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Spatiotemporal Variability in Seawater Carbonate Chemistry at Two Contrasting Reef Locations  
in Bocas del Toro, Panama

A Thesis submitted in partial satisfaction of the requirements for the degree

Master of Science

in

Marine Biology

by

Katelin Pedersen

Committee in charge:

Professor Andreas Andersson, Chair  
Professor Greg Rouse  
Professor Martin Tresguerres

2019

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2019

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## LIST OF ABBREVIATIONS

CaCO <sub>3</sub>	Calcium carbonate
CO <sub>2</sub>	Carbon dioxide
DIC	Dissolved inorganic carbon
DO	Dissolved oxygen
NCC	Net community calcification
NCP	Net community production
OA	Ocean acidification
SD	Standard deviation
TA	Total alkalinity
Ω <sub>a</sub>	Saturation state of seawater with respect to aragonite

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## ABSTRACT OF THE THESIS

Spatiotemporal Variability in Seawater Carbonate Chemistry at Two Contrasting Reef Locations  
in Bocas del Toro, Panama

by

Katelin Ann Pedersen

Master of Science in Marine Biology

University of California San Diego, 2019

Professor Andreas Andersson, Chair

There is growing concern for how coral reefs may fare in a high-CO<sub>2</sub> world. The majority of laboratory and mesocosm experiments have revealed negative effects on the growth and calcification of reef builders exposed to elevated CO<sub>2</sub> conditions. However, coral reefs are highly dynamic systems and the interplay between different biogeochemical and physical processes on reefs results in large variability of seawater carbonate chemistry on different functional scales. This can create localized seawater conditions that can either enhance or alleviate the effects of ocean acidification (OA). Consequently, in order to predict how coral reef ecosystems may respond to OA in the future, it is necessary to first

establish a baseline of natural carbonate chemistry conditions. This includes characterizing the range and variability of carbonate chemistry and the physical and biogeochemical controls across a broad range of environments over both space and time. Here, we have characterized the spatial and temporal physiochemical variability of two contrasting coral reef locations in Bocas del Toro, Panama that differed in their benthic community composition, reef morphology, and exposure to open ocean conditions, using a combination of research approaches including stationary autonomous sensors and spatial surveys during the month of November 2015. Mean and diurnal temporal variability in both physical and chemical seawater parameters were remarkably similar between sites and sampling depths, although, the magnitude of spatial variability was quite different between the sites. Spatial gradients in physiochemical parameters at Punta Caracol reflected the cumulative modification from terrestrial runoff and benthic metabolism. Based on graphical vector analysis of salinity normalized TA-DIC data, reef metabolism was dominated by organic carbon cycling over inorganic carbon cycling at both sites, where the outer reef reflected net heterotrophy likely owing to remineralization of organic matter from terrestrial inputs. Altogether, the results of this study highlight the strong influence of terrigenous runoff on reef metabolism and seawater chemistry conditions and demonstrate the importance of considering external inputs of alkalinity in reefs when interpreting TA-DIC data in systems with large freshwater inputs. Predicting future changes to coral reef ecosystems requires an understanding of the natural complexity of these systems in which various physical, ecological and biogeochemical drivers interact creating large variability in seawater chemistry over space and time.

## Chapter 1: Introduction

Coral reefs are one of the most biologically diverse and economically important marine ecosystems, providing numerous services and goods for human communities through coastal protection, habitat provision, fisheries, building materials, biochemical compounds, and tourism (Moberg and Folke 1999; Pandolfi et al. 2005; Hoegh-Guldberg et al. 2007). Yet, since the onset of the industrial revolution, coral reefs worldwide have experienced drastic changes in function and health, including reductions in coral cover (Hoegh-Guldberg 2005; Wilkinson 2008),  $\text{CaCO}_3$  accretion rates (Perry et al. 2018; Toth et al. 2018), structural complexity (Alvarez-Filip Lorenzo et al. 2009), and biodiversity (Loya et al. 2001; Hughes et al. 2018). The deterioration of coral reefs has been attributed to a number of global and local stressors including climate change, runoff, sedimentation, pollution, disease and overfishing (Hoegh-Guldberg 1999; Hughes et al. 2003; Bellwood et al. 2004; Wilkinson 2008). In addition to these perturbations, rising atmospheric carbon dioxide ( $\text{CO}_2$ ) as a result of fossil fuel combustion, deforestation, and land-use changes (Orr et al. 2005; Le Quéré et al. 2009), is driving shifts in seawater carbonate chemistry, leading to a decrease in seawater pH and saturation state with respect to  $\text{CaCO}_3$  minerals ( $\Omega$ ), commonly referred to as ocean acidification (OA). OA could have direct negative effects on some marine organisms and ecosystems (Hoegh-Guldberg et al. 2007; Doney et al. 2009; Hofmann et al. 2010; Kroeker et al. 2013), and will also alter biogeochemical cycling of C, N and P (e.g., Doney et al. 2009; Beman et al. 2011).

For coral reefs, the paramount concern about OA has been its potential to drive reefs from a state of net calcium carbonate ( $\text{CaCO}_3$ ) accretion to one of net erosion (Kleypas et al. 1999; Bruno and Selig 2007; Fabry et al. 2008; Silverman et al. 2009) through decreased biogenic calcification rates (Pandolfi et al. 2011; Kennedy et al. 2013; Chan and Connolly 2013), and increased rates of  $\text{CaCO}_3$  dissolution and bioerosion (Andersson et al. 2009; Wisshak et al. 2012; Andersson and Gledhill 2013; Eyre et al. 2018). Although some calcifying organisms have exhibited mixed responses to experiments simulating OA conditions (Ries et al. 2009; Andersson et al. 2011), most tropical corals and calcifying algae have shown mostly decreased rates of calcification in response to elevated  $\text{CO}_2$ , and decreased pH and  $\Omega$  conditions in

the laboratory (Pandolfi et al. 2011; Chan and Connolly 2013; Kroeker et al. 2013; Johnson et al. 2014). However, it is clear that calcifying taxa and species exhibit different sensitivity to OA (McCulloch et al. 2012; Chan and Connolly 2013), and thus, will experience negative effects at different threshold levels (Fabricius et al. 2011). Furthermore, seawater carbonate chemistry is highly variable between and across different habitats on coral reefs, making it challenging to predict both current and future seawater chemistry conditions. In fact, many model projections and experimental treatment scenarios on the response of reef organisms to OA are based primarily on open ocean trends (e.g., Hoegh-Guldberg et al. 2007; Silverman et al. 2009; Ricke et al. 2013) despite fundamental differences in carbonate chemistry dynamics between the open ocean and coral reefs.

In most coral reef environments, benthic and pelagic metabolism, geomorphology and hydrodynamics, interact to modify seawater carbonate chemistry over spatial scales ranging from millimeters to kilometers, and on timescales of minutes to days (Yates et al. 2007; Anthony et al. 2011; Hofmann et al. 2011; Shaw et al. 2012; Duarte et al. 2013; Falter et al. 2013; Page et al. 2018). In addition, some reefs are strongly influenced by terrestrial-based runoffs and/or riverine inputs that also may significantly modify the local seawater chemistry (Drupp et al. 2011; Fagan and Mackenzie 2007). Biogeochemical processes on coral reefs have the capacity to drive fluctuations in CO<sub>2</sub> parameters (e.g., pCO<sub>2</sub>, pH, and  $\Omega_a$ ) over diel and/or seasonal timescales such that the extremes often exceed or equal conditions expected in the open ocean by the end of the century (Andersson and Mackenzie 2012; Price et al. 2012; Shaw et al. 2012; Bopp et al. 2013; Albright et al. 2015). The degree to which seawater carbonate chemistry is modified is tightly linked to the depth, residence time, and the benthic community composition, where coral cover and the relative abundances of calcifying to non-calcifying organisms results in the differential modification of seawater (Anthony et al. 2011; Lowe and Falter 2015; Page et al. 2018). These differences can have consequences for downstream communities, as the dominant biogeochemical processes may exacerbate or alleviate the effects of OA (Anthony et al. 2011; Manzello et al. 2012; Hendriks et al. 2014; Camp et al. 2016; Rivest et al. 2017; Takeshita et al. 2018; Cyronak et al. 2018). Consequently, to understand how OA may affect coral reefs and its inhabitants, it is imperative

to first understand the current conditions these systems experience, including the natural range and variability of seawater carbonate chemistry, and the control and the relative influence of different drivers on the natural variability (Andersson and Mackenzie 2012; Page et al. 2016, 2017, 2018). Recent development of faster, and more accurate autonomous sensors for *in-situ* measurements of pH and oxygen (Martz et al. 2010) has advanced the ability to capture high frequency variability over extended periods of time, providing greater capacity to evaluate the environmental drivers and extremes experienced by reef organisms. Previous studies include evaluating organismal and community functions across natural CO<sub>2</sub> gradients (e.g., Manzello et al. 2008), communities associated with volcanic CO<sub>2</sub> seeps/vents (e.g., Fabricius et al. 2011; Kroeker et al. 2011; Kerrison et al. 2011), highly vegetated areas such as seagrass meadows, kelp forests and mangroves (e.g., Hendriks et al. 2014; Kapsenberg and Hofmann 2016; Koweeck et al. 2017), shallow coral reef flats (e.g., Page et al. 2018), and naturally low pH “Ojo” springs (e.g., Crook et al. 2012). Other studies have characterized the natural variability of seawater carbonate chemistry across a range of habitats with differing benthic community composition with the aim to evaluate whether some habitats could serve as refugia from OA (Yates et al. 2014; Camp et al. 2016), while others have attempted to assess the biological impacts of seawater carbonate chemistry variability on calcification rates (Shamberger et al. 2014). Establishing a baseline of contemporary environmental conditions is essential if we are to make robust predictions about the fate of coral reefs. Furthermore, it is a critical aspect in the design of more ecologically relevant manipulation experiments through the incorporation of the natural temporal variability and ranges experienced by these organisms (Andersson et al. 2015).

The goal of this study was to characterize the high-resolution spatiotemporal variability in seawater carbonate chemistry at two distinctly different reef environments with disparate benthic community composition, reef morphology and exposure to open ocean conditions. Using a combination of autonomous sensors and spatial surveys, we characterized the seawater carbonate chemistry at two coral reef sites in Bocas del Toro, Panama over the month of November 2015. One site, Punta Caracol, is a small lagoonal reef situated within Bahia Almirante and is in close proximity to dense mangroves and

seagrass beds, whereas, Punta Vieja, is a large reef site in direct contact with the open ocean. We hypothesize that heterogeneity in the benthic community structure and physical environment between the two sites would produce localized differences in seawater carbonate chemistry conditions.

## **Chapter 2: Materials and Methods**

### **2.1 Site Descriptions**

#### ***Bocas del Toro, Panamá***

The Bocas del Toro Archipelago is located along Panama's northwest Caribbean coast. Almirante Bay in the northwest side of the archipelago has an approximate surface area of 446 km<sup>2</sup> and is subject to freshwater discharge, terrestrial inputs and high sedimentation rates from several rivers, creeks and streams that drain into the bay (Fig. 1) (Guzmán and Guevara 1998; D'Croz et al. 2005). Along the Boca del Drago inlet, a sediment plume is typically present as a result of high sediment runoff from the Changuinola river north of Bocas del Toro and from the Sixaola river in Costa Rica (Seemann et al. 2014). This sheltered semi-lagoonal system created by the barrier of islands and shoaling sand cays is shielded from the strong waves and wind outside the archipelago, which supports the growth of dense mangrove forests dominated by the red mangrove *Rhizophora mangle* (Guzmán and Jiménez 1992; Dominici-Arosemena and Wolff 2005; Collin 2005). Water circulation, predominantly driven by tides in Almirante Bay, occurs through passages between islands and sand cays, with one main inlet at Boca del Drago, and outlets on either end of Isla Bastimentos (Seemann et al. 2014). The tidal range for the archipelago is small (0.4 m) with complex seasonal variation between diurnal and semidiurnal tides of varying amplitudes (D'Croz et al. 2005). The climate of Bocas del Toro includes frequent and strong rainfall with irregular seasonal patterns (Kaufmann and Thompson 2005; Dominici-Arosemena and Wolff 2005; D'Croz et al. 2005).

#### ***Punta Caracol***

Punta Caracol is a small, shallow reef site (~0.07 km<sup>2</sup>) situated along the east coast of Isla Colon in the Almirante Bay of Bocas del Toro, Panamá (9.377°N, 82.30°W) (Fig. 1). It is characterized by a

sequential zonation of varying habitats moving away from the mangrove-dense shoreline to fine-grained sediments and seagrasses (<1 m depth), sandy sediments and large colonies of *Porites*, *Orbicella*, *Diploria*, *Montastrea* and *Colpophyllia* (2-4 m), which transition to a mixed community of coral reef organisms and muddy sediments as depth increases from 4 to 12 m (Guzmán and Guevara 2005; Loh and Pawlik 2012; Neal et al. 2014) (Fig. 1). Nestled at the mouth of Big Bright, a large drainage basin, Punta Caracol receives a flux of nutrients and organic material from nearby plantations (Guzmán and Jiménez 1992; Gochfeld et al. 2007). Other factors influencing this site include high fishing pressure, coastal development and sedimentation from terrestrial runoff (Seemann et al. 2014; Kline 2004).

### ***Punta Vieja***

The Punta Vieja reef is situated along the southeast coast of Isla Bastimentos (9.259°N, 82.1081°W) (Fig. 1). In contrast to Punta Caracol, Punta Vieja is situated outside Almirante Bay approximately 10 km from the town of Bocas. Correspondingly, Punta Vieja's location allows for greater exposure to the open ocean and is surrounded mostly by uninhabited forest and is adjacent to many mangrove crop-ups and keys (Kline 2004; Díaz 2005). The benthic habitat composition differs from Punta Caracol; the reef flat (2-5 m) is dominated mostly by *Acropora cervicornis* and *Acropora palmata*, but also contains small patches of other corals along with gorgonians. Beyond 5 m, depth drops off rapidly with high densities of corals, which further transitions to a muddy bottom beyond the reef structure at ~12 m.

## **2.2 Sampling strategy**

### ***Autonomous sampling of water column parameters***

To measure short-term variability in seawater biogeochemistry, high-frequency temporal data was collected by deploying stationary autonomous instruments at both Punta Caracol and Punta Vieja from 3-20 November 2015 (Fig.1). Two stations at each site (3 m and 8.4 m at Punta Caracol, and 2.6 m and 7.6 m at Punta Vieja) were equipped with SeapHOx sensors (Martz et al. 2010) that measured temperature (°C), salinity (psu), pressure, dissolved oxygen (DO; ml L<sup>-1</sup>), and pH every 30 minutes. SeapHOx pH measurements were calibrated to discrete seawater samples collected next to the instrument

during sampling, with pH determined from the internal reference electrode and reported on the total pH scale (Bresnahan et al. 2014). A low-resolution and a high-resolution 1 MHz AquaDopp (Nortek) current profiler were deployed at Punta Caracol and Punta Vieja, respectively. All sensors were secured to the bottom at each station using cinder blocks.

### ***Spatial sampling of surface seawater carbonate chemistry***

In order to capture the spatial variability in seawater chemistry throughout the diurnal period, surveys were carried out by boat in the morning and afternoon from 11-17 November 2015. Surface seawater samples were collected at 24 stations across an area of  $\sim 0.07 \text{ km}^2$  at Punta Caracol ( $n = 5$  surveys), and 25 stations across an area of  $16 \text{ km}^2$  at Punta Vieja ( $n = 4$  surveys). In addition to the 25 stations at Punta Vieja, samples were also collected at an offshore station to serve as a reference for open ocean conditions (Fig. 1). Three additional seawater sampling surveys between Punta Caracol and Punta Vieja were carried out to capture the transitional gradient between the sites. At each sampling location, sea surface temperature ( $\pm 0.2^\circ\text{C}$ ), salinity ( $\pm 0.1 \text{ psu}$ ) and DO ( $\pm 0.2 \text{ ml L}^{-1}$ ) were measured with a YSI Professional Plus multi-parameter probe. Surface seawater samples were collected with a Niskin bottle from a depth of  $\sim 0.5 \text{ m}$  and transferred immediately to 250-mL Pyrex borosilicate glass bottles, per standard protocols (Dickson et al. 2007), and were immediately preserved with 100  $\mu\text{L}$  of saturated solution of  $\text{HgCl}_2$  to arrest any metabolic activity. All samples were sealed with grease coated borosilicate stoppers and rubber bands to prevent gas exchange.

The samples were shipped to the Scripps Coastal and Open Ocean Biogeochemistry lab for analysis of dissolved inorganic carbon (DIC) and total alkalinity (TA). Concentrations of DIC were measured using an automated infrared inorganic carbon analyzer (AIRICA, Marianda) system with a LI-COR 7000 (Li-COR) infrared  $\text{CO}_2$  analyzer as the detector. Total alkalinity was analyzed via an open-cell potentiometric acid titration using an 876 Dosimat (Metrohm) and Electrode Plus pH electrode (Metrohm) (Dickson et al. 2007). Accuracy of the instruments, calculated as the mean offsets ( $\pm 1 \text{ SD}$ ) from Dickson Certified Reference Material (CRM), was  $-0.9 \pm 2.4 \mu\text{mol kg}^{-1}$  ( $n = 51$ ) and  $-2.1 \pm 2.7 \mu\text{mol kg}^{-1}$  ( $n = 136$ ) for TA and DIC, respectively.



## 2.3 Calculations and data analysis

The MATLAB CO2SYS program (Lewis and Wallace 1998) was used to calculate seawater  $p\text{CO}_2$ , aragonite saturation state ( $\Omega_a$ ) and pH (defined on the total  $\text{H}^+$  scale) based on *in situ* seawater temperature, salinity, DIC, and TA. Dissociation constants were adopted from Mehrbach et al. (1973), refit by Dickson and Millero (1987). In order to evaluate the influence of biogeochemical processes on seawater TA and DIC, these parameters were normalized to the average salinity at the offshore reference station (34.4). Two different freshwater end-members were used to assess the effect of salinity normalization assuming different freshwater TA and DIC concentrations: (1) assuming zero TA and negligible DIC in the freshwater endmember and (2) a non-zero endmember based on observed relationships between TA, DIC, and salinity. Salinity-normalized TA and DIC concentrations were calculated using the equation:

$$C_n = \frac{(C_m - C_{fw}) \times S_{sw}}{S_m} + C_{fw} \quad (1)$$

where  $C_m$  is the measured solute concentration (TA or DIC in  $\mu\text{mol kg}^{-1}$ ),  $C_{fw}$  is the solute concentration of the freshwater being added to the system ( $\mu\text{mol kg}^{-1}$ ),  $S_{sw}$  is the salinity of the seawater the data is being normalized to (i.e., 34.4 psu), and  $S_m$  is the measured salinity (Friis et al. 2003; Jiang et al. 2014).

When we normalize the data using the zero endmember, the equation reduces to:

$$C_n = \frac{C_m \times S_{sw}}{S_m} \quad (2)$$

which is often applied in coral reef biogeochemistry assuming the solute concentration of the freshwater added to the system is zero (e.g., Friis et al. 2003). For the non-zero endmember calculation, freshwater solute concentrations were determined from the relationship of salinity and TA and DIC at each site, where  $C_{fw}$  is the y-intercept of the solute-salinity linear regression (Jiang et al. 2014). Type II major axis linear regression analysis was performed on nTA and nDIC data in MATLAB using the lsqfitma.m MODEL-2 least squares fit code (<https://www.mbari.org/index-of-downloadable-files/>).

## Chapter 3: Results

During the deployment period from 3-19 November 2015, weather was mostly partly cloudy with intermittent rainstorms and an average wind speed of  $1.9 \pm 1.1 \text{ m s}^{-1}$  predominantly from the southeast (Smithsonian Physical Monitoring Program). Total rainfall over the course of the study reached 99.4 mm with the heaviest rainfall occurring on the 11th (Smithsonian Physical Monitoring Program; Fig. 3). Tides in Bocas del Toro were mixed semidiurnal with an average tidal range of  $0.31 \pm 0.10 \text{ m}$  during the study (Fig. 3). Currents at Punta Caracol were predominantly oriented alongshore towards the north-northwest, ranging in speed from 0 to  $0.12 \text{ m s}^{-1}$  (avg. =  $0.03 \text{ m s}^{-1} \pm 0.02 \text{ m s}^{-1}$ ) while currents at Punta Vieja were generally slower, ranging from 0 to  $0.08 \text{ m s}^{-1}$  (avg. =  $0.02 \text{ m s}^{-1} \pm 0.02 \text{ m s}^{-1}$ ) with net flow directed from west to east (Fig. 2).

### **3.1 Temporal variability of environmental parameters from stationary autonomous sensors**

#### ***Punta Caracol***

Mean seawater temperature was similar at 3 and 8 m depth at Punta Caracol, averaging  $30.3 \text{ }^{\circ}\text{C}$  (Fig. 3; Table 1), and decreased by  $0.7 \text{ }^{\circ}\text{C}$  throughout the study period. Diel trends in temperature were apparent, with the shallower site (3 m) experiencing greater fluctuations than the deeper site (8 m) with an average diel range ( $\pm 1 \sigma$ ) of  $0.7 \pm 0.2 \text{ }^{\circ}\text{C}$  and  $0.4 \pm 0.1 \text{ }^{\circ}\text{C}$ , respectively. Mean seawater salinity was greater at the deeper site ( $34.3 \pm 0.2$ ) than the shallow site ( $33.9 \pm 0.3 \text{ psu}$ ). Distinct diel trends in DO and pH were evident at both locations in Punta Caracol (Fig. 3). The mean DO concentration and the mean diel range were slightly higher at 3 m ( $169.6 \pm 5.9 \text{ } \mu\text{mol kg}^{-1}$  and  $44.4 \pm 11.4 \text{ } \mu\text{mol kg}^{-1}$ , respectively) compared to 8 m ( $160.0 \pm 6.5 \text{ } \mu\text{mol kg}^{-1}$  and  $38.3 \pm 6.9 \text{ } \mu\text{mol kg}^{-1}$ , respectively; Table 1). During any one diel cycle, the range in DO concentration for the 3 m and 8 m sites varied from  $20.9$  to  $67.8 \text{ } \mu\text{mol kg}^{-1} \text{ day}^{-1}$  and  $24.8$  to  $51.2 \text{ } \mu\text{mol kg}^{-1} \text{ day}^{-1}$ , respectively. Similarly, mean daily pH for the two depths were comparable (3 m avg. =  $7.96 \pm 0.03$ ; 8 m avg. =  $7.97 \pm 0.01$ ; Table 1), although, the shallower site experienced larger variability (avg. diel range =  $0.10 \pm 0.07$ ; Table 1). The range in pH over any given day varied from  $0.05$  to  $0.32$  (3 m) and  $0.05$  to  $0.09$  (8 m).

#### ***Punta Vieja***

Average seawater temperature was similar between the two sampling depths ( $30.3\text{ }^{\circ}\text{C} \pm 0.2\text{ }^{\circ}\text{C}$  and  $30.2\text{ }^{\circ}\text{C} \pm 0.2\text{ }^{\circ}\text{C}$  for 3 m and 8 m, respectively; Table 1), whereas average salinity was slightly higher at 8 m depth ( $35.0 \pm 0.4$  psu; Table 1) compared to 3 m depth ( $34.2 \pm 0.2$ ; Table 1). DO and pH followed diel cycles with little apparent influence from tides. Mean DO concentrations were slightly higher for the shallow site ( $169.1 \pm 5.2\text{ }\mu\text{mol kg}^{-1}$ ) compared to the deeper site ( $159.8 \pm 8.8\text{ }\mu\text{mol kg}^{-1}$ ; Table 1). The average diel range in DO concentration at the two depths (Table 1) varied from 28.9 to 62.1  $\mu\text{mol kg}^{-1}\text{ day}^{-1}$  at 3 m and 32.4 to 80.7  $\mu\text{mol kg}^{-1}\text{ day}^{-1}$  at 8 m. Mean pH was similar between the two temporal sampling depths ( $7.96 \pm 0.01$  and  $7.95 \pm 0.02$ , for 3 m and 8 m, respectively), with little difference in diel variability ( $0.05 \pm 0.01$  and  $0.07 \pm 0.02$ , respectively; Table 1). Over any given day, the pH varied by 0.04 to 0.07 units and 0.05 to 0.11 units for the 3 m and 8 m sites, respectively.

### **3.2 Spatial Variability of Carbonate Chemistry Parameters from Boat Surveys**

#### ***Punta Caracol***

The average surface seawater temperature for all surveys was  $30.2 \pm 0.5\text{ }^{\circ}\text{C}$ , with an average range of  $1.1 \pm 0.6\text{ }^{\circ}\text{C}$  (Table 1). In general, seawater temperature was lower in the morning than the afternoon. During the afternoon surveys, surface seawater temperature showed an even spatial distribution while the first two morning surveys (November 11 and 12) revealed distinct spatial gradients with areas of colder surface seawater. These two surveys followed an intense rain event on the nights of November 10 and 11 (Fig. 3). Coincident with the colder temperatures, salinity was also lower with the lowest salinity observed during the morning of November 12 ( $28.5 \pm 0.1$  psu), and the greatest spatial gradient ranging from 28.5 to 33.9 psu observed on the morning of November 12 (Fig. 4). The average seawater salinity for all surveys was  $32.8 \pm 1.6$  psu with the range in salinity varying from 0.6 to 5.4 psu for any given survey.

The spatial distribution of TA essentially tracked that of temperature and salinity, with the two surveys in the morning on November 11 and 12 revealing the lowest average TA ( $2092 \pm 55\text{ }\mu\text{mol kg}^{-1}$ ) and the greatest spatial gradient, respectively (Fig. 4). During the afternoon surveys, the spatial gradients

were less defined although a distinct trend was noted on the 12th, but for the final morning survey on the 13<sup>th</sup>, any spatial gradient was virtually absent across sampling stations except for at one station, where one suspicious outlier skewed the data (Fig. 4). The average TA for the spatial surveys was  $2185 \pm 55 \mu\text{mol kg}^{-1}$  with a range of 55 to  $154 \mu\text{mol kg}^{-1}$  (Table 1). DIC and DO mostly tracked the observed gradients in other parameters, although some deviation from this was observed during the afternoon on November 12 and morning of November 13 (Fig. 4). In general, DIC and DO mirrored each other with high DIC corresponding to low DO and vice versa. In the mornings, DIC was highest and DO lowest at the stations along the shore and decreased and increased, respectively, in the offshore direction. Conversely, these gradients were reversed in the afternoon surveys (Fig. 4). The lowest average DIC and DO was observed on the morning of November 11 ( $1883 \pm 20 \mu\text{mol kg}^{-1}$  and  $147.3 \pm 8.3 \mu\text{mol kg}^{-1}$ , respectively) following the rain event. The average DIC for all surveys was  $1914 \pm 26 \mu\text{mol kg}^{-1}$  and the average DO  $166.8 \pm 18 \mu\text{mol kg}^{-1}$  (Table 1).

The spatial variability in pH was large with an average range of  $0.11 \pm 0.04$  (Table 1) and varied in magnitude between surveys from 0.07 to 0.16 units over any given survey. Similarly,  $\text{pCO}_2$  and  $\Omega_a$  were both highly variable within and between surveys. The observed range during any given survey varied from 64.50 to  $231.80 \mu\text{atm}$ , and 0.35 to 1.43, respectively. In general, gradients in pH were parallel to those of  $\Omega_a$ , and reversed for  $\text{pCO}_2$ , which mostly followed the observed gradients in salinity and TA (Fig. 5). However, variance from this was observed during the morning of November 13 (Fig. 5) where gradients followed those of DIC and DO, with the lowest pH and  $\Omega_a$  and highest  $\text{pCO}_2$  recorded at the inshore stations, which increased and decreased, respectively, in the offshore direction (Fig. 5). The lowest average pH and  $\Omega_a$ , and highest  $\text{pCO}_2$ , was recorded on the morning of November 11 ( $7.89 \pm 0.03$ ,  $2.60 \pm 0.24$ , and  $574.02 \pm 47.14 \mu\text{atm}$ , respectively) following the rain event. Average pH,  $\Omega_a$  and  $\text{pCO}_2$  for all spatial surveys was  $7.96 \pm 0.04$ ,  $3.22 \pm 0.39$ , and  $486.53 \pm 56.85 \mu\text{atm}$ , respectively (Table 1).

### ***Punta Vieja***

In general, seawater temperature followed the daily light cycle with cooler temperatures in the early mornings and warmer temperatures in the afternoon. The average seawater temperature throughout

the spatial surveys was  $29.9^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$  which was marginally higher than the offshore reference station average of  $29.7^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ . Seawater temperature was generally uniform throughout the surveys, however, larger gradients began to form in the afternoon of November 17, where elevated temperatures were localized near the inner stations (Fig. 6). Average salinity was  $34.2 \pm 0.1$  which was slightly lower than the offshore reference value of  $34.4 \pm 0.0$  (Table 1). Spatial gradients in salinity were small with higher concentrations near the west/northwest stations (Fig. 6) but was otherwise generally consistent between surveys with an average range of  $0.1 \pm 0.1$  (Table 1).

The spatial distribution in TA closely followed salinity where the lowest concentrations were observed near the offshore stations and increased moving inshore. The largest gradient in TA was recorded during the afternoon survey on November 17, where TA ranged from 2139 to 2225  $\mu\text{mol kg}^{-1}$  (Fig. 6). The average TA for the spatial surveys was  $2216 \pm 10 \mu\text{mol kg}^{-1}$  (Table 1). Gradients in DIC closely matched those of TA, where the lowest concentrations were observed offshore, and increased in the inshore direction (Fig. 6). Conversely, gradients in DO were weaker and reversed in direction with increased concentration in the offshore direction (Fig. 6). The average DIC and DO was generally consistent between surveys, where the average for all surveys was  $1934 \pm 9 \mu\text{mol kg}^{-1}$  and  $177.6 \pm 6.2 \mu\text{mol kg}^{-1}$ , respectively (Table 1).

In contrast to TA and DIC, pH displayed clear, opposite gradients of high to low in the offshore direction, with the exception of one station in the final afternoon survey on November 17 which skewed the data (Fig. 7). The spatial range in pH varied between surveys from 0.06 to 0.11; however, average pH remained consistent throughout the surveys ( $7.96 \pm 0.00$ ; Table 1). Gradients in  $\Omega_a$  followed the same spatial pattern as pH, but with less definition, whereas  $\text{pCO}_2$  mirrored those of pH (Fig. 7). The average  $\Omega_a$  and  $\text{pCO}_2$  for all surveys was  $3.29 \pm 0.04$  and  $479.79 \pm 2.81 \mu\text{atm}$ , respectively, and the range during any one survey varied from 0.36 to 0.64, and 75.74 to 154.82  $\mu\text{atm}$ , respectively (Table 1).

### **3.3 Comparing Punta Caracol and Punta Vieja**

Despite both systems maintaining similar averages in salinity and temperature throughout both

the temporal and spatial studies, Punta Caracol exhibited greater variability in both parameters over space and time. Both sites exhibited stratification, with cooler, fresher water lying on top of warmer, saltier water (Fig. 3). Overall, average TA, DIC, DO, and  $\Omega_a$  were slightly higher at Punta Vieja compared Punta Caracol (Table 1), yet, Punta Caracol experienced greater spatial variability in all parameters despite a smaller survey area. Nonetheless, mean DO and pH throughout the temporal studies were nearly identical between sites and sampling depths, and the average pH from the spatial surveys were parallel between both sites (Table 1). However, the temporal variability was considerably higher at Punta Caracol (max range of 0.32) compared to Punta Vieja (max range of 0.11) (Fig. 3).

To further assess variability between the sites, seawater samples collected between Punta Caracol and Punta Vieja on a transect showed that, on average, TA and DIC were greater in the morning than the afternoon ( $2215 \pm \mu\text{mol kg}^{-1}$  and  $2203 \mu\text{mol kg}^{-1}$  for TA, and  $1905 \pm 7 \mu\text{mol kg}^{-1}$  and  $1927 \pm 18 \mu\text{mol kg}^{-1}$  for DIC, respectively; Fig. 8), whereas average pH was lower in the morning than in the afternoon ( $7.98 \pm 0.02$  and  $8.00 \pm 0.02$  for pH, respectively). A distinct gradient in both TA and DIC was observed during the morning and afternoon which revealed a decrease from Punta Caracol towards Punta Vieja, however, the gradient was stronger for DIC, where the stations closest to Punta Vieja showed the greatest drawdown from the morning to the afternoon (Fig. 8). The spatial distribution of pH did not display as clear of a gradient in the afternoon as it did in the morning, where pH was higher at the stations closest to Punta Caracol and decreased in the direction towards Punta Vieja.

### **3.4 Assessing reef metabolism based on TA-DIC relationships**

To further understand the relative influences of reef metabolic processes on the observed spatial and temporal seawater carbonate chemistry variability, TA-DIC diagrams were plotted against vectors depicting theoretical effects of net community calcification (NCC) and net community production (NCP) on seawater chemistry (Fig. 9) (Suzuki and Kawahata 2003). NCC refers to the balance between gross calcification and gross  $\text{CaCO}_3$  dissolution and NCP refers to the balance between primary production and total respiration (e.g., Cyronak et al. 2018). The relative balance between NCC and NCP is reflected in the slope of the TA-DIC regressions, such that a slope approaching 2 indicates a system dominated by

inorganic carbon cycling (NCC), whereas a slope approaching 0 represents a system dominated by organic carbon cycling (NCP) (Cyronak et al. 2018). Given the large inputs of freshwater to the system, TA-DIC data were normalized to salinity to remove effects from freshwater dilution and precipitation that occurred over the study. However, traditional salinity normalization using 0 as an end-member could potentially be overestimating the nTA and nDIC concentrations (Friis et al. 2003; Richardson et al. 2017) as rivers are known to be a source of alkalinity and inorganic carbon. Therefore, a second salinity normalization was done on the TA-DIC data using the y-intercept from the TA-S and DIC-S relationships as the “non-zero” freshwater endmember.

The slopes of the TA-DIC type II major axis linear regressions at Punta Caracol varied significantly between the normalized and non-normalized data. Plotting the raw TA-DIC data produced a slope of 2.48 with an  $R^2$  of 0.67. In contrast, normalizing the data shifted the data such that the zero endmember revealed a strong positive correlation ( $R^2 > 0.96$ ) with a slope of 0.71 (Fig. 9), and the non-zero endmember further reduced the slope to 0.64 with an  $R^2$  of 0.59 (Fig. 9). Conversely, the slope of the normalized data at Punta Vieja did not change regardless of endmember used (slope = 0.86;  $R^2 = 0.58$ ; Fig. 9), however, it did slightly decrease from the raw data (slope = 1.01; Fig. 9). Relative to the open ocean endmember, Punta Caracol mostly exhibited excess alkalinity during both the morning and afternoon, although the values in the morning were typically higher than during the afternoon. Some instances of alkalinity depletion were observed during both morning and afternoon. DIC was generally depleted during the afternoon indicating net organic carbon production while excess DIC was observed in the morning as a result of net respiration at night. In contrast, excess TA and DIC relative to the open ocean was observed at Punta Vieja for the majority of observations regardless of the time of the day, although early morning values were typically higher with respect to both TA and DIC. These observations may indicate that this system was dominated by heterotrophy and  $\text{CaCO}_3$  dissolution.

## **Chapter 4: Discussion**

The goal of this study was to characterize the spatial and temporal variability in seawater carbonate chemistry parameters at two contrasting coral reef sites in Bocas del Toro, Panama, using a combination of sampling schemes (i.e., autonomous benthic sensors and surface spatial surveys). Despite large differences in their geographical setting (e.g., geomorphology, proximity to rivers and open ocean) and benthic community composition (i.e., mix of mangrove, sea grass, and corals vs. coral dominated system), the observed average conditions and diel variability of seawater parameters were remarkably similar, especially below the surface (Fig. 3; Table 1). Surface measurements, however, revealed larger differences in the variability of physical and chemical parameters across space (Table 1). The differences in spatial variability between the two sites appeared to be mainly driven by freshwater inputs at Punta Caracol and differences in depth across the sampling areas. This was evident from salinity gradients coincident with gradients in TA, DIC, and DO (as well as pH,  $\Omega_a$ , and pCO<sub>2</sub>) following rain events (Fig. 4, 5). A small creek just north of the sampling grid at Punta Caracol appeared to be the source of the majority of this freshwater input, which explains the lower mean, and greater variability in salinity and other parameters at this site compared to Punta Vieja. During dry periods at Punta Caracol, the spatial variability in DIC, DO and pH was likely driven by benthic metabolism and enhanced by depth differences across the survey area, where the shallowest depths showed the greatest change in concentration from morning to afternoon (Fig. 4, 5). Notably though, while TA, DIC and DO on average were slightly lower at Punta Caracol compared to Punta Vieja, the averages of surface seawater pH,  $\Omega_a$  and pCO<sub>2</sub> were similar at the two sites (Table 1), although the variability was much greater at the former location. Given this larger variability, one could interpret that the benthic community at Punta Caracol was exposed to a wider range of conditions, but it is evident from the autonomous sensors at 3 m and 8 m depths that this was not the case, as the most prominent differences were restricted to the very top surface layer (Table 1).

Although the direct influence of freshwater appeared restricted to the surface chemistry at Punta Caracol, there are many other ways freshwater inputs can modify biogeochemical processes and seawater chemistry. In particular, terrestrially-derived freshwater inputs are often enriched in organic matter and/or



nutrients and could amplify net respiration through increased remineralization of organic matter, while stimulating primary production via nutrient addition (e.g., Fabricius 2005; Cai et al. 2010; Larsen and Webb 2009; Ringuet and Mackenzie 2005; Fagan and Mackenzie 2007). Such metabolic alterations can shift the dominant biogeochemical processes on a reef, and consequently, the seawater chemistry. Given the large inputs of freshwater at Punta Caracol and its effect on surface chemistry variability, it was expected that this location might experience a greater influence of organic matter and nutrient inputs on biogeochemical processes than Punta Vieja. This would be further amplified by its partial isolation from the Caribbean Sea and being completely surrounded by terrestrial environments. However, the pH and oxygen data (i.e., mean and average diel range) from 3 m and 8 m depths did not reveal any clear evidence of differences in net reef metabolism between the two sites resulting from terrestrial inputs (e.g., lower pH and oxygen). Typically, these parameters, including the diel variability, are influenced by additional factors such as community composition and biomass, flow rates and trajectory, as well as the seawater residence time at each site (Zhang et al. 2012; Lowe and Falter 2015; Page et al. 2018). Yet, the average flow rate between the sites differed by only  $0.01 \text{ m s}^{-1}$ , and the flow direction was predominantly unidirectional (Fig. 2), so it is unlikely that current speeds affected the biogeochemical variability significantly. Depending on flow trajectory and mixing rates with different end members (e.g., freshwater or offshore water), the chemical memory of the seawater and inorganic carbon chemistry could be different (i.e., the cumulative modification of properties such as DIC and TA). These changes are not necessarily discernible from oxygen and pH data alone (Andersson et al. 2014), and the short-term diel variability in these parameters are not affected by flow trajectory. Despite apparent differences in benthic communities and habitats between the two sites, the diel variability in pH and oxygen were similar at all sensor locations, which, therefore, do not reveal any differences in net reef metabolism or the dominant biogeochemical processes occurring at each site. Similarly, a recent study from Kane'ohe Bay in Hawaii did not detect substantial differences in seawater pH and oxygen variability between a range of different reef habitats (Page et al., 2018). Instead, it was proposed that the prevailing biogeochemical conditions and temporal variability were most strongly correlated with water depth, and thus, controlled by the

biomass-to-water-volume ratio rather than the benthic community composition, with the exception of areas of extremely high coral cover (Page et al., 2018).

Based on system scale analysis of surface seawater TA-DIC data relative to open ocean conditions, Punta Vieja reflected net heterotrophy at all times while Punta Caracol appeared autotrophic during afternoon surveys and heterotrophic during morning surveys (Fig. 10). However, one must recognize that the data from Punta Caracol ( $\sim 0.07 \text{ km}^2$ ) represent one small, active reef community (i.e., the data reflect variability at smaller, more localized spatial scales) while the data from Punta Vieja ( $\sim 16 \text{ km}^2$ ) represent an integrated signal from multiple habitats and communities over a much larger spatial scale (see Cyronak et al., 2018 and Takeshita et al. 2018 for a detailed discussion). The observed net heterotrophy at this larger scale can only be attributed to external input and remineralization of organic material, which is expected, given the local geography and adjacent terrestrial environments (Suzuki et al. 2001; Suzuki and Kawahata 2003; Fagan and Mackenzie 2007). Irrespective of the trophic status, both locations appeared to undergo net dissolution of  $\text{CaCO}_3$  minerals as inferred from alkalinity depletion relative to offshore samples and based on the assumption that  $\text{CaCO}_3$  formation and dissolution were the only processes affecting TA. Although this assumption is valid for most coral reef environments, the potential large input of dissolved organic material and nutrients in Bocas del Toro could significantly affect the TA balance and must be noted (Brewer and Goldman 1976; Cai and Wang 1998). However, by salinity normalizing TA-DIC data to a derived non-zero TA-DIC end-member, this effect is partly accounted for, although the composition of the end-member is clearly associated with uncertainty. Regardless, observations of net heterotrophy from other reef environments have frequently been associated with net  $\text{CaCO}_3$  dissolution (Courtney et al. 2018) as the decomposition of organic material drives seawater  $\Omega$  in sediments and microenvironments below equilibrium, causing  $\text{CaCO}_3$  dissolution (Andersson and Gledhill 2013; Eyre et al. 2018). Heterotrophy on reefs can also be driven by lateral advection of food from highly productive offshore blooms onto reefs resulting in increased feeding by corals (e.g., Yeakel et al. 2015; Fox et al. 2018). The prevailing hypothesis suggests that this would lead to increased reef-scale calcification rather than dissolution (e.g., Yeakel et al., 2015). However, despite

conditions of net reef-scale  $\text{CaCO}_3$  dissolution as a result of terrestrially derived organic material, some studies suggest that this additional nutrition could still prove beneficial to the success and growth of individual corals (Watanabe et al. 2006; Shamberger et al. 2014).

Multiple lab experiments have shown increased tolerance to acidification if corals are provided additional nutrition (e.g., Edmunds 2011; Drenkard et al. 2013; Towle et al. 2015) and similar inferences have been made from field studies (e.g., Crook et al., 2012; Shamberger et al., 2014). For example, Shamberger et al. (2014) reported healthy coral communities within a semi-enclosed bay in Palau exposed to low seawater  $\Omega$ , but with a potential plentiful supply of nutrients from the surrounding terrestrial environments. Similarly, in Puerto Morelos, Mexico, where seawater is frequently undersaturated owing to inflow of naturally acidic groundwater, the presence of healthy corals has been hypothesized as a result of elevated nutrient concentrations in the groundwater providing nutritional energy that may offset any potential negative effects of acidification (Crook et al. 2012). Despite the persistence of corals under these conditions, only few species appeared tolerant to such low levels of seawater  $\Omega$  and pH, as coral density and biodiversity increased with distance away from the source of groundwater (Crook et al. 2012). Similar decreasing trends in biodiversity have been observed at reefs influenced by  $\text{CO}_2$  vents in Papua New Guinea (Fabricius et al. 2011), which appear related to species-specific tolerance to low pH conditions (e.g., *Porites*) rather than the supply of additional nutritional resources as the abundance of corals was not affected. In contrast, at a  $\text{CO}_2$  vent site in Okinawa, Japan, soft corals dominated the coral community under acidified conditions (Inoue et al. 2013). Based on the carbonate chemistry data of the present study, it is not possible to ascertain whether the distinct visual differences between the reef community and structure between Punta Caracol and Punta Vieja are related to this, as the means and variability of biogeochemical parameters were remarkably similar. However, these data only represent a snapshot in time, and a longer study would be required to fully characterize these differences.

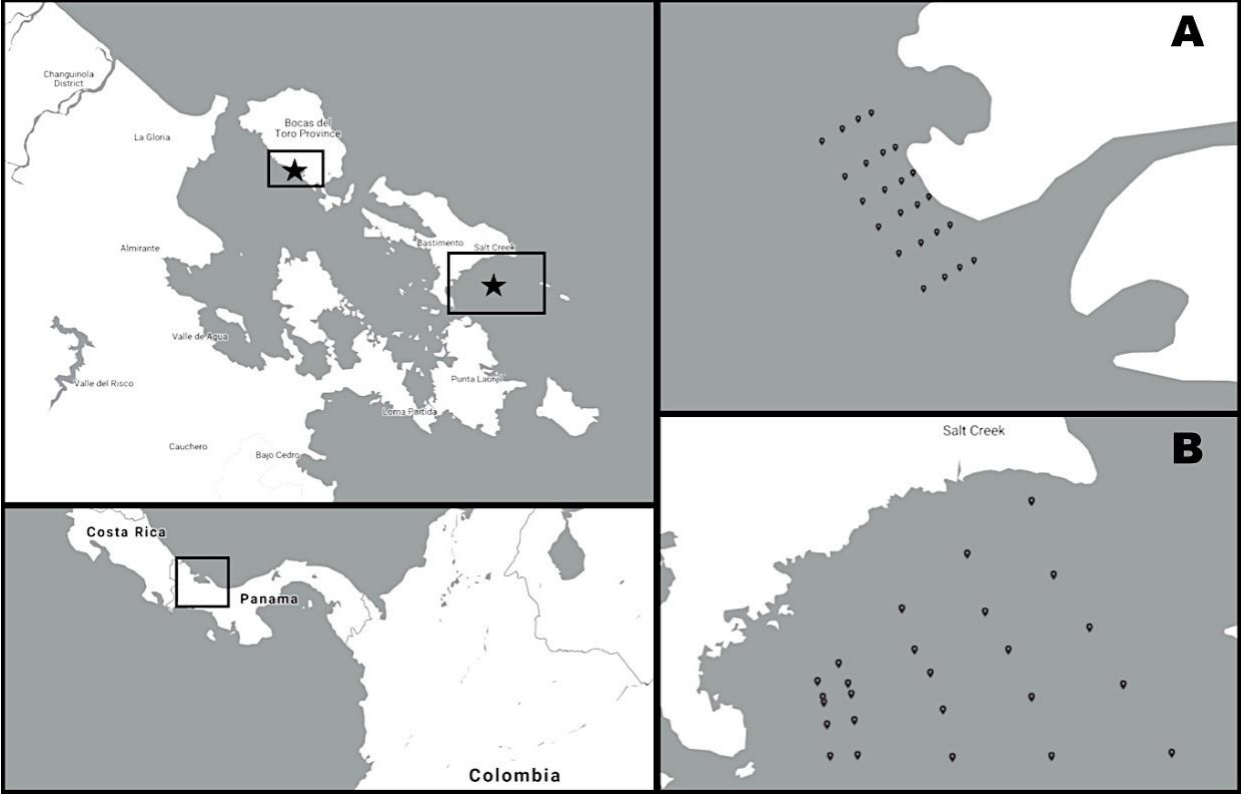
In the context of OA, it is of interest to understand whether reefs influenced by large terrestrial inputs, such as the reefs in Bocas del Toro, are more or less sensitive to the long-term changes in seawater  $\Omega$  and pH of adjacent offshore waters. Input of nutrients and organic matter certainly influence water quality, including seawater  $\Omega$  and pH, and may ultimately control the community structure and distribution, potentially favoring species that are more tolerant to secular changes in seawater chemistry. Drastic changes in community structure of reef systems have been observed in multiple places such as the wider Caribbean (Jackson et al. 2014), Reunion Island (Montaggioni et al. 1993; Chazottes et al. 2002), and in Kane'ohē Bay, Hawaii (Smith et al. 1981; Jokiel et al. 1993) where multiple drivers including terrigenous input of organic material (e.g., sewage) and nutrient discharge have correlated with declines in coral cover and reef growth (Smith et al. 1981; Montaggioni et al. 1993; Jokiel et al. 1993; Chazottes et al., 2002; Jackson et al., 2014) although some species have persisted through these perturbations. In the case of Bocas, reefs around the archipelago have recently undergone a shift in dominance from *Porites* to *Agaricia tenuifolia* in mid-depth waters (Aronson et al. 2004). This is thought to be because the latter are more tolerant of high nutrient concentrations and high sedimentation rates than other Caribbean corals (Sebens et al. 2003).

Although the effects of OA on coral reefs and calcifying organisms is mostly expected to be negative, observations from locations where natural acidification occurs (e.g., Fabricius et al., 2011; Crook et al., 2012; Shamberger et al., 2014) suggest that the magnitude of the impacts could differ considerably across reef systems and species. OA will not only alter mean carbonate chemistry parameters across most environments but will also increase the variability in seawater pH and pCO<sub>2</sub> due to reduced seawater buffering capacity. The interplay between the various local (e.g., over-fishing, diseases, runoff, sedimentation) and global stressors (warming and OA), combined with complex biological, chemical, and physical processes on a reef creates large variability over space and time, challenging our ability to predict the fate of coral reefs in the future. Continuing to measure seawater chemistry conditions across a broad range of habitats and environmental conditions on spatial and

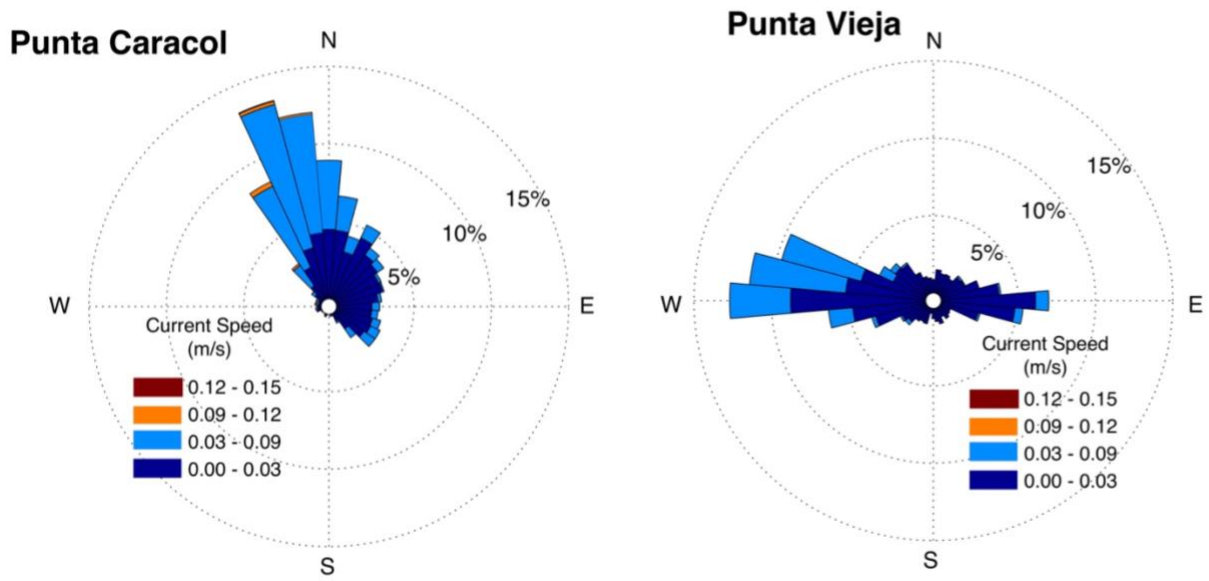
temporal scales is critical to further our progress in understanding natural variability. Moreover, spatiotemporal variability across an array of habitats can provide context for more ecologically relevant experimental conditions that incorporate natural ranges, and exposure times, and can help us understand the distribution of organisms.

## **Conclusion**

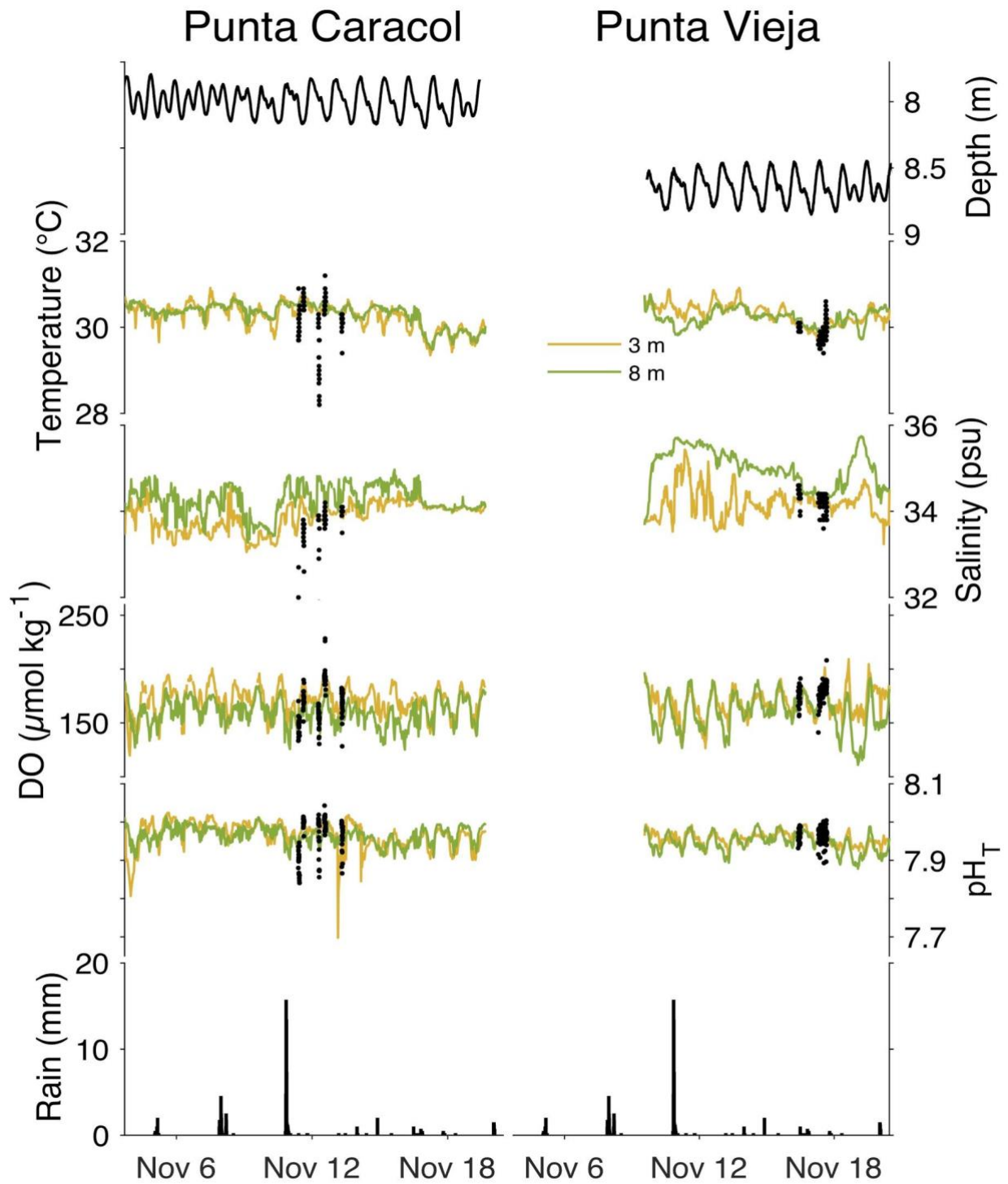
The seawater constituting the reefs in Bocas del Toro does not represent typical oligotrophic coral reef conditions; rather, the reefs are heavily influenced by a number of natural and anthropogenic stressors. In particular, heavy rainfall and terrigenous runoff exerted a large influence on the spatial variability in seawater chemistry and trophic status of the sites at the time of the study. Despite differences in the magnitude of surface variability between the sites, seawater conditions (mean and diel) below the surface were remarkably similar. Vector analysis of TA-DIC data revealed further similarities in their biogeochemical processes. Although comparisons between the sites, and to other reefs around the world, should consider the spatial scale in which the surface samples were collected. Overall, the results of this study highlight the various ways in which freshwater inputs can modify biogeochemical processes and seawater chemistry on a reef, and demonstrates how biogeochemistry within reefs with large freshwater inputs can be easily misinterpreted or misunderstood unless they are evaluated with the consideration of possible external inputs of TA and DIC to the system. In future research efforts, it is evident that characterization of the different end members as well as the contribution from inorganic nutrients and organic acids and bases to TA will be important steps to fully understand the dominant biogeochemical processes at the reefs in Bocas del Toro.



**Figure 1.** Map showing the location of the two reef sites in Bocas del Toro, Panama: Punta Caracol (A) and Punta Vieja (B).

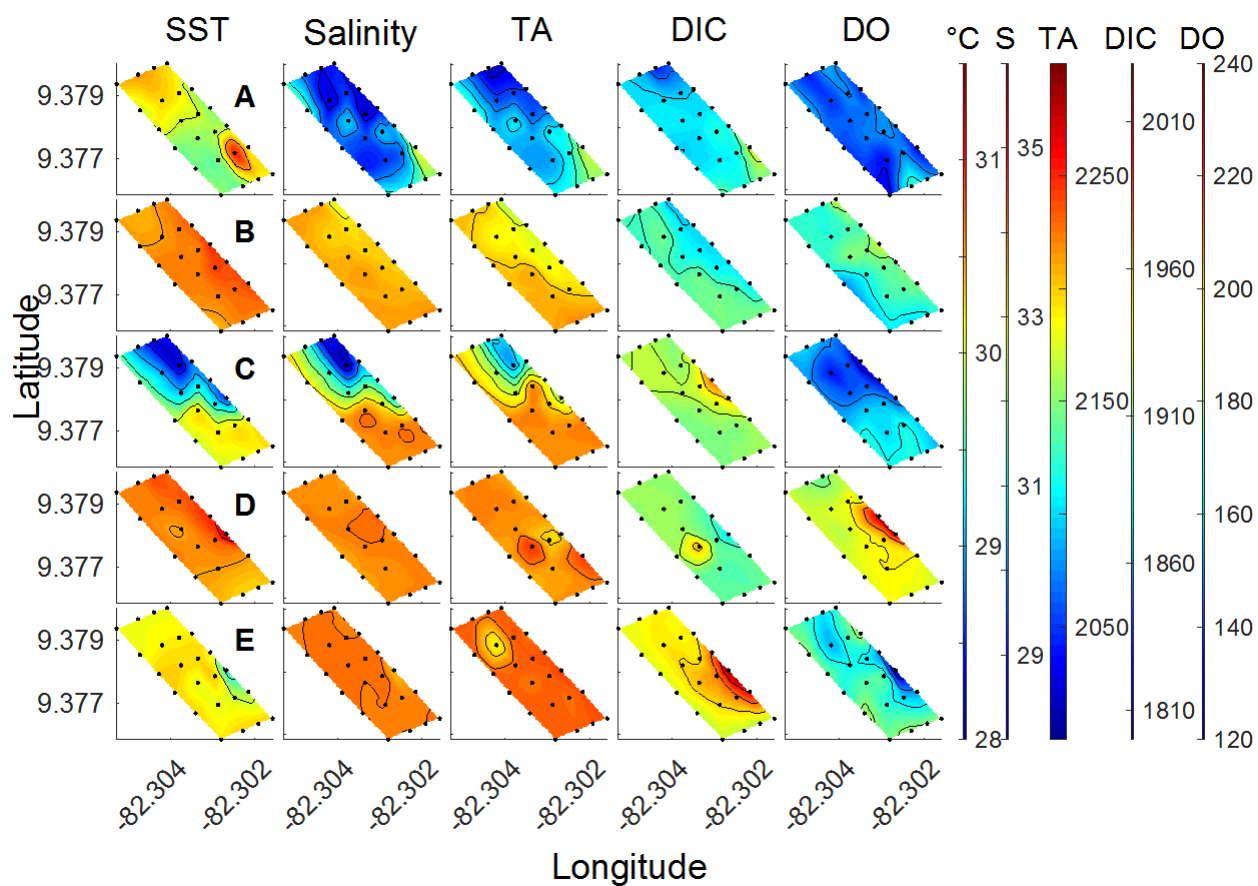


**Figure 2.** Current rose diagrams of Punta Caracol and Punta Vieja showing the direction in which the current is moving, and the ranges in speed. The ranges in current speed are represented by the different colors, and the dotted circles indicate the percentage of time during which the currents measured fell in each speed and direction bin.

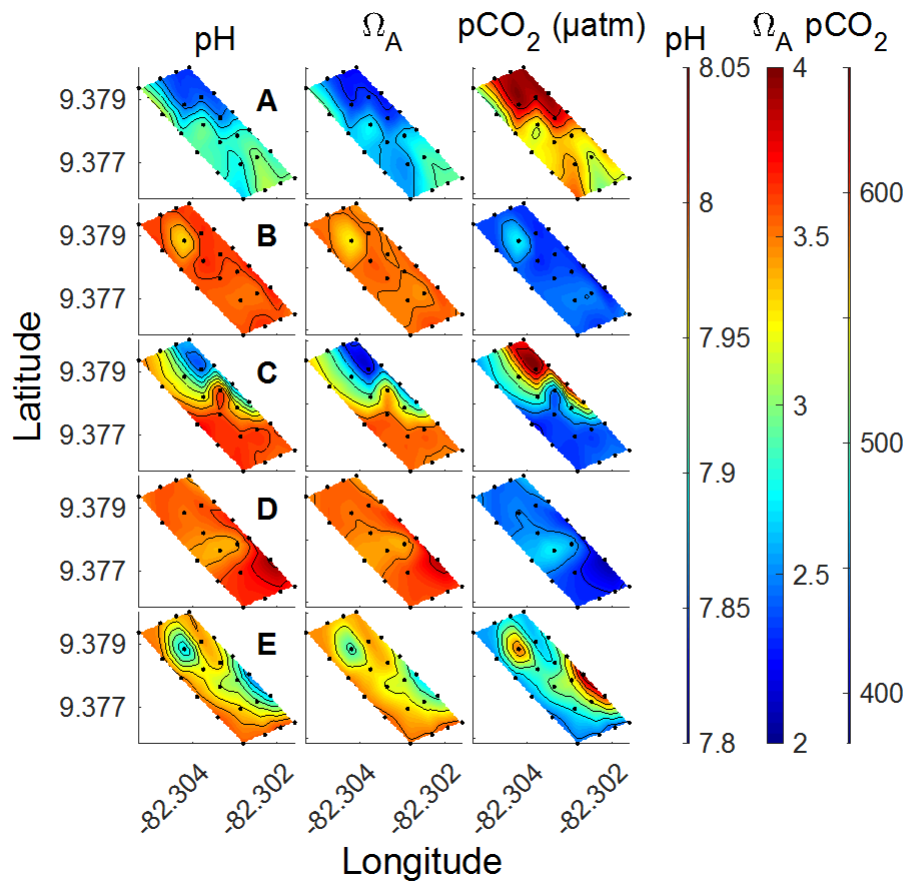


**Figure 3.** Time series profiles for each site showing tides, temperature, salinity, DO,  $\text{pH}_T$  and total rainfall measured at the four stationary autonomous sensors. The yellow line indicates the 3 m sampling depth and the green represents the 8 m sampling depth. Black dots are the surface samples from the spatial surveys.

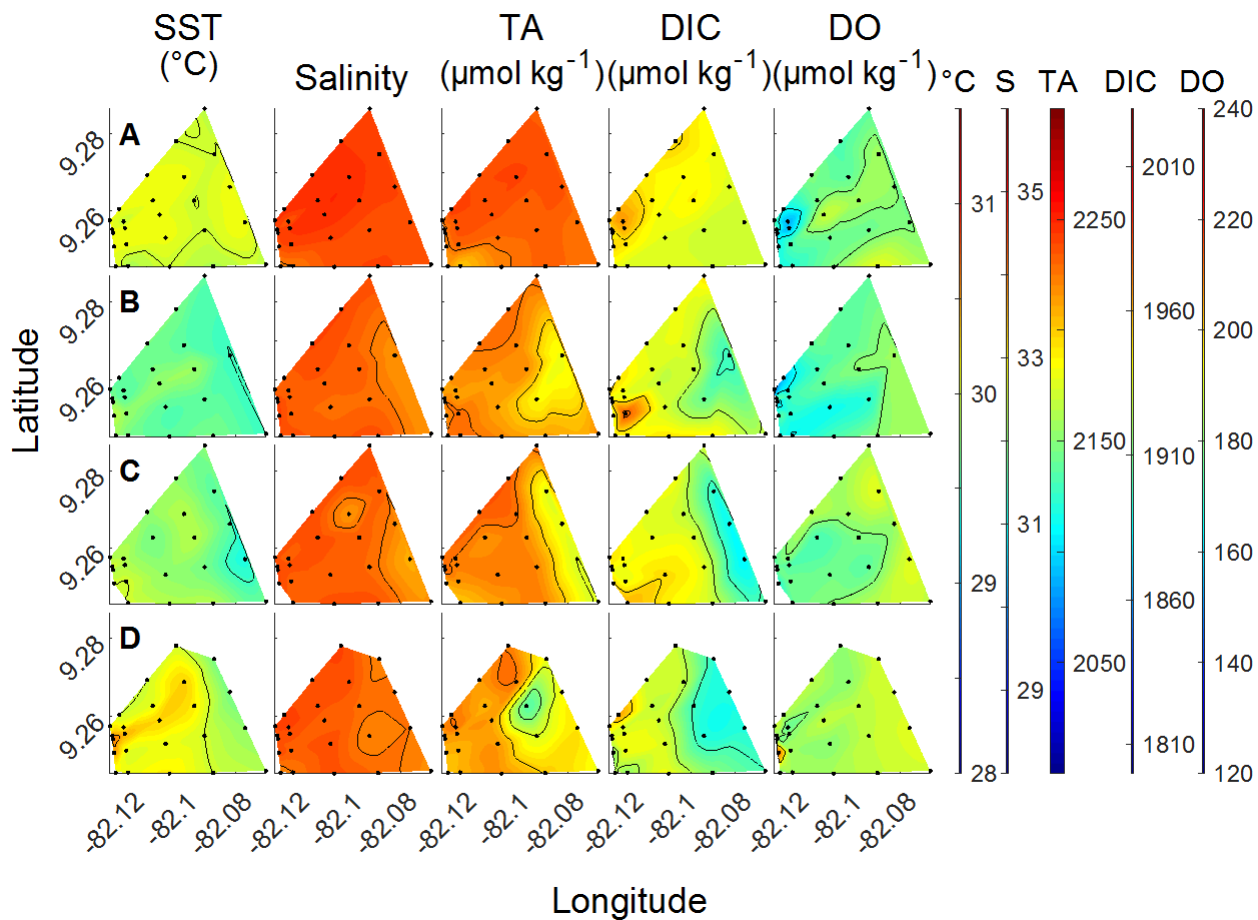




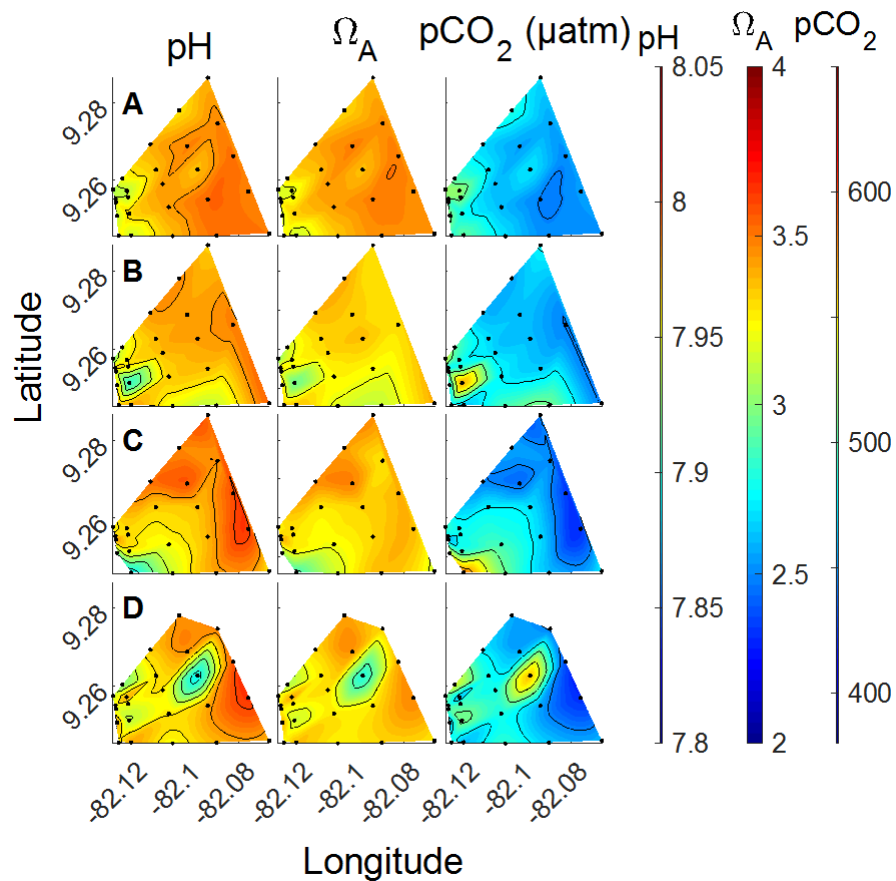
**Figure 4.** Spatial contour plots from gridded interpolations (cubic interpolations using Matlab griddata) of temperature, salinity, TA, DIC and DO across the spatial sampling stations over the course of the spatial surveys (A-E) at Punta Caracol. The black contour lines represent a change in each parameter unit as follows: 0.5 °C, 1 psu, 25  $\mu\text{mol kg}^{-1}$  for TA and DIC, and 15  $\mu\text{mol kg}^{-1}$  for DO. Survey times are as follows: (A) 9:30 AM 11 November 2015; (B) 2:30 PM 11 November 2015; (C) 6:45 AM 12 November 2015; (D) 1:00 PM 12 November 2015; (E) 7:20 AM 13 November 2015.



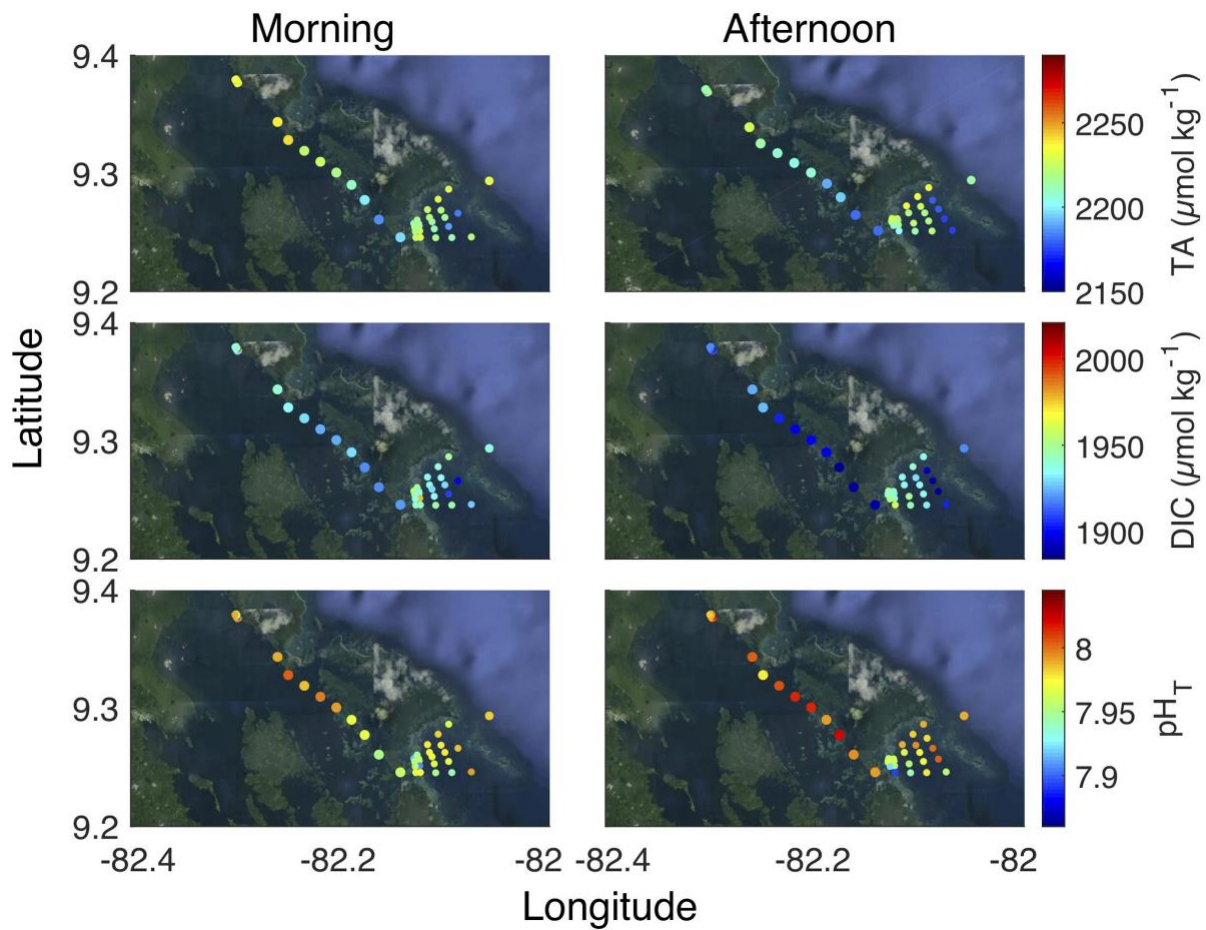
**Figure 5.** Continued spatial contour plots from gridded interpolations (cubic interpolations using Matlab griddata) of  $pH_T$ ,  $\Omega_a$ , and  $pCO_2$  across the spatial sampling stations at Punta Caracol over the course of all surveys (A-E). The black contour lines represent a change in each parameter as follows: 0.02, 0.3, and 30  $\mu\text{atm}$ , respectively. Survey times are as follows: (A) 9:30 AM 11 November 2015; (B) 2:30 PM 11 November 2015; (C) 6:45 AM 12 November 2015; (D) 1:00 PM 12 November 2015; (E) 7:20 AM 13 November 2015.



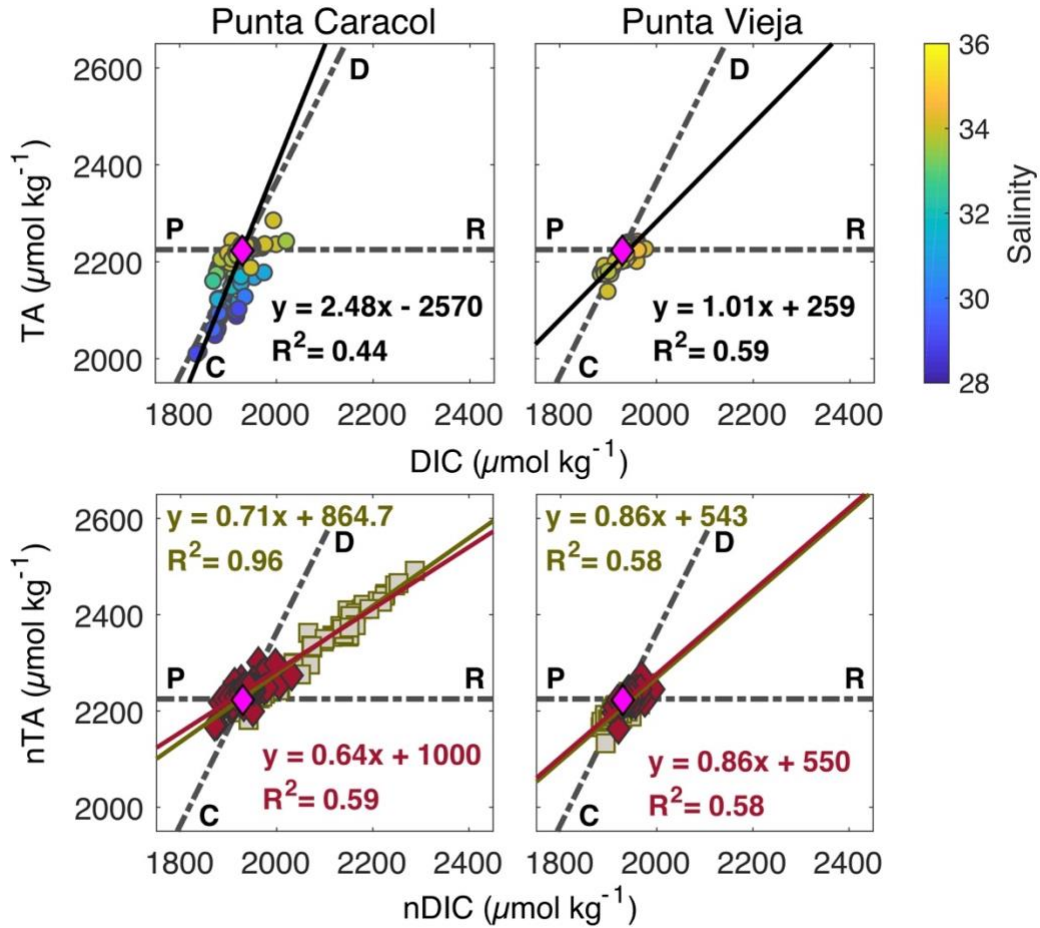
**Figure 6.** Spatial contour plots from gridded interpolations (cubic interpolations using MATLAB griddata) of temperature, salinity, TA, DIC and DO across the spatial sampling stations over the course of the spatial surveys (A-D) at Punta Vieja. The black contour lines represent a change in each parameter unit as follows: 0.5 °C, 1 psu, 25 μmol kg<sup>-1</sup> for TA and DIC, and 15 μmol kg<sup>-1</sup> for DO. Survey times are as follows: (A) 9:30 AM 16 November 2015; (B) 7:00 AM 17 November 2015; (C) 11:00 AM 17 November 2015; (D) 2:30 PM 17 November 2015.



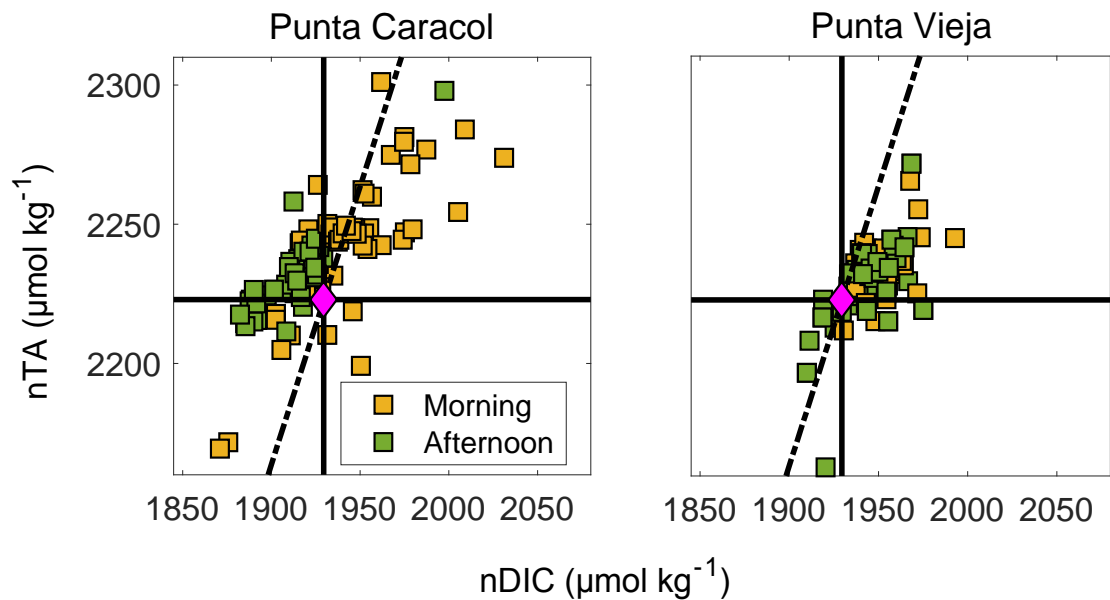
**Figure 7.** Continued spatial contour plots from gridded interpolations (cubic interpolations using MATLAB griddata) of  $pH_T$ ,  $\Omega_a$ , and  $pCO_2$  across the spatial sampling stations at Punta Vieja over the course of all surveys (A-D). The black contour lines represent a change in each parameter as follows: 0.02, 0.3, and 30  $\mu\text{atm}$ , respectively. Survey times are as follows: (A) 9:30 AM 16 November 2015; (B) 7:00 AM 17 November 2015; (C) 11:00 AM 17 November 2015; (D) 2:30 PM 17 November 2015.



**Figure 8.** Comparison of morning and afternoon concentrations of TA ( $\mu\text{mol kg}^{-1}$ ), DIC ( $\mu\text{mol kg}^{-1}$ ), and  $\text{pH}_T$  shown as a transitional continuum from Punta Caracol to Punta Vieja, including the offshore reference station.



**Figure 9.** Salinity normalized and non-salinity normalized TA-DIC diagrams using data collected from the spatial surveys. The pink diamond represents the offshore reference station average TA and DIC. Dashed lines show the organic (P/R; production/respiration) and inorganic (C/D; calcification/dissolution) metabolic pathways. Solid black lines in the upper plots show the best fit line from a type II major axis linear regression. The bottom two plots show salinity normalized TA-DIC relationships using two different endmembers. Green squares show the salinity normalized zero-endmember data, and the red diamonds show the salinity normalized non-zero endmember data.



**Figure 10.** Zoom of salinity normalized non-zero endmember TA-DIC data from Punta Caracol and Punta Vieja. Yellow squares represent data from morning surveys ( $n = 3$  at Punta Caracol and  $n = 2$  at Punta Vieja), and green squares represent data from afternoon surveys ( $n = 2$  at Punta Caracol and  $n = 2$  at Punta Vieja). The pink diamond reflects the offshore reference station average TA and DIC concentration, with the solid black lines extending the value to the edge of the plot. The dashed black line depicts the theoretical inorganic (calcification/dissolution) metabolic pathway.

**Table 1.** Summary table of the average ( $\pm$  SD) and average range ( $\pm$  SD) of measured biogeochemical parameters from the spatial and temporal studies at both sites. For the spatial surveys, range was calculated as the average range during each individual sampling survey (Punta Caracol, n = 5; Punta Vieja, n = 4), and for the temporal sampling regime range was calculated as the average diel range over a full 24 hr period (Punta Caracol, n = 17; Punta Vieja, n = 12).

		Punta Caracol		Punta Vieja			
		Spatial	Temporal	Spatial		Temporal	
			3m	8m		3m	8m
<b>Average</b>	Temperature ( $^{\circ}$ C)	30.2 $\pm$ 0.5	30.3 $\pm$ 0.2	30.3 $\pm$ 0.3	29.9 $\pm$ 0.2	30.3 $\pm$ 0.2	30.2 $\pm$ 0.2
	Salinity	32.8 $\pm$ 1.6	33.9 $\pm$ 0.3	34.3 $\pm$ 0.2	34.2 $\pm$ 0.1	34.2 $\pm$ 0.2	35.0 $\pm$ 0.4
	DO ( $\mu$ mol/kg)	166.8 $\pm$ 18.0	169.6 $\pm$ 5.9	160.0 $\pm$ 6.5	177.6 $\pm$ 6.2	169.1 $\pm$ 5.2	159.8 $\pm$ 8.8
	DIC ( $\mu$ mol/kg)	1914 $\pm$ 26	-----	-----	1934 $\pm$ 9	-----	-----
	TA ( $\mu$ mol/kg)	2185 $\pm$ 55	-----	-----	2216 $\pm$ 10	-----	-----
	pH(T)	7.96 $\pm$ 0.04	7.96 $\pm$ 0.03	7.97 $\pm$ 0.01	7.96 $\pm$ 0.00	7.96 $\pm$ 0.01	7.95 $\pm$ 0.02
	$\Omega_a$	3.22 $\pm$ 0.39	-----	-----	3.29 $\pm$ 0.04	-----	-----
	pCO <sub>2</sub> ( $\mu$ atm)	486.53 $\pm$ 56.85	-----	-----	479.79 $\pm$ 2.81	-----	-----
<b>Average Range</b>	Temperature ( $^{\circ}$ C)	1.1 $\pm$ 0.6	0.7 $\pm$ 0.2	0.4 $\pm$ 0.1	0.5 $\pm$ 0.3	0.5 $\pm$ 0.2	0.4 $\pm$ 0.2
	Salinity	2.4 $\pm$ 2.2	0.6 $\pm$ 0.3	0.8 $\pm$ 0.3	0.1 $\pm$ 0.1	0.9 $\pm$ 0.5	0.7 $\pm$ 0.4
	DO ( $\mu$ mol/kg)	44.0 $\pm$ 8.8	44.4 $\pm$ 11.2	38.3 $\pm$ 6.9	32.8 $\pm$ 8.1	44.3 $\pm$ 13.2	49.6 $\pm$ 14.7
	DIC ( $\mu$ mol/kg)	82 $\pm$ 25	-----	-----	64 $\pm$ 21	-----	-----
	TA ( $\mu$ mol/kg)	98 $\pm$ 45	-----	-----	58 $\pm$ 20	-----	-----
	pH(T)	0.11 $\pm$ 0.04	0.10 $\pm$ 0.07	0.07 $\pm$ 0.01	0.09 $\pm$ 0.02	0.05 $\pm$ 0.01	0.07 $\pm$ 0.02
	$\Omega_a$	0.77 $\pm$ 0.42	-----	-----	0.51 $\pm$ 0.13	-----	-----
	pCO <sub>2</sub> ( $\mu$ atm)	151.66 $\pm$ 69.79	-----	-----	121.19 $\pm$ 33.57	-----	-----



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