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Groundwater and porewater as a major source of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands)

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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 fresh groundwater discharge (as traced by radon) and shallow porewater exchange (as quantified from advective chamber incubations) 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 $7.76 \text{ mmol m}^{-2} \text{ d}^{-1}$, 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 $1080 \text{ mmol m}^{-2} \text{ d}^{-1}$. 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 dependant on the time of day. On a daily basis, groundwater can contribute approximately 70% to 80% of the TA taken up by corals within the lagoon. 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 $p\text{CO}_2$ 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 $p\text{CO}_2$, which alters the carbonate chemistry of seawater leading to a reduction in pH at a rate of roughly 0.002 pH y^{-1} (Feely et

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We used a non-steady state radon mass balance model from Burnett and Dulaiova (2003) to determine groundwater flux rates in $\text{cm}^3 \text{m}^{-2} \text{d}^{-1}$. The model incorporated sources of ^{222}Rn from groundwater and ^{226}Ra decay 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 ^{222}Rn derived fluxes of groundwater TA into the lagoon.

2.4 Sample analysis

Both water-column and benthic chamber samples were immediately brought back into the laboratory. Dissolved oxygen ($\pm 1\%$) was measured directly following collection using a Hach Luminescent Dissolved Oxygen (LDO[®]) probe. Samples for nutrients were filtered with a $0.45 \mu\text{m}$ cellulose acetate filter and frozen at -20°C until analysed following the methods of Eyre and Ferguson (2005) using a Lachat Flow Injection Analysis (FIA) system. Samples for total alkalinity (TA) and pH were filtered through a $0.45 \mu\text{m}$ 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 Metrohm 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 Metrohm Titrand automatic titrator and pH electrode. Pre-standardized $0.01 \text{mol l}^{-1} \text{HCl}$ 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 $\delta^{13}\text{C}$ DIC ($\pm 1.2\%$) were $0.7 \mu\text{m}$ filtered with a Whatman GF/F syringe filter, preserved using $50 \mu\text{l}$ of saturated HgCl_2 with no head space, and stored at 4°C . Samples were acidified with 5% ($v:v$) phosphoric acid and the resulting CO_2 was analysed via continuous flow wet-oxidation isotope ratio mass spectrometry (CF-WO-IRMS) using an Aurora 1030 W total organic carbon (TOC) analyzer coupled to a

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Thermo Delta V Plus IRMS (Oakes et al., 2010). DIC concentrations were estimated with the Excel macro CO_2 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), CO2SYS also generated Ω_{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 (TA_{C}) for the chamber samples was calculated by subtracting the alkalinity, as determined in CO2SYS, contributed by $\text{B}(\text{OH})_4^-$, OH^- and total dissolved phosphorus (TDP) from TA.

3 Results

3.1 Advective chambers

The flux rates of TA_{C} , 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 TA_{C} decreased throughout the day and began to increase in the late afternoon (Fig. 2a). TA_{C} 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 for the night (Fig. 2c). H^+ fluxes showed the same trend as DO fluxes with slight variation in the night (Fig. 2d). In all cases, the flux rates in the 40 RPM chamber exhibited the largest range over a diel cycle (Fig. 2).

Figure 3 shows the hourly flux rates of TA_{C} , DIC, and DO plotted against the average photosynthetic active radiation (PAR) measured during the same time as the flux was calculated. All three solutes show a distinct hysteretic pattern, with lower rates of all fluxes in the morning at comparable PAR levels in the afternoon (Fig. 3). The fluxes of

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of the sediment was generally smaller in the Cook Islands, with the highest percentage between 250 μm –500 μm compared to Heron which was mostly in the 1–2 mm range. Even though permeability was similar (Glud et al., 2008), differences in grain size may affect the flow of water through the sediments and subsequent TA fluxes. Daily fluxes of TA from the sediments ranged from -1.55 to $7.76 \text{ mmol m}^{-2} \text{ d}^{-1}$, with the highest rates in the 40 rpm chamber (Table 2). Daily Cook Island TA_C fluxes are lower than flux rates in Heron Island, although the daily TA_C flux rate from the 40 RPM chambers are similar in magnitude.

The hysteretic pattern of solute fluxes in the advective chambers is indicative of processes in the sediments being influenced by the previous state of the system (Fig. 3). Lower fluxes in the morning than in the afternoon for TA, DIC, and DO may be due to the decrease in DO and Ω_{Ar} overnight and subsequent change in the system as photosynthesis increases DO in the pore waters (Cyronak et al., 2013). Similar patterns in coral photosynthesis and calcification have been observed over a diel cycle (Levy et al., 2004; Schneider et al., 2009). Levy et al. (2004) attributed the lower photosynthesis rates in the morning to a breakdown of photosynthetic machinery at night and subsequent build-up during the day, while the hysteresis in calcification rates were attributed to changes in respiration rates of corals at specific times during a diel cycle (Schneider et al., 2009). Similar processes may be occurring in the microbiota living in the sediments as well, which would contribute to the observed hysteresis. Also, because DO is consumed through sulphide oxidation (Ku et al., 1999), high sulphide production and the subsequent build-up in the porewaters overnight might also lead to the observed hysteresis in flux rates. If sulphide 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 (Fig. 3).

The slope of DIC vs. TA_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_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

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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 flux rates were not as well correlated to 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 sulphides in the sediments (Ku et al., 1999). Additional investigations on the role sulphides play in alkalinity cycling on coral reefs are warranted.

4.2 Estimating a mixed groundwater end member

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 $\delta^{13}\text{C}$ DIC versus $1/[\text{DIC}]$, can be used to estimate the $\delta^{13}\text{C}$ 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 end members (shallow and deep) to the water-column can be estimated by using the $\delta^{13}\text{C}$ of added DIC generated from the Keeling plot as the $\delta^{13}\text{C}$ of the mixed end member. 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 end member in subsequent mixing models, which matched well to the measured pore water values in the bores (Table 1).

A two-source mixing model can be used to estimate the water-column concentrations of TA based on radon concentrations measured over the sampling period. Radon concentrations from the water-column were divided by the mixed end member concentration (47 % EM1 : 53 % EM2), and a percent groundwater input were then multiplied by the end member of TA (Table 1). When a range of end members was used for the water-column TA, 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

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concentration of TA fit within that range (Fig. 9a). A variable end member model was also calculated based on the change in TA 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 in the morning for the water-column TA 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 in change of TA in the water-column that excludes the effects of groundwater was estimated as $-20 \text{ mmol m}^{-2} \text{ h}^{-1}$ during the day and $20 \text{ mmol m}^{-2} \text{ h}^{-1}$ at night. When the variable end member was applied to the water-column portion of the radon 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values of DIC in the groundwater are indicative of an organic source of carbon, as carbonate minerals tend to have $\delta^{13}\text{C}$ values from 0‰ to 2‰ (Weber and Woodhead, 1969; Eadie and Jeffrey, 1973; Ogrinc et al., 2003). In addition, a potential uncoupling of sulphate reduction from sulphide oxidation would generate carbonate alkalinity with a depleted $\delta^{13}\text{C}$ value due to the organic C source, perhaps reflecting the depleted $\delta^{13}\text{C}$ DIC values found in the groundwater (Ku et al., 1999).

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 ($179202 \text{ dpm m}^{-3}$) (Table 1). Fluxes of groundwater ranged from $0\text{--}46 \text{ cm d}^{-1}$ and were highest during low tides

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(Fig. 11a). This is consistent with tidal pumping driving 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 end member concentration of TA ($5467 \text{ } \mu\text{mol l}^{-1}$) to estimate the fluxes of TA into the water-column (Fig. 11b). Fluxes ranged from $0\text{--}105 \text{ mmol m}^{-2} \text{ h}^{-1}$ over a tidal cycle, with the highest fluxes observed during the lowest tides.

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). Also, 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 (Tait et al., 2012). This long residence time means TA derived from groundwater can act as a potential source of carbonates to the lagoon, raising the Ω_{Ar} of the lagoon above oceanic levels and helping to buffer against ocean acidification. However, groundwater may also act as a source of CO_2 , which would inhibit the buffering capacity of SGD associated 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 potentially 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 exchange processes of groundwater that could alter TA fluxes to the

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Table 1. Measurements of solutes in the groundwater end members (EM), EM1 $n = 3$, EM2 $n = 1$. $\delta^{13}\text{C}$ DIC of the mixed endmember was estimated from the y-intercept of a Keeling plot. The 47% EM1 : 53% EM2 are concentrations calculated from the $\delta^{13}\text{C}$ DIC estimated end member values.

	Depth (m)	DIC ($\mu\text{mol l}^{-1}$)	$\delta^{13}\text{C}$ DIC	TA ($\mu\text{mol l}^{-1}$)	^{222}Rn (dpm m^{-3})	pH
Ground Water EM1	1	9381 \pm 354	-10.12 \pm 1.02	7134 \pm 60	49 585 \pm 1743	7.325
Ground Water EM2	2.5	4251	-6.3	3989	294 146 \pm 4601	7.593
47% EM1 : 53% EM2	–	6661	-8.09	5467	179 202	7.480

15526

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.

Location	Chamber	TA_C Efflux ($\text{mmol m}^{-2} \text{h}^{-1}$)	TA_C Uptake ($\text{mmol m}^{-2} \text{h}^{-1}$)	Daily TA_C Flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	Source
Cook Islands	Diffusive	3.32	-4.01	-1.16	This study
	40 RPM	3.96	-4.78	7.76	
	60 RPM	3.17	-4.01	-1.55	
Heron Island	Diffusive	5.21	-4.83	5.13	Cyronak et al. (2013)
	40 RPM	4.93	-5.65	8.84	
	80 RPM	5.61	-7.36	8.78	

15527

Table 3. Concentrations of TA ($\mu\text{mol l}^{-1}$) measured in groundwater throughout the world. * Designates concentrations measured as HCO_3^- .

TA ($\mu\text{mol l}^{-1}$)	System type	Location	Reference
2150–2949	Subtropical estuary	South Carolina, USA	Cai et al. (2003)
90–8920	Subtropical estuary	Kunsan, Korea	Kim et al. (2004)
4.020	Subtropical estuary	Southern China	Liu et al. (2012)
753–7026*	Inland mountains	Central Mexico	Mahlknecht et al. (2004)
2550–23300	Tidal flat	Wadden Sea, Germany	Moore 2011
95–2000*	Tropical island	Guadeloupe	Rad et al. (2007)
1400–13000*	Tropical island	Martinique	Rad et al. (2007)
800–4016*	Tropical island	Reunion	Rad et al. (2007)
2290*	Coastal lagoon	Brazil	Santos et al. (2008)
1.32–2162	Tropical island	Hawaii	Schopka and Derry (2012)
3989–7134	Tropical island	Cook Islands	This study

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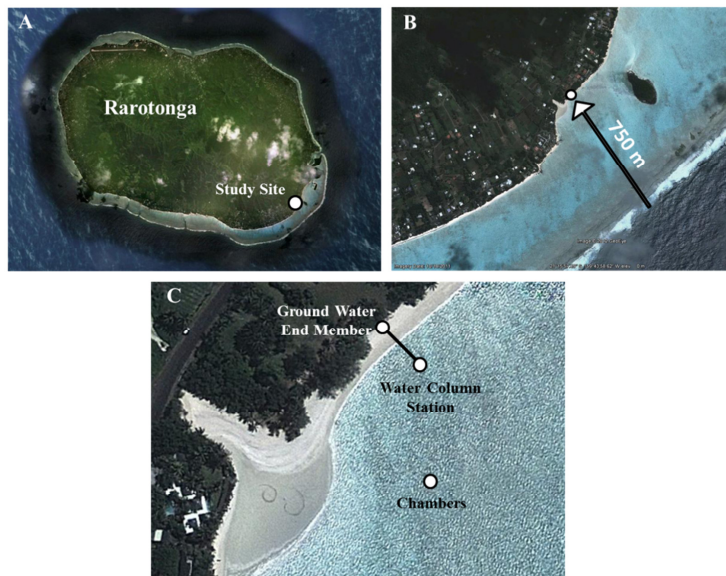


Fig. 1. A map of Rarotonga showing the location of Muri Lagoon and the sampling site.

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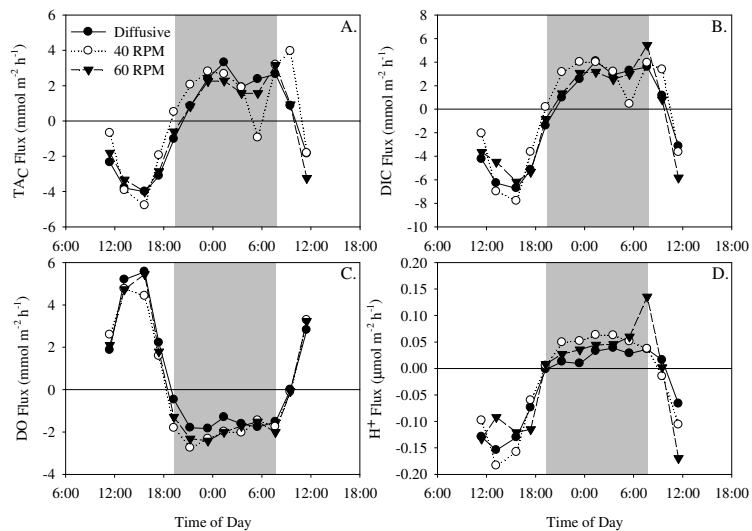


Fig. 2. Hourly, integral derived flux rates of TA_C , DIC, DO and H^+ from the advective chambers. Grey bars represent night hours. All fluxes are in $\text{mmol m}^{-2} \text{h}^{-1}$ besides H^+ which are in $\mu\text{mol m}^{-2} \text{h}^{-1}$.

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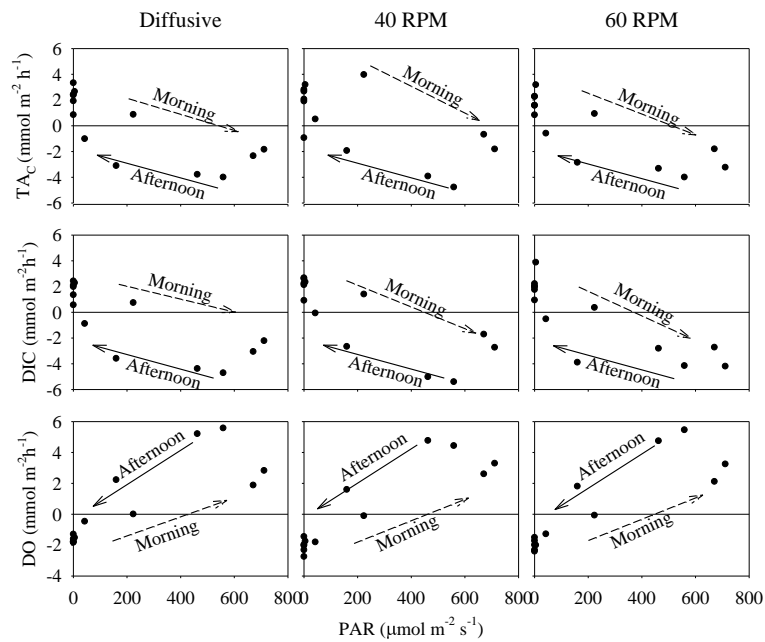


Fig. 3. Flux rates of TA_C , DIC, and DO plotted against the average PAR values measured during the same time period as the flux. Flux rates are in $mmol\ m^{-2}\ h^{-1}$.

15531

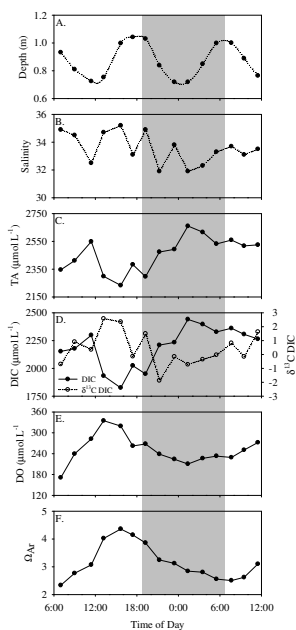


Fig. 4. (A) Depth, (B) salinity, (C) TA, (D) DIC, (E) DO, and (F) Ω_{Ar} measured in the discrete water samples taken from the water-column. Grey bars represent night hours.

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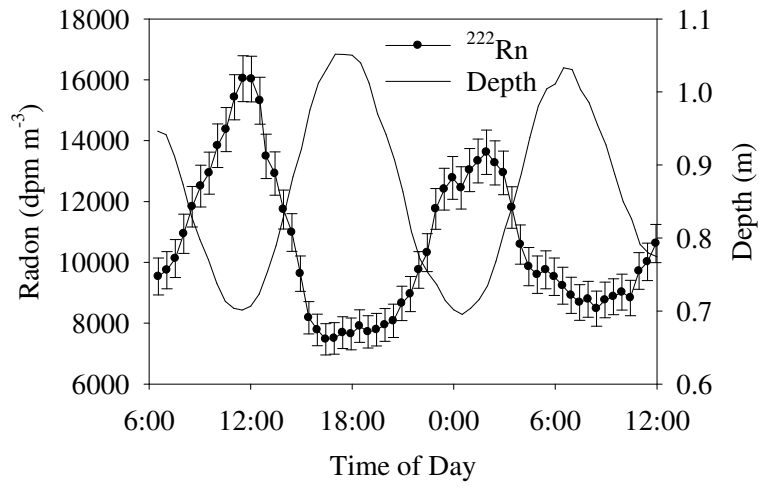


Fig. 5. Radon concentrations and depth measured at the water-column monitoring site over the course of the study.

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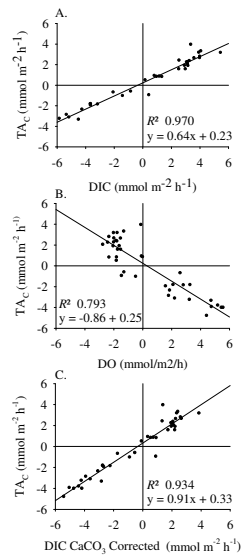


Fig. 6. Linear regressions of **(A)** TA_C vs. DIC, **(B)** TA_C vs. DO, and **(C)** TA_C vs. DIC corrected for $CaCO_3$ dissolution from all stirring rates of the advective chamber incubations. Equations and R^2 values are displayed for each regression.

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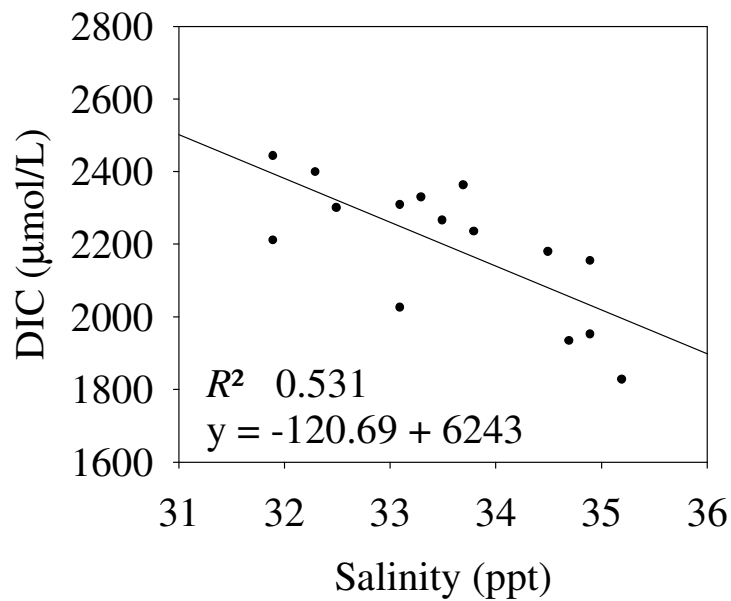


Fig. 7. Regression of salinity vs. concentrations of DIC in the water-column measured over the course of the study. The regression equation and R^2 value are displayed.

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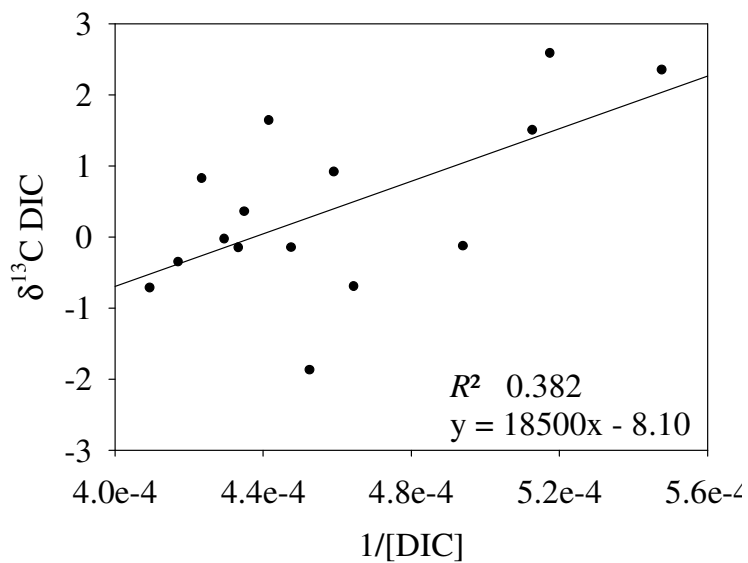


Fig. 8. Keeling plot of $\delta^{13}\text{C DIC}$ vs. $1/[\text{DIC}]$ measured in the water-column.

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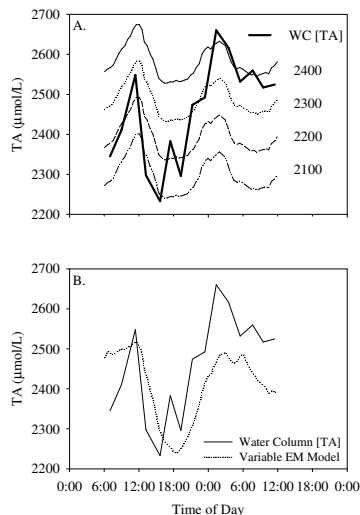


Fig. 9. Concentration of TA in the water-column during the course of the study plotted along with the estimated concentration of TA based on the ^{222}Rn derived mixing model. **(A)** Four separate mixing models using a range of TA concentrations for the oceanic end member from 2100–2400 $\mu\text{mol l}^{-1}$, **(B)** the variable oceanic end member model. All TA concentrations are in $\mu\text{mol l}^{-1}$.

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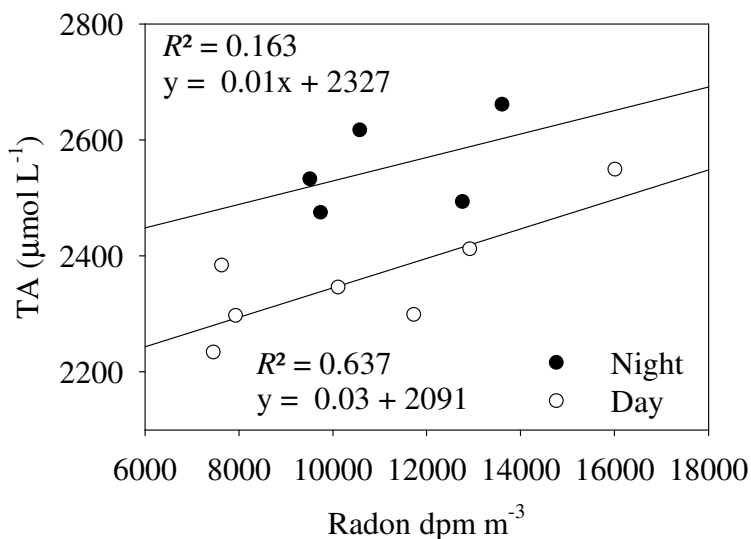


Fig. 10. TA vs. ^{222}Rn concentrations in the water-column, separate regressions were made for day time and night time hours. The three daylight time points taken during the second sampling day were removed from the regressions.

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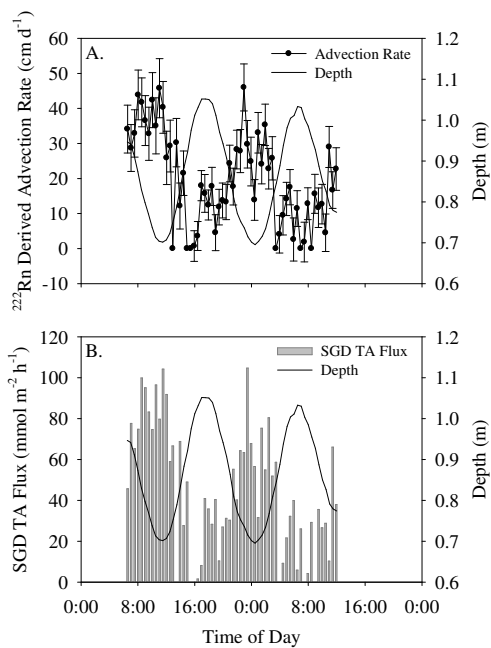


Fig. 11. (A) SGD advection rates in cm d^{-1} estimated using the model from Burnett and Du-laiova (2003) plotted alongside depth measured during the study. **(B)** Hourly SGD derived flux rates of TA into the water-column plotted with depth over the course of the study.

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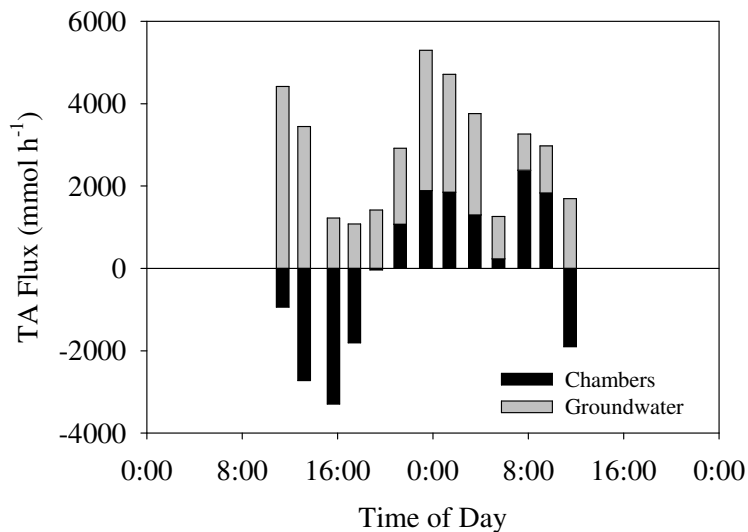


Fig. 12. Hourly flux rates of TA from advective sediments and SGD over a 750 m transect from the study site to reef crest. 100 % cover was assumed for advective sediments and SGD was estimated as mixing 50 m offshore.

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