, 2003], and there are varying mechanisms through which groundwater can be exchanged with open water [Santos *et al.*, 2012a]. SGD can refer to fresh groundwater delivered by terrestrial hydraulic gradients [Burnett *et al.*, 2003], as well as to the tidally driven recirculation of seawater through sediments [Robinson *et al.*, 2007; Santos *et al.*, 2010]. Radon ( $^{222}\text{Rn}$ ) has been used as a tracer for groundwater in coastal systems due to its naturally high concentrations in groundwater compared to surface waters and its unreactive nature [Cable *et al.*, 1996; Burnett *et al.*, 2006]. Because  $^{222}\text{Rn}$  is produced through contact with sediments, it can trace both fresh groundwater as well as tidally recirculated seawater [Santos *et al.*, 2010]. Studies assessing SGD advection rates on coral reefs report a broad range from 52 to 4732  $\text{L m}^{-1} \text{h}^{-1}$  and suggest that SGD can be an important source of nutrients to coral reef ecosystems [Lewis, 1987; D'Elia and Wiebe, 1990; Paytan *et al.*, 2006]. Past studies have speculated that groundwater can influence the water column carbonate chemistry of coral reef ecosystems [Smith and Pesret, 1974; Watanabe *et al.*, 2013], but none have demonstrated a clear link between the two. It has been shown that the point sources of SGD from geological features known as "ojos" can affect water column carbonate chemistry; however, these features are highly localized [Crook *et al.*, 2012].

We hypothesize that SGD is a broadly occurring and overlooked driver of  $p\text{CO}_2$  dynamics in the surface waters of coral reef ecosystems. We assessed this hypothesis in two contrasting coral reef lagoons: a Pacific Island fringing reef (Rarotonga) subject to large fresh groundwater inputs and a Great Barrier Reef atoll-like system (Heron Island) with little to no fresh groundwater inputs. This study examined the variability of  $p\text{CO}_2$  and  $^{222}\text{Rn}$  over tidal and diel cycles within these two coral reef systems. We build on recent papers that examined net ecosystem calcification at Heron Island [McMahon *et al.*, 2013] and assessed the influence of groundwater exchange on alkalinity at Rarotonga [Cyronak *et al.*, 2013].

## 2. Materials and Methods

### 2.1. Study Sites

Rarotonga (21°14'S, 159°47'W), the largest island in the South Pacific Cook Island archipelago, has an area of 67.19  $\text{km}^2$ , with ~36 km of shoreline (Figure 1). The island is surrounded by a fringing coral reef lagoon, which extends from 30 to 900 m to the reefal crest. The Cook Island chain was formed through volcanic

activity and is composed of extinct volcanoes rising  $>5000$  m from the ocean floor [Thompson *et al.*, 1998]. Rarotonga has a deeply dissected terrain, with steep ridges and deep valleys, and a maximum elevation of 650 m above sea level [Thompson *et al.*, 1998]. Rarotonga is characterized by a rainy (November to April) and dry (May to October) season, with a mean annual rainfall amount of  $\sim 2100$  mm  $\text{yr}^{-1}$ . Our study site was located on the southwestern side of the island in Muri Lagoon. Muri Lagoon has an average depth of about 1.4 m and covers an area of  $1.75$  km<sup>2</sup> [Holden, 1992]. The flow in Muri Lagoon is dominated by wave setup and runs from the reefal crest northwest toward shore and then northeast along the shore toward a channel, which opens to the ocean [Holden, 1992]. Previous studies have relied on a heat balance [Befus *et al.*, 2013] and geochemical tracers [Tait *et al.*, 2013] to assess SGD in Muri Lagoon. The tidal cycle in Muri Lagoon is semidiurnal with a range of 0.56 m measured during this study. In order to avoid confusion, the sampling site is referred to as Rarotonga or Rarotonga lagoon throughout the rest of this paper.

Heron Island (23°27'S, 151°55'E) is a coral cay located along the southern portion of the Great Barrier Reef,  $\sim 72$  km east of mainland Australia (Figure 1). The island itself consists mainly of coarse carbonate sands and has an area of  $0.16$  km<sup>2</sup>, a coastline of  $\sim 2.2$  km, and a maximum elevation of 3.6 m above sea level. Heron Island receives a mean annual rainfall amount of  $\sim 1028$  mm, with more precipitation occurring during the summer and fall months (November to April). Data collection at both sites was performed during similar seasons (i.e., months of higher precipitation), and the amount of rainfall was similar during both time series (3.0 mm at Rarotonga and 2.1 mm at Heron Island). Heron Island is surrounded by a large coral lagoon (26.4 km<sup>2</sup>), which has an average depth of 1.7 m [Wild *et al.*, 2004]. The benthic makeup of the lagoon is  $\sim 25\%$  living coral cover, while the rest is predominately carbonate sands [Wild *et al.*, 2004; Eyre *et al.*, 2008; Glud *et al.*, 2008]. The permeability and porosity of the sands are high, which allows seawater to easily flow through the sediments [Santos *et al.*, 2010]. The flow in the western half of the lagoon is influenced by a channel, which drains the lagoon at low tide. Our study site was on the southern side of Heron Island, which receives a strong lagoonal signal due to tidally influenced currents flowing east across the site. The tidal range measured during this study was about 2.1 m.

## 2.2. Time Series Observations

Sampling in the water column at Rarotonga was conducted from 15 to 19 March 2012, while sampling in the water column at Heron Island was conducted from 17 to 26 April 2012. Due to limitations in gear, groundwater time series were not run concurrently with the water column time series. The beach groundwater time series study at Rarotonga was performed on 21 March 2012 and lasted for 16 h, while the groundwater at Heron Island was monitored for 28 h starting on 12 April 2012. In order to monitor the fluctuations in the groundwater chemistry, a 0.5 m deep bore was dug at the high-tide mark directly on shore from the sampling site at Rarotonga. Due to the coarse nature of the Heron Island sediments (i.e., large chunks of coral that prevented a bore from being installed onshore of the water column study site), a preinstalled bore 30 m landward of the low-tide mark on the opposite side of the island was used. The bore at Heron Island was 7.5 m in depth.

During the water column time series at both study sites, all instrumentation was deployed  $\sim 10$  m offshore of the low-tide mark and 0.2 m from the bottom. A Vantage Pro (Davis Instruments) weather station was used to measure atmospheric wind speed, temperature, and pressure directly onshore of each sampling site. The monitoring of physicochemical parameters was done using a Hydrolab DS5X (Hach Environmental) and an Aqua Troll 200 (In-Situ Inc.). Data for depth, temperature ( $\pm 0.5\%$ ), and salinity ( $\pm 0.5\%$ ) were collected every 5 min. Dissolved oxygen (DO) ( $\pm 1\%$ ) was measured every 5 min using a Hach Luminescent Dissolved Oxygen (LDO<sup>®</sup>) probe connected to the Hydrolab. The pH ( $\pm 0.003$ ) was measured every 5 min using a SAMI2-pH sensor, which determines pH spectrophotometrically using metacresol purple as the indicator [Martz *et al.*, 2003; Seidel *et al.*, 2008]. The SAMI2 is factory calibrated to measure pH in the total hydrogen ion scale.

The  $p\text{CO}_2$  and  $^{222}\text{Rn}$  were measured concurrently through a shower head type gas equilibration device (GED) [Santos *et al.*, 2012b]. Seawater was pumped from each sampling site into the GED at a rate of  $\sim 2$  L  $\text{min}^{-1}$  using a bilge pump. Air was recirculated through a closed loop from the GED through a Drierite<sup>™</sup> column and into a Licor 7000 CO<sub>2</sub> detector and a RAD7  $^{222}\text{Rn}$  detector. The Licor 7000 is a differential, nondispersive infrared gas analyzer that was set to measure  $p\text{CO}_2$  ( $\pm 1\%$ ) at 1 min intervals. Prior to each field campaign, the Licor was calibrated across a range of premixed CO<sub>2</sub> gasses (306, 502 and 2017  $\mu\text{atm}$ ). The RAD7 was factory

**Table 1.** The Average (Ave.), Maximum (Max), Minimum (Min), and Range of Parameters Measured in the Water Column at Rarotonga and Heron Island During This Study

	Rarotonga				Heron Island			
	Ave.	Min	Max	Range	Ave.	Min	Max	Range
Depth (m)	0.69	0.42	0.98	0.56	0.95	0.15	2.20	2.05
Temp (°C)	27.4	24.1	31.0	6.9	25.4	20.7	28.5	7.8
pH	7.96	7.76	8.17	0.41	8.04	7.75	8.36	0.60
Salinity	35.6	34.3	36.6	2.3	34.6	34.2	35.2	1.0
Wind speed ( $\text{m s}^{-1}$ )	4.0	2.0	5.8	3.7	2.3	0.0	6.6	6.6
DO ( $\mu\text{mol L}^{-1}$ )	204	118	331	214	209	84	365	282
$p\text{CO}_2$ ( $\mu\text{atm}$ )	549	327	833	507	471	178	956	778
$^{222}\text{Rn}$ ( $\text{dpm m}^{-3}$ )	12662	5638	36291	30653	1003	255	2360	2105
$\Omega_{\text{Ar}}$	3.5	1.7	6.7	5.0	4.1	2.0	8.0	6.0
SGD advection rate ( $\text{cm d}^{-1}$ )	$16.7 \pm 4.7$	0.0	68.8	68.8	$29.7 \pm 10.3$	0.0	166.5	166.5
Air-sea $\text{CO}_2$ flux ( $\text{mmol m}^{-2} \text{d}^{-1}$ )	$8.8 \pm 3.4$	-3.3	24.7	27.9	$2.5 \pm 2.1$	-13.9	31.2	45.2

calibrated and measures polonium daughters ( $^{218}\text{Po}^+$  and  $^{214}\text{Po}^+$ ), which are converted into  $^{222}\text{Rn}$  concentrations using radioactive decay equations. Radon concentrations were integrated over 30 min intervals to ensure acceptable counting statistics. In order to compare all of the data on similar time scales, an hourly average was taken from measurements a half hour before and after the RAD7 began each cycle.

In order to measure fluctuations in groundwater chemistry, a peristaltic pump was used to pump water from the bores at  $\sim 1 \text{ L min}^{-1}$  into the GED. The lower flow rate used for groundwater could drive a lag in  $^{222}\text{Rn}$  response time of up to 1 h; however,  $^{222}\text{Rn}$  values were used as measured, because 1 h running averages were used during all subsequent data analysis. The SAMI2-pH was connected in line with the peristaltic pump in order to measure pH in the groundwater bores. The total alkalinity (TA,  $\pm 0.2\%$ ) was measured during the groundwater time series every 2 h by Gran Titration using a Metrohm automatic titrator and 0.01 M HCl standardized to Dickson Certified Reference Material (Batch 111). Samples for  $\text{NO}_x$  were also taken every 2 h and were filtered with a  $0.45 \mu\text{m}$  cellulose acetate filter and frozen at  $-20^\circ\text{C}$  until analyzed following the methods of *Eyre and Ferguson* [2005] using a Lachat FIA system. In Rarotonga, TA and  $\text{NO}_x$  were also directly measured in the freshwater end member [*Cyronak et al.*, 2013].

### 2.3. Data Analysis

All  $p\text{CO}_2$  values were corrected according to the temperature and pressure measured in the GED using equations from *Pierrot et al.* [2009]. The  $\Omega_{\text{Ar}}$  was estimated using the Excel macro  $\text{CO}_2$  System (CO2SYS) [*Pierrot et al.*, 2006] with inputs of  $p\text{CO}_2$  and pH and the constants from *Mehrbach et al.* [1973] refit by *Dickson and Millero* [1987]. The estimates of  $\Omega_{\text{Ar}}$  calculated using these two parameters of the carbonate system have been shown to be robust [*Cullison Gray et al.*, 2011]. Air-sea  $\text{CO}_2$  fluxes were calculated according to the following equation:

$$\text{Flux} = k \alpha (p\text{CO}_{2(\text{water})} - p\text{CO}_{2(\text{air})}) \quad (1)$$

where  $k$  is the gas transfer velocity for  $\text{CO}_2$ ,  $\alpha$  is the solubility coefficient [*Weiss*, 1974],  $p\text{CO}_{2(\text{water})}$  is the partial pressure of  $\text{CO}_2$  in the water column, and  $p\text{CO}_{2(\text{air})}$  is the partial pressure of  $\text{CO}_2$  in the air, which was assumed to be constant at the Mauna Loa 2012 average of 393.8 ppm [*Keeling et al.*, 2001]. Due to the shallow depths and relatively strong currents at the study sites, we used the wind speed-based  $k_{600}$  parameterization from *Raymond and Cole* [2001], which was derived from a compilation of estuarine and riverine studies. All  $k_{600}$  values were corrected for the Schmidt number of  $\text{CO}_2$  at in situ temperatures and salinities [*Wanninkhof*, 1992; *Jahne et al.*, 1997]. Positive air-sea  $\text{CO}_2$  fluxes represent fluxes from the seawater into the atmosphere, while negative fluxes represent fluxes into the seawater from the atmosphere. SGD fluxes were determined using a nonsteady state  $^{222}\text{Rn}$  mass balance model described in detail by *Burnett and Dulaiova* [2003]. The model has been successfully applied to both Heron Island [*Santos et al.*, 2010] and Rarotonga [*Tait et al.*, 2013] in previous studies. The model estimates SGD fluxes based on the temporal change in  $^{222}\text{Rn}$  inventories in the water column (1 h time steps) after accounting for all known  $^{222}\text{Rn}$  sources and sinks (i.e., atmospheric evasion, mixing,  $^{222}\text{Rn}$  decay, and  $^{226}\text{Ra}$ ). The missing  $^{222}\text{Rn}$  fluxes are then divided by the groundwater end member concentration to obtain SGD advection rates in units of  $\text{cm d}^{-1}$ .

**Table 2.** Averages and Standard Deviations of Parameters Measured in the Groundwater at Rarotonga and Heron Island<sup>a</sup>

	Rarotonga	Heron Island
Depth (m)	0.34 ± 0.12	4.63 ± 0.39
Temp (°C)	25.4 ± 0.09	25.6 ± 0.03
pH	7.309 ± 0.01	7.602 ± 0.05
Salinity	28.3 ± 2.7	33.1 ± 0.2
TA (μmol L <sup>-1</sup> )	3339 ± 249	2243 ± 96
pCO <sub>2</sub> (μatm)	3515 ± 205	1397 ± 199
NO <sub>x</sub> (μmol L <sup>-1</sup> )	28.2 ± 4.5	76.5 ± 27.6
<sup>222</sup> Rn (dpm m <sup>-3</sup> )	130836 ± 16460	27204 ± 3231
pCO <sub>2</sub> -EM (μatm)	5501 ± 183	1397 ± 199
<sup>222</sup> Rn-EM (dpm m <sup>-3</sup> )	242836 ± 19561	27204 ± 3231
Free-CO <sub>2</sub> -EM (μmol L <sup>-1</sup> )	173.9 ± 5.2	40.6 ± 5.1

<sup>a</sup>The NO<sub>x</sub> concentration from Rarotonga is the average of direct measurements (*n* = 4) from the freshwater end member, while the Heron Island NO<sub>x</sub> concentration is the average during the groundwater time series. The pCO<sub>2</sub>-EM, <sup>222</sup>Rn-EM, and free-CO<sub>2</sub>-EM are the groundwater end members calculated as described in the text.

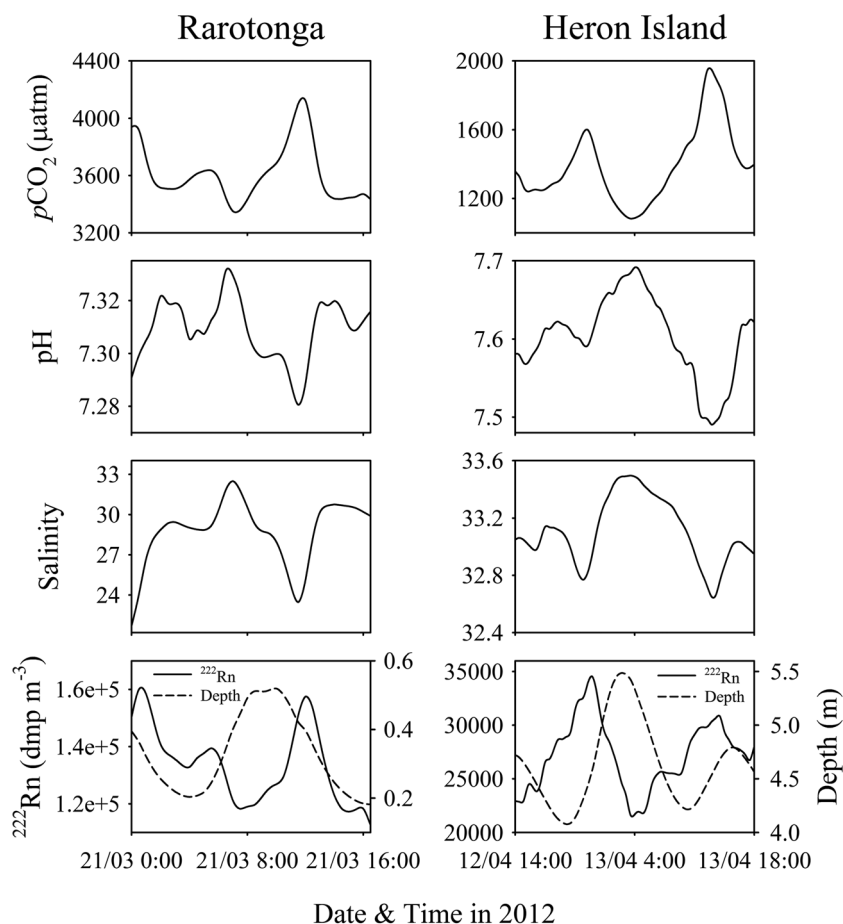
### 3. Results

#### 3.1. Groundwater Time Series

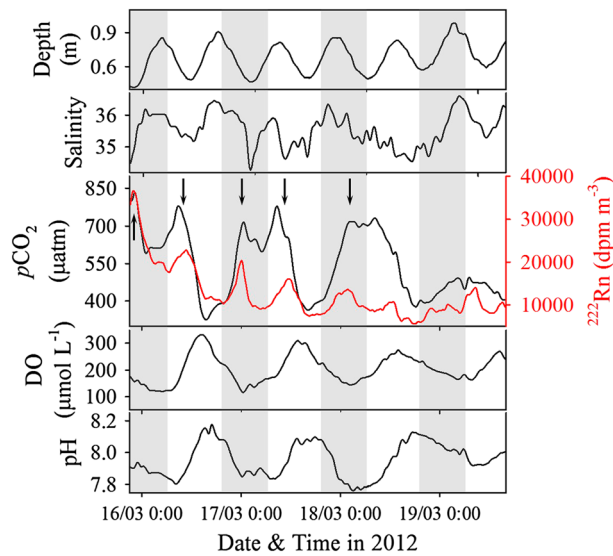
In the Rarotonga groundwater, pCO<sub>2</sub> and <sup>222</sup>Rn were 6 and 10 times higher than in the water column, respectively (Tables 1 and 2). The pCO<sub>2</sub> ranged from 3083 to 4024 μatm, while the <sup>222</sup>Rn ranged from 80,111 to 159,937 dpm (disintegrations per minute) m<sup>-3</sup> over a tidal cycle and was highest during the ebb tide (Figure 2). The pH and salinity followed similar but opposite trends of pCO<sub>2</sub>, with salinity ranging from 21.7 to 32.5 and pH ranging from 7.28 to 7.33 (Figure 2). Both pH and salinity were lower in the groundwater than in the water column (Tables 1 and 2). Average TA was 3339 μmol L<sup>-1</sup> during the

bore time series and was ~5500 μmol L<sup>-1</sup> in the freshwater end member. The average NO<sub>x</sub> concentration was 28.2 μmol L<sup>-1</sup> in the freshwater end member.

In the Heron Island groundwater, pCO<sub>2</sub> and <sup>222</sup>Rn were approximately 3 times and 27 times higher than in the water column, respectively (Tables 1 and 2). The highest pCO<sub>2</sub> coincided with the peaks in <sup>222</sup>Rn and the lowest

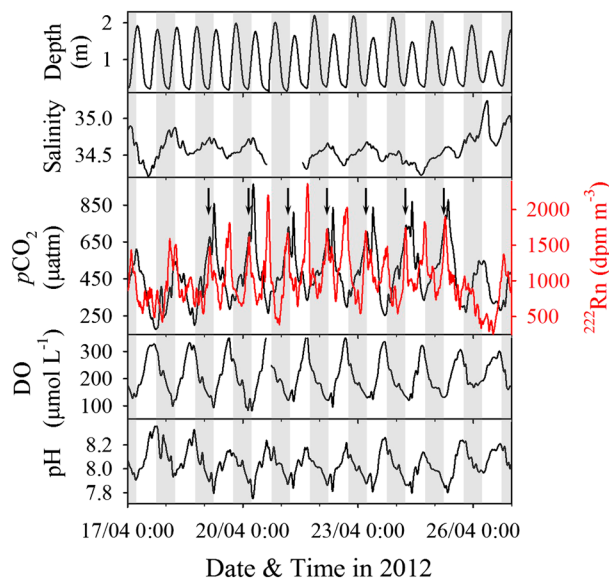


**Figure 2.** The pCO<sub>2</sub>, pH, salinity, <sup>222</sup>Rn, and depth measured in the groundwater at Rarotonga and Heron Island.



**Figure 3.** The  $p\text{CO}_2$ , DO, pH,  $^{222}\text{Rn}$  (red), salinity, and depth measured in the water column at Rarotonga over the course of this study. All time is in local time, and gray bars represent nighttime hours. The arrows indicate times when  $p\text{CO}_2$  and  $^{222}\text{Rn}$  vary concurrently. The line graphs represent data points every half hour, which are averages for 30 min before and after each respective time point (see Methods for more detail).

tidal cycles (Figure 3). Tidal range was highest in the beginning of the time series and decreased toward the end, with a range of 0.56 m over the course of the study. In the Rarotonga water column,  $p\text{CO}_2$  ranged from 327 to 833  $\mu\text{atm}$  with an average of 549  $\mu\text{atm}$  and followed a cycle that was indicative of both tidal and diel drivers (Figure 3). This average  $p\text{CO}_2$  was well in excess of the expected concentration if the water column was in equilibrium with the atmosphere ( $\sim 394 \mu\text{atm}$ ), resulting in a relatively low-average seawater pH (7.96). During

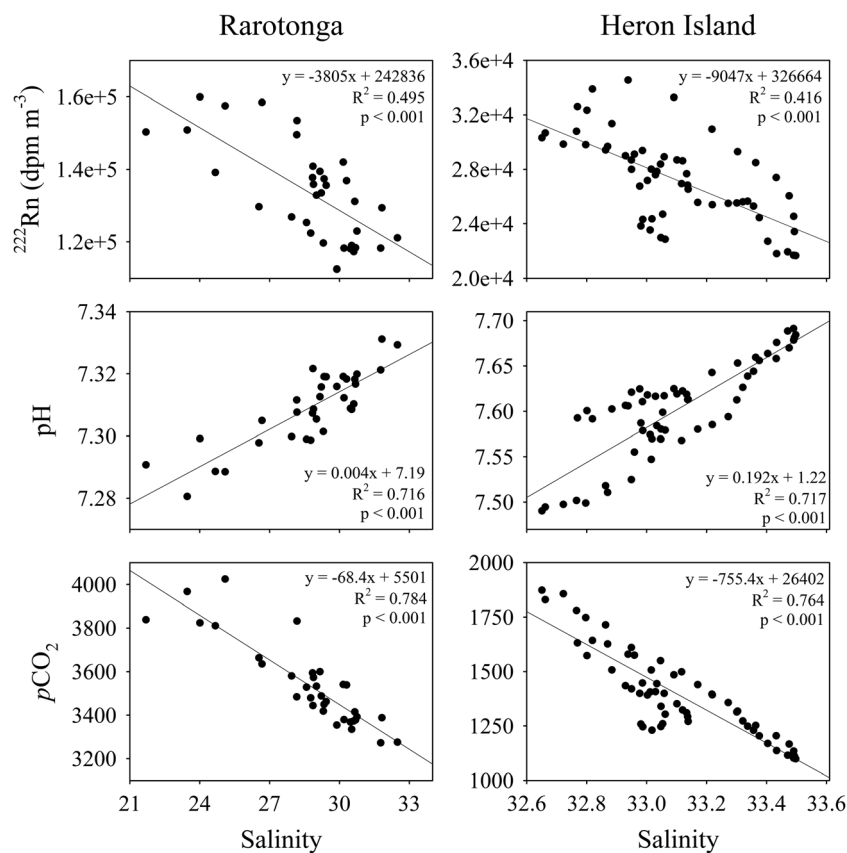


**Figure 4.** The  $p\text{CO}_2$ , DO, pH,  $^{222}\text{Rn}$  (red), salinity, and depth measured in the water column at Heron Island over the course of this study. All time is in local time, and gray bars represent nighttime hours. The arrows indicate times when  $p\text{CO}_2$  and  $^{222}\text{Rn}$  vary concurrently; note how the arrows shift with the tidal cycle. The line graphs represent data points every half hour, which are averages for 30 min before and after each respective time point (see methods for more detail).

salinities (Figure 2). Salinity in the groundwater ranged from 32.7 to 33.5 and was lowest during the ebb tide with an average of 33.1 during the time series. The pH followed a trend similar to salinity and varied between 7.49 and 7.69 during the time series.  $^{222}\text{Rn}$  steadily increased during the low tide and was highest during the flood tide (Figure 2). The temporal variability of solutes in the groundwater indicates an active mixing of groundwater and seawater within the beach sands over tidal time scales. The average concentration of TA was 2243  $\mu\text{mol L}^{-1}$ , and  $\text{NO}_x$  was 76.5  $\mu\text{mol L}^{-1}$  during the Heron Island groundwater time series.

### 3.2. Water Column Time Series

The water column time series at Rarotonga covered 4 days and 7 tidal cycles (Figure 3). The  $p\text{CO}_2$  was generally lower during the final two diel cycles when the tidal range and low-tide  $^{222}\text{Rn}$  peaks were smaller. The trends in DO and pH were more consistent with biological drivers, increasing and decreasing smoothly over a diel cycle (Figure 3). The minimum and maximum DO concentrations during the time series were 118 and 331  $\mu\text{mol L}^{-1}$  with an average of 204  $\mu\text{mol L}^{-1}$ . The pH ranged 0.41 units over the course of the study, with a minimum value of 7.76 and maximum of 8.17.  $^{222}\text{Rn}$  concentrations were highest during ebb tides, and the average  $^{222}\text{Rn}$  concentration in the water column was 12,662  $\text{dpm m}^{-3}$ . The highest



**Figure 5.** Linear regressions of  $^{222}\text{Rn}$ ,  $p\text{CO}_2$ , and pH versus salinity in the groundwater time series at Rarotonga and Heron Island.

$^{222}\text{Rn}$  concentrations were measured on the first day during the tidal cycle with the greatest range, and as the tidal ranges became smaller, the  $^{222}\text{Rn}$  concentrations decreased (Figure 3).

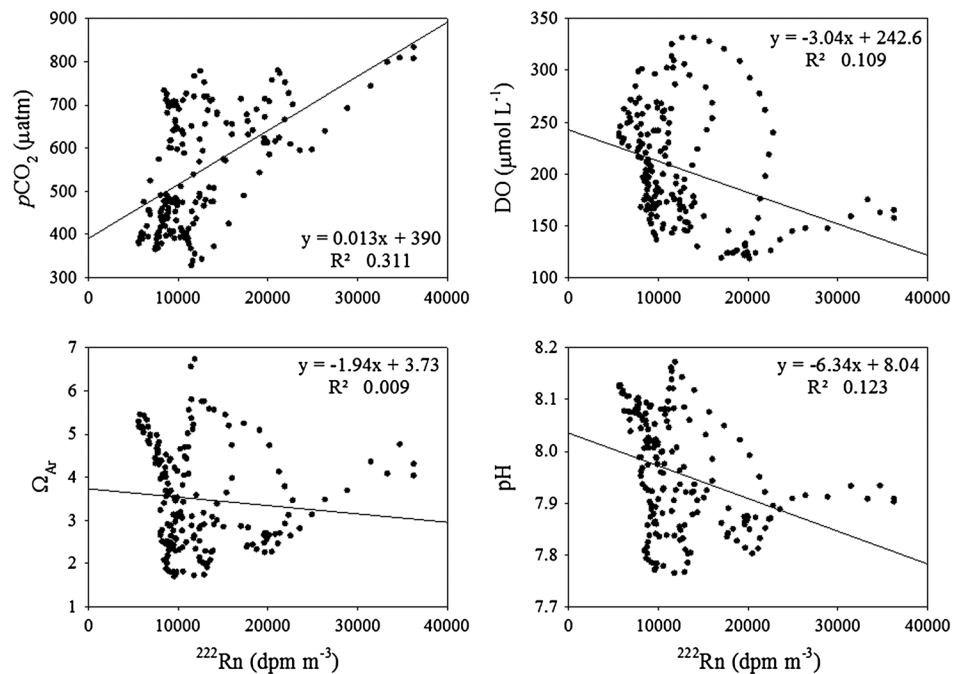
The water column time series at Heron Island covered 10 days and 19 tidal cycles. Tidal range was greatest during the first half of the time series (Figure 4). All parameters exhibited variations indicative of biological drivers, with  $p\text{CO}_2$  decreasing until the late afternoon and then increasing throughout the night (Figure 4). The average  $p\text{CO}_2$  over the course of the study was 471  $\mu\text{atm}$  in the Heron Island water column, which was lower than at Rarotonga (549  $\mu\text{atm}$ ). However,  $p\text{CO}_2$  in the Heron Island water column exhibited a larger range (178 to 956  $\mu\text{atm}$ ) than at Rarotonga (327 to 833  $\mu\text{atm}$ ). Heron Island  $p\text{CO}_2$  showed small but detectable variations unrelated to biological drivers, some of which coincided with the peaks in  $^{222}\text{Rn}$  concentrations and shifted with the tidal cycle (Figure 4). DO and pH variability were opposite of  $p\text{CO}_2$ , and average pH was higher in the Heron Island water column (8.04) than in the Rarotonga water column (7.96) (Table 1). The average  $^{222}\text{Rn}$  concentration was 1003  $\text{dpm m}^{-3}$  with minimum and maximum concentrations of 255 and 2360  $\text{dpm m}^{-3}$ .  $^{222}\text{Rn}$  concentrations were highest at the beginning of the flood tide and lowest during high tides (Figure 4).

## 4. Discussion

### 4.1. Drivers of SGD Exchange

SGD exchange processes in both Rarotonga and Heron Islands were clearly influenced by tidal processes (Figures 2–4). Tidal pumping can refer to multiple but fundamentally distinct processes [Santos *et al.*, 2012a]. Both seawater recirculation and terrestrial hydraulic gradient driven SGD can fall under the more general term of tidal pumping due to the influence of tides on both processes [Santos *et al.*, 2009]. Tides affect seawater recirculation as seawater infiltrates the beach face during high tides and is discharged



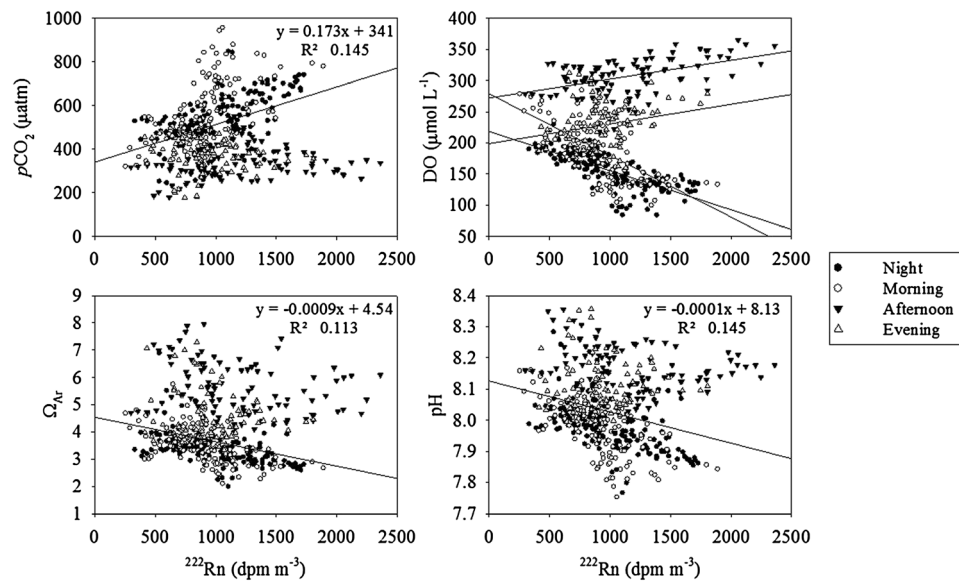


**Figure 6.** Linear Regressions of  $p\text{CO}_2$ , DO,  $\Omega_{\text{Ar}}$ , and pH versus  $^{222}\text{Rn}$  in the water column at Rarotonga.

during low tides. Likewise, steeper hydraulic gradients at low tide can cause greater amounts of fresh groundwater to be discharged than during high tides.  $^{222}\text{Rn}$  concentrations during the groundwater time series at Rarotonga were highest during the ebb tide (Figure 2), which is indicative of positively pressured fresh groundwater being held off by sea level at high tides. The Heron Island groundwater showed a different trend, with  $^{222}\text{Rn}$  concentrations highest during the flood tide (Figure 2). This is indicative of a slow release of high  $^{222}\text{Rn}$  groundwater and seawater recirculation being the dominant exchange mechanism of SGD at Heron Island.

When plotted against salinity,  $^{222}\text{Rn}$  exhibited a significant negative linear trend in the groundwater of both systems (Figure 5). Fresh groundwater end members can be extrapolated from the y intercept (i.e., when salinity = 0). In Rarotonga, the estimates of a  $^{222}\text{Rn}$  groundwater end member ( $242,836 \pm 19,561$  dpm m<sup>-3</sup>) using this method agree well with those measured in fresh groundwater (179,202 to 294,146 dpm m<sup>-3</sup>) [Cyronak *et al.*, 2013], which is consistent with previous studies using a similar approach in systems where fresh SGD is the main source of  $^{222}\text{Rn}$  [Peterson *et al.*, 2009]. This is further evidence of fresh groundwater and a terrestrial hydraulic gradient driving SGD at Rarotonga [see Santos *et al.*, 2012a, Figure 1]. When  $^{222}\text{Rn}$  is plotted against the salinity in the Heron Island groundwater, there is a disagreement between the observed and extrapolated end member concentrations. The concentration of the  $^{222}\text{Rn}$  end member extrapolated to 0 salinity is 3-fold higher than the highest measured groundwater  $^{222}\text{Rn}$  concentration and is ~7.5-fold higher than the average groundwater  $^{222}\text{Rn}$  concentration [Santos *et al.*, 2010]. This is further evidence of seawater recirculation being the dominant driver of SGD, because there would be no freshwater end member to extrapolate  $^{222}\text{Rn}$  values back to at Heron Island. These observations are consistent with the isolated, narrow freshwater lens observed at Heron Island [Santos *et al.*, 2010]. Therefore, the end members for Rarotonga groundwater were calculated from the y intercept of each parameter versus salinity measured during the groundwater time series, while the end members for Heron Island were calculated as the average concentrations measured over the groundwater time series (Table 2).

Linear regressions between  $^{222}\text{Rn}$  and salinity in the Rarotonga ( $R^2 = 0.008$ , data not shown) and Heron Island ( $R^2 = 0.016$ , data not shown) water columns showed no significant correlation, possibly due to the small range of salinity in both systems (Table 1). However, the temporal variations of  $^{222}\text{Rn}$  concentrations in the water column revealed that the highest  $^{222}\text{Rn}$  concentrations at Rarotonga coincided with ebb tides and the highest  $^{222}\text{Rn}$  concentrations at Heron Island coincided with the beginning of flood tides (Figures 3 and 4).



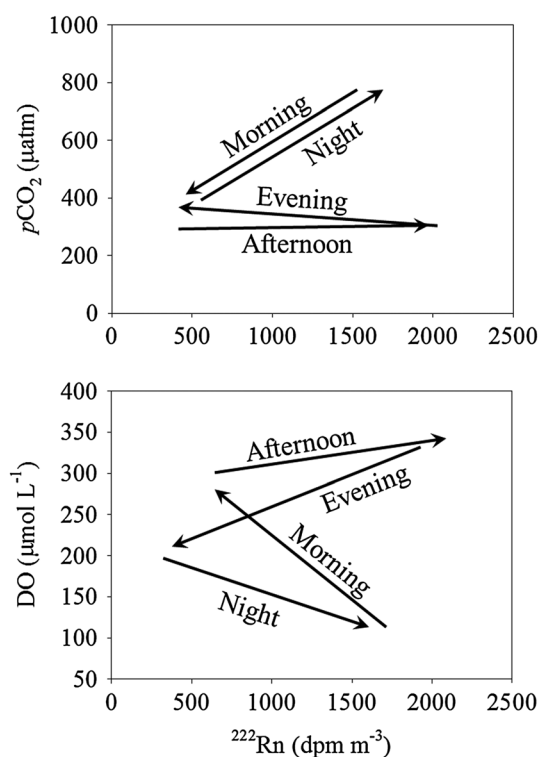
**Figure 7.** Linear regressions of  $p\text{CO}_2$ , DO,  $\Omega_{\text{Ar}}$ , and pH versus  $^{222}\text{Rn}$  in the water column at Heron Island. Regression equations displayed for  $p\text{CO}_2$ ,  $\Omega_{\text{Ar}}$ , and pH are shown with values in the afternoon removed. Measurements are divided into night (22:00 to 06:00), morning (06:00 to 12:20), afternoon (12:20 to 17:20), and evening (17:20 to 22:00). Regressions for the DO versus  $^{222}\text{Rn}$  correlations are as follows: night ( $\text{DO} = -0.07(^{222}\text{Rn}) + 218$ ,  $R^2 = 0.55$ ), morning ( $\text{DO} = -0.1(^{222}\text{Rn}) + 279$ ,  $R^2 = 0.35$ ), afternoon ( $\text{DO} = -0.03(^{222}\text{Rn}) + 272$ ,  $R^2 = 0.21$ ), and evening ( $\text{DO} = -0.03(^{222}\text{Rn}) + 199$ ,  $R^2 = 0.06$ ).

Also, the salinity had a greater range in the Rarotonga water column (2.4) when compared to the Heron Island water column (1.0) (Table 1). This also indicates that a terrestrial hydraulic gradient driving fresh groundwater exchange is a major driver of SGD in Rarotonga, while seawater recirculation is dominant in Heron Island. In support of this hypothesis, using a combination of  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  isotopes,  $^{222}\text{Rn}$  concentrations, and electrical resistivity mapping, *Tait et al.* [2013] estimated that fresh groundwater was a significant source of SGD to the Rarotonga lagoon. *Tait et al.* [2013] also found that the average  $^{222}\text{Rn}$  concentrations in shallow saline groundwater were lower than the highest surface water concentrations, implying that the recirculated seawater cannot explain the  $^{222}\text{Rn}$  enrichments observed in the Rarotonga water column.

#### 4.2. Contrasting $p\text{CO}_2$ Dynamics in Rarotonga and Heron Island

The  $p\text{CO}_2$  in the Rarotonga water column was positively correlated with  $^{222}\text{Rn}$  concentrations (Figure 6). Since the highest  $^{222}\text{Rn}$  concentrations were associated with greater tidal ranges, which would influence SGD inputs, there are probably different correlations between  $p\text{CO}_2$  and  $^{222}\text{Rn}$  based on tidal height. However, over the course of the entire study, there was a statistically significant correlation ( $R^2 = 0.301$ ,  $p < 0.01$ ), indicating that SGD is a source of free  $\text{CO}_2$  to the Rarotonga water column (Figure 6). Over the course of the time series,  $p\text{CO}_2$  in the water column was negatively correlated with salinity ( $R^2 = 0.402$ ,  $p < 0.01$ , data not shown), also indicating that fresh groundwater is a source of free  $\text{CO}_2$ . The significant correlations between  $p\text{CO}_2$  and both  $^{222}\text{Rn}$  and salinity, despite multiple other drivers of  $p\text{CO}_2$  dynamics over the course of a diel cycle (i.e., reefal metabolism), indicate that SGD is an important source of free  $\text{CO}_2$ . It seems that due to the high  $p\text{CO}_2$  of the fresh groundwater ( $\sim 5500$   $\mu\text{atm}$ ), SGD in Rarotonga can act as a delivery mechanism of free  $\text{CO}_2$  to the water column.

The dynamics of  $p\text{CO}_2$  and  $^{222}\text{Rn}$  in the Heron Island water column were more complex than in Rarotonga (Figure 7). Salinity and  $p\text{CO}_2$  were not well correlated in the water column ( $R^2 = 0.07$ , data not shown), indicating that fresh SGD does not play a role in driving the  $p\text{CO}_2$  dynamics of the Heron Island water column. However, there were distinct correlations of  $p\text{CO}_2$  with  $^{222}\text{Rn}$  depending on the time of the day. The  $p\text{CO}_2$  was positively correlated with  $^{222}\text{Rn}$  concentrations when the afternoon time points (times of highest primary production) were removed (Figure 7). During the afternoon, there was no statistically significant correlation between  $^{222}\text{Rn}$  and  $p\text{CO}_2$  ( $R^2 = 0.01$ ). DO concentrations were negatively correlated with  $^{222}\text{Rn}$  during the night and morning and positively correlated in the afternoon and evening (Figure 7). The high  $p\text{CO}_2$ /low DO and low  $p\text{CO}_2$ /high DO



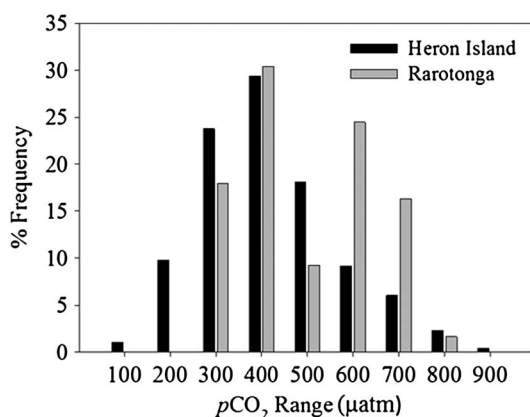
**Figure 8.** Diagram showing the relationship between  $p\text{CO}_2$ , DO, and  $^{222}\text{Rn}$  over different times of the day in the Heron Island water column.

concentrations associated with high  $^{222}\text{Rn}$  in the Heron Island water column indicate that SGD may stimulate coral reef metabolism. Figure 8 illustrates how  $p\text{CO}_2$  and DO concentrations in the water column are related to  $^{222}\text{Rn}$  concentrations (and thus SGD) over the course of a day. High nutrient and organic loads from SGD could stimulate photosynthesis during the day and respiration at night, which would influence  $p\text{CO}_2$  and DO correlations with  $^{222}\text{Rn}$  differently over a diel cycle (see next paragraph, Figures 7 and 8).

Average solute concentrations from the groundwater time series at both Rarotonga and Heron Island are reported in Table 2. Salinity and pH were both lower in the Rarotonga groundwater than in the Heron Island groundwater. The groundwater in Rarotonga had  $\sim 3$  times the average  $p\text{CO}_2$  and  $\sim 5$  times the  $^{222}\text{Rn}$  concentrations as that in Heron Island. The  $p\text{CO}_2$  end member in Rarotonga was almost 5 times of that in Heron Island, perhaps influencing the higher-average  $p\text{CO}_2$  observed in the Rarotonga water column (Tables 1 and 2). In general, the Heron Island water column

exhibited a larger range of  $p\text{CO}_2$  than in Rarotonga. However, the Rarotonga water column had a higher-average  $p\text{CO}_2$  over the course of the study, which is indicative of the different drivers of SGD. A constant input of high- $p\text{CO}_2$  groundwater from SGD in Rarotonga could have resulted in the higher-average water column  $p\text{CO}_2$ , while potentially reducing the range. Conversely, because of the lower  $p\text{CO}_2$  in the Heron Island groundwater and large amount of biological activity driving water column  $p\text{CO}_2$  variability, the range of  $p\text{CO}_2$  was higher, while the average was lower. Interestingly, SGD stimulated the uptake and release of  $\text{CO}_2$  through the controls on the biological processes in the Heron Island water column (Figures 7 and 8). We hypothesize that the differences between the influence of SGD on  $p\text{CO}_2$  dynamics in Rarotonga and Heron Island were related to the different  $\text{NO}_x$  concentrations in the groundwater at both locations (Table 2). The fluxes of  $\text{NO}_x$  from the Heron Island groundwater were calculated to be some of the highest in undisturbed ecosystems due to large local seabird populations [Santos *et al.*, 2010], although these loads are not reflected in water column  $\text{NO}_x$  concentrations ( $\sim 0.8 \mu\text{mol L}^{-1}$ ) due to rapid biological assimilation and high rates of  $\text{NO}_x$  loss via denitrification [Eyre *et al.*, 2008; Eyre *et al.*, 2013]. Based on  $^{222}\text{Rn}$  and  $\text{NO}_x$  end members in the groundwater (Tables 1 and 2), the average SGD-derived fluxes of  $\text{NO}_x$  were  $4.7 \pm 1.3 \text{ mmol m}^{-2} \text{ d}^{-1}$  to the Rarotonga water column and  $22.7 \pm 7.9 \text{ mmol m}^{-2} \text{ d}^{-1}$  to the Heron Island water column. Therefore, the delivery of large amounts of  $\text{NO}_x$  from SGD to the Heron Island water column may stimulate both heterotrophic and autotrophic activity, while the lower fluxes of  $\text{NO}_x$  to the Rarotonga water column have less of an effect on reefal metabolism.

The frequency distributions of  $p\text{CO}_2$  offer another way to examine the differences between the influence of SGD on water column carbonate chemistry at Rarotonga and Heron Island. The  $p\text{CO}_2$  distribution in the Rarotonga water column was bimodal, with peaks between 300–400  $\mu\text{atm}$  and 600–700  $\mu\text{atm}$  (Figure 9). This implies that two distinct phases occurred in Rarotonga, one with high SGD inputs and high  $p\text{CO}_2$  values and another with low SGD inputs and low  $p\text{CO}_2$  values. This supports the hypothesis that steep hydraulic gradients of groundwater acted as a source of free  $\text{CO}_2$  to the Rarotonga water column at low tide. Heron Island however followed a smoother Gaussian distribution with the frequency of higher concentrations



**Figure 9.** Percent frequency distributions of  $p\text{CO}_2$  values at the two study sites in the water column. Each value represents  $p\text{CO}_2$  measurements that had the same value in the hundreds place (i.e., 100 represents values between 100 to 199).

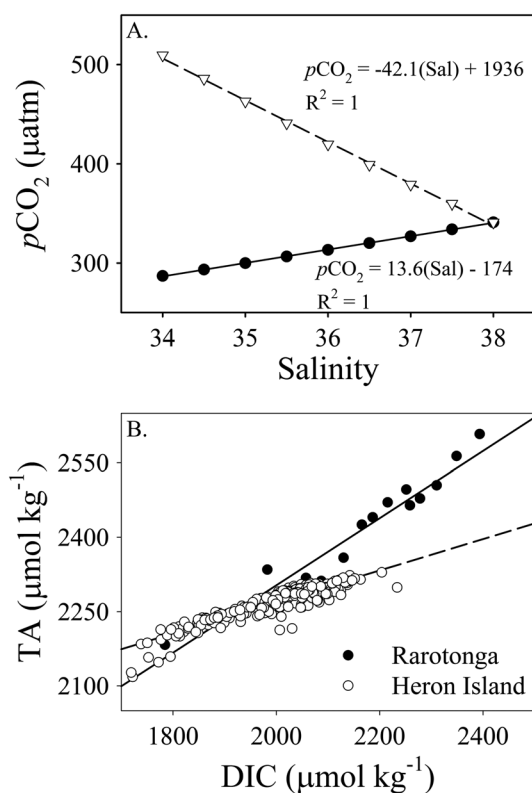
trailing off after 400  $\mu\text{atm}$  (Figure 9). This supports the hypothesis that diel  $p\text{CO}_2$  variability in the Heron Island water column is predominantly influenced by biological activity.

The two distinct ways in which SGD can influence  $p\text{CO}_2$  variability in coral reefs has implications for how OA will impact each ecosystem over the long term. Rarotonga had a consistently higher  $p\text{CO}_2$ , which may reduce community calcification, while  $p\text{CO}_2$  at Heron Island was highly dependent on biological activity, which could both raise and lower community calcification rates at different times of the day. Systems like Rarotonga with elevated  $p\text{CO}_2$  may offer sites analogous to volcanic vents used to predict the in situ effects of OA on reefal ecosystems [Hall-Spencer et al., 2008; Fabricius et al., 2011]. In fact, systems throughout the world with differing SGD inputs may offer natural gradients of average  $p\text{CO}_2$ , while still maintaining the diel variability observed on most reefal flats. This would offer novel ways to study the impact of OA because, unlike volcanic vents and ocos [Hall-Spencer et al., 2008; Crook et al., 2012], calcification rates of entire coral reef lagoons could be compared against a natural range of average  $p\text{CO}_2$  and pH values. However, SGD would also deliver freshwater and other solutes such as nutrients into the lagoons, which could confound any comparisons between different ecosystems.

### 4.3. Influences of Groundwater Chemistry

The influence of groundwater on the  $p\text{CO}_2$  dynamics of coral reef water columns is not only highly dependent on the groundwater chemistry but can also be influenced by freshwater dilution and changes in seawater buffering capacity. Calculations were performed in CO2SYS in order to assess the influence of pure dilution and a reduction in buffering capacity on  $p\text{CO}_2$ . A seawater end member with starting TA ( $2300 \mu\text{mol L}^{-1}$ ), dissolved inorganic carbon (DIC;  $1950 \mu\text{mol L}^{-1}$ ), salinity (38), and temperature ( $25^\circ\text{C}$ ) was diluted to a range of salinities (34–38) assuming dilution by a freshwater end member with no TA and DIC. The linear regression between salinity and  $p\text{CO}_2$  indicates that between the salinities of 34 and 38, a decrease in salinity of 1 unit results in a decrease in  $p\text{CO}_2$  of  $\sim 13 \mu\text{atm}$ , the opposite of what was observed at Rarotonga (Figure 10a). However, if a freshwater end member with chemistry similar to Rarotonga groundwater (TA =  $5500 \mu\text{mol}$ , DIC =  $5617 \mu\text{mol}$ ) is used, a decrease in salinity of 1 unit results in an increase in  $p\text{CO}_2$  of  $\sim 42 \mu\text{atm}$ , similar to the results from the Rarotonga groundwater time series (Figures 5 and 10a). Therefore, any changes to water column carbonate chemistry due to SGD are highly dependent on the specific groundwater chemistry including salinity, DIC, and TA concentrations. Because  $^{222}\text{Rn}$  is a conservative, unambiguous tracer of SGD inputs, the correlations between  $^{222}\text{Rn}$  and carbonate system parameters represent bulk changes in carbonate chemistry due to both dilution and groundwater chemistry.

The plots of TA versus DIC offer a way to separate out the effects of biological (e.g., photosynthesis and respiration) from geochemical (e.g.,  $\text{CaCO}_3$  precipitation and dissolution) processes on the carbonate system [Gattuso et al., 1996; Suzuki and Kawahata, 2003; Andersson and Gledhill, 2013]. Because geochemical processes affect both TA and DIC concentrations ( $\Delta\text{DIC} = \Delta\text{TA}/2$ ) and biological processes affect only DIC, the slope of the TA versus DIC relationship can offer insights into the processes behind changes in water column carbonate chemistry. As presented in other studies, discrete samples for TA and DIC were taken from both the Rarotonga [Cyronak et al., 2013] and Heron Island [McMahon et al., 2013] water columns during the respective time series presented here (Figure 10b). The relationship in Rarotonga ( $\text{TA} = 0.68(\text{DIC}) + 947$ ,  $R^2 = 0.926$ ) indicates that the carbonate system is influenced 66% by biological processes, while the relationship in Heron Island ( $\text{TA} = 0.32(\text{DIC}) + 1635$ ,  $R^2 = 0.842$ ) indicates 84% biological influence. This further supports the hypothesis that biological processes are a more dominant driver of carbonate system variability in the Heron Island water column than in Rarotonga. However, the more apparent influence of “geochemical” processes in



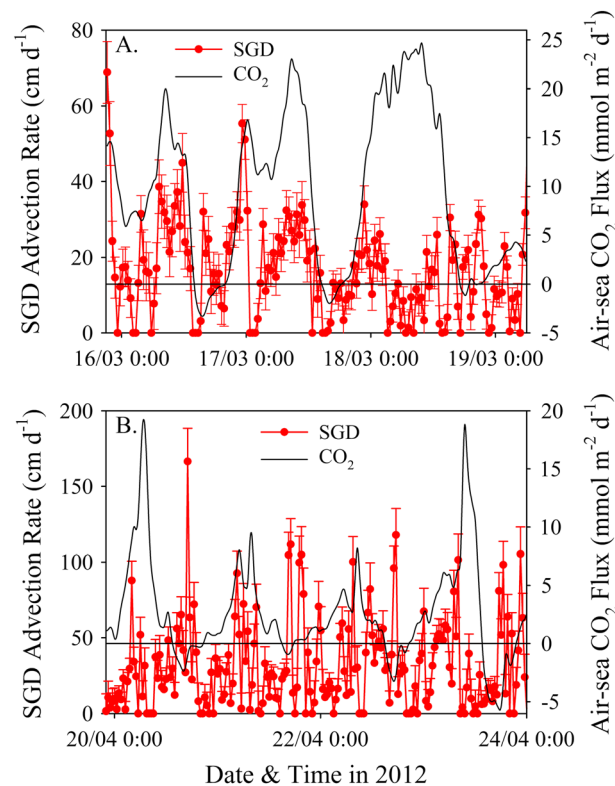
**Figure 10.** (a) Modeled effect of freshwater dilution on  $p\text{CO}_2$  using CO2SYS and two freshwater end members. An end member with both DIC and TA set to 0 (circles), and an end member with chemistry similar to Rarotonga groundwater (triangles; TA = 5500  $\mu\text{mol}$ , DIC = 5617  $\mu\text{mol}$ ) was used. (b) TA versus DIC concentrations in both the Rarotonga and Heron Island water columns. Data are from discrete samples taken during the same time series as presented in this study but previously published by Cyronak *et al.* [2013] and McMahon *et al.* [2013].

influencing pH and  $\Omega_{\text{Ar}}$  over a diel cycle [Gray *et al.*, 2012; Shaw *et al.*, 2012], this suggests that SGD lowers the buffering capacity of the water column and may represent a positive feedback to OA at Rarotonga. There are other aspects that need to be taken into account in order to properly address any buffering capacity. For instance, excess  $\text{CO}_2$  would be released to the atmosphere, while TA would remain in the water column. Both lagoonal circulation patterns and residence time also play large roles in any buffering capacity of SGD-derived TA [Andersson and Mackenzie, 2012].

In contrast to Rarotonga, the average TA in the groundwater of Heron Island was only 2243  $\mu\text{mol L}^{-1}$ , which is similar to the TA of the water column (2185 to 2323  $\mu\text{mol L}^{-1}$ ) (Figure 10 and Table 2) [McMahon *et al.*, 2013]. Therefore, SGD is unlikely to be a significant source of TA to the Heron Island water column. In the water column, pH ( $R^2 = 0.145$ ,  $p < 0.01$ ) and  $\Omega_{\text{Ar}}$  ( $R^2 = 0.113$ ,  $p < 0.01$ ) were both negatively correlated with  $^{222}\text{Rn}$  when the afternoon time points (i.e., most productive times of the day) were removed, indicating that SGD also acts as a positive feedback to OA in Heron Island. In the afternoon, any SGD inputs that stimulate production could increase the pH and  $\Omega_{\text{Ar}}$ ; however, there is no statistically significant correlation between pH or  $\Omega_{\text{Ar}}$  and  $^{222}\text{Rn}$  during that time period (Figure 7). This may be because SGD is also a source of free  $\text{CO}_2$  to the water column at the same time that it stimulates production. The influence of local geology most likely plays a large factor in determining the carbonate chemistry of the local groundwater and thus the influence of SGD on water column carbonate chemistry. The release of free  $\text{CO}_2$  was likely influenced by the rates of microbial respiration in both landmasses. However, the high rates of sulphate reduction in Rarotonga groundwater most likely reduced the amount of free  $\text{CO}_2$  fluxed to the water column due to the production of alkalinity and associated buffering [Cyronak *et al.*, 2013].

Rarotonga is most likely due to the differences in groundwater chemistry and the large amount of TA delivered by SGD into the water column [Cyronak *et al.*, 2013] and not necessarily increases in  $\text{CaCO}_3$  precipitation and dissolution. The TA versus DIC plots further demonstrate the diverse influences of SGD on water column carbonate chemistry, and that care must be taken when using the TA versus DIC relationship to determine biological versus geochemical influences on the carbonate system of whole ecosystems.

The groundwater at Rarotonga is high in TA ( $\sim 5500 \mu\text{mol L}^{-1}$ ), and SGD has been shown to increase the TA of the lagoon water column (Figure 10) [Cyronak *et al.*, 2013]. It has been hypothesized that any source of TA to a coral reef lagoon may be able to buffer coral ecosystems against the decreases in pH due to OA [Kleypas and Langdon, 2006; Andersson *et al.*, 2007], due to the increases in  $\text{HCO}_3^-$  and  $\text{CO}_2^{3-}$  ions and their ability to absorb  $\text{H}^+$  ions as  $\text{CO}_2$  is added to seawater. However, both pH and  $\Omega_{\text{Ar}}$  of the water column exhibited negative, although not significant trends with  $^{222}\text{Rn}$  concentrations (Figure 6). The impact of SGD on pH and  $\Omega_{\text{Ar}}$  may be explained by the concurrent flux of  $\text{CO}_2$  with TA. Even though there are many drivers



**Figure 11.** SGD advection rates derived from the steady state model of Burnett and Dulaiova [2003] and air-sea CO<sub>2</sub> fluxes derived from the calculations of Raymond and Cole [2001] with the atmospheric CO<sub>2</sub> concentration assumed to be constant at 393.8 ppm in (a) the Rarotonga water column and (b) the Heron Island water column. Only a portion of the Heron Island time series is shown in order to better reveal the diel trends. Error bars on the SGD advection rates represent uncertainty derived from the model.

[Burnett and Dulaiova, 2003] estimated average SGD advection rates to be  $16.7 \pm 4.7 \text{ cm d}^{-1}$  at Rarotonga and  $29.7 \pm 10.3 \text{ cm d}^{-1}$  at Heron Island. Using the end member concentrations of free CO<sub>2</sub> in the groundwater (Table 2), SGD delivered an average of  $29.0 \pm 8.2 \text{ mmol free CO}_2 \text{ m}^{-2} \text{ d}^{-1}$  to the Rarotonga water column and an average of  $12.1 \pm 4.2 \text{ mmol free CO}_2 \text{ m}^{-2} \text{ d}^{-1}$  to the Heron Island water column. In support of these SGD-derived free CO<sub>2</sub> fluxes is a TA mass balance calculated over 1 day at the same sampling site during this study [Cyronak et al., 2013]. The mass balance agreed well with the SGD-derived TA fluxes calculated from <sup>222</sup>Rn inputs, indicating that the <sup>222</sup>Rn fluxes derived from the freshwater end member are reliable. Even though average <sup>222</sup>Rn-derived SGD fluxes in Rarotonga (mostly fresh SGD) were roughly half of those in Heron Island (saline SGD), the ~3-fold higher SGD-derived CO<sub>2</sub> fluxes were consistent with the ~3-fold higher average air-sea CO<sub>2</sub> fluxes in Rarotonga. Since the net ecosystem production of coral reefs is close to zero, the main reason reefs are thought to be sources of CO<sub>2</sub> to the atmosphere is due to CO<sub>2</sub> released during calcification [Frankignoulle et al., 1994; Gattuso et al., 1999]. Our results demonstrate that SGD can also contribute to the air-sea flux of CO<sub>2</sub> from coral reefs. Interestingly, any reduction in calcification due to a lower pH and  $\Omega_{Ar}$  from SGD could further reduce pCO<sub>2</sub> levels in the water column. More studies to assess the impact of SGD on air-sea CO<sub>2</sub> fluxes in coral reef ecosystems over longer time scales are needed.

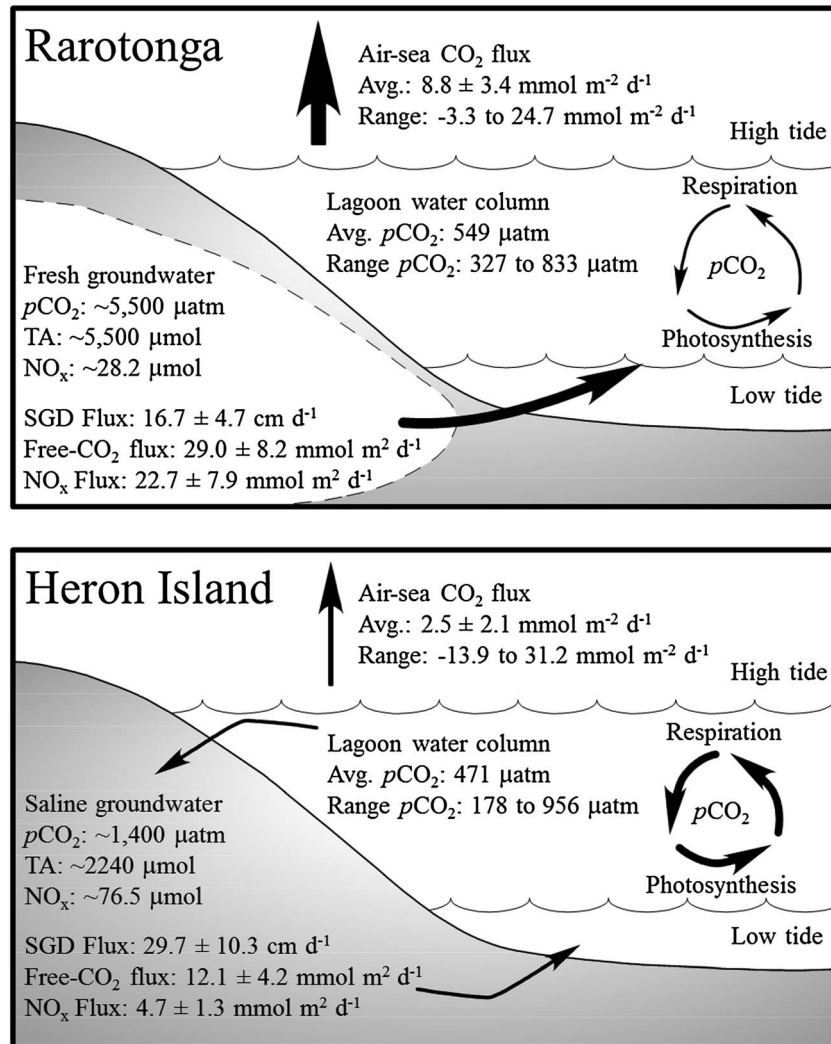
#### 4.5. Implications of SGD to Community Level Metabolism Measurements

These results have implications to studies that calculate community level metabolic and calcification rates in coral reefs. There are generally two methods, besides incubations, used to calculate coral reef community metabolic and calcification rates. The Lagrangian, or flow respirometry method, refers to the measuring changes in solute concentrations as seawater flows across reefal habitats [Barnes and Devereux, 1984;

#### 4.4. SGD and Air-Sea CO<sub>2</sub> Fluxes

Average air-sea CO<sub>2</sub> fluxes over the course of this study indicate that both lagoons were a source of CO<sub>2</sub> to the atmosphere (Figure 11). Rarotonga ( $8.8 \pm 3.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) had a ~3-fold higher average air-sea flux of CO<sub>2</sub> than Heron Island ( $2.5 \pm 2.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ ). Air-sea CO<sub>2</sub> fluxes in other reefs have been shown to vary over a diel cycle, ranging from  $-2.1$  to  $6.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ , and are thought to be predominantly biologically controlled [Gattuso et al., 1993, 1995; Frankignoulle et al., 1996; Bates, 2002]. Air-sea CO<sub>2</sub> fluxes at both Rarotonga and Heron Island varied over diel cycles, with higher fluxes observed at night (Figure 11). However, the majority of these fluxes were positive over the entire diel cycle, even when photosynthesis was occurring. Coral reef ecosystems have also been shown to switch between sources and sinks of CO<sub>2</sub> dependant on the time of year [Bates, 2002; Drupp et al., 2013]. However, it was not within the scope of this study to assess the seasonal variability of air-sea CO<sub>2</sub> fluxes at Rarotonga and Heron Island.

A nonsteady state <sup>222</sup>Rn mass balance



**Figure 12.** Conceptual models showing how SGD influences  $p\text{CO}_2$  dynamics in the water column at Rarotonga and Heron Island.

Gattuso *et al.*, 1996]. This is usually done by measuring changes in seawater chemistry as an instrument package is floated across the reef [Gattuso *et al.*, 1996; Chisholm and Barnes, 1998] or as seawater flows between two stations [Yates and Halley, 2006; Shamberger *et al.*, 2011]. SGD could easily impact Lagrangian studies if there were significant groundwater inputs as the water mass flowed across the reef. The slack, or low-tide method, refers to measuring changes in carbonate chemistry over time during low tides when coral communities are isolated from mixing with the open ocean [Kinsey, 1978; Ohde, 1995; Silverman *et al.*, 2012]. The selection of the sampling site in the studies using the slack tide approach is critical as SGD fluxes tend to be highest at low tides [Burnett *et al.*, 2003].

A possible example of discrepancies in calculated coral reef calcification rates, possibly due to SGD inputs, can be found in the literature. To determine community metabolic rates, Chisholm and Barnes [1998] floated an instrument package across Lizard Island lagoon in the northern Great Barrier Reef. There were large discrepancies in the rates of calcification determined by two separate techniques, a combined DO/pH technique and via changes in alkalinity. The rates of organic matter decomposition and nitrification evoked to explain these discrepancies were determined to be unrealistic [Gattuso *et al.*, 1999], but no alternative explanations were suggested. Due to the relatively high rainfall preceding the study, the proximity of the instruments to land, and the relatively high elevation of Lizard Island (360 m, somewhat similar to Rarotonga), it is possible to assume that there were some SGD inputs during their study. If SGD impacts the seawater chemistry of Lizard Island lagoon similarly to the locations investigated here, any changes in DO/pH would be

less affected by SGD than changes in  $p\text{CO}_2$  and TA (Figures 3 and 4). If the package was floated across an area of high SGD inputs, it could account for the anomalies observed by *Chisholm and Barnes* [1998].

#### 4.6. Conclusions

The anomalies of  $p\text{CO}_2$  in both systems studied here were indicative of broadly occurring SGD inputs as supported by (1) temporal variations of  $^{222}\text{Rn}$  and  $\text{CO}_2$ ; (2) correlations between  $^{222}\text{Rn}$ , salinity, and  $p\text{CO}_2$ ; (3)  $p\text{CO}_2$  dynamics in the groundwater; (4) frequency distributions of  $p\text{CO}_2$  values in the water column; (5) TA versus DIC plots; and (6) air-sea  $\text{CO}_2$  fluxes compared to SGD-derived free  $\text{CO}_2$  fluxes. The exchange mechanism of SGD influenced carbonate chemistry differently in each system, impacting  $p\text{CO}_2$  variability through both the direct delivery of free  $\text{CO}_2$  and the stimulation of coral reef metabolism (e.g., photosynthesis and respiration). In summary, the distinct ways that SGD can influence water column  $p\text{CO}_2$  are highly dependent on groundwater chemistry, SGD flux rates, and the driving forces of groundwater exchange, which are variable across different coral reef ecosystems (Figure 12). More comprehensive studies on seasonal time scales and larger spatial scales are necessary to further examine the effects of SGD on seawater carbonate chemistry across a diverse range of coral reefs.

The high SGD-derived fluxes of free  $\text{CO}_2$  into the two coral reef ecosystems may represent a positive feedback to OA (i.e., decreases local pH and  $\Omega_{\text{Ar}}$ ) on a local scale. Carbonate system variability caused by SGD may also influence ecosystem level calculations of metabolism and calcification. This has important implications for OA research, as measuring net ecosystem calcification rates is critical to understanding how OA will impact coral reefs. In fact, systems with variable SGD inputs may have naturally variable  $p\text{CO}_2$  levels, potentially allowing for in situ studies on the impact of OA on coral reefs over ecosystem wide scales. Finally, local drivers of coral reef carbonate chemistry may offer more approachable management solutions to mitigating the effects of OA on coral reefs [*Kelly et al.*, 2011]. In conclusion, this overlooked driver of carbonate system dynamics may have important implications to studies assessing the impact that OA will have on the biogeochemistry of coral reefs.

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