

Carbonate chemistry and coral reefs in the Pacific coast of Costa Rica

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To the memory of Dieter.... a beloved friend

"Spread your wings and fly away, fly away, far away"

- Queen

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ABSTRACT

Coral reefs are important tropical ecosystems holding about 25% of the world marine biodiversity. Their tridimensional biogenic structures are built of calcium carbonate and they are threatened by global warming and ocean acidification. Current projections on the future development of coral reefs suffer among others from the scarcity of local observations, especially along the Costa Rican coast in the Eastern Tropical Pacific (ETP).

The aim of this thesis was to investigate the carbonate chemistry in coastal waters and their effect on the reef development along this coast. It reveals a strong gradient from reefs influenced by upwelling in the north towards reefs affected by river discharges in the south. Due to this gradient we selected three study sites: Santa Elena in the north, Marino Ballena in the south and Matapalo between these two sites. Parameters required to determine the carbonate system (pH, $p\text{CO}_2$, TA and DIC) including temperature, salinity and nutrients were measured during the dry and rainy season. Furthermore, the benthic composition was quantified by reef surveys and in situ studies were carried out to identify the effect of local environmental variables on reef organisms.

Our results evidenced that coastal upwelling and metabolic reactions (photosynthesis and respiration) are the main drivers in the north (Santa Elena), whereas calcification and carbonate dissolution in addition to river discharges exert a strong control on the carbonate chemistry in the south (Marino Ballena). The dominant coral species in the south (*Porites lobata* and *Pavona clavus*) cope with enhanced suspended matter concentrations, a low salinity, and a low aragonite saturation state (Ω_a). Reef-builders in the north (*Pavona gigantea*, *Pavona clavus* and *Pocillopora* sp.) are also tolerant to low Ω_a but are adapted to low sea water temperatures and eutrophic conditions. However, enhanced nutrient inputs into reefs enhance productivity, which in turn favors the growth of larger and more effective benthic bioeroders. In addition to strong currents, this enhances erosion and explains the low reef accretion rates in the ETP compared to the Western Tropical Pacific. The progressing ocean acidification, changes in the strength of upwelling and enhanced inputs from land threaten the sensible balance between reef accretion and erosion along the Costa Rican coast. In the future these processes and their combined impact on reefs need to be monitored and studied in more detail, in order to find ways to better protect these coral reefs.

ZUSAMMENFASSUNG

Korallenriffe sind wichtige tropische Ökosysteme, die ca. 25% aller bekannten und im Ozean vorkommenden Arten beherbergen. Sie bilden dreidimensionale biogene Strukturen, die im wesentlichen aus Kalziumkarbonat bestehen. Die globale Erwärmung und die Versauerung der Ozeane bedrohen das Wachstum der Korallen und somit auch den Bestand der Riffe. Direkte Beobachtungen, die die Reaktionen von Riffen auf globale Veränderungen beschreiben, sind jedoch bisher selten und fehlen zur Validierung von Modellen, die die zukünftige Entwicklung von Korallenriffen vorhersagen.

Das Ziel dieser Arbeit war es, die Karbonatchemie in Küstengewässern und deren Auswirkungen auf die Riffentwicklung entlang der Küste Costa Ricas zu untersuchen. Die Riffe entlang der costa-ricanischen Küsten sind zeitlich und räumlich variierenden Einflüssen ausgesetzt. Im Norden dominiert der saisonale Auftrieb von nährstoffreichem und korrosivem Tiefenwasser während im Süden die Einträge von Flüssen die Riffentwicklung nachhaltig beeinflussen. Um das Spektrum variierender Einflussgrößen zu erfassen, wurden drei Untersuchungsgebiete ausgewählt: Santa Elena im Norden, Marino Ballena im Süden und Matapalo zwischen diesen beiden Gebieten. Die zur Bestimmung des Karbonatsystems (pH, pCO₂, TA und DIC) erforderlichen Parameter, einschließlich Temperatur, Salzgehalt und Nährstoffkonzentrationen, wurden während der Trocken- und Regenzeit gemessen. Darüber hinaus wurde die Artenzusammensetzung der Riffe ermittelt und weitere Studien vor Ort durchgeführt, um den Einfluss lokaler Umweltgrößen auf individuelle Rifforganismen zu identifizieren.

Es konnte gezeigt werden, dass die Karbonatchemie im Norden (Santa Elena) im wesentlichen durch den Auftrieb sowie die Photosynthese und Respiration beeinflusst wird, während im Süden (Marino Ballena) die Bildung und Lösung von Kalk zusätzlich zu den Flusseinträgen eine starke Kontrolle über die Karbonatchemie und die Riffzusammensetzung ausüben. Die im Süden vorherrschenden Korallenarten (*Porites lobata* und *Pavona clavus*) kommen mit erhöhten Schwebstoffkonzentrationen, einem niedrigen Salzgehalt und einer geringeren Aragonitsättigung (Ω_a) zurecht. Riffbildende Korallen im Norden (*Pavona gigantea*, *Pavona clavus* und *Pocillopora* sp.) weisen ebenfalls eine Toleranz gegenüber einer niedrigen Ω_a auf, sind aber an niedrige Wassertemperaturen und nährstoffreichere Bedingungen angepasst. Nährstoffeinträge in Riffe begünstigen das Algenwachstum, was wiederum das Wachstum größerer und effektiverer Bioerodierer begünstigt und somit die Erosion erhöht. Dies spiegelt sich auch in Riffbildung wieder, die im westlichen tropischen Pazifik deutlich ausgeprägter ist, als im östlichen tropischen Pazifik, in dem Auftrieb ein weitverbreitetes Phänomen ist.

Die fortschreitende Versauerung der Ozeane, Veränderungen in der Stärke des Auftriebs und erhöhte Einträge vom Land gefährden das empfindliche Gleichgewicht

zwischen Riffbildung und Erosion entlang der costa-ricanischen Küste. In Zukunft müssen diese Prozesse und ihre kombinierten Auswirkungen auf Riffe genauer überwacht und untersucht werden, um Wege zu finden, diese Korallenriffe besser zu schützen.

LIST OF PUBLICATIONS**First authored:**

Sánchez-Noguera C, Stuhldreier I, Jiménez C, Cortés J, Morales A, Wild C, Rixen T (2018) Natural ocean acidification at Papagayo upwelling system (north Pacific Costa Rica): implications for reef development. *Biogeosciences* 15: 2349-2360, doi.org/10.5194/bg-15-2349-2018

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Stuhldreier I, Sánchez-Noguera C, Roth F, Jiménez C, Rixen T, Cortés J, Wild C (2015) Dynamics in benthic community composition and influencing factors in an upwelling-exposed coral reef on the Pacific coast of Costa Rica. *PeerJ* 3:e1434, doi 10.7717/peerj.1434

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1. SCIENTIFIC BACKGROUND

1.1 Carbonate chemistry and coral reefs

The ocean carbonate chemistry is a complex system that comprises equilibrium reactions controlling the concentrations of the dissolved inorganic carbon species in seawater (CO_2 , H_2CO_3 , HCO_3^- and CO_3^{2-}) (Kleypas et al., 2006). Biological processes such as photosynthesis, respiration, precipitation and dissolution of carbonates influence the carbonate system (Fig. 1.1) (Smith and Key, 1975; Zeebe, 2012).

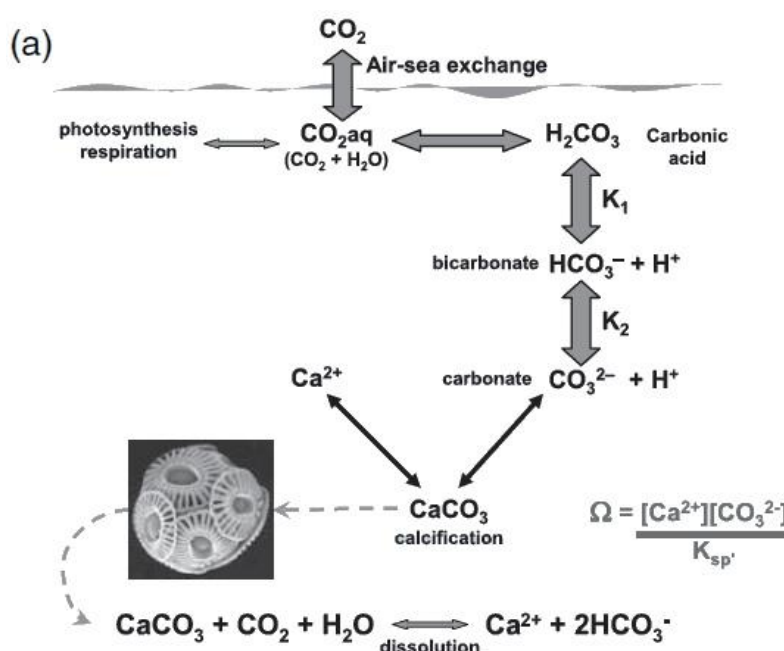


Figure 1.1 Simplified diagram of the carbonate system in the ocean. Taken from Kleypas et al. (2006).

The concentration of total dissolved inorganic carbon (DIC) and total alkalinity (TA) can be used to describe the carbonate system and to calculate pH, CO_2 concentration as well as the saturation state of the carbonate minerals calcite (Ω_c) and aragonite (Ω_a) (Fig. 1.2). DIC is defined as the molar sum of the dissolved inorganic carbon species, whilst TA is related to the charge balance in seawater. It can be defined as the concentration of bases able to accept H^+ when performing a titration with 0.1 N HCl to the carbonic acid endpoint (Zeebe and Wolf-Gladrow, 2001). CO_2 invasion, respiration of organic matter and carbonate dissolution are the main processes increasing DIC concentration in seawater; while vice versa CO_2 emission, photosynthesis and the precipitation of carbonate decreases DIC concentrations. In contrast to DIC, CO_2 fluxes across the air sea interface do not affect the TA and the influence of photosynthesis and respiration on the TA is much weaker as those of carbonate precipitation and dissolution.

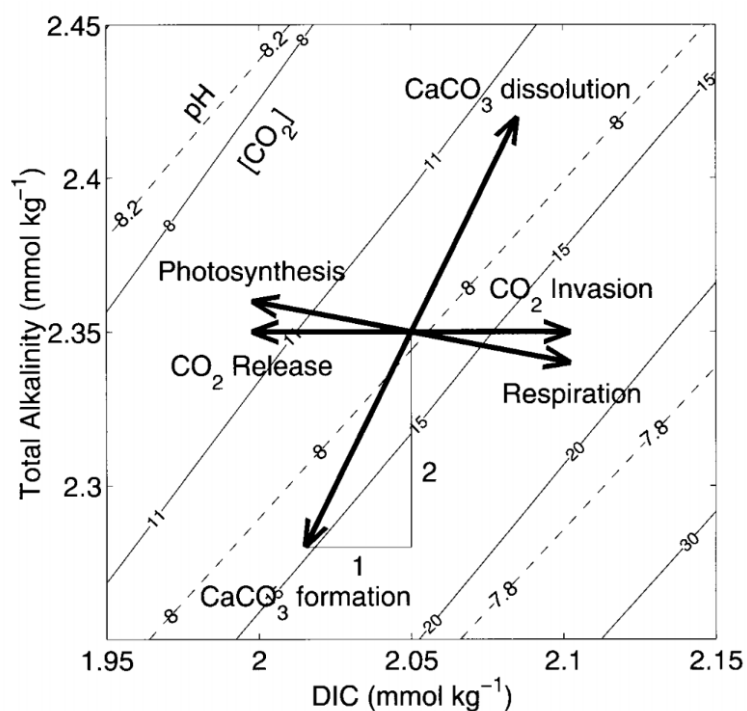
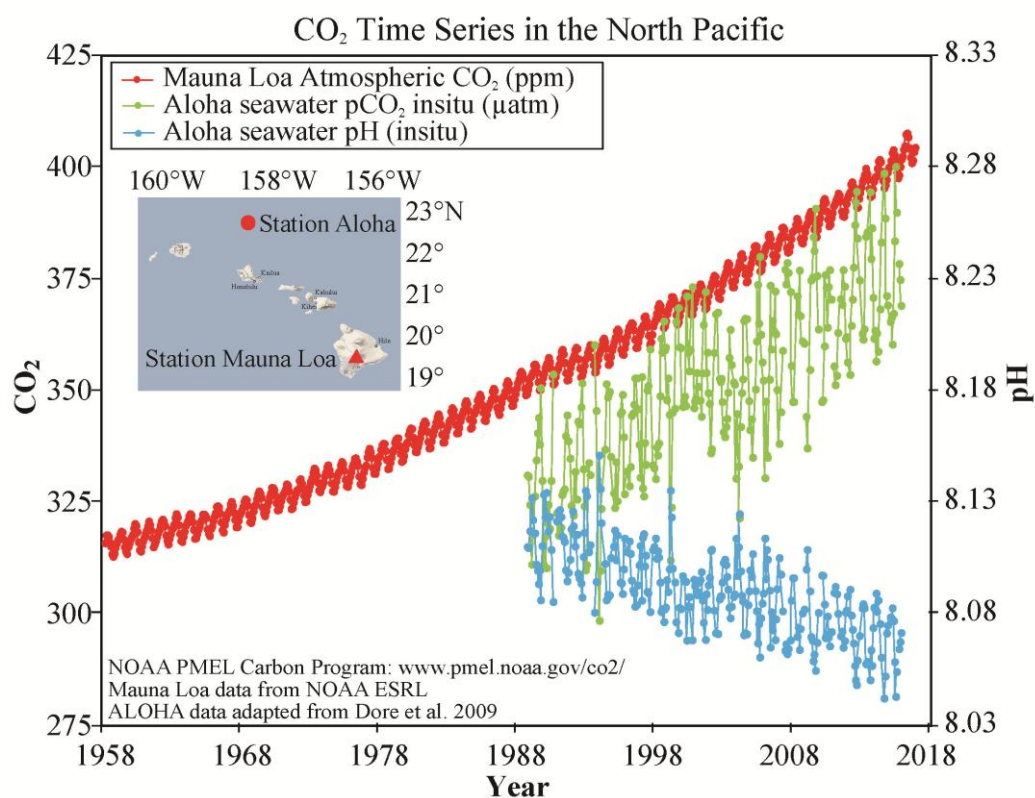


Figure 1.2. Processes influencing Total alkalinity and Dissolved Inorganic Carbon in seawater. Taken from Zeebe & Wolf-Gladrow (2001).

Since coral reefs are among the most productive ecosystems in the world and main sites of calcification they influence the carbonate system in the ocean, but are also very sensitive to changes of the carbonate system caused by human induced emissions of CO_2 into the atmosphere and global warming. Historical records of seawater pH and atmospheric CO_2 over the last 60 years leave no doubts on a progressing human induced ocean acidification (Fig. 1.3) (Kleypas et al., 2006).

A large number of studies have shown a close link between coral calcification, seawater pH and Ω_a (Cyronak et al., 2016; Gattuso et al., 1998; Langdon, 2002; Schneider and Erez, 2006). Based on the current reef distribution and prevailing environmental conditions in reefs it is stated that formation of reef structures is precluded when e.g. the annual mean Ω_a falls below 2.82 (Guan et al., 2015; Kleypas et al., 1999b). Nevertheless, photosynthesis and respiration as well as carbonate precipitation and dissolution often cause a pronounced daily cycle and on this time scale such long-term thresholds values are often passed over (Albright et al., 2013; Kleypas et al., 2011; Kline et al., 2015). It is assumed that buffering mechanisms operate in benthic reef communities and prevent such overshoots on the long-term run. Whether these processes offer a protection of reefs against ocean acidification is an open question (Anthony et al., 2011a). In order to find answers to this question more local studies are required to improve the knowledge about the buffer capacity of reefs against global changes.



Data: Mauna Loa (ftp://afjp.cmdl.noaa.gov/products/trends/co2/co2_mm_mlo.txt) ALOHA (http://hahana.soest.hawaii.edu/hot/products/HOT_surface_CO2.txt)
 Ref: J.E. Dore et al, 2009. Physical and biogeochemical modulation of ocean acidification in the central North Pacific. *Proc Natl Acad Sci USA* **106**:12235-12240.

Figure 1.3. Impact of the increasing atmospheric CO₂ on the ocean pH, based on time series from the North Pacific (Hawaii). Atmospheric CO₂ time series is shown in red, partial pressure of CO₂ in seawater in green and seawater pH in blue. Taken from the NOAA PMEL Carbon Program.

1.2 Coral reefs from the Eastern Tropical Pacific: the case of Costa Rica

The Eastern Tropical Pacific (ETP) has been described as a region lacking well-developed coral reefs (Dana, 1975) due to the environmental restrictive conditions, the high frequency and intensity of disturbances, the intense bioerosion and slow recovery rates that preclude their development (Cortés, 1997; Manzello, 2010a; Manzello et al., 2008). However, paleogeological records and field work revealed not only the persistence of reefs at the edge of non-suitable conditions for reef accretion, but also surprisingly fast accretion rates of reefs in the ETP (Glynn, 1977; Glynn et al., 1983; Jiménez and Cortés, 2003b; Toth et al., 2012, 2015). A recent overview suggests that coral ecosystems from the ETP are highly resilient, despite being exposed to a large combination of natural and anthropogenic disturbances at the local and global scale (Glynn et al., 2017a). In the ETP the most extensive coral ecosystems are located in Costa Rica, Panamá, Colombia and around oceanic islands such as Isla del Coco (Cortés, 1997, 2003; Glynn et al., 2017a; Glynn and Ault, 2000; Toth et al., 2017). ETP coral reefs are characterized by their small size, simple structure, discontinuous distribution and low diversity. Usually they are built up by few coral species including branching

(*Pocillopora* sp.) or massive corals (*Porites lobata*, *Pavona clavus* and *Pavona gigantea*) (Alvarado et al., 2006, 2010, 2011; Cortés, 1990, 1996, 1997, 2003; Cortés et al., 1994).

In Costa Rica coral reef research started about 50 years ago, and currently there is a vast number of publications covering a wide range of topics such as reef structure and species composition (Alvarado et al., 2005; Cortés, 1990, 1996; Cortés and Murillo, 1985; Guzmán and Cortés, 1989b, 1989a; Jiménez, 2001a), growth history and bioerosion processes (Cortés et al., 1994; Fonseca and Cortés, 1998), reproduction (Bezy, 2009; Glynn et al., 1991, 1994, 1996, 2011), coral reef diseases (Gateño et al., 2003), biodiversity (Cortés, 2009; Cortés and Guzmán, 1998; Dominici-Arosemena et al., 2005), symbionts (Sunagawa et al., 2008) and the impact of disturbances over coral reefs (Fernández-García et al., 2012; Fernández and Cortés, 2005; Guzmán et al., 1990; Guzmán and Cortés, 1992, 2001; Sánchez-Noguera et al., 2018a). A general overview on the distribution pattern of coral reefs along the Pacific coast in the country suggests that the influence of coastal currents and therefore coastal topography are key aspects in the development of consolidated carbonate structures (Cortés et al., 2010). Coral communities and isolated coral colonies are widely distributed along this coast, but real coral reef formations are restricted to the northernmost and southernmost areas where sheltered locations are abundant (Fig. 1.4) (Alvarado et al., 2006; Cortés and Guzmán, 1998; Cortés and Jiménez, 2003; Cortés and Murillo, 1985; Jiménez, 2001a).

Both, branching and massive species, built reefs along this coast; however, the main reef-building corals vary between locations. In northern locations (Santa Elena, Islas Murciélago, Bahía Culebra and Matapalo) coral reefs are built by *Pocillopora* sp., *P. gigantea* and *P. clavus*, whereas in southernmost sections (Marino Ballena, Isla del Caño and Golfo Dulce) of the same coast the carbonate structures are mainly produced by *P. lobata*, *P. clavus* and *Pocillopora* (Cortés, 1996; Cortés et al., 2010). A particular condition of northern reefs is that they are exposed to extreme local environmental changes on a yearly basis, when the coastal upwelling of Papagayo develops over the dry season (Jiménez et al., 2010; Jiménez and Cortés, 2003b).

In terms of coral reefs, the most outstanding areas from the northern section of this coast are Santa Elena, Bahía Culebra and Matapalo. Bahía Culebra is one of the best-studied locations and holds a high coral biodiversity, with 16 scleractinian species reported (Jiménez, 2001a). In Matapalo, located 12 km south from Bahía Culebra, branching corals built a carbonate structure with a length of almost 1.7 km (Jiménez, 2007). About >250 km south of Matapalo is Marino Ballena National Park, an area with abundant presence of coral communities and corals reefs built by *P. lobata* and *P. clavus* (Alvarado et al., 2005). In the southern section of this coast reefs are best developed around the Isla del Caño and in the Golfo Dulce (Alvarado et al., 2006; Cortés, 1990; Cortés et al., 1994, 2009), however reefs at these sites were not included in this thesis due to logistic constraints. Costa Rican coral reefs are strongly influenced by climate anomalies such as El Niño Southern Oscillation – ENSO (Guzmán et al., 1987; Jiménez and Cortés, 2001), and suffer from harmful algal blooms (HAB) (Guzmán et al.,

1990; Vargas-Montero et al., 2008) and invasive species (e.g. *Caulerpa sertularioides*) (Fernández and Cortés, 2005).

The persistence of coral reefs around the world relies on a steady balance between accretion and erosion processes (Glynn, 1997). Compared to Western Tropical Pacific low reef accretion in the Eastern Tropical Pacific indicates the sensibility of this system in the ETP. Multiple global and local stressors threaten it (Alvarado et al., 2012; Manzello et al., 2008, 2017) but combined effects of these stressors and threshold values are still largely unknown. A research focused on the carbonate chemistry of this area will contribute to understand the current threshold of these coral reefs. This kind of information will help to refine the models predicting the future impacts of climate change, particularly ocean acidification, on coral reefs from the ETP.

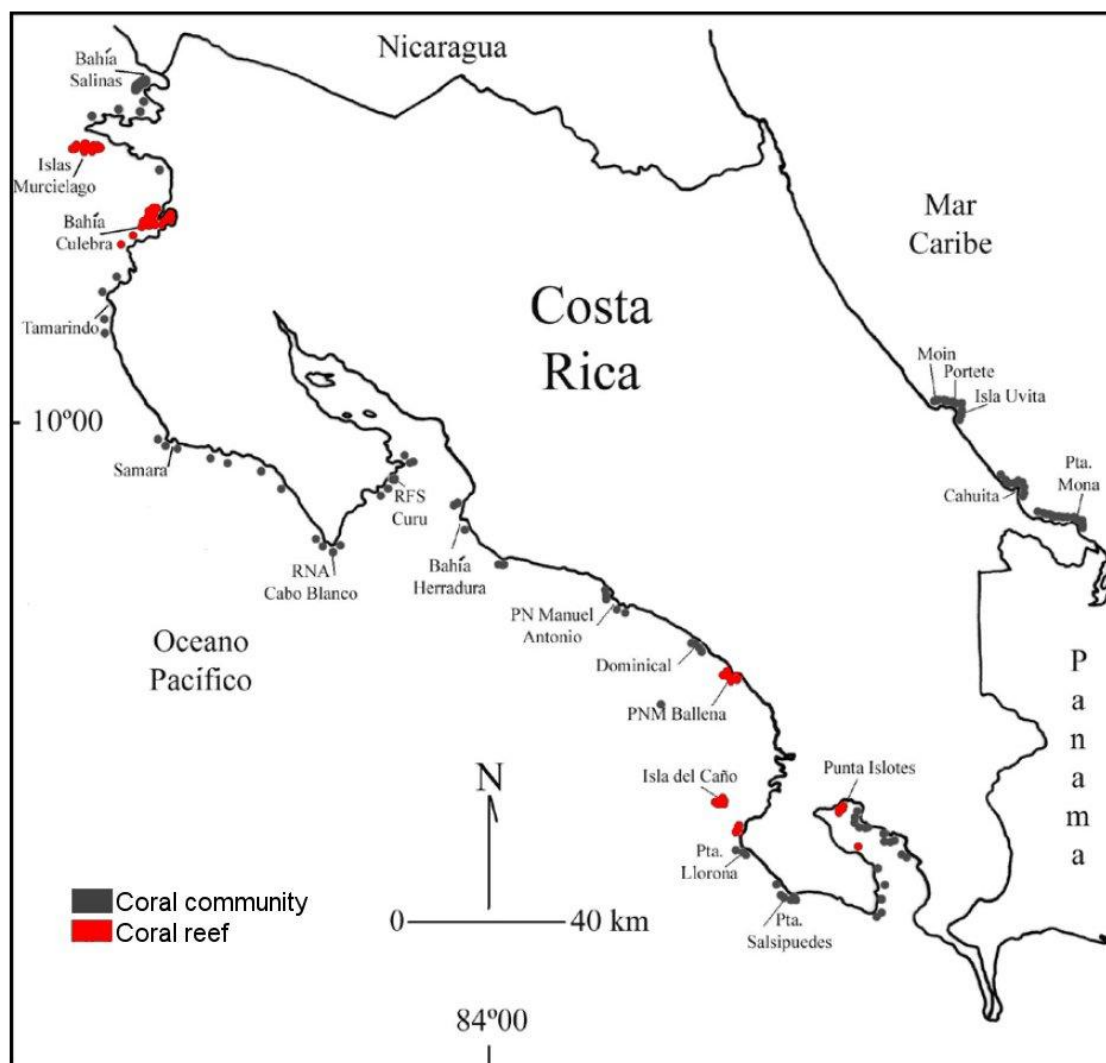


Figure 1.4. Coral ecosystems distribution along the Pacific coast of Costa Rica. Modified from Alvarado et al. (2006).

1.3 Papagayo Upwelling System: a study location for ocean acidification scenarios

The ETP is influenced by seasonal coastal upwelling systems, resulting from the interaction between ocean currents and the prevailing trade winds (Lavín et al., 2006). From December to April, the easterly winds promoted by boreal winter cold fronts pass through the central American mountain gaps and raise the thermocline depth in the Pacific coast (Amador et al., 2006). As a result, three small-scale coastal upwelling systems develop: the 1) upwelling off Tehuantepec in México, 2) the Papagayo upwelling system which is centered at the border between Nicaragua and Costa Rica and 3) the Panamá upwelling in the Gulf of Panamá (Brenes et al., 1990; Fiedler and Talley, 2006; Vargas, 2002). Associated with the development of these upwelling systems are pronounced changes in the ocean current regime, the chemical and physical properties of ocean waters as well as the composition and functioning of pelagic and benthic ecosystems (Alfaro et al., 2012; Manzello, 2010b; Manzello et al., 2008; Norzagaray-López et al., 2017; Rixen et al., 2012). During the development of the Papagayo upwelling system seawater temperatures decrease by up to 9°C and can drop down to values of < 14.0°C (Alfaro and Cortés, 2012; Jiménez, 2001c). This drastic decrease in seawater temperature is accompanied by increases in nutrient concentrations (Fernández-García et al., 2012) and pCO₂ whereas dissolved oxygen concentrations and Ω_a dropped down to values of 144 $\mu\text{mol l}^{-1}$ and 2.1 (Rixen et al., 2012).

Despite these extreme conditions corals in the Gulf of Papagayo are known for their high growth rates as mentioned before (Jiménez and Cortés, 2003b). This suggests that there must be a trade-off mechanism, which highlights this location as a perfect site for studying the potential sensitivities of reefs to ocean acidification. It has even been stated that reefs in the ETP represent a real-world example of coral reef development under extreme conditions, which could be an analog for future reefs in a high CO₂ world (Manzello et al., 2017). However, the natural laboratory is threatened. A recent evaluation of the benthic ecosystems in the Gulf of Papagayo revealed a significant deterioration of coral reefs (Alvarado et al., 2018; Sánchez-Noguera et al., 2018a). Similarly, as in other ETP locations there could be several factors affecting reef development and resilience within the region, including thermal stress, bioerosion and poor recruitment (Bezy, 2009; Glynn, 1994; Manzello et al., 2008). However, apart from one three-day study on the carbonate system by Rixen et al. (2012) there are no information about the impact of high-CO₂ and low- Ω_a waters on the reef development along the Costa Rican coast.

2. OBJECTIVES

Coral reefs are among the most remarkable engineers in tropical ecosystems and also provide several goods and services to humanity (Moberg and Folke, 1999; Spurgeon, 1992). They protect coasts against storms, tsunamis and coastal erosion, act as nurseries ground for commercially important species and as magnet for tourists. Unfortunately, they are also recognized as highly vulnerable to local stressors such as siltation and overexploitation and the impacts of climate change (IPCC, 2018).

The majority of projections on the response of the ocean to ocean acidification are based on measurements undertaken in the open ocean. Data from coastal regions are scarce. Only recently the number of studies on the carbonate chemistry is increasing to fill knowledge gaps on processes controlling the variability of pH and $p\text{CO}_2$ in coastal areas (Carstensen and Duarte, 2019; Gray et al., 2012; Norzagaray-López et al., 2017; Vargas et al., 2016). This includes also papers published as part of this thesis (Sánchez-Noguera et al., 2018b; Stuhldreier et al., 2015b; Wizemann et al., 2018). The overall goal of this thesis is to characterize the carbonate chemistry and its influence on reef development along the Costa Rican coast in the ETP. The following specific objectives were proposed, in order to achieve the overarching goal:

1. to determine the local variability of the carbonate chemistry along the Pacific coast of Costa Rica,
2. to identify the driving factors of the previously reported differences in coral reef composition, and
3. to identify bioerosion patterns in a marginal reef and quantify the role of carbonate chemistry as factor causing bioerosion.

3. APPROACH AND OUTLINE OF PUBLICATIONS

The present study was carried out in the framework of the COSTACID project (Costa Rican Coral Reefs Under Natural Acidification). This project was funded by the Leibniz Association and developed in close collaboration between the Leibniz Centre for Tropical Marine Research (ZMT, Bremen, Germany) and the Centro de Investigación en Ciencias del Mar y Limología (CIMAR, San José, Costa Rica) from Universidad de Costa Rica. Fieldwork was carried out in three locations in the Pacific coast of Costa Rica from March 2013 to May 2014 covering the dry and rainy seasons and the corresponding upwelling and non-upwelling season, respectively. It included the deployment of Submersible Autonomous Moored Instruments (SAMI-pH and SAMI-CO₂) and sampling of discrete samples on regular intervals. The study locations were chosen based on two main features: 1) presence of coral reefs and 2) the degree to which upwelling influenced the study. In addition to the determination of pH, $p\text{CO}_2$, TA, DIC, temperature, salinity and nutrient concentrations reef surveys were conducted to quantify the benthic composition and an in situ growth experiment was performed.

Outline of manuscripts

The key aspects and findings of this thesis are discussed in three chapters outlined as scientific manuscripts. The first and third one (Sections 4 and 6) are already published, while the second one is under revision by coauthors. Five additional publications resulting from the COSTACID project are also included in the general discussion of this thesis, as they are key complement of the core chapters. Altogether, the three core manuscripts of the thesis and the additional publications provide an integral overview to understand the impacts of the local variability of the carbonate chemistry on Costa Rican coral reefs.

For the first publication of this thesis (Section 4) in situ measurements of pH and $p\text{CO}_2$ were used, in order to characterize the carbonate chemistry at the Papagayo upwelling system (Sánchez-Noguera et al., 2018b). The data was collected with SAMI-pH and SAMI-CO₂ sensors (www.sunburstensors.com) during two non-upwelling seasons (2012 and 2013) and analyzed in combination with data from a previous three-day study (Rixen et al., 2012). Originally, it was planned to deploy the sensors for an entire year but bio-fouling thwarted the plans and forced us to return the sensors to Sunburst for maintenance (Fig. 3.1).

For the second study (Section 5), we collected discrete water samples in three different locations (Santa Elena, Matapalo and Marino Ballena), over an eight-day period during dry and rainy season. Additionally, we also carried out coral reef surveys in each location, to quantify benthic coverage and species composition. The goal of this study was to describe the spatial and temporal variability of the carbonate chemistry and other parameters (temperature, salinity and inorganic nutrients) and

their influence on the reef development along the Pacific coast of Costa Rica. Finally, in the third study (Section 6) we investigated the influence of upwelling on bioerosion and the carbonate budget in a marginal reef (Matapalo). For this study, carbonate bodies comprised by skeletal coral substrates were deployed in Matapalo reef for four months, over the upwelling season 2013-2014. The carbonate bodies were recovered every month, the settlement succession of calcifying organisms was documented by photographs and erosion rates calculated from weight loss. Macro and microbioerosion were determined through Micro Computerized Tomography (μ CT) scans and Scanning Electron Microscopy (SEM) of cast-embeddings.



Figure 3.1. Bio-fouling on SAMI sensors deployed during non-upwelling season.

Manuscript I

Natural ocean acidification at Papagayo upwelling system (north Pacific Costa Rica): implications for reef development

Celeste Sánchez-Noguera, Ines Stuhldreier, Jorge Cortés, Carlos Jiménez, Álvaro Morales, Christian Wild, Tim Rixen

Contributions: Celeste Sánchez-Noguera and Tim Rixen designed the study, analyzed the data, prepared figures and /or tables and wrote the paper. Celeste Sánchez-Noguera collected and analyzed samples. Ines Stuhldreier, Jorge Cortés, Carlos Jiménez, Álvaro Morales and Christian Wild reviewed the paper.

Current status: published in Biogeosciences 15: 2349-2360 (2018).

Manuscript II

Carbonate chemistry gradient along the Pacific coast of Costa Rica influences reef development

Celeste Sánchez-Noguera, Ines Stuhldreier, Jorge Cortés, Carlos Jiménez, Christian Wild, Tim Rixen

Contributions: Study was designed by Celeste Sánchez-Noguera and Tim Rixen. Fieldwork was carried out by Celeste Sánchez-Noguera and Ines Stuhldreier. Celeste Sánchez-Noguera performed laboratory measurements and data analysis. Manuscript was written by Celeste Sánchez-Noguera with advice from coauthors.

Current status: to be submitted.

Manuscript III

Rapid bioerosion in a tropical upwelling coral reef

André Wizemann, Sri D. Nandini, Ines Stuhldreier, Celeste Sánchez-Noguera, Max Wisshak, Hildegard Westphal, Tim Rixen, Christian Wild, Claire E. Raymond

Contributions: Study was designed by Ines Stuhldreier, Celeste Sánchez-Noguera, Hildegard Westphal, Tim Rixen, Christian Wild, Claire Raymond. Investigation was performed by André Wizemann, Sri D. Nandini, Ines Stuhldreier, Celeste Sánchez-Noguera, Max Wisshak and Claire E. Raymond. Data curation and formal analysis were carried out by André Wizemann, Sri D. Nandini, Ines Stuhldreier, Celeste Sánchez-Noguera, Max Wisshak, Tim Rixen and Claire E. Raymond. The original draft was written by André Wizemann; in the review and edition participated Sri D. Nandini, Ines Stuhldreier, Max Wisshak, Hildegard Westphal, Tim Rixen, Christian Wild, Claire E. Raymond.

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4. NATURAL OCEAN ACIDIFICATION AT PAPAGAYO UPWELLING SYSTEM (NORTH PACIFIC COSTA RICA): IMPLICATIONS FOR REEF DEVELOPMENT

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Abstract

Numerous experiments have shown that ocean acidification impedes coral calcification, but knowledge about in situ reef ecosystem response to ocean acidification is still scarce. Bahía Culebra, situated at the northern Pacific coast of Costa Rica, is a location naturally exposed to acidic conditions due to the Papagayo seasonal upwelling. We measured pH and $p\text{CO}_2$ in situ during two non-upwelling seasons (June 2012, May-June 2013), with a high temporal resolution of every 15 and 30 min, respectively, using two Submersible Autonomous Moored Instruments (SAMI-pH, SAMI-CO₂). These results were compared with published data from the 2009 upwelling season. Findings revealed that the carbonate system in Bahía Culebra shows a high temporal variability. Incoming offshore waters drive inter- and intra-seasonal changes. Lowest pH (7.8) and highest $p\text{CO}_2$ (658.3 μatm) values measured during a cold-water intrusion event in the non-upwelling season were similar to those minimum values reported from upwelling season (pH = 7.8, $p\text{CO}_2$ = 643.5 μatm), unveiling that natural acidification also occurs sporadically in the non-upwelling season. This affects the interaction of photosynthesis, respiration, calcification, and carbonate dissolution and the resulting diel cycle of pH and $p\text{CO}_2$ in the reefs of Bahía Culebra. During non-upwelling season the aragonite saturation state (Ω_a) rises to values of >3.3 and during upwelling season fall below 2.5. The Ω_a threshold values for coral growth were derived from the correlation between measured Ω_a and coral linear extension rates which were obtained from the literature and suggest that future ocean acidification will threaten the continued growth of reefs in Bahía Culebra. These data contribute to build a better understanding of the carbonate system dynamics and coral reefs key response (e.g. coral growth) to natural low-pH conditions, in upwelling areas in the Eastern Tropical Pacific and beyond.

4.1 Introduction

Ocean acidification (OA) caused by human-induced increase of atmospheric CO₂ (Feely et al., 2009; Sabine et al., 2004) is considered one of the major threats to marine calcifying organisms and ecosystems (Doney et al., 2012; Fabry et al., 2008; Gattuso et al., 2015; Hofmann et al., 2010). Among all marine habitats, tropical coral reefs are recognized as the most endangered (Hoegh-Guldberg et al., 2007; Kleypas and Yates, 2009; Pörtner et al., 2014), since in addition to reduced calcification (Doney et al., 2009; Gattuso et al., 2014a; Langdon et al., 2000; Marubini et al., 2008), a lower pH also weakens the reef framework by favoring bioerosion and enabling carbonate dissolution (Barkley et al., 2015; Gattuso et al., 2014b; Manzello et al., 2014). According to the IPCC business-as-usual scenario, about 90% of the ocean's surface waters will become undersaturated with respect to aragonite in the next decades (Gattuso et al., 2015), emphasizing the need to study the response of natural ecosystems to OA. Nowadays, aragonite undersaturated surface waters occur naturally

in some parts of the ocean, as consequence of underwater volcanic seeps (Enochs et al., 2015; Fabricius et al., 2011, 2015; Hall-Spencer et al., 2008) or upwelling that drags corrosive deep water into the surface mixed layer (Fassbender et al., 2011; Feely et al., 2008; Harris et al., 2013; Hauri et al., 2009).

Aside from some studies at volcanic seeps (Enochs et al., 2015; Fabricius et al., 2011, 2015; Kroeker et al., 2011) or at reefs in the Eastern Tropical Pacific (ETP) (Manzello, 2008, 2010a, 2010b; Manzello et al., 2008, 2014), our understanding of OA impacts on corals derives mainly from laboratory and seawater enclosure experiments (Hall-Spencer et al., 2015; Pörtner et al., 2014). These results are used to predict ecosystem responses to future OA (Kleypas et al., 2006; Kleypas and Langdon, 2006), but their reliability is challenged by the artificial conditions under which the experiments are conducted. For example, the duration of studies is often too short to allow a full adaptation or acclimatization of the organisms/systems to the changing environmental conditions, and the missing connectivity between ecosystems in seawater enclosures restricts natural interactions between organisms (Hofmann et al., 2010; Kleypas et al., 2006; Kleypas and Langdon, 2006). In situ studies in natural low-pH conditions are able to overcome some of these problems and the ETP is well known for its CO₂-enriched and acidic subsurface waters (Takahashi et al., 2014). Upwelling events decreases the carbonate saturation state (Ω) along the Central American coast (Manzello, 2010b; Manzello et al., 2008; Rixen et al., 2012), and have the potential to produce poorly cemented coral reefs with low accretion rates that are subject to rapid bioerosion (Alvarado et al., 2012; Manzello et al., 2008).

Corals in the northern part of the Costa Rican Pacific coast are developing under the influence of the seasonal Papagayo upwelling (Jiménez et al., 2010; Rixen et al., 2012; Stuhldreier et al., 2015a, 2015c). To contribute to the general understanding of OA impacts on coral reefs, we investigated the variability of the carbonate system in the upwelling-influenced Bahía Culebra, Costa Rica. The main objectives of this study were 1) to describe the behavior of the carbonate system on diurnal and seasonal time scales, 2) to characterize the controlling processes, and 3) to determine ecological impacts of changing carbonate systems. Furthermore, our results will allow us to draw some conclusions concerning future thresholds of coral reef development within this bay.

4.2 Methods

Study site

Bahía Culebra, located in the Gulf of Papagayo, North Pacific coast of Costa Rica (Fig. 4.1), is strongly influenced by the northeasterly Papagayo winds. The strongest wind jets develop during the boreal winter (Amador et al., 2016) and are driven by large-scale variations of the trade winds (Alfaro and Cortés, 2012; Chelton et al., 2000). When Papagayo winds blow through the mountain gap between southern Nicaragua

and northern Costa Rica, the resulting strong offshore winds on the Pacific side lead to upwelling of cold and nutrient-enriched subsurface waters between December and April (Ballesterio and Coen, 2004; Brenes et al., 1990; Kessler, 2006; McCreary et al., 1989). These cyclonic eddies also influence the magnitude and location of the Costa Rica Dome (CRD), which is located ca. 300 km off the Gulf of Papagayo (Fiedler, 2002b). However, the CRD changes its distance to the Costa Rican coast throughout the year, as a result of differences in wind forcing (Fiedler, 2002b; Wyrтки, 1964). During the dry season, particularly between February and April, offshore moving water masses strengthen upwelling at the coast and shoal the thermocline in the Gulf of Papagayo (Fiedler, 2002b; Wyrтки, 1965, 1966). In May-June, during the onset of the rainy season the CRD moves offshore (Fiedler, 2002b; Fiedler and Talley, 2006) and the North Equatorial Countercurrent (NECC) can carry tropical water masses into Bahía Culebra until December, when again upwelling sets in (Wyrтки, 1965, 1966).

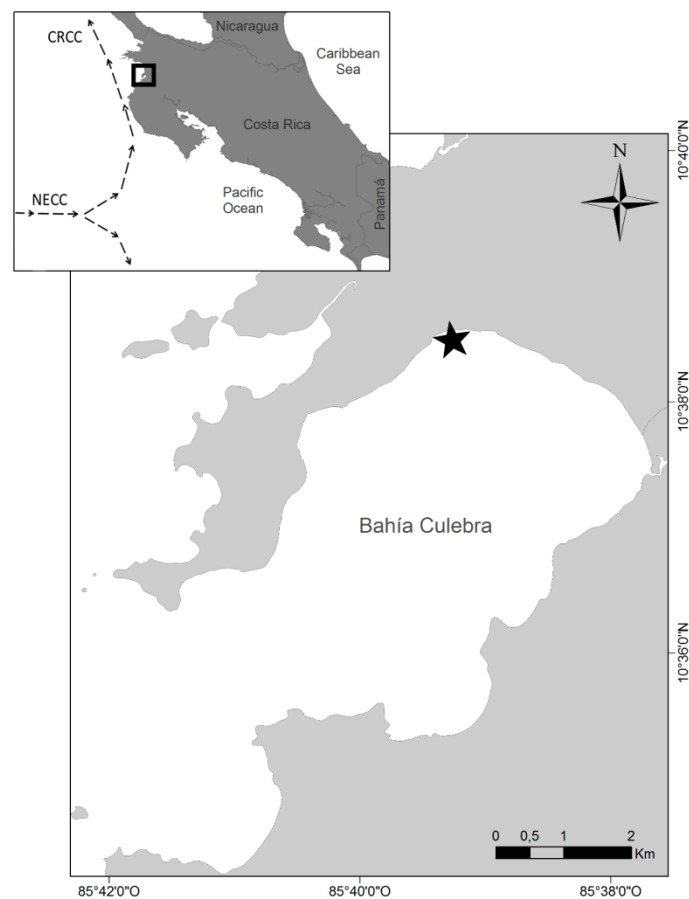


Figure 4.1. Location of Bahía Culebra (square) in the Gulf of Papagayo, North Pacific coast of Costa Rica (insert). Measurements were made at Marina Papagayo (star). Main ocean currents influencing the Gulf of Papagayo (dashed arrows): NECC= North Equatorial Counter Current, CRCC= Costa Rica Coastal Current.

Measurements

We measured in situ pH, $p\text{CO}_2$ and seawater temperature (SWT) during two non-upwelling periods (15 days in June 2012 and 7 days in May-June 2013, Fig. 4.2). Measurements were undertaken with two Submersible Autonomous Moored Instruments (SAMI-pH and SAMI- CO_2) (www.sunburstsensors.com), in sampling intervals of 15 (June 2012) and 30 minutes (May-June 2013). SAMI-sensors were deployed at the pier of Marina Papagayo ($85^\circ 39' 21.41''\text{W}$; $10^\circ 32' 32.89''\text{N}$), on top of a carbonate sandy bottom in the inner part of Bahía Culebra (Fig. 4.1). The water-depth varied approximately between 5-8 m depending on the tide, but sensors, hooked to the pier, moved up and down with the tide and were always at the same depth, 1.5 m below the surface. SAMI instruments measured pH (total hydrogen ion scale) and $p\text{CO}_2$ spectrophotometrically by using a colorimetry reagent method (DeGrandpre et al., 1995, 1999; Seidel et al., 2008). Salinity from discrete samples was measured with a WTW probe (Cond3310) and was used for correction of pH values. Calculation of aragonite saturation state (Ω_a) from parameters measured in situ with SAMI sensors is accurate (Cullison Gray et al., 2011; Gray et al., 2012), but discrete water samples were collected as often as possible to validate the instruments (Fig. 4.3). 250 mL borosilicate bottles were filled with seawater at 30 cm below the surface and preserved with 200 μl of 50% saturated HgCl_2 solution to inhibit biological activity (Dickson et al., 2007). Samples were stored at 3-4 $^\circ\text{C}$ until analysis. Total alkalinity (TA) and Dissolved inorganic carbon (DIC) were measured using a VINDTA 3C (Versatile Instrument for the Determination of Total dissolved inorganic carbon and Alkalinity; Marianda, Kiel, Germany) coupled with a UIC CO_2 coulometer detector (UIC Inc., Joliet, USA). Both instruments were calibrated with Dickson Certified Reference Material (Batch 127) (Dickson et al., 2003). DIC concentrations as well as TA and Ω_a were calculated with the CO2SYS program as a function of measured pH and $p\text{CO}_2$; with dissociation constants of Mehrbach et al. (1973) for carbonic acid as refit by Dickson and Millero (1987), and Dickson (1990) for boric acid.

Wind speeds were obtained from a station of the Instituto Meteorológico Nacional (National Meteorological Institute of Costa Rica), located at the nearby Liberia airport. The Módulo de Información Oceanográfica of the University of Costa Rica (www.miocimar.ucr.ac.cr) supplied the tidal data. All coral growth values were taken from the literature; linear extension rates from Bahía Culebra were measured by Jiménez and Cortés (2003), whilst coral growth in Panamá and Galápagos was measured by Manzello (2010a). For the correlation between coral growth and Ω_a , we used the mean Ω_a values from Panamá and Galápagos previously reported by Manzello (2010b).

Data analysis

We compared our data with values measured during upwelling season in 2009 (Rixen et al., 2012). In 2009 $x\text{CO}_2$ was measured by an underway $p\text{CO}_2$ system (SUNDANS)

equipped with an infrared gas analyzer (LI-7000), and pH was measured using an Orion ROSS electrode an Orion StarTM. Correlations between tidal cycles and physicochemical parameters (pH, $p\text{CO}_2$, T, wind) during non-upwelling periods were tested via Pearson Correlation in Python. Differences in parameters (temperature, pH, $p\text{CO}_2$, TA, DIC, Ω_a) between all periods (2009, 2012, 2013) were tested with a General Linear Model (GLM), in the statistical package R. The GLM was evaluated using graphical methods to identify violations of assumptions of homogeneity of variance and normality of residuals. All GLM assumptions were met. Additionally, we developed a simple model to improve our understanding of processes controlling the observed diel trends, as seen in the time series data of pH and $p\text{CO}_2$ (Figs. 4.2, 4.4). The model simulates combined effects of metabolic processes (photosynthesis, respiration, calcification and dissolution) on the carbonate chemistry. Input parameters for starting the model were the calculated DIC (in 2012: $2037 \mu\text{mol kg}^{-1}$ at 7:00 h and $2019 \mu\text{mol kg}^{-1}$ at 15:00 h; in 2013: $1883 \mu\text{mol kg}^{-1}$ at 5:00 h and $1805 \mu\text{mol kg}^{-1}$ at 15:00 h) and TA (in 2012: $2284 \mu\text{mol kg}^{-1}$ at 7:00 h; in 2013: $2193 \mu\text{mol kg}^{-1}$ at 5:00) values, corresponding to the highest and lowest measured $p\text{CO}_2$ during the day. Calculation of TA and DIC from the pair pH and $p\text{CO}_2$ is prone to errors (Cullison Gray et al., 2011; Millero, 2007), however the values used as input parameters in the model are in range with those reported from other studies in tropical areas (Cyronak et al., 2013b; Manzello, 2010b). The difference between the two DIC concentrations (ΔDIC) was assumed to be caused by photosynthesis/respiration and the resulting formation and decomposition of particulate organic carbon (POC) as well as calcification/dissolution and the precipitation and dissolution of particulate inorganic carbon (PIC, Eq. 4.1). R_{OI} describes the ratio between the production of organic carbon (POC) and precipitation of calcium carbonate carbon (PIC), and was used to link ΔPOC to ΔPIC ($R_{\text{OI}} = \text{POC}/\text{PIC}$) (Eq. 4.2, 4.3). The R_{OI} was further constrained by the determined change of TA (ΔTA). Therefore, it was considered that photosynthesis and respiration of one mole of carbon increases and reduces TA by 0.15 units, respectively (Broecker and Peng, 1982). Calcification and dissolution of one mole of carbon decreases and increases TA by two units (Eq. 4.4). To verify the results from the model, we used the output ΔDIC and ΔTA to calculate new $p\text{CO}_2$ and pH values, which were further compared to the measured ones (Fig. 4.5). The best fit between modeled and measured values was achieved with a respective R_{OI} of -2.6 for 2012 and 1.0 for 2013, whereas the assumption of calcium carbonate dissolution caused the negative sign.

$$\Delta\text{DIC} = \Delta\text{POC} + \Delta\text{PIC} \quad (4.1)$$

$$\Delta\text{PIC} = \left(\frac{\Delta\text{POC}}{R_{\text{OI}}} \right) \quad (4.2)$$

$$\Delta\text{POC} = \Delta\text{DIC} / \left(1 + \left(\frac{1}{R_{\text{OI}}} \right) \right) \quad (4.3)$$

$$\Delta TA = (\Delta POC * 0.15) - \left(\left(\frac{\Delta POC}{R_{OI}} \right) * 2 \right) \quad (4.4)$$

This was calculated on hourly time steps, separately for 2012 and 2013, using the mean SWT (2012 = 29.61 ± 0.93 °C, 2013 = 30.08 ± 0.27 °C) and salinity (2012 = 32.5, 2013 = 32.5).

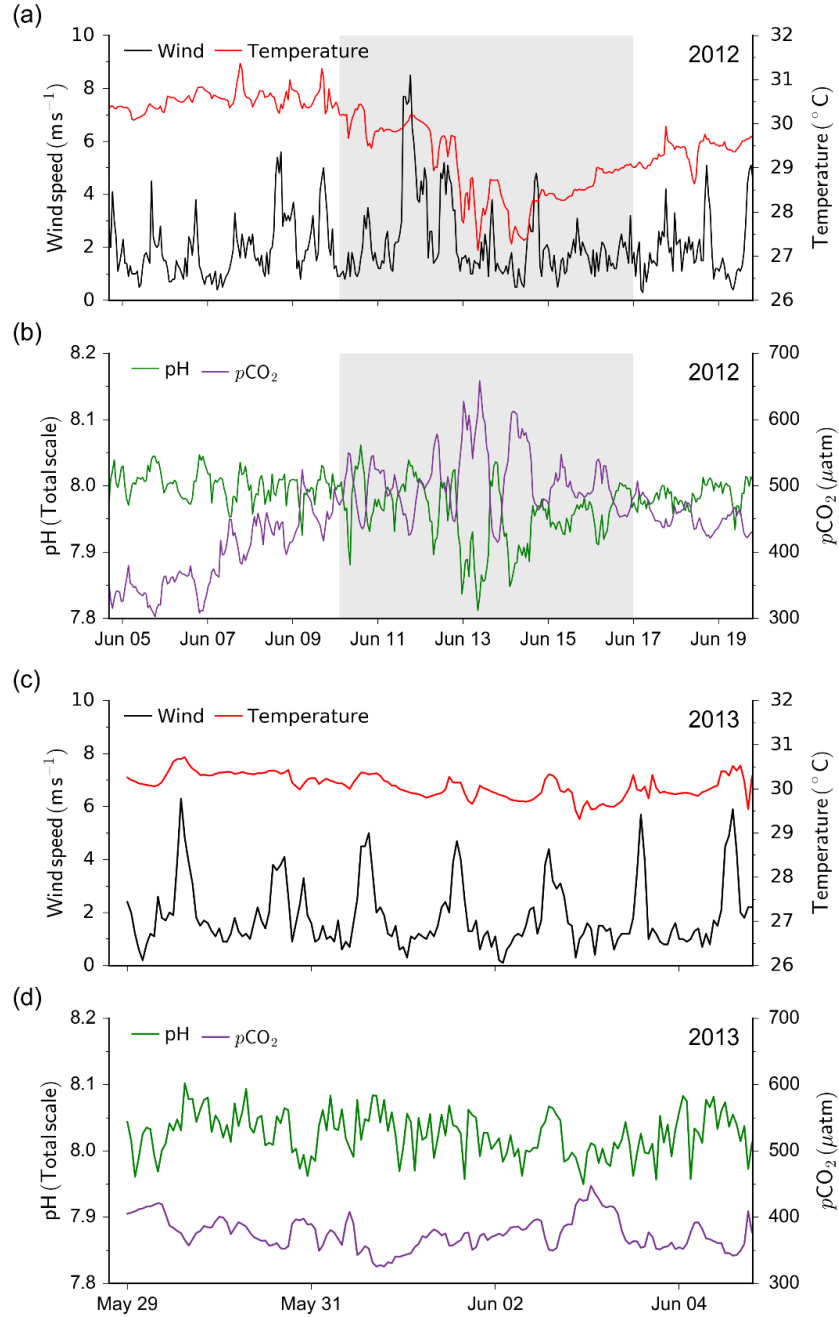


Figure 4.2. Measured parameters (wind speed, SWT, pH and pCO_2) during the non-upwelling seasons of June 2012 (a, b) and May-June 2013 (c, d), at Bahía Culebra. Shaded area in (a) and (b) indicates the 2012 upwelling-like event.

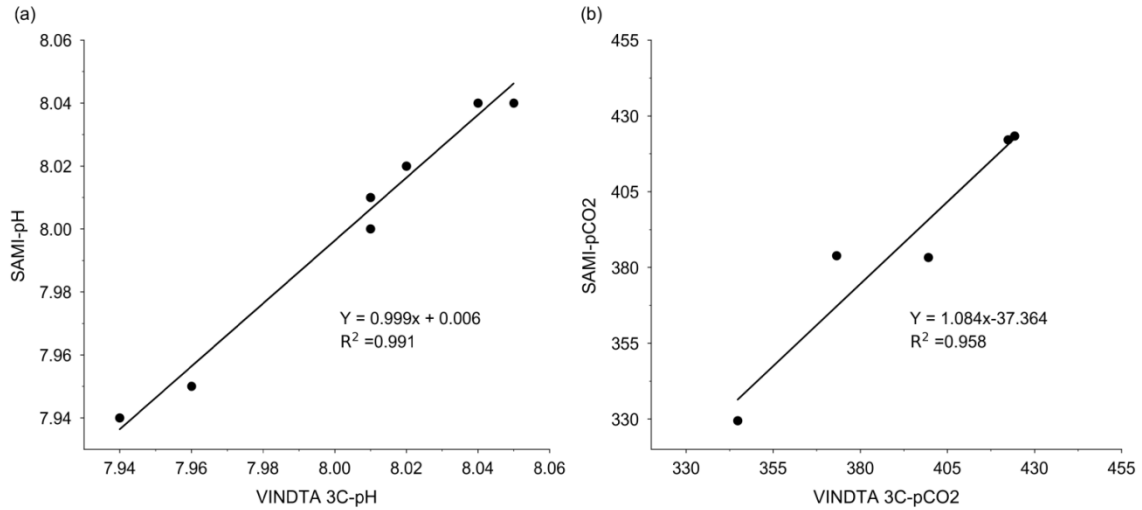


Figure 4.3. Validation of in situ measurements of pH (a) and $p\text{CO}_2$ (b) using discrete water samples. SAMI sensors measured pH and $p\text{CO}_2$ directly in the water column. The pH and $p\text{CO}_2$ values used for validation were calculated with the CO2SYS program as a function of measured TA and DIC; discrete samples were measured with a VINDTA 3C system.

4.3 Results

Carbonate chemistry during non-upwelling season

In June 2012, average SWT was 29.61 ± 0.93 (average \pm standard deviation) $^{\circ}\text{C}$ and ranged from 27.13°C to 31.37°C . In May-June 2013 SWT ranged from 29.3°C to 30.7°C (average $30.08 \pm 0.27^{\circ}\text{C}$). During both periods, the salinity was 32.5 ± 0.8 . During the study periods, the wind intensified during the afternoons reaching speeds of up to 8.5 m s^{-1} and 6.0 m s^{-1} in 2012 and 2013, respectively (Fig. 4.2). Average pH and $p\text{CO}_2$ in June 2012 were 7.98 ± 0.04 and $456.38 \pm 69.68 \mu\text{atm}$, respectively; the corresponding averages for May-June 2013 were 8.02 ± 0.03 and $375.67 \pm 24.25 \mu\text{atm}$ (Table 4.1). Since the tidal cycle was not significantly correlated with the variability of pH, $p\text{CO}_2$, T or wind ($p > 0.05$) during the periods of observations (Table 4.2), it was excluded from further discussions. Mean Ω_a values were 3.32 ± 0.46 in June 2012 and 3.50 ± 0.49 in May-June 2013 (Table 4.1).

Table 4.1. Measured and calculated (*) parameters, during upwelling (2009) and non-upwelling seasons (2012, 2013) at Bahía Culebra, Costa Rica.

	pH (Total scale)	$p\text{CO}_2$ (μatm)	CO_2 ($\mu\text{mol kg}^{-1}$)	T ($^{\circ}\text{C}$)	DIC* ($\mu\text{mol kg}^{-1}$)	TA* ($\mu\text{mol kg}^{-1}$)	Ω^*
2009	7.91	578.49	16.44	25.09	2098.71	2328.42	2.71
Mean \pm SD	± 0.32	± 42.82	± 1.35	± 0.57	± 103.81	± 118.45	± 0.29
2012	7.98	456.38	11.77	29.61	1924.65	2204.54	3.32
Mean \pm SD	± 0.04	± 69.68	± 1.99	± 0.93	± 195.07	± 212.18	± 0.46
2013	8.02	375.67	9.56	30.08	1800.92	2102.66	3.50
Mean \pm SD	± 0.03	± 24.25	± 0.64	± 0.27	± 142.78	± 174.79	± 0.49

Table 4.2. Correlations between tide height and four parameters during non-upwelling season (2012, 2013).

Year	pH	$p\text{CO}_2$	T	Wind
2012	-0.004	0.037	-0.005	0.033
2013	0.111	0.026	-0.093	-0.126

All p-values > 0.05

Seasonal variation of the carbonate system

Measured parameters showed significant differences between study periods ($p < 0.05$). The SWT range differed among years (Table 4.1); 2013 was the warmest study period, followed by 2012 and 2009. Lowest measured pH was 7.81 in June 2012, 7.84 in April 2009 and 7.95 in May-June 2013. We also compared DIC and TA, in order to estimate to which extend the observed variations of $p\text{CO}_2$ were caused by changes in temperature and/or DIC concentrations. Mean DIC values were $2098.71 \pm 103.81 \mu\text{mol kg}^{-1}$ in April 2009, $1924.65 \pm 195.07 \mu\text{mol kg}^{-1}$ in June 2012 and $1800.92 \pm 142.78 \mu\text{mol kg}^{-1}$ in May-June 2013. Similarly, mean TA values were $2328.42 \pm 118.45 \mu\text{mol kg}^{-1}$ in April 2009, $2204.54 \pm 212.18 \mu\text{mol kg}^{-1}$ in June 2012 and $2102.66 \pm 174.79 \mu\text{mol kg}^{-1}$ in May-June 2013. According to average values, April 2009 was the period with most acidic water and greater CO_2 enrichment, followed by June 2012 and May-June 2013 (Table 4.1). Mean Ω_a values were 2.71 ± 0.29 during upwelling season (April 2009) and 3.41 ± 0.13 during non-upwelling season (June 2012, May-June 2013), resulting in annual average Ω_a of 3.06 ± 0.49 at Bahía Culebra. Time series of pH and $p\text{CO}_2$ in June 2012 and May-June 2013 showed a pronounced daily cycle (Fig. 4.4), which in addition to previously described data will be discussed in the following paragraphs.

4.4 Discussion

Natural OA beyond the upwelling season

The observed differences in pH and $p\text{CO}_2$ between 2012 and 2013 suggest that the non-upwelling season exhibits a strong interannual variability (Table 4.1). In 2012 pH was lower and $p\text{CO}_2$ higher than in 2013 (Fig. 4.2b, c). The June 2012 time-series data showed that SWT decreased and $p\text{CO}_2$ increased from 300 to 650 μatm in less than a week, after several days of strong afternoon winds (Fig. 4.2a). Similarly, this increase in $p\text{CO}_2$ was accompanied by a dropped in pH from 8.04 to 7.83 (Fig. 4.2a). This suggests that an enhanced wind-driven vertical mixing entrained cooler and CO_2 -enriched waters from greater water-depth into the surface layer. The associated SWT drop from 31.4°C to 27.1°C was similar to that observed during the onset of the 2009 upwelling event (26.2°C to 23.7°C ; Rixen, Jiménez, and Cortés 2012). Nevertheless, the higher SWT during the 2012 non-upwelling season suggests that the entrained water originated from a shallower water-depth, compared with the water upwelled in 2009. The $p\text{CO}_2$ values with up to 650 μatm reached the same level during both events,

which is partially caused by the higher SWT in 2012. However, DIC concentrations in 2012 ($1924.65 \pm 195.07 \mu\text{mol kg}^{-1}$) were lower than those in 2009 ($2098.71 \pm 103.81 \mu\text{mol kg}^{-1}$), but exceeded those in 2013 ($1800.92 \pm 142.78 \mu\text{mol kg}^{-1}$, Table 1). During the seven days that lasted the cold-water intrusion event in 2012 (June 10-17), the DIC concentrations dropped from $2355.39 \mu\text{mol kg}^{-1}$ down to $1715.30 \mu\text{mol kg}^{-1}$. This implies that in addition to high SWT, the entrainment of CO_2 -enriched subsurface water increased the $p\text{CO}_2$ not only during the upwelling periods, but also during the 2012 non-upwelling season.

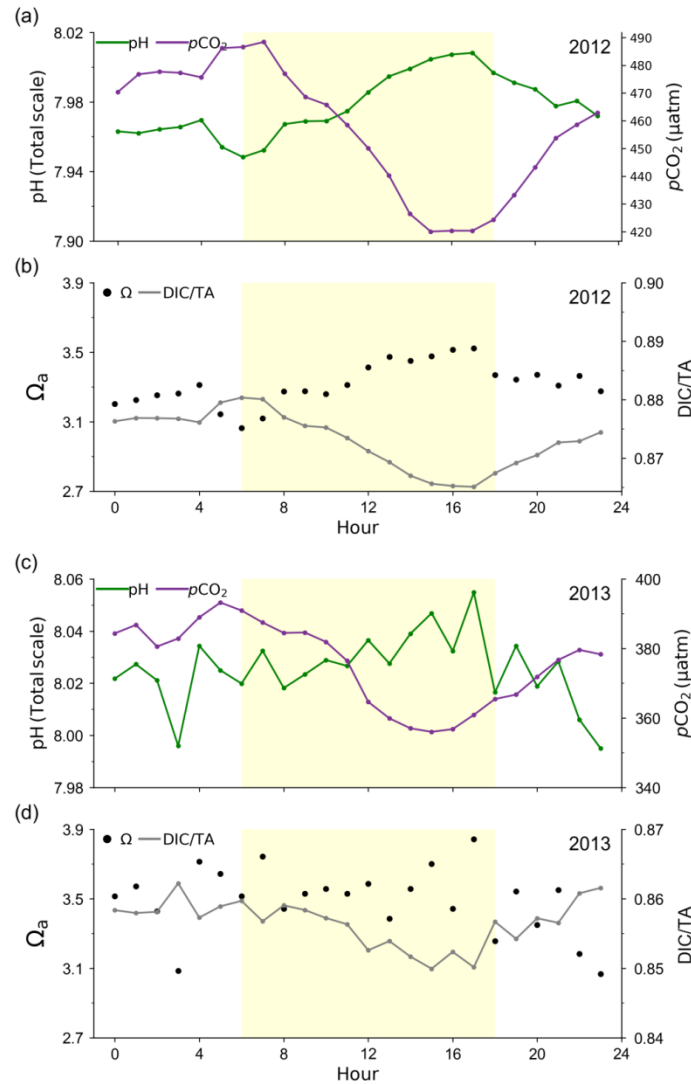


Figure 4.4. Diel pattern of parameters measured in Bahía Culebra. Data points are hourly averages of 15 and 7 consecutive days in 2012 (a, b) and 2013 (c, d), respectively. The shaded area represents daylight hours.

Since in 2012 the $p\text{CO}_2$ had already increased by June 7th and the SWT decreased two days later (June 10th), the inflow of CO_2 -enriched waters seems to have increased the $p\text{CO}_2$ already prior to the strengthening of local winds (Fig. 4.2b). Later, local wind-induced vertical mixing seems to have amplified the impact of the inflowing CO_2 -enriched water mass on the $p\text{CO}_2$ in the surface water by increasing its input into

surface layers. Accordingly, the CO₂-enriched waters were apparently supplied from a different location than they are during upwelling season. Since the NECC carries offshore waters towards the Costa Rican shore during the non-upwelling season (Fiedler, 2002b; Wyrski, 1965, 1966), it is assumed that the CO₂-enriched subsurface water originated somewhere south of our study area in the open ETP. The absence of such a cold-event during the non-upwelling season in 2013 suggests that the occurrence of this kind of events might be an irregular feature (Fig. 4.2c, d), and the driving forces are still elusive. Nevertheless, these types of events have the potential to affect the metabolic processes in the bay as will be discussed in the following section, which analyzes the daily cycles during the non-upwelling seasons in 2012 and 2013.

Processes behind the variability of the carbonate system

In 2012, the pH and the $p\text{CO}_2$ values followed a pronounced diurnal cycle with highest pH and lowest $p\text{CO}_2$ values during the late afternoon and lowest pH and highest $p\text{CO}_2$ values around sunrise in the early morning (Fig. 4.4a). Such daily cycles are typical for tropical regions and are assumed to be caused by photosynthesis during the day and respiration of organic matter during the night (Albright et al., 2013; Cyronak et al., 2013a; Shaw et al., 2012). The aragonite saturation state as well as the DIC/TA ratio followed this pattern, with higher Ω_a and lower DIC/TA ratio values during the day as well as lower Ω_a and higher DIC/TA values at night (Fig. 4.4b). Although the $p\text{CO}_2$ cycles in 2013 followed a similar pattern to 2012, pH cycles were less predictable (Fig. 4.4).

To characterize the relative importance of the processes responsible for the observed changes in pH and $p\text{CO}_2$ (photosynthesis, respiration, calcification and dissolution) we used the model described earlier, which is based on the determined DIC concentrations during times when pH and $p\text{CO}_2$ revealed their daily minima and maxima, respectively. For example, if photosynthesis of organic matter dominates the transition from early morning maxima of $p\text{CO}_2$ to late afternoon minima of $p\text{CO}_2$ it should be associated with a decline in DIC. Whether photosynthesis was accompanied with enhanced calcification can be detected by an associated decrease of TA. Since decreasing DIC raises the pH and a decrease in TA lowers the pH, such photosynthetic enhanced calcification hardly affects the pH and could explain the weak daily cycle observed in 2013. Alternatively, if photosynthesis is accompanied by carbonate dissolution during the day, this would amplify the daily cycle of pH and $p\text{CO}_2$ as seen during the cold-water intrusion event in 2012. Likewise, an increased photosynthesis resulting from higher nutrient concentrations (Pennington et al., 2006) could also be causing the observed large amplitude during the event in 2012. However, in our case the determined TA and DIC concentrations constrain the impact of the formation of organic matter (POC = photosynthesis - respiration) and calcification (PIC = calcification - dissolution) on the carbonate system. This sets the boundaries within which the observed diurnal cycle of pH and $p\text{CO}_2$ has to be explained (Fig. 4.5c, d). In order to reconstruct the diurnal cycle of pH and $p\text{CO}_2$ within these boundaries we assumed a

photosynthetic-enhanced calcification during the day and vice versa, dissolution and respiration at night. Thereby the best fit between pH and $p\text{CO}_2$ measured in 2013 and the respective calculated values could be obtained by using a R_{OI} of 1. This approach failed to explain the diurnal cycle of pH and $p\text{CO}_2$ as observed during the 2012 cold-water intrusion event (June 10-17). The only solution we found to explain these pronounced diurnal cycles within the given DIC and TA boundaries was to assume that photosynthesis and dissolution prevailed during the day and respiration and calcification occurred at night. The R_{OI} of -2.6 resulted in the best fit between the measured and calculated pH and $p\text{CO}_2$ for the 2012 event, whereas the negative sign reflects the contrasting effects of calcification and dissolution on the DIC concentration.

Dissolution taking place during daytime is peculiar but not completely unusual, as it has been reported on tropical sandy bottoms under ambient (Cyronak et al., 2013b; Yates and Halley, 2006a) and high- CO_2 conditions (Comeau et al., 2015). Similarly, dark-calcification is not entirely uncommon and occurs in both, sandy bottoms and coral reefs (Albright et al., 2013; Yates and Halley, 2006b). Accordingly, the entrainment of CO_2 -enriched water from the NECC seems to shift the carbonate chemistry of Bahía Culebra from a system where photosynthesis and calcification are the controlling processes during light hours to a system in which daytime is dominated by photosynthesis and dissolution. The net effect, as observed, is an enhanced $p\text{CO}_2$ and lower Ω_a during periods characterized by the inflow of CO_2 -enriched waters (Table 4.1). This has strong ecological implications for local coral reef ecosystems.

Ecological implications for coral reefs

Coral reefs in Bahía Culebra were dominated by *Pocillopora* spp. and *Pavona clavus* (Jiménez, 2001a; Jiménez et al., 2010), whereas *Porites lobata* is the main reef forming coral in the southern part of the Costa Rican Pacific coast (Cortés and Jiménez, 2003; Glynn et al., 2017a). Although the reefs in the north are naturally exposed to periodic high- CO_2 conditions during upwelling events (Rixen et al., 2012), as well as during cold water intrusions in non-upwelling season, the linear extension rates of *Pocillopora* spp. and *P. clavus* exceeded those of the same species in other regions (Fig. 4.6) (Glynn, 1977; Jiménez and Cortés, 2003b; Manzello, 2010a; Rixen et al., 2012). This suggests that local corals are adapted and/or acclimatized to the upwelling of cold and acidic waters.

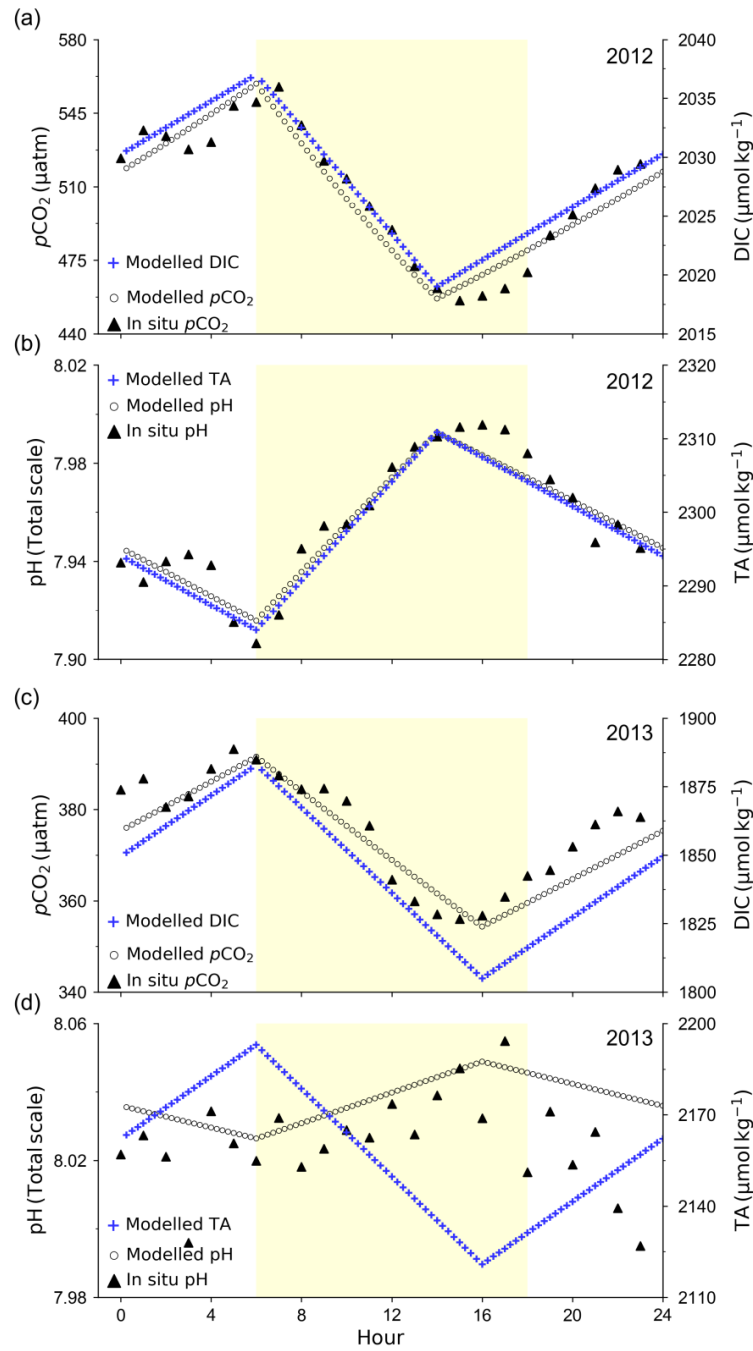


Figure 4.5. Expected diel behaviour of the carbonate system in 2012 (a, b) and 2013 (c, d), based on measured parameters. Modeled parameters are shown as blue crosses and empty circles; the reference parameter used to adjust the model is shown in black triangles. Shaded area represents daylight hours.

Aragonite saturation state (Ω_a) is known as one of the main variables influencing coral growth and therefore reef distribution around the world (Kleypas et al., 1999a). By integrating the data from the present study and values previously reported by Rixen et al. (2012), we estimated that the annual mean Ω_a in Bahía Culebra is 3.06. Additionally, earlier studies in the ETP measured Ω_a values and coral extension rates from locations that are under the influence of upwelling events (Manzello, 2010a),

whilst extension rates from Bahía Culebra were measured by Jiménez and Cortés (2003). The correlation between our estimated Ω_a with the available data from Bahía Culebra, Panamá and Galápagos indicates that coral extension rates in each of those locations are predictable by their corresponding Ω_a values (Fig. 4.6).

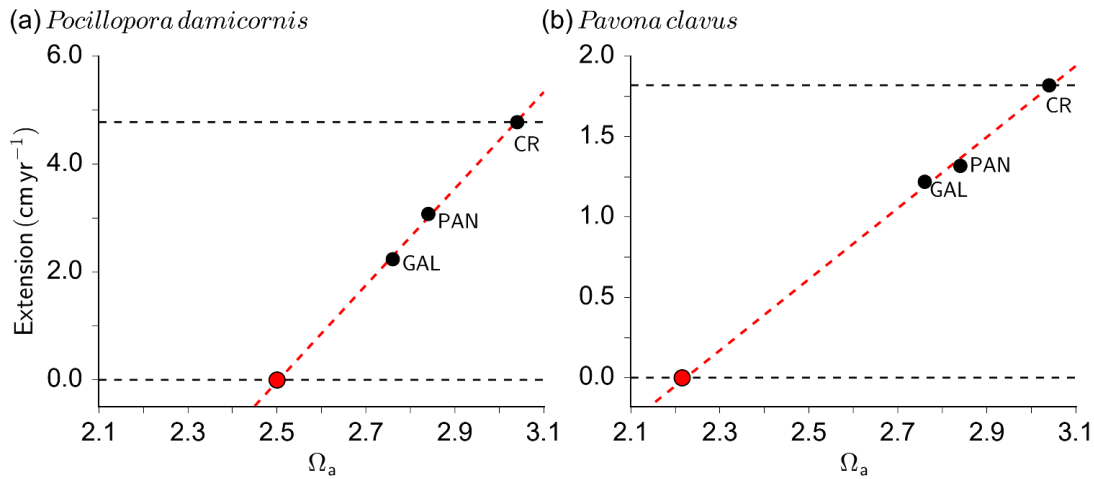


Figure 4.6. Mean aragonite saturation states (Ω_a) – from present and former studies - versus previously reported mean linear extension rates of (a) *Pocillopora damicornis* and (b) *Pavona clavus* from upwelling areas in Costa Rica (CR) (Jiménez and Cortés, 2003), Panamá (PAN) and Galápagos (GAL) (Manzello, 2010a). Red broken line shows the regression equation as estimated by Rixen et al. (2012). Red mark represents our estimated Ω_a threshold for Bahía Culebra, when coral growth equals zero.

The dependency of coral growth on Ω_a and the mean Ω_a (2.71) during the upwelling season (Table 4.1) suggests that upwelling of acidic waters should reduce corals' relatively high annual mean growth rates in Bahía Culebra. The increased Ω_a during non-upwelling season in turn must enhance linear extension and explains corals' high annual mean growth rates. The Ω_a values from this study suggest that most favorable conditions for coral growth occur during non-upwelling season, the period that coincides with development of the rainy season. This implies that during the main growing season the eutrophication and siltation caused by human impacts on river discharges, as well as the development of harmful algal blooms, could also strongly affect the corals' annual mean growth rates (Cortés and Reyes-Bonilla, 2017).

Despite the corals' high annual mean linear extension rates, studies carried out in 1973 showed that the thickness of the reef framework within our study area was with 0.6 to 3 m (mean 1.8 m) among the lowest in the ETP, where Holocene framework accumulation in *Pocillopora*-dominated reefs could reach up to 9 m (Glynn et al., 1983; Toth et al., 2017). During the last decade it further decreased (Alvarado et al., 2012), and during the period of our observation the reef frameworks of *Pocillopora* spp. in Bahía Culebra hardly exceeded a thickness of 0.5 m. This denotes that although *Pocillopora* spp. and *P. clavus* are adapted to the entrainment of acidic waters, these reefs are growing in an environment at the limit of reef-building corals tolerance in

terms of temperature, nutrient loads and pH (Manzello et al., 2017). Gaps in coral reef accretion at the ETP are known from the geological record (Toth et al., 2012, 2015, 2017). They have been linked to increased ENSO variability (Toth et al., 2012, 2015) and stronger upwelling conditions (Glynn et al., 1983), favoring dissolution and erosion of reef frameworks while at the same time restricting coral growth.

The y-intercept of the regression equation derived from the correlation between linear extension rates and Ω_a furthermore implies that linear extension of *P. damicornis* and *P. clavus* should approach zero under a carbonate saturation state of $\Omega_a < 2.5$ (*P. damicornis*) and < 2.2 (*P. clavus*). According to climate predictions, the global Ω_a will reach values < 2.0 by the end of this century (IPCC, 2014), and major upwelling systems such as those off California and South America will intensify (Wang et al., 2015). Combined effects of ocean acidification and impacts of stronger upwelling on Ω_a in the ETP and on Ω_a in Bahía Culebra are difficult to predict. Worldwide, OA is expected to reduce coral reefs' resilience by decreasing calcification and increasing dissolution and bioerosion (Anthony et al., 2011b; Kleypas et al., 1999a; Yates and Halley, 2006a). Coral reefs from the ETP are affected by chronic and acute disturbances, such as thermal stress and natural ocean acidification resulting from ENSO and upwelling events, respectively (Manzello, 2010b; Manzello et al., 2008). Historically, these reefs have shown a high resilience to both stressors by separately, but their coupled interaction can cause coral reef lost within the next decades. The ETP have the lowest Ω_a of the tropics, near to the threshold values for coral reef distribution, therefore the reefs from this region may be the most affected by the increasing levels of anthropogenic CO_2 and also show the first negative impacts of this human induced OA (Manzello et al., 2017). This emphasizes the importance of the Paris agreement and all the global efforts to reduce the CO_2 emission into the atmosphere (Figueres et al., 2017).

4.5 Conclusions

The present study provides data from in situ measurements from a system that is naturally exposed to low-pH conditions, and seeks to characterize the carbonate chemistry within a bay (Bahía Culebra) and its potential impact on the reefs. This study builds on previous field studies in the upwelling areas of Panamá (Manzello, 2010b; Manzello et al., 2008) and Papagayo (Rixen et al., 2012). Our results indicate that physical processes, such as the coastal upwelling and the exchange of water between the bay and the open ocean, influence the carbonate chemistry on timescales of weeks to months, where metabolic processes (photosynthesis and calcification) influence the diurnal cycle. To which extend benthic and pelagic processes control the diurnal cycle, cannot be established based on our data. However, the results from the present study also suggest that coral reefs from Bahía Culebra are exposed to a high intra- and interannual variability in the carbonate system. Challenging conditions for reef development are not restricted to the upwelling season, they occur sporadically also

during non-upwelling season, when pH and CO₂ concentrations reach values comparable to those during upwelling events. Previous studies reported that the linear extension rates measured in Bahía Culebra were among the highest in the ETP, thus is likely that coral growth in this bay is enhanced with increased Ω_a during periods with no entrainment of low-pH waters. However, coral growth must be measured during both seasons in order to confirm this assumption. Threshold values of Ω_a when coral growth likely approaches zero were derived from the correlation of Ω_a and previously measured annual linear extension rates. The Ω_a threshold values from the present study and the fact that high-CO₂ waters are occasionally hauled in to the bay during non-upwelling season; suggest that coral reef development in Bahía Culebra is potentially threatened by anthropogenic OA.

Acknowledgements

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5. CARBONATE CHEMISTRY GRADIENT ALONG THE PACIFIC COAST OF COSTA RICA INFLUENCES REEF DEVELOPMENT

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To be submitted

Abstract

Reef development is controlled by a variety of environmental conditions, but carbonate chemistry data is scarce in most coastal areas from the Eastern Tropical Pacific. Consequently, this study contributes to understand the role of local conditions shaping the benthic community structure along the Pacific coast of Costa Rica, where physicochemical parameters were measured in situ and from discrete water samples over a year period, during dry and rainy season. This study characterizes the carbonate chemistry at three locations: Santa Elena in the north, Marino Ballena in the south and Matapalo between these two locations. The obtained results show a high variability of the seawater chemistry along this coast, with pH that ranges between 7.85 and 8.04. Coastal upwelling, photosynthesis and respiration are the main drivers of the carbonate systems in northern locations. Conversely, in southern locations the enhanced river discharges in combination with calcification and dissolution exert a strong control on the carbonate chemistry, with dissolution occurring mainly during the rainy season. Compared to these locations, Matapalo displays a relatively low seasonality of the carbonate chemistry and is confirmed as a “transition location” in the gradient of upwelling influence along this coast. Our results also suggest that the distribution of key reef-building species along this coast is mainly controlled by nutrient inputs caused by upwelling (north) and river discharges (south) in combination with omega, salinity and turbidity. The dominant coral species in the north (*Pavona* spp. and *Pocillopora* spp.) are highly tolerant to low omega and nutrient-enriched cold waters. Main reef-builders in southern locations (*Porites* cf. *lobata* and *Panovoa clavus*) cope better with low salinity, low omega and loads of suspended matter.

5.1 Introduction

Eastern Tropical Pacific (ETP) coral reefs extend from México to northern Perú and are characterized by their small size and simple structure with discontinuous distribution. The relatively low diversity of corals in the ETP was increasingly attributed to the prevalence of extreme physical conditions along this coast (Cortés, 1997; Dana, 1975; Glynn et al., 2017a). Eastern boundary upwelling systems limit e.g. expansion of coral reefs in the north (California Upwelling system) and towards the south (Humboldt Upwelling system). In between, major local wind-driven upwellings occur off Mexico, at the border between Nicaragua and Costa Rica (Papagayo Upwelling) and in the Gulf of Panama (Panama Upwelling). The climate anomaly El Niño Southern-Oscillation (ENSO) strongly influences upwelling in the ETP (Fiedler and Lavín, 2017; Glynn et al., 2017b). In the course of negative ENSO episodes referred to as El Niño, upwelling weakens and seawater temperature increases above the average. ENSO-induced warming events have caused bleaching and significant coral mortality in Costa Rica (Jiménez, 2001b; Jiménez et al., 2001; Jiménez and Cortés, 2001, 2003a). On the other

hand, positive ENSO episodes referred to as La Niña intensify local upwelling conditions.

The northern Pacific coast of Costa Rica is strongly influenced by the Papagayo upwelling system, whose impact diminishes towards the south (Cortés, 2016). While coral reef formations are restricted to northern and southern locations (Cortés et al., 2010; Cortés and Jiménez, 2003) in the middle sections of the littoral isolated colonies of scleractinian corals are widely spread. Branching corals of the genus *Pocillopora* are widely distributed and build reef structures in both, the northern and southern locations. Massive species on the other hand, vary from north to south, with *Pavona gigantea*, *Pavona clavus* and *Gardineroseris planulata* as the main reef builders in the north, while *Porites cf. lobata* is the main reef-building coral in the south. This strong north-south gradient in coral distribution summarized in Cortés and Jiménez (2003) and Glynn et al. (2017a) raises the question of to which extent the carbonate chemistry and temperature control the reef development along the Pacific coast of Costa Rica? In order to address this question, we measured total alkalinity (A_T), dissolved inorganic carbon (C_T), temperature, salinity and nutrient concentrations at three locations along the coast during the dry and rainy season. Additionally, benthic surveys were carried out in some representative coral reefs at each location. The compiled data will allow the spatial and seasonal comparison of physicochemical conditions and coral reef status and to elucidate which factors control the differences of the benthic community structure along the Costa Rican coast.

5.2 Materials and Methods

Study locations

Three study locations were chosen along the Costa Rican Pacific coast (Fig. 5.1): Santa Elena and Matapalo in the north and Marino Ballena in the south. Most coral reefs from northern locations are constructed by branching species (*Pocillopora* spp.), although there are also reefs of massive corals (*Pavona* spp.) (Cortés, 1997; Cortés et al., 2010; Jiménez, 1997, 2001a). In the south, Marino Ballena comprises several coral communities and reefs built by *Porites cf. lobata* and *Pavona clavus* (Alvarado et al., 2005, 2006; Cortés et al., 2010).

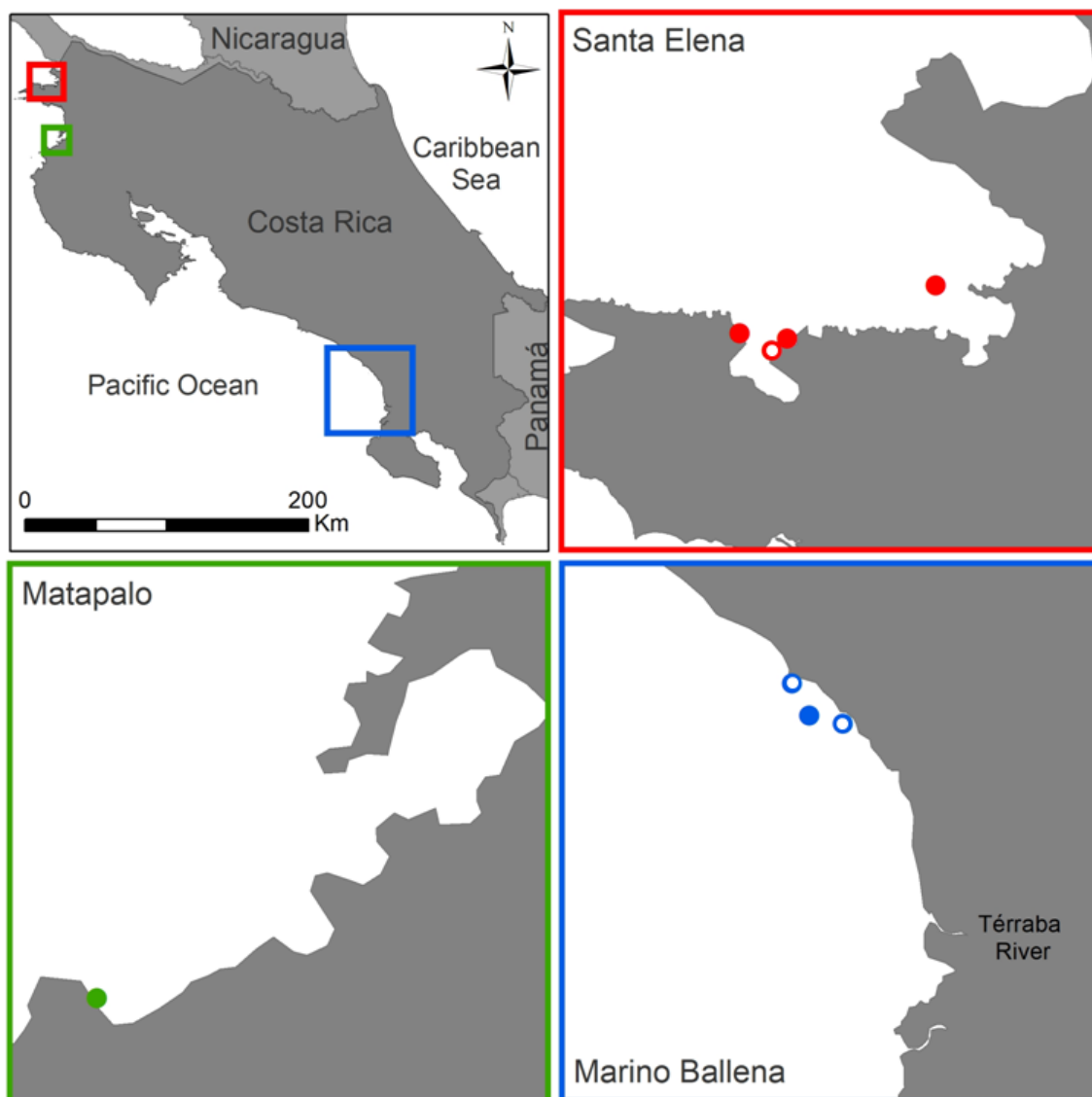


Figure 5.1. Studied locations in the north (Santa Elena, Matapalo) and south (Marino Ballena) Pacific coast of Costa Rica. Circles indicate the sampling sites in each location (full = water sampling + benthic survey, empty = water sampling).

Water sampling

Water samples were collected for eight consecutive days in each location, during high and low tide, both in rainy (July-August 2013) and dry (January-February 2014) season. When possible, samples were collected at two different depths, 0.5 m below the surface and directly over the reef, the latter depth differed between sites (3-10 m). The number of sampling sites in each location was determined by the presence of coral reefs (Table 5.1), for a total of four sampling sites in Santa Elena (Bajo Rojo, Matapalito, Pochote, Cabros), one in Matapalo and three in Marino Ballena (Tómbolo, Bajo Mauren, Tres Hermanas). Sampling was carried out with a 10 L volume Niskin bottle following the protocol described by Dickson et al. (2007). Water for determination of carbonate chemistry parameters was collected in 250 mL air-tight borosilicate bottles, fixed immediately after collection with 200 μ L of a 50% saturated

HgCl₂ solution (35 gL⁻¹ HgCl₂) and stored cold until analysis. Nutrient samples were filtered in the field through a 0.45 µm pore size filter and frozen until analysis. Samples for salinity determination were collected in 50 mL plastic bottles and measured in the laboratory with a WTW probe (Cond3310). Seawater temperature (SWT) was measured *in situ* using HOBO® Pendant Temperature data loggers (Bajo Rojo, Matapalito, Matapalo, Bajo Mauren) and a WTW probe (Cond3310) (Matapalito, Pochote, Tómbolo, Tres Hermanas).

Table 5.1. Samples collected along the Pacific coast of Costa Rica during the study period. Sampling was carried out in rainy (July-August 2013) and dry (January-February 2014) season.

LOCATION (No. sites)	Non-upwelling (Rainy season 2013)	Upwelling (Dry season 2014)	TOTAL
Santa Elena (4)	75 (7-14 August)	64 (5-13 January)	138
Matapalo (1)	32 (29 July-05 August)	28 (20-28 February)	60
Marino Ballena (3)	76 (18-25 August)	27 (10-17 January)	103

Reef surveys

Benthic community composition was quantified at three reefs in Santa Elena (Bajo Rojo, Matapalito, Cabros), one in Matapalo (Matapalo) and one in Marino Ballena (Bajo Mauren) (Fig. 5.1). Due to fieldwork logistics, reef surveys were conducted in a different temporal resolution at each location (monthly at Santa Elena and Matapalo, yearly at Marino Ballena, Table 5.2) and averaged over all available data points. Benthic surveys were conducted following the chain method (Rogers et al., 1994) with five replicates per transect. A 10 m length chain with a known number of links was laid on top of the reef following its contours; nine categories (live coral at species level, dead coral, bleached coral, macroalgae, coralline algae, turf algae, substrate, cyanobacteria and others) were used to quantify the species composition under each link. Afterwards, the corresponding number of links for each category was converted to relative benthic cover.

Laboratory measurements

A_T and C_T were measured with a VINDTA 3C system (Versatile instrument for the determination of total dissolved inorganic carbon and titration alkalinity), coupled with a UIC CO₂ coulometer (model CM5015) and a METROHM® Titrino (model 716 DMS). Instruments were calibrated with Dickson Certified Reference Material (Batch 127) (Dickson et al. 2003). The fCO₂, pH and Ω_a (aragonite saturation state) were calculated with CO2SYS as a function of measured parameters (A_T, C_T, salinity, nutrients and

SWT), with dissociation constants of Mehrbach et al. (1973) for carbonic acid as refit by Dickson and Millero (1987), and Dickson (1990) for boric acid.

Five inorganic nutrients (phosphate, PO_4^{3-} ; silicate, $\text{SiO}(\text{OH})_3^-$; ammonium, NH_4^+ ; nitrite, NO_2^- and nitrate, NO_3^-) were measured through a reagent based method with a Lachat's QuikChem[®] 8500 Series 2 Flow Injection Analysis (FIA) System, following the Standard Operation Procedure from Centro de Investigación en Ciencias del Mar y Limnología (CIMAR) of the University of Costa Rica (PON Nut-08).

All meteorological data (wind speed, wind direction and rainfall) were provided by the Instituto Meteorológico Nacional (National Meteorological Institute of Costa Rica), from two stations located in the North Pacific (Santa Rosa and Liberia) and in the South Pacific (Damas station).

Table 5.2. Reef surveys carried out at each location during the study period. Sampling was carried out between April 2013 and April 2014.

REEF (Location)	Temporal resolution	Transects (TOTAL)
Bajo Rojo (Santa Elena)	Monthly	12
Matapalito (Santa Elena)	Every 3 and 6 months	6
Cabros (Santa Elena)	Monthly	11
Matapalo (Matapalo)	Monthly	12
Bajo Mauren (Marino Ballena)	Yearly	2

Analyzes

All measured (SWT, salinity, phosphate, nitrate, nitrite, silicate, ammonium, A_T , C_T) and calculated (pH, $f\text{CO}_2$, Ω_a) physicochemical parameters were averaged by site, tide (low, high) and season (dry, rainy) and also by location and season. For statistical comparisons we used the salinity normalized values (nA_T , nC_T) ($nA_T = A_T \times 35/S$, $nC_T = C_T \times 35/S$). Statistical differences between locations and season were tested by Kruskal-Wallis.

Spatial and temporal variation in environmental parameters and benthic community composition were analyzed using the software PRIMER 7 and PAST. Prior to analysis, means of physicochemical parameters were log-transformed and standardized and resemblance matrices were calculated based on Bray-Curtis similarity. Differences in environmental parameters between locations and seasons were examined with Non-Metric Multidimensional Scaling (nMDS) and tested with Two-Way Crossed Analysis of Similarities (ANOSIM) and Permutation Multivariate

Analyses of Variance (PERMANOVA). Additionally, environmental parameters were graphically examined using Principal Component Analysis (PCA) and box-plots.

To estimate the contribution of the main biological processes driving the carbon cycle in our study locations on an annual basis we used the approach proposed by Albright et al. (2013), based on the fact that net organic carbon production (photosynthesis-respiration) and net inorganic carbon production (calcification-dissolution) processes affect A_T and C_T in a different way (Suzuki and Kawahata, 2004). According to the theoretical stoichiometric relationship between these processes and A_T and C_T , when calcification occurs C_T is reduced by two mol and A_T by one mol, whereas photosynthesis decreases C_T by one mol while A_T increases only by 0.15 mol (Zeebe and Wolf-Gladrow, 2001). Therefore, the slope of the C_T - A_T relationship indicates the balance between the net organic and inorganic carbon metabolism. The ratio between these metabolic processes (organic carbon production:inorganic carbon production) is given by the equation $(2/m)-1$, where m is the slope of the C_T - A_T relationship (Albright et al., 2013).

For analysis of the benthic community composition, we calculated average coverage of each benthic category, Shannon-Wiener diversity index (H') and Pielou's evenness (J') for each location and compared them using a non-parametric test Kruskal-Wallis. The average values of benthic composition were overlaid on top of the nMDS plot to find patterns in species composition between locations.

Finally, it is important to keep in mind that all meteorological data used in this study were obtained from the closest stations to our study areas, not measuring the conditions exactly at our sampling locations. Santa Rosa meteorological station for example, is about 20 km southeast from Santa Elena. For this reason, we have used wind speed and rainfall data to explain general patterns and tendencies, but not for direct statistical correlations.

5.3 Results

Environmental parameters

Average (\pm standard deviation) of measured parameters, independent of seasons, showed that in the northernmost location (Santa Elena) the coastal waters are cooler (25.3 ± 3.3 °C, $H = 6.71$, $p = 0.03$) and more saline (34.3 ± 0.8 psu, $H = 22.51$, $p < 0.01$) than the other locations (Supplementary Table 5.1, 5.2). Matapalo, located more than 55 km south from Santa Elena and more than 280 km north from Marino Ballena, resembles Santa Elena in terms of salinity (34.0 ± 0.2 psu) but with an average SWT (28.4 ± 0.6 °C) which is comparable to Marino Ballena (27.9 ± 0.8 °C). At Marino Ballena, the southernmost location, coastal waters are less saline (29.4 ± 1.7 psu) as compared to the other locations (Supplementary Table 5.1, 5.2). Concentrations of PO_4^{3-} and NO_3^- were the highest in Santa Elena, whereas Marino Ballena holds the

highest average concentrations of $\text{SiO}(\text{OH})_3^-$ and NO_2^- (Supplementary Table 5.1, 5.2). The $n\text{A}_\text{T}$ values in Santa Elena ($< 2200 \mu\text{mol kg}^{-1}$) were similar to those determined in Matapalo but lower than in Marino Ballena ($< 2300 \mu\text{mol kg}^{-1}$). On the other hand, in Santa Elena and Marino Ballena $n\text{C}_\text{T}$ showed concentrations of $> 2000 \mu\text{mol kg}^{-1}$ whereas $n\text{C}_\text{T}$ concentrations were lower in Matapalo ($< 2000 \mu\text{mol kg}^{-1}$) (Supplementary Table 5.1, 5.2).

In contrast to Matapalo, $n\text{A}_\text{T}$ and $n\text{C}_\text{T}$ revealed pronounced seasonal changes in Santa Elena and Marino Ballena (Supplementary Table 5.1, 5.3). During the dry season Santa Elena experienced an increase in salinity, $n\text{A}_\text{T}$ and $n\text{C}_\text{T}$ as well as sharp drop in SWT. At Marino Ballena an increase of $n\text{A}_\text{T}$ and $n\text{C}_\text{T}$ was accompanied by a slight decrease of salinity and SWT during the rainy season, whereas SWT, salinity, $n\text{A}_\text{T}$ and $n\text{C}_\text{T}$ remains similar during both seasons in Matapalo ($p > 0.05$, Supplementary Table 5.1, 5.3).

Meteorological parameters indicate that Marino Ballena was the location with the lowest wind speeds ($1.3 \pm 0.7 \text{ m s}^{-1}$) and highest rainfall ($18.5 \pm 15.4 \text{ mm day}^{-1}$) during the study periods. Matapalo was the other extreme with highest wind speed ($5.3 \pm 3.1 \text{ m s}^{-1}$) and lowest rainfall ($0.6 \pm 1.5 \text{ mm day}^{-1}$). At Santa Elena wind speeds and rain were $2.3 \pm 1.3 \text{ m s}^{-1}$ and $1.8 \pm 3.6 \text{ mm day}^{-1}$, respectively (Supplementary Table 5.1, 5.2, 5.3).

The nMDS plot shows spatial and temporal differences in physicochemical parameters, resulting in three separate groups according to location and season (Supplementary Figure 5.1). Marino Ballena sites form a single unit indistinctly of season, grouped with Matapalo-dry season data points. Matapalo-rainy and Santa Elena-rainy fall in one group. Finally, Santa Elena-dry season points represent another group (Supplementary Figure 5.1). Significant differences in physicochemical parameters between locations were confirmed with the analysis of similarities ($R = 0.94$, $p = .001$) and PERMANOVA ($F = 33.8_{26,31}$, $p = .001$). The latter analysis also revealed significant differences between seasons ($F = 91.9_{26,31}$, $p = .001$) and a significant interaction between location and season ($F = 84.7_{26,31}$, $p = .001$). Plotting of individual parameters by location (Fig. 5.2) shows that the magnitude of physicochemical variation varies when moving from north to south. Santa Elena reefs are exposed to a high variation of environmental conditions with extreme values (Supplementary Table 5.1), while the range of variation in Matapalo is lower than in Santa Elena with salinity and $n\text{A}_\text{T}$ as the most stable parameters. The fluctuation of most environmental conditions in Marino Ballena is also lower when compared to Santa Elena.

According to the PCA (Fig. 5.3), five main water parameters explained 92.3% of the variance of the environmental conditions in coastal waters along the Costa Rican Pacific. Silicate (0.646), $n\text{A}_\text{T}$ (-0.322) and $n\text{C}_\text{T}$ (-0.301) contributed 69.3% to the variance (PC1); whilst phosphate (0.456), nitrate (0.437) and silicate (-0.466) explained a further 23.0% (PC2). Graphical analysis of salinity normalized values ($n\text{A}_\text{T}$ vs. $n\text{C}_\text{T}$) (Fig. 5.4)

indicates that Marino Ballena had higher nA_T than the other locations, with a steep increase in nA_T and nC_T during rainy season. Santa Elena was the location with highest nC_T values occurring specifically during dry season. Measured parameters in Matapalo were the lowest and had similar values during both seasons, overlapping with values measured in Santa Elena during rainy season.

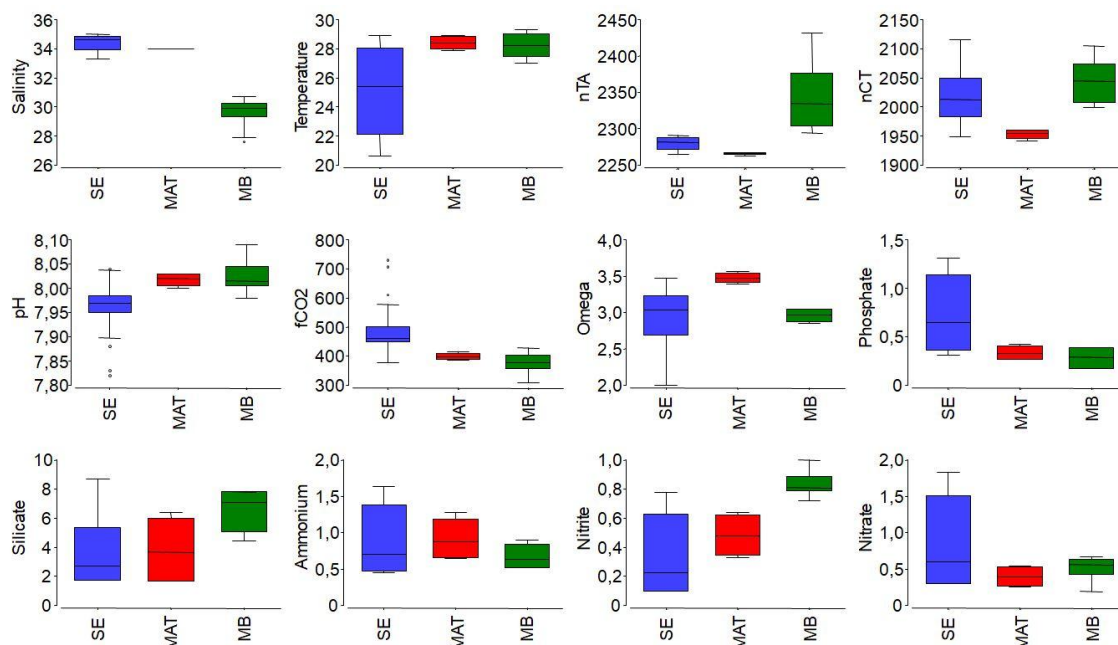


Figure 5.2. Gradient distance to upwelling in the variation of the water parameters along the Pacific coast of Costa Rica. SE = Santa Elena, MAT = Matapalo, MB = Marino Ballena. See Fig. 5.1 for location of study areas.

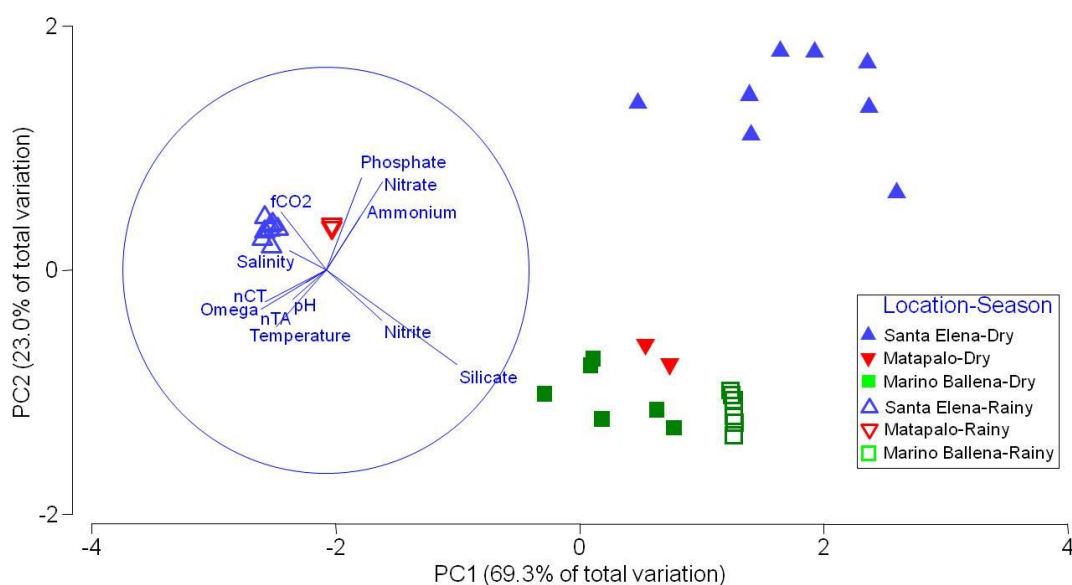


Figure 5.3. Spatial and temporal variation of environmental parameters. Analysis by location, season and tide based on Principal Component Analysis (PCA). PC1 correlates positively to silicate (0.646) and negatively to nA_T (-0.322) and nC_T (-0.301). PC2 correlates positively to phosphate (0.456) and nitrate (0.437) and negatively to silicate (-0.466).

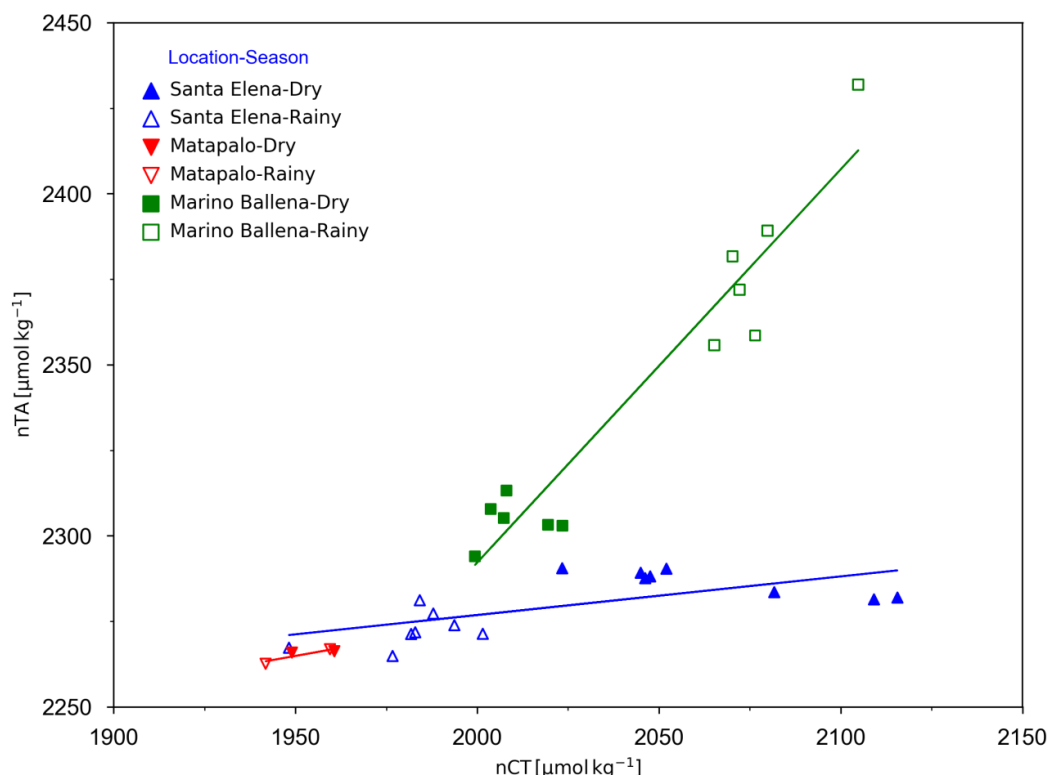


Figure 5.4. Dissolved inorganic carbon versus total alkalinity measured in three locations at the Pacific coast of Costa Rica. A_T and C_T were normalized to a salinity of 35 ($nA_T = A_T \times 35/S$, $nC_T = C_T \times 35/S$; S corresponds to the salinity measured in situ). The slope of the C_T - A_T relationship indicates the balance between the organic (photosynthesis-respiration) and inorganic (calcification-dissolution) metabolism. The ratio between organic carbon production:inorganic carbon production is given by the equation $(2/m)-1$.

Benthos composition

In all locations, the categories “Bleached” and “Others” accounted for less than 0.1% and < 1.0% of benthic coverage, respectively, and were excluded from all graphical analysis but the nMDS overlay. There were no significant differences in benthic composition between locations (Kruskal-Wallis, $H = 0.02734$, $p = 0.9864$). Richness (S), diversity (H') and evenness (J') were also similar for all locations (Table 5.3). Reefs in Santa Elena are mainly composed by live coral ($32.0 \pm 28.8\%$), turf ($24.3 \pm 29.0\%$), coralline algae ($16.7 \pm 14.8\%$), substrate ($15.4 \pm 13.9\%$) and dead coral ($11.0 \pm 21.3\%$). Matapalo reef has three major categories, coralline algae ($34.1 \pm 11.6\%$), live coral ($30.4 \pm 6.9\%$) and turf ($30.2 \pm 10.9\%$). The reef evaluated in Marino Ballena is similar to Matapalo reef in terms of the categories that dominate the benthos, although there are differences in the percentages of cover (CA = $48.5 \pm 6.3\%$, live coral = $23.5 \pm 3.2\%$, turf = $17.5 \pm 7.7\%$). Macroalgae were only observed in Santa Elena ($0.1 \pm 0.3\%$) and Matapalo ($2.9 \pm 3.5\%$). Cyanobacteria were present in all locations but had a very low coverage; the highest value was quantified in Marino Ballena ($2.0 \pm 1.7\%$) (Fig. 5a). Regarding coral species, the reefs in the north are mainly built by *Pavona gigantea* and *Pocillopora* spp. with a minor contribution of *Pavona varians*, whereas southern reefs

are built by *P. clavus* and *P. cf. lobata* with minor contribution of *Psammocora stellata* and *Porites panamensis* (Fig. 5.5b).

Table 5.3. Species richness (S), diversity (H') and evenness (J') in coral reefs at three locations in the Pacific coast of Costa Rica.

LOCATION	S	H'	J'
Santa Elena	9	0.68	0.72
Matapalo	9	0.56	0.59
Marino Ballena	7	0.57	0.68

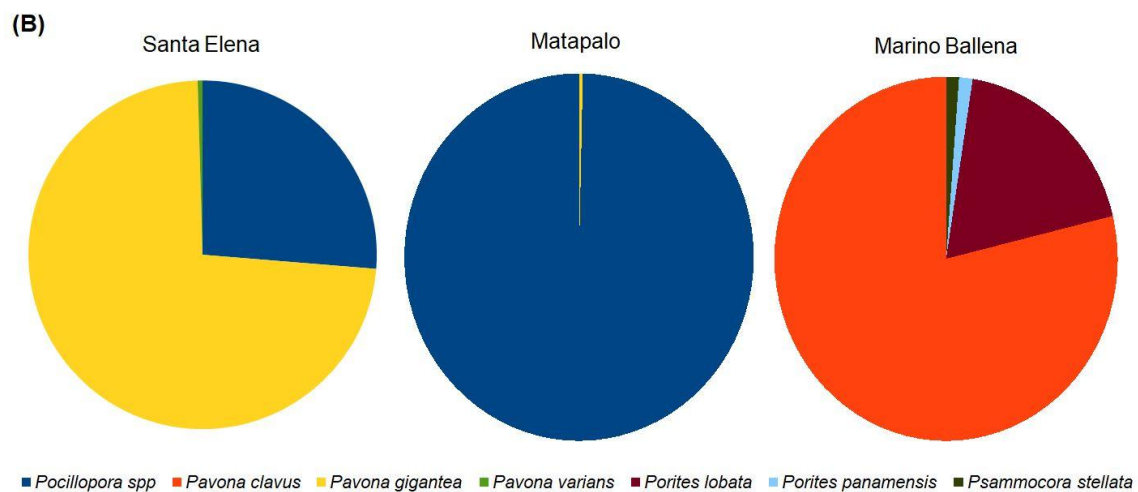
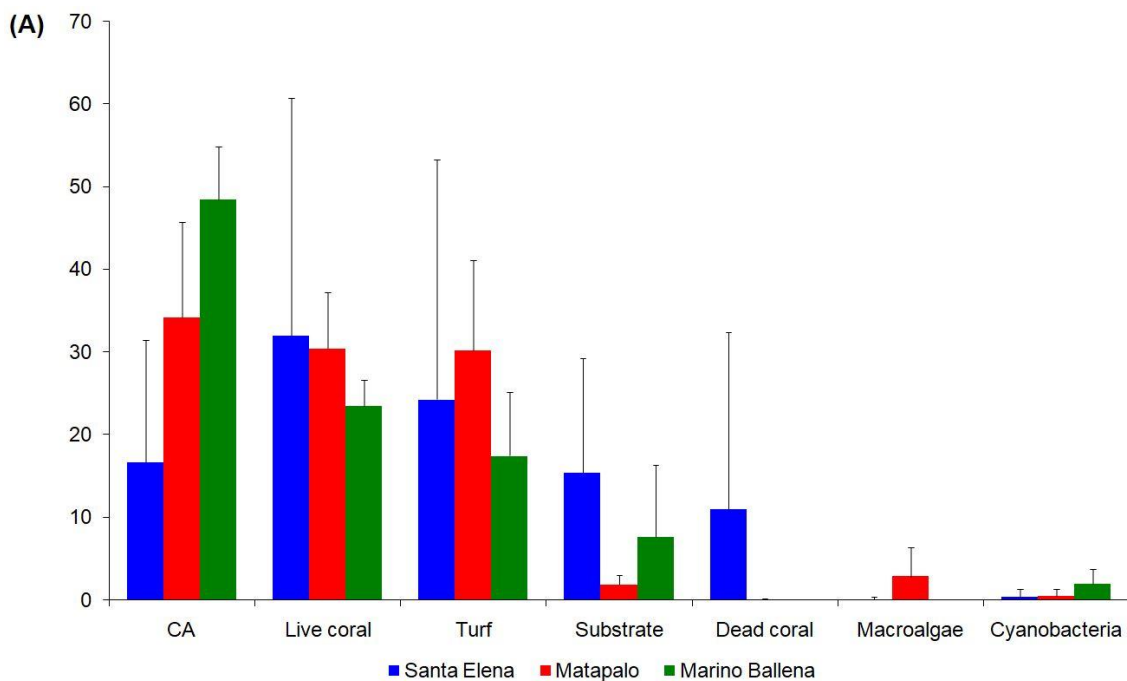


Figure 5.5. Benthic cover along the Pacific coast of Costa Rica. (A) Percentages of benthic cover in coral reefs from three locations; CA = coralline algae. (B) Contribution (%) of coral species to benthic community.

5.4 Discussion

Evidence of a geographical gradient in the environmental conditions along the Pacific coast

The differences in local environmental conditions reflect a gradient of upwelling influence from north to south (Fig. 5.2). Seasonality seems to be controlled by the occurrence of upwelling in the north and by the development of the rainy season in the south. Our results demonstrate that upwelling influences are not restricted to the decrease in SWT and increase in nutrient concentrations (Fernández-García et al., 2012; Jiménez, 2001c), but is also characterized by an increase in nC_T with an associated drop in pH and omega. Furthermore, a parallel study by Stuhldreier et al. (2015b) demonstrated that there is a gradient in the upwelling intensity between Santa Elena and Matapalo, with a more pronounced variability in physicochemical parameters in Santa Elena. Our results allow the comparison not only between northern locations but also with southern sites. Consequently, Matapalo can be recognized as a “transition location” between the northern (strongly influenced by the upwelling) and the southern (non-upwelling area) Pacific. In the following we will discuss the individual environmental parameters in more detail.

Seawater temperature and salinity: SWT exhibits a reverse seasonality between northern (Santa Elena and Matapalo) and southern (Marino Ballena) locations. Coastal waters in the north are colder from December to April due to the upwelling and start to get warmer around May (Alfaro et al., 2012; Alfaro and Cortés, 2012) during the transition to the rainy season. The range of SWT fluctuations in Santa Elena is very high during upwelling season (Cortés et al., 2014; Stuhldreier et al., 2015b) and although the lowest value measured during our study was 18°C, previous studies indicated that SWT in this area can drop down to values of < 14.0°C in the course of upwelling events (Jiménez, 2001c). Conversely, in southern sites the coastal waters experience a slight cooling during the second half of the year, as the rainy season develops.

This cooling during the rainy season is related to the greater freshwater input from numerous rivers near Marino Ballena. The Térraba River, for example, is located about 10 km southwest from Marino Ballena and drains one of the largest basins in the country (Krishnaswamy et al., 2001). Mean annual precipitation and flow discharge are significantly higher than any other basin in the north (Waylen and Laporte, 1999). The average water temperature of this river is 25°C (Umaña-Villalobos and Springer, 2006) and the river discharge is enhanced between the months of May and November (Rojas and Rodríguez, 2008), producing the cooling of the surface waters and decrease of salinity to values of 26.0 psu (this study; Alvarado and Aguilar, 2009).

Nutrients: our results confirm that the high variability of nutrient concentrations in Santa Elena during the dry season is driven by the Papagayo upwelling, with a significant increase of the mean values by 69% (phosphate), 80% (nitrate) and 65% (ammonium) as compared to the non-upwelling rainy season. On the other hand, the

inorganic nutrient concentrations in Marino Ballena increased during the rainy season as a result from runoff and river discharge. In these southern sites, land erosion and runoff strongly contribute to the nutrient input carried by the Térraba River discharge (Alvarado et al. 2009) and other rivers in the area. Consequently, the average concentration of silicate was 48% higher as compared to the dry season (Fig. 5.3), and phosphate and nitrate also had a significant increase in their concentrations during the rainy season of up to 125% and 74%, respectively. Despite the mechanisms by which inorganic nutrients affect coral reefs are subject to debate, there is a general consensus that unbalanced nutrient enrichment from anthropogenic sources poses negative effects for coral reef functioning (D'Angelo and Wiedenmann, 2014). For example, high nutrient loads have the potential to affect corals indirectly by decreasing their skeletal density (Manzello et al., 2014), favoring primary producers which can outcompete stony corals (Fernández-García et al., 2012) and increasing bioerosion by facilitating shifts to larger and more effective bioeroders (Wizemann et al., 2018).

Carbonate chemistry parameters: the spatial and temporal analysis of our data supports two major assumptions: 1) there is an upwelling-driven geographic gradient in alkalinity, dissolved inorganic carbon and pH, and 2) seasonal variability in carbonate chemistry in northern locations are mainly driven by the Papagayo upwelling during the dry season and by the river discharges during the rainy season in the south. Dynamics of Ω_a and pH in coastal areas are driven by several processes: i) upwelling of high- CO_2 waters (Feely et al., 2008; Harris et al., 2013; Rixen et al., 2012; Sánchez-Noguera et al., 2018b), ii) metabolic processes (planktonic communities and coral reefs) (Albright et al., 2013, 2015; Gray et al., 2012) and iii) inputs from land (Carstensen and Duarte, 2019; Dong et al., 2017; Vargas et al., 2016). In this study, the northernmost (Santa Elena) and southern (Marino Ballena) locations both experienced low Ω_a values; however, the source of these reduced values and its variability differed between locations. In Santa Elena, the lower pH and Ω_a was linked to the upwelling of waters with high- CO_2 concentrations (Rixen et al., 2012), whereas in Marino Ballena the dilution effect by freshwater input (river discharges and runoff, both increased during rainy season) was likely responsible for the observed decrease in Ω_a values (Chierici and Fransson, 2009; Harris et al., 2013).

By analyzing the coupled changes of alkalinity and dissolved inorganic carbon (Fig. 5.4) in combination with the estimated organic carbon production:inorganic carbon production ratios, we can shed light on which processes are exerting a major control over the carbonate system in our study locations. The high temporal variability of nC_T measured in Santa Elena alongside an organic carbon production:inorganic carbon production ratio of 16.71, indicates that in addition to upwelling of CO_2 enriched waters, organic metabolism is responsible for the observed seasonal fluctuation in this location. It is also with the analysis of the effect of different processes in alkalinity and dissolved inorganic carbon (Fig. 5.4) that we confirm that respiration in Santa Elena

increased in upwelling season, while photosynthesis was enhanced during the rainy season. Similarly, in the California Current System the high concentration of dissolved inorganic carbon is mostly attributed to respiration-derived CO_2 (Hauri et al., 2009). As in other upwelling systems, is very likely that the enrichment of dissolved inorganic carbon and alkalinity measured in Santa Elena results from respiration processes and the dissolution of CaCO_3 in deep waters (Hauri et al., 2009; Millero et al., 1998), respectively. In Matapalo, an organic:inorganic ratio of 9.49 still emphasizes the relevance of the organic metabolism for the carbonate chemistry in northern locations. Additionally, the small variability measured in alkalinity and dissolved inorganic carbon in combination with higher pH (> 8.0) and Ω_a (> 3.4) values, suggests that CaCO_3 is precipitated all year around. Finally, the coupled increase of alkalinity and dissolved inorganic carbon recorded in Marino Ballena, suggest that the dissolution of CaCO_3 is a regular process taking place at water depth < 15 m during rainy season. An estimated organic carbon production:inorganic carbon production ratio of 0.74 confirmed this assumption. Dissolution and thus inorganic carbon processes seem to exert a main control on the carbonate chemistry in Marino Ballena during the rainy season (Fig. 5.4).

The dissolution of carbonates explains the compared to other locations high $n\text{A}_\text{T}$ and $n\text{C}_\text{T}$ in Marino Ballena during rainy season, but the question remains why $n\text{A}_\text{T}$ and $n\text{C}_\text{T}$ are also enhanced during the dry season. Considering that the Térraba River drains the largest karstic region in Costa Rica (about 185 km^2 of extension) (Bolz and Calvo, 2018; Ulloa et al., 2011) is very likely that surface and groundwater discharges supply dissolved carbonates to the reefs (Krishnaswamy et al., 2001). Since in Marino Ballena the pH is as low as in Santa Elena, river discharges must also contain a significant contribution of dissolved inorganic carbon from the respiration of soil organic matter.

Environmental conditions shape coral reef composition in the Costa Rican Pacific coast

Despite all study locations had similar benthic richness and diversity; the main reef-building corals were different along the Costa Rican Pacific coast (Fig. 5.5b). Reefs from northern locations are dominated by massive and branching species, whereas reefs from the southern part of this coast are mostly comprised by, but no restricted to, massive ones (Glynn et al., 2017a). Some branching-coral reefs have been reported in southern locations (Cortés and Jiménez, 1996; Guzmán and Cortés, 1989a) but they are surpassed in number by massive-coral reefs and these locations were not surveyed during this study due to logistic reasons. The aforementioned coral distribution patterns raise two main questions: 1) why massive coral species building reefs in the north (*P. gigantea* and *P. clavus*) are different from massive species in the south (*P. cf. lobata* and *P. clavus*) (Fig. 5.5)? and 2) why branching corals are not among the main reef-builders in the south?

The measured physicochemical parameters revealed spatial and temporal differences in the environmental conditions along the Costa Rican Pacific coast; however it seems insufficient to understand why the main reef-building species differ between locations. In order to find a possible explanation for these coral distribution patterns, we also compared our local values with the environmental conditions determined in coral reefs on a global scale (Table 5.4) (Guan et al., 2015). These global values were used to update the ReefHab model (Kleypas, 1995, 1997), originally developed to predict the potential distribution of coral reefs according to the available environmental data. Kleypas' work was a milestone which stated for the first time the environmental tolerance limits for coral reefs, and therefore contributed to understand and predict their global distribution. The comparison of the environmental conditions in the Pacific coast of Costa Rica (this study) with the global tolerance limits derived from the updated ReefHab model (Guan et al., 2015) (Table 5.4) revealed that the composition of the dominant coral species in our study locations can be mainly explained by differences in phosphate, omega and salinity, as these parameters divert from the global tolerance thresholds in different ways.

Table 5.4. Global thresholds of environmental parameters for coral reefs and environmental conditions in three coral reefs from the Pacific coast of Costa Rica.

Parameter	Global (Guan et al. 2015)	Santa Elena (average)	Matapalo (average)	Marino Ballena (average)
Temperature (range)	21.7-29.6	22.0-28.1	28.0-28.8	27.5-29.0
Salinity (range)	28.7-40.4	33.9-34.9	34.0-34.0	29.1-34.0
NO ₃ ⁻ (max)	4.51	1.47	0.52	0.64
PO ₄ ³⁻ (max)	0.63	1.14	0.40	0.39
Omega (min)	2.82	2.38	3.44	2.93

Our results confirm that main reef-builders in the north Pacific coast of Costa Rica (*P. gigantea* and *Pocillopora* spp.) are highly tolerant to the episodic exposition to low-omega cool waters and eutrophic conditions occurring during upwelling events (Jiménez, 2001c; Rixen et al., 2012; Stuhldreier et al., 2015a, 2015b). Conversely, the dominant species in Marino Ballena (*P. cf. lobata* and *P. clavus*) thrive in southern locations because they cope very well with the combination of low-omega and low salinities, in addition to the terrigenous input during rainy season (Alvarado et al., 2009). This also agrees to results obtained from other studies. For example, in Papua New Guinea *P. lobata* cope with low pH around underwater seeps (Fabricius et al.,

2011) and in the Pacific coast of Panamá *Pavona* corals exhibited a high tolerance to the combination of thermal stress and acidification during upwelling (Manzello, 2010a), which could explain the success of these genera in Santa Elena and Marino Ballena.

Now that we have attempted to explain the differences in the distribution of the main reef-building massive species, we can move on to our second question, regarding the minor contribution of branching corals in southern locations. In Costa Rica, most reefs built by *Pocillopora* spp. have experienced severe mortalities, frequently attributed to warming during ENSO events and to recurrent occurrence of harmful algal blooms (Guzmán et al., 1987, 1990, Jiménez et al. in prep.). Nevertheless, the current distribution of branching corals and the remaining structures of former reefs can be used as a proxy to identify the most favorable conditions for the success of these species along this coast. Something to keep in mind is that branching corals are not completely absent from the south and they even manage to build small reefs southwest of Marino Ballena (Cortés and Jiménez, 1996; Guzmán and Cortés, 1989a), but massive species are more successful building reef structures at these locations. Therefore, the broad distribution of branching corals along this coast suggests that they cope well with the varied range of conditions in all the study locations. But why are branching corals not frequently found among the main reef-builders in the south? There is an additional factor to consider, which was not measured in this study but definitively makes a difference between northern and southern locations: the contribution of terrigenous materials by river discharge. River discharge are higher in the south as in the north. Alvarado et al. (2005) have previously discussed that the scarceness of *Pocillopora* in Marino Ballena could be related to the low light penetration depth in the water column, due to high concentrations of suspended matter derived from river discharges (Alvarado et al., 2009) (Alvarado et al., 2009) (Alvarado, Fernández, and Cortés 2009) (Alvarado et al., 2009) (Alvarado et al., 2009) (Alvarado et al., 2009) (Alvarado et al., 2009). Accordingly *Pocillopora* seems to be very sensitive to low salinity and low light conditions, whereas massive species such as *P. cf. lobata* - which is one of the main reef-builders in that area - are known to be very tolerant to low salinities (Marcus and Thorhaug, 1982) and high sedimentation (Cortés, 1990).

The results presented in our study provide an interesting hint to adaptation limits of individual coral species to local environmental conditions, as the saturation state of carbonates. For example, the lowest average omega value occurred during upwelling season in Santa Elena (2.38, Table 5.4) and is lower than local (Sánchez-Noguera et al., 2018b) and global threshold values for reef development (2.82, Table 5.4) (Guan et al., 2015). The success of the massive and branching species to build coral reefs along the Pacific coast is a good example of adaptation to high local variability, but this does not guarantee their survival under climate change scenarios, when the rate of changes will be enhanced (Howes et al., 2015). For example, a recent study revealed that at present

the lapse between global bleaching events is about six years, shortening the temporal window for reef recovery after associated mass mortality (Hughes et al., 2018).

5.5 Conclusions

The results from our study demonstrate that seawater chemistry in coastal waters from the Costa Rican Pacific coast display a high variability, which is mainly driven by the Papagayo upwelling system during the dry season in the north and river discharge during the rainy season in the south. Matapalo reef is located between the northernmost (Santa Elena) and the southern location (Marino Ballena) and reveals a relatively low seasonality, which seem to have favored reef development and enhanced the resilience capability. Local coral reefs are adapted to the gradient caused by upwelling in the north and river discharges in the south. However, their level of tolerance to this variability seems to be species specific. Main reef builders in northernmost locations (*P. gigantea*, *Pocillopora* spp. and *P. clavus*) are highly tolerant to low-omega, low water temperature and eutrophic conditions during upwelling events. In contrast, main reef building species in Marino Ballena (*P. cf. lobata* and *P. clavus*) seem to cope well with the combination of low-omega, low salinity and high sedimentation due to inputs from land during the rainy season.

Reef formation demonstrates that corals from the Pacific coast of Costa Rica are adapted to local environmental conditions, but this in turn does not mean that they are tolerant to external perturbations driving environmental conditions towards reef specific limits. Accordingly, Costa Rican coral reefs have experienced several bleaching events during ENSO years in the last three decades. This implies that environmental conditions in the ETP are close to the limits that warm water reef ecosystems can tolerate. With respect to future conservation and reef protection, Matapalo and Marino Ballena appear to be very promising locations due to the relatively stable carbonate chemistry conditions and the buffering effect against ocean acidification caused by inputs of dissolved carbonates from land. However, this calls for integrated coastal management actions which reduce the pressures of local stressors such as siltation, pollution, fishing and tourism.

Acknowledgements

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5.6 Supplementary Tables and figures

Supplementary Table 5.1. Average values of measured and calculated (*) environmental parameters (mean \pm SD) at three locations in the Pacific coast of Costa Rica. SWT measured *in situ* and the other parameters from discrete water samples. Meteorological data collected at meteorological stations located near the study locations was provided by the Instituto Meteorológico Nacional.

	Salinity (psu)	STW (°C)	nA _T ($\mu\text{mol kg}^{-1}$)	nC _T ($\mu\text{mol kg}^{-1}$)	pH* (Total scale)	Omega*
ANNUAL						
Santa Elena	34.3 \pm 0.8	25.3 \pm 3.3	2278.93 \pm 16.63	2027.41 \pm 64.22	7.94 \pm 0.10	2.84 \pm 0.61
Matapalo	34.0 \pm 0.2	28.4 \pm 0.6	2265.62 \pm 14.61	1954.15 \pm 27.99	8.02 \pm 0.04	3.46 \pm 0.22
Marino Ballena	29.4 \pm 1.7	27.9 \pm 0.8	2359.71 \pm 67.48	2059.33 \pm 55.19	8.03 \pm 0.08	2.95 \pm 0.31
DRY SEASON (upwelling)						
Santa Elena	34.9 \pm 0.3	22.2 \pm 1.7	2285.42 \pm 17.92	2079.06 \pm 54.93	7.90 \pm 0.12	2.38 \pm 0.57
Matapalo	34.0 \pm 0.2	28.0 \pm 0.5	2266.09 \pm 15.68	1955.59 \pm 29.33	8.02 \pm 0.04	3.44 \pm 0.21
Marino Ballena	30.2 \pm 0.7	29.0 \pm 0.4	2304.88 \pm 19.68	2009.80 \pm 26.90	8.01 \pm 0.05	2.99 \pm 0.22
RAINY SEASON (non-upwelling)						
Santa Elena	33.9 \pm 0.7	28.1 \pm 0.8	2273.48 \pm 13.29	1984.03 \pm 30.48	7.98 \pm 0.06	3.22 \pm 0.29
Matapalo	34.0 \pm 0.2	28.8 \pm 0.3	2265.22 \pm 13.85	1952.89 \pm 27.18	8.01 \pm 0.04	3.48 \pm 0.23
Marino Ballena	29.1 \pm 1.9	27.5 \pm 0.5	2379.19 \pm 67.76	2076.93 \pm 51.91	8.04 \pm 0.08	2.93 \pm 0.33

Supplementary Table 5.1 (continued)

	PO_4^{3-}	SiO(OH)_3^-	NH_4^+	NO_2^-	NO_3^-	Rain (mm day ⁻¹)	Wind (m s ⁻¹)
ANNUAL							
Santa Elena	0.71 ± 0.51	3.60 ± 3.16	0.89 ± 0.54	0.34 ± 0.31	0.83 ± 0.78	1.8 ± 3.6	2.3 ± 1.3
Matapalo	0.33 ± 0.11	3.72 ± 2.31	0.90 ± 0.39	0.47 ± 0.22	0.40 ± 0.19	0.6 ± 1.5	5.3 ± 3.1
Marino Ballena	0.33 ± 0.10	7.15 ± 1.53	0.60 ± 0.18	0.82 ± 0.22	0.57 ± 0.17	18.5 ± 15.4	1.3 ± 0.7
DRY SEASON (upwelling)							
Santa Elena	1.14 ± 0.47	5.80 ± 3.61	1.37 ± 0.43	0.63 ± 0.22	1.47 ± 0.77	0.0 ± 0.0	3.4 ± 0.8
Matapalo	0.40 ± 0.12	6.05 ± 1.06	1.18 ± 0.40	0.62 ± 0.22	0.26 ± 0.16	0.0 ± 0.0	7.1 ± 3.2
Marino Ballena	0.18 ± 0.07	5.29 ± 2.07	0.82 ± 0.25	0.86 ± 0.42	0.36 ± 0.22	0.5 ± 0.9	1.3 ± 0.7
RAINY SEASON (non-upwelling)							
Santa Elena	0.35 ± 0.05	1.75 ± 0.00	0.48 ± 0.10	0.10 ± 0.00	0.30 ± 0.00	3.3 ± 4.3	1.5 ± 1.0
Matapalo	0.27 ± 0.05	1.69 ± 0.25	0.65 ± 0.10	0.34 ± 0.12	0.52 ± 0.10	1.1 ± 1.9	3.7 ± 1.9
Marino Ballena	0.39 ± 0.00	7.81 ± 0.00	0.52 ± 0.02	0.80 ± 0.07	0.64 ± 0.06	24.9 ± 12.9	1.3 ± 0.7

Supplementary Table 5.2. Statistical differences of environmental parameters between locations. Asterisks indicate significant differences ($p < 0.05$).

	Salinity (psu)	STW (°C)	nA_T ($\mu\text{mol kg}^{-1}$)	nC_T ($\mu\text{mol kg}^{-1}$)	pH (Total scale)	Omega
ANNUAL						
H	22.51	6.71	24.8	10.85	15.96	9.57
P	< 0.01*	0.03*	< 0.01*	< 0.01*	< 0.01*	< 0.01*
DRY SEASON (upwelling)						
H	12.35	12.35	12.35	11.75	9.4	10.89
P	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*
RAINY SEASON (non-upwelling)						
H	10.75	12.07	12.24	12.24	8.294	12.24
p	0.01	< 0.01*	< 0.01*	< 0.01*	0.04*	< 0.01*

Supplementary Table 5.2 (continued)

	PO_4^{3-}	$SiO(OH)_3^-$	NH_4^+	NO_2^-	NO_3^-	Rain (mm day ⁻¹)	Wind (m s ⁻¹)
ANNUAL							
H	6.12	8.70	0.87	18.78	2.42	4.97	15.1
p	0.04*	0.01*	0.65	< 0.01*	0.29	0.07	< 0.01*

DRY SEASON (upwelling)							
H	12.35	1.09	10.66	6.98	11.41	7.35	12.35
p	< 0.01*	0.58	< 0.01*	0.03*	< 0.01*	< 0.01*	< 0.01*
RAINY SEASON (non-upwelling)							
H	12.35	12.35	12.49	12.49	12.49	12.01	5.32
p	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	0.15

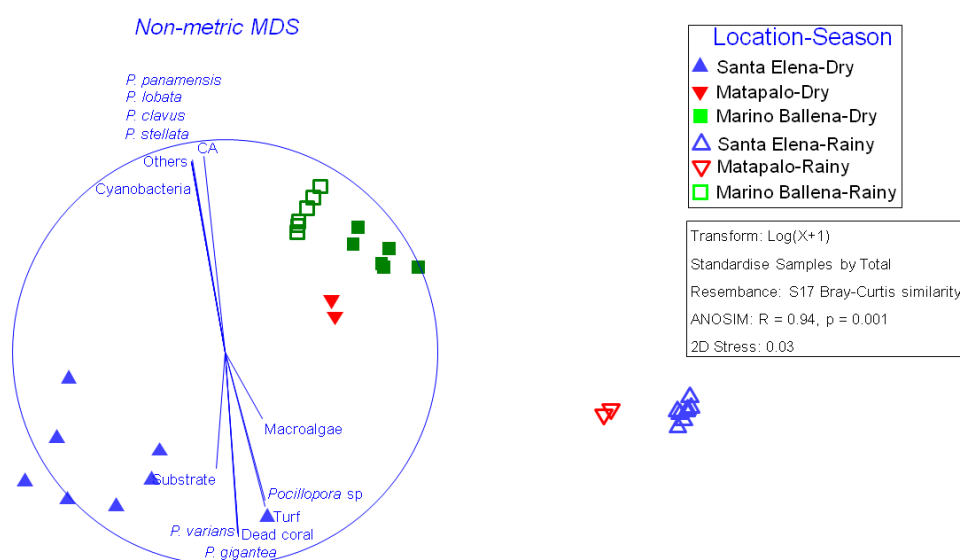
Supplementary Table 5.3. Statistical differences of environmental parameters between seasons. Asterisks indicate significant differences ($p < 0.05$).

	Salinity (psu)	STW (°C)	nA _T (μmol kg ⁻¹)	nC _T (μmol kg ⁻¹)	pH (Total scale)	Omega
SE						
H	7.29	6.72	8.47	9.10	4.04	8.78
P	< 0.01*	< 0.01*	< 0.01*	< 0.01*	0.04*	< 0.01*
MAT						
H	-	2.4	0	0.6	0.15	0.6
P	-	0.12	1	0.44	0.68	0.44
MB						

H	5.77	8.31	8.31	8.31	3.10	1.85
p	0.02*	< 0.01*	< 0.01*	< 0.01*	0.07	0.17

Supplementary Table 5.3 (continued)

	PO_4^{3-}	SiO(OH)_3^-	NH_4^+	NO_2^-	NO_3^-	Rain (mm day ⁻¹)	Wind (m s ⁻¹)
SE							
H	7.87	6.72	11.12	7.29	9.10	8.78	11.12
P	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*
MAT							
H	2.4	2.4	2.4	2.4	2.4	2.4	2.4
P	0.10	0.12	0.12	0.12	0.12	0.10	0.12
MB							
H	8.31	8.31	8.31	0.92	8.31	8.31	0.02
p	< 0.01*	< 0.01*	< 0.01*	0.32	< 0.01*	< 0.01*	0.87



Supplementary Figure 5.1. Spatial differences in benthic composition related to variation of environmental parameters. Differences in environmental parameters between locations and over seasons, according to a Non-Metric Multidimensional Scaling (nMDS) tested with Two-Way Crossed Analysis of Similarities (ANOSIM) and Permutation Multivariate Analyses of Variance (PERMANOVA).

6. RAPID BIOEROSION IN A TROPICAL UPWELLING CORAL REEF

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Abstract

Coral reefs persist in an accretion-erosion balance, which is critical for understanding the natural variability of sediment production, reef accretion, and their effects on the carbonate budget. Bioerosion (i.e. biodegradation of substrate) and encrustation (i.e. calcified overgrowth on substrate) influence the carbonate budget and the ecological functions of coral reefs, by substrate formation/consolidation/erosion, food availability and nutrient cycling. This study investigates settlement succession and carbonate budget change by bioeroding and encrusting calcifying organisms on experimentally deployed coral substrates (skeletal fragments of *Stylophora pistillata* branches). The substrates were deployed in a marginal coral reef located in the Gulf of Papagayo (Costa Rica, Eastern Tropical Pacific) for four months during the northern winter upwelling period (December 2013 to March 2014), and consecutively sampled after each month. Due to the upwelling environmental conditions within the Eastern Tropical Pacific, this region serves as a natural laboratory to study ecological processes such as bioerosion, which may reflect climate change scenarios. Time-series analyses showed a rapid settlement of bioeroders, particularly of lithophagine bivalves of the genus *Lithophaga/Leiosolenus* (Dillwyn, 1817), within the first two months of exposure. The observed enhanced calcium carbonate loss of coral substrate (>30%) may influence seawater carbon chemistry. This is evident by measurements of an elevated seawater pH (>8.2) and aragonite saturation state ($\Omega_{\text{arag}} > 3$) at Matapalo Reef during the upwelling period, when compared to a previous upwelling event observed at a nearby site in distance to a coral reef (Marina Papagayo). Due to the resulting local carbonate buffer effect of the seawater, an influx of atmospheric CO₂ into reef waters was observed. Substrates showed no secondary cements in thin-section analyses, despite constant seawater carbonate oversaturation ($\Omega_{\text{arag}} > 2.8$) during the field experiment. Micro Computerized Tomography (μ CT) scans and microcast-embeddings of the substrates revealed that the carbonate loss was primarily due to internal macrobioerosion and an increase in microbioerosion. This study emphasizes the interconnected effects of upwelling and carbonate bioerosion on the reef carbonate budget and the ecological turnovers of carbonate producers in tropical coral reefs under environmental change.

6.1 Introduction

Tropical coral reefs are among the most productive biogenic calcium carbonate (CaCO₃) producing ecosystems in the world. At the same time the biogenic skeletal CaCO₃ is degraded by means of bioerosion (Neumann, 1966), rendering this process an integral component of the CaCO₃ budget. CaCO₃ bioerosion is a dynamic process pertaining to complex ecological impacts within coral reefs (Tribollet and Golubic, 2011). The intensity and pace of bioerosion influences the cycling of biogenic CaCO₃ and supports the formation of sediment in large buildups such as carbonate platforms

and reef structures (Hallock, 2001; Schlager, 2003; Tucker and Wright, 2009). From the reef ecosystem or colony scale, bioerosion, by way of endolithic (i.e. inside hard substrate) micro- and macrobioerosion, as well as epilithic (i.e. on hard substrate) attachment etching and grazing activity, effects the physical resistance of coral reef framework to extrinsic erosion such as storm surges, thereby further promoting sediment production (Scott and Risk, 1988). However, calcifying bioeroding and encrusting species also bind and cement loose sediments (i.e. form calcareous overgrowth), and create new habitats with consolidated substrate (Davidson et al., 2018; Rasser and Riegl, 2002). In most tropical oligotrophic settings colonization of coral skeletons by bioeroders and encrusters typically occurs within days and is considered to develop a mature community within several months to years (Tribollet and Golubic, 2005). In marginal tropical reef systems colonization and development of a community may be even more rapid and intense. Many marginal reefs are exposed to pronounced environmental changes such as meridional migration of the circulation systems in the ocean and the atmosphere (Guinotte et al., 2003). Upwelling systems can influence such reef ecosystems, temporarily favoring organotrophic composed carbonate communities (Humphreys et al., 2016; Reijmer et al., 2012; Reymond et al., 2016; Westphal et al., 2010). Typically, the ensuing marginal reef settings are non-framework or low-relief coral communities (Perry and Larcombe, 2003). Marginal reefs present an excellent opportunity to investigate carbonate dynamics over time, as transitions in the reef community may occur on a regular base (Glynn and Manzello, 2015). This is pertinent to study as reef bioerosion processes are expected to accelerate under future ocean acidification (Reyes-Nivia et al., 2013; Wisshak et al., 2012) and eutrophication scenarios (Chazottes et al., 2008).

The aim of this study is to investigate how upwelling influences bioerosion patterns and the CaCO_3 budget of bioerosion on substrates in a marginal reef setting located in the Gulf of Papagayo, Costa Rica, Eastern Tropical Pacific (ETP). Therefore, skeletal coral substrates were placed onto the benthic cover in a local coral reef during the upwelling season from December 2013 to March 2014. Monthly recovery of substrates enabled the documentation of the bioeroder and encruster succession at a high temporal resolution. For analysis of macro- and microbioerosion patterns, Micro Computerized Tomography (μCT), thin-sections and cast-embeddings were used together with Scanning Electron Microscopy (SEM). Concomitant measurements of the seawater parameters such as nutrients, temperature, pH, dissolved inorganic carbon (DIC) and total alkalinity (A_T) with calculations of the bioerosion CaCO_3 budget of substrates (net CaCO_3 weight change) allowed further discussion on the correlation of the bioerosive activity to the influence of the ambient seawater properties. Finally, a conceptual environmental model illustrates how bioerosion processes take part in the functioning of marginal reef ecosystems in the ETP.

6.2 Materials and Methods

Environmental setting and study site

The ETP is one of the most productive tropical marine regions due to upwelling of macronutrient-rich subsurface waters into the euphotic zone (Fiedler and Lavín, 2017; Pennington et al., 2006). All along the ETP, continental shelf coral reef ecosystems have developed within the periphery of the optimal environmental conditions for coral growth (in respect to thermal range and turbidity). One of the larger tropical coral reefs off the Pacific coast of Costa Rica is located in the semi-sheltered Bay of Matapalo, which is part of the Gulf of Papagayo (Fig 6.1) (Stuhldreier et al., 2015b, 2015a).

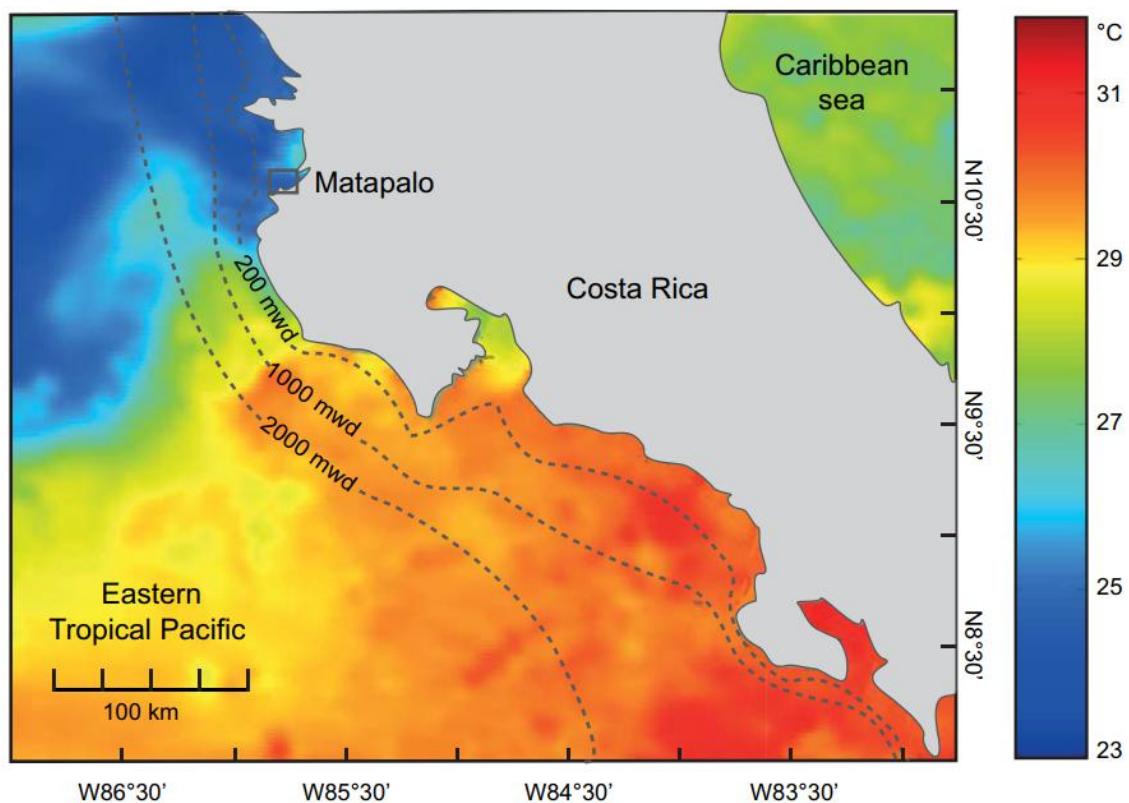


Figure 6.1. Map of the Eastern Tropical Pacific coast of Costa Rica with the location of the study site, Matapalo Reef (10°32'21"N, 85°45'59"W), in the Gulf of Papagayo (small inset). Mean sea surface temperatures (SST) on the right side indicate the oceanic hydrothermal setting during the major upwelling period (17 February 2014). The SST data were derived from daily global maps with a grid map resolution of 1 km (GHRSSST, Level 4, G1SST) produced by the JPL Regional Ocean Modeling System group available from <http://ocean.jpl.nasa.gov/SST/>. The data was visualized with the Ocean Data View software.

During the dry season (December-April; northern winter), the Gulf of Papagayo is exposed to upwelling when the Papagayo jet, a trade wind from the mainland, intensifies (Fig. 6.1) (Glynn, 1977; Glynn and Ault, 2000; Manzello et al., 2008). During

this period, wind-driven upwelling and the seasonal extension of the Costa Rica Dome brings cool (22-26°C), low pH (<8), and nutrient-rich subsurface water into the Gulf of Papagayo (Fiedler, 2002a; Kessler, 2002). Consequently these conditions allow the formation of extensive but poorly developed reefs (Stuhldreier et al., 2015a). In these reefs, bioerosion is an integral part of the reef framework and carbonate sediment production (Alvarado et al., 2017; Glynn, 1990). Sediments at the reef site were comprised of dead coral branches of the genus *Pocillopora* alternating with patches of fine carbonate sand (S6.2 Fig). Such fields of coral rubble form typical substrate of many reefs within the ETP (Enochs, 2012; Glynn, 1976).

Pre-experimental preparations

Similar to the sedimentary substrate at the study site (i.e. coral rubble of *Pocillopora* branches; S6.2 Fig), skeletal framework of a dead *Stylophora pistillata* grown in the marine experimental facility at the Leibniz Centre for Tropical Marine Research (ZMT) in Germany was used in the field experiment (CITES permit number 10314/IV/SATS-LN/2009). Despite being non-native in the ETP, *S. pistillata* is a branching species with calices of comparable size (within a range of ~1.0 to 1.5 mm; e.g. Baird and Babcock, 2000). This coral colony was cut into small cylindrical blocks of approximately 1 cm in diameter and 3 cm in length. To remove any soluble components and organic tissue, the coral substrates were cleaned for 48 h with hydrogen peroxide (H₂O₂ 30%). This was done to avoid abnormal causes for an attraction of bioerosive/encrusting settlers (e.g. molecular/organic sensorial attraction). Subsequently, the cleaned substrates were weighed (Mettler Toledo, AT 21 Comperator; accuracy >0.1 mg) before being deployed in the reef.

Experimental setup

Exposure experiments were conducted during the northern winter upwelling period from December 2013 to April 2014. For this purpose, a total of 16 *S. pistillata* substrates were fixed within custom made plastic frames with angler line, whereby a hole was drilled pre-experimentally in the middle part of each substrate (S6.1 Fig). The frames were placed at Matapalo Reef ~5 m below sea level (bsl) and suspended approximately 0.5 m above the seafloor. To allow undisturbed settlement the coral substrates were uncaged. To identify settling succession and CaCO₃ erosion rates, four replicate coral substrates were retrieved consecutively after one, two, three, and four months of exposure, respectively. However, over the exposure period four of the coral substrates were lost due to external forces (e.g. currents, fish bites, crumbling) resulting in a reduced number of replicates for some of the months. Originally, substrates were deployed in a higher temporal replication at the described study site and also at Bahía Santa Elena (10°56'526"N, 85°48'838"W), located north of Matapalo Reef. Due to major loss of substrates, this study has to focus on the results from Matapalo Reef during the upwelling period. S10 Fig exemplarily presents one substrate

deployed at Bahía Santa Elena on December 11th 2013. The sample was recovered on February 13th 2014 after two months of exposure. Other substrates deployed at Bahía Santa Elena were lost after the second month.

Water parameter measurements

Nutrient concentration, physico-chemical seawater parameters

Seawater nutrient concentration and physico-chemical parameters, such as seawater temperature and salinity, were measured by Stuhldreier et al. (2015b) directly above the reef substrate on a weekly basis. Total scale pH (pH_{Manta}) was measured between December 2013 and April 2014 by deploying a Manta 2 Water Quality Multiprobe (Eureka Environmental Engineering) 0.5 m above the reef substrate. Stuhldreier et al. (2015b) provided further details regarding data processing. Since the pH_{Manta} measurements did not meet the accuracy requested in Dickson et al. (Dickson, 2010), discrete water samples were collected during daytime next to the Manta multiprobe at a water depth of ~6 m. Occasionally, additional surface water samples were collected at a depth of 0.5 m. The results obtained from the surface and bottom water samples were averaged and are presented in Table 6.1. Total alkalinity (A_T) and total dissolved inorganic carbon (DIC) were determined with a titration unit VINDTA 3C (Marianda, Kiel, Germany), which includes a UIC CO₂ coulometer detector (UIC Inc., Joliet, USA). The VINDTA 3C was calibrated using the Dickson Certified Reference Material (Batch 127) (Dickson et al., 2003). Sánchez-Noguera et al. (2018b) describe the method in further detail. This method meets the requested standard (Dickson, 2010) and the program CO₂SYS was used to calculate the $\text{pH}_{\text{VINDTA}}$ (total scale), the $p\text{CO}_2$ and aragonite saturation state (Ω_{arag}). For the calculations, the daily mean seawater temperature and salinity obtained from the Manta multiprobe were used, except on February 3rd and March 31st 2014. At these two days the Manta multiprobe was not deployed and a WTW sensor was used to measure seawater temperature and salinity (Sánchez-Noguera et al., 2018b).

Table 6.1. Monitored and calculated ($\text{pH}_{\text{VINDTA}}$, $f\text{CO}_2$, Ω_{arag}) seawater parameters for carbon chemistry at the study site of Matapalo Reef, Costa Rica. See also S6.2 Table and Fig 6.2a for comparison of pH_{Manta} and $\text{pH}_{\text{VINDTA}}$.

Date (d/m/y)	Time	Depth (m)	A_T ($\mu\text{mol/kg}$)	DIC ($\mu\text{mol/kg}$)	SST (°C)	SSS	pH-cal (total scale)	$f\text{CO}_2$ -cal (μatm)	Ω_{arag} -cal
02/12/2013	16:10	6.00	2211.18	1971.99	25.63	32.52	7.97	479.48	2.81
09/12/2013	15:30	6.00	2106.38	1805.37	27.87	31.08	8.09	330.82	3.49
16/12/2013	15:30	6.00	2093.72	1822.51	28.20	31.00	8.03	385.15	3.18
23/12/2013	15:30	6.00	2072.18	1785.09	28.16	30.68	8.07	343.27	3.35
30/12/2013	15:30	6.00	2078.75	1783.16	28.53	30.70	8.08	335.76	3.45
06/01/2014	14:30	5.00	2086.62	1789.08	28.51	31.19	8.07	339.57	3.45
20/01/2014	13:13	3.25	2213.52	1890.27	26.41	31.92	8.12	318.66	3.73
21/01/2014	08:30	3.25	2218.88	1918.48	26.41	30.54	8.10	345.66	3.55

23/01/2014	11:23	3.25	2209.45	1917.96	26.64	33.31	8.04	391.36	3.34
24/01/2014	13:00	3.25	2224.72	1938.93	25.98	32.02	8.06	381.87	3.33
25/01/2014	11:45	3.25	2207.52	1903.20	26.80	30.50	8.10	340.08	3.59
26/01/2014	12:15	3.25	2169.64	1864.63	27.46	32.98	8.06	360.27	3.49
27/01/2014	12:30	3.25	2185.60	1874.89	27.19	33.13	8.07	353.02	3.55
28/01/2014	08:50	3.25	2198.65	1915.50	27.00	33.90	8.02	412.88	3.24
03/02/2014	12:30	5.50	2179.02	1889.40	27.00	33.65	8.03	390.48	3.30
31/03/2014	12:28	3.00	2256.14	1924.72	25.40	33.67	8.11	337.41	3.75
17/04/2014	10:02	2.25	2263.01	1956.66	27.95	33.64	8.03	404.54	3.55

Post-experimental sample treatment and bioerosion CaCO_3 substrate budget analyses

All coral substrates retrieved were air dried and shipped back to ZMT for further analyses. At ZMT, the coral substrates were digitally photographed and weighed after bleaching with H_2O_2 (30%) for 72 h, which removed organic material (S6.9 Fig). Net erosion rates were calculated from the weight loss of the substrate (normalized to milligrams of CaCO_3 removed per substrate and day). Additionally, percentages of CaCO_3 loss rate per substrate, and monthly means were calculated. A one-way ANOVA test using JMP (version 9.0.2) was conducted to statistically assess the change in CaCO_3 during the four months exposure period. Homogeneity of variance of the means is assumed ($F_{3,8} = 4.10$) based on the Levene's test ($\text{Prob} > F = 0.05$) followed by a Tukey HSD means comparison for each month, which distinguished if means were significantly different from each other. However, it is noted that there is a small sample size and therefore a likelihood of a type II error.

Micro Computerized Tomography (μCT) scanning

Micro Computerized Tomography (μCT) scans were conducted from one control substrate (pre-experiment) and from one substrate of each exposure period (i.e. from each of the monthly recoveries) throughout the field experiment. On top of the substrates a small CaCO_3 body was mounted with modeling clay to facilitate beam hardening correction during the reconstruction process. Substrates were scanned using a Skyscan[®] 1772 μCT scanner (located at Kiel University; Department of Geoscience) with a voxel size of 7-8 μm in 0.9 mm rotational steps and 360° rotation. The raw scan data was reconstructed at ZMT Bremen using the software nRecon with 43% beam hardening correction, no data smoothing and maximum ring artifact reduction accuracy. Voxel-based 3D volume models were visualized with the software CTVox and a color map was applied to discriminate morphological changes due to encrustation and bioerosion (S6.4-S6.8 Figs; S6.10 Fig).

Microbioerosion analyses

Microbioerosion was investigated using Scanning Electron Microscopy (SEM) of cast-embeddings and petrographic thin-sections of the coral substrates. Partially etched (5% HCl solution for approx. 30s) epoxy-resin casts were prepared in a vacuum chamber following the protocol in Wisshak (2012), except for the application of an alternative epoxy resin (R & G cast resin “water-clear” UN3082 + 2735). The casts, showing the positive infill of the bioerosion traces were rinsed with purified water, dried, mounted, and sputter-coated with gold for investigation by SEM with the use of the secondary electron detector at 20 keV (Tescan Vega3 XMU).

For the investigation of microbioerosion from thin-sections, longitudinal and latitudinal petrographic thin-sections of the previously μ CT scanned coral substrates were prepared. For this, substrates were embedded in epoxy and subsequently sections were polished to a thickness of 45 μ m. Thin-sections for SEM analyses were gold-sputtered for 30 s and analyzed using the Back-Scattered Electron detector (BSE) at 10 keV.

For analyses of surface microbioerosion, coral substrates were mounted on SEM stubs with conductible modeling clay (Leit-C plast). The surface of the substrates was then examined using low-vacuum mode and the BSE detector at 20 keV.

6.3 Results

Physico-chemical seawater parameters

Mean seawater temperature during the first two months (December 2013 to January 2014) was 27.2 °C (Fig 6.2a). In February 2014 seawater temperature dropped down to 21.6 °C. This temperature decrease was accompanied by increasing concentrations of dissolved nutrients, indicating a major upwelling event (i.e. cold water intrusions), which lasted for about three to four weeks (Fig 6.2). In 2009, a similar upwelling event was observed 15 km to the northeast at Marina Papagayo, at a site within ~200 m distance to a coral reef, where mean seawater temperature decreased from about 26.3 °C to 23.7 °C (Rixen et al., 2012). Since oxygen-depleted and nutrient-enriched subsurface waters are corrosive (Feely et al., 2008), seawater pH decreased and $p\text{CO}_2$ increased during this upwelling event in 2009. In contrast, during the upwelling event observed in February 2014 at Matapalo Reef, the pH_{Manta} increased from 8.11 to 8.30 (Fig 6.2a). Unfortunately, no DIC and A_T data were obtained during this pronounced upwelling event in 2014 (Fig 6.2a, Table 6.1, S6.2 Table). Prior to and after the upwelling event, pH_{Manta} corresponded with the $\text{pH}_{\text{VINDTA}}$ derived from DIC and A_T measurements. Thus, it is unlikely that the increase of pH_{Manta} during the upwelling is a measurement error. A pH of up to 8.3 was not measured at Marina Papagayo during 2009, 2012 and 2013 (Rixen et al., 2012; Sánchez-Noguera et al., 2018b). Even if this pH_{Manta} reading is considered as erroneously high, it indicates that the pH did rise during the 2014 upwelling event, and not drop as expected. The $\text{pH}_{\text{VINDTA}}$ derived from

DIC and A_T measurements represent daytime values. State of the art pH measurements (Dickson, 2010) at Marina Papagayo (pH 7.9 – 8.05) during the non-upwelling periods in 2012 and 2013, (Sánchez-Noguera et al., 2018b) and the upwelling event in 2009 (Rixen et al., 2012) indicated a diurnal pH variability of less than ± 0.15 . During the non-upwelling periods the pH was generally lower at night and increased from the early morning hours until the late afternoon. During the upwelling season the intrusion of corrosive subsurface water largely masked the diurnal trend (Rixen et al., 2012).

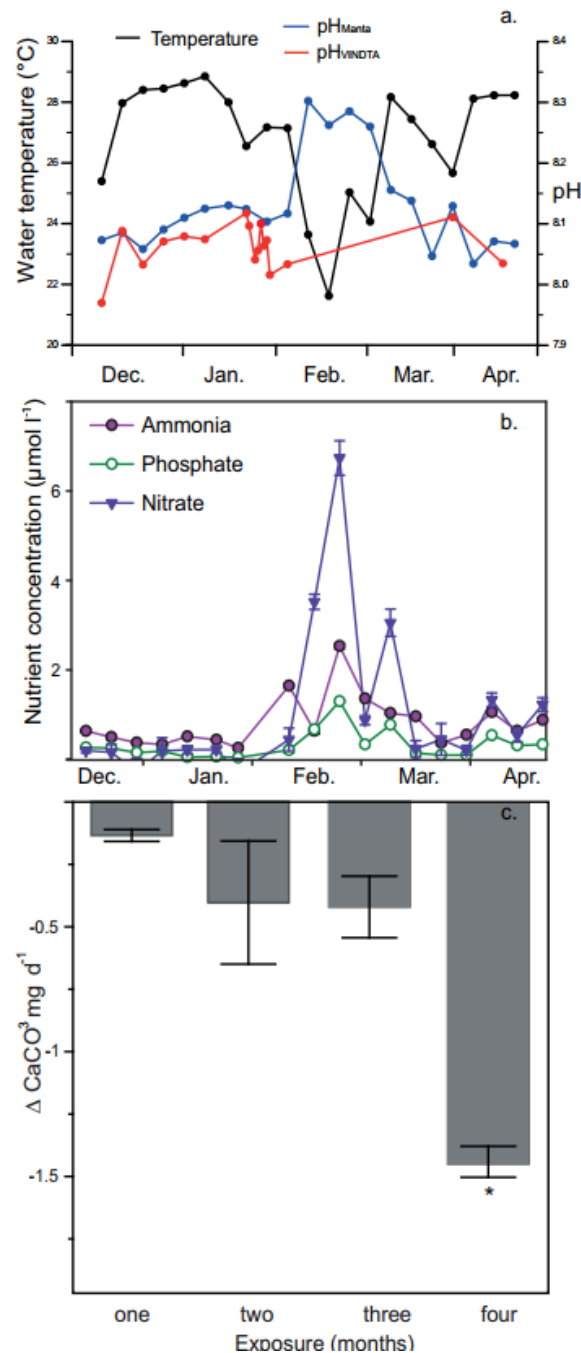


Figure 6.2. Graphs showing a) daytime means of seawater temperature, pH_{Manta} (total scale) and $\text{pH}_{\text{VINDTA}}$ (total scale), b) nutrient concentrations of nitrate, ammonia and phosphate, and c) bioerosion CaCO_3 budget of the experimental coral substrate

through time (with standard deviation, black bars). Temperature, pH_{Manta} and nutrient data modified after Stuhldreier et al. (2015b).

At Matapalo Reef, Ω_{arag} derived from A_T and DIC measurement ranged between 2.8 and 3.7 (mean 3.4 ± 0.2 ; Table 1) over the experimental period and mostly exceeded the global means of ~ 2.9 (Kleypas and Langdon, 2006). The $f\text{CO}_2$ varied between 318.7 and 479.5 μatm with an average of $367.7 \pm 40.4 \mu\text{atm}$ (Table 6.1). During the period of observation the atmospheric CO_2 concentrations increased from ~ 394 to ~ 401 ppm as measured at Mauna Loa in the central Pacific Ocean (NOAA, Earth System Research Laboratory, Global Monitoring Division). This indicates an influx of atmospheric CO_2 into the seawater surrounding Matapalo Reef. In contrast, during the upwelling event in 2009 at Marina Papagayo seawater $p\text{CO}_2$ exceeded atmospheric CO_2 and thus CO_2 was emitted. In addition to upwelling, the intrusion of subsurface water via enhanced wind mixing increased seawater $p\text{CO}_2$ from $\sim 320 \mu\text{atm}$ to $\sim 600 \mu\text{atm}$ during the non-upwelling period in 2009 (Rixen et al., 2012), similar to observations in 2012 (Sánchez-Noguera et al., 2018b).

Nutrient concentrations

Mean concentrations of nitrate were $0.09 \pm 0.10 \mu\text{mol/L}$ in the first month, $0.97 \pm 0.87 \mu\text{mol/L}$ in the second month, $2.72 \pm 1.47 \mu\text{mol/L}$ in the third month (upwelling pulse), and $0.63 \pm 0.24 \mu\text{mol/L}$ in the fourth month (Fig 6.2b). With the onset of upwelling during the third month, nitrate concentrations peaked at $6 \mu\text{mol/L}$ (Fig 6.2b). Mean concentrations of ammonia were $0.47 \pm 0.05 \mu\text{mol/L}$ in the first month, $0.74 \pm 0.31 \mu\text{mol/L}$ in the second month, $1.47 \pm 0.36 \mu\text{mol/L}$ in the third month (upwelling pulse), and $0.65 \pm 0.01 \mu\text{mol/L}$ in the fourth month (Fig 6.2b). Concentrations of ammonia peaked in the third month at $\sim 3 \mu\text{mol/L}$ corresponding with the onset of upwelling (Fig 6.2b). Mean concentrations of phosphate were $0.18 \pm 0.04 \mu\text{mol/L}$ in the first month, $0.24 \pm 0.15 \mu\text{mol/L}$ in the second month, $0.63 \pm 0.26 \mu\text{mol/L}$ in the third month (upwelling pulse), and $0.26 \pm 0.11 \mu\text{mol/L}$ in the fourth month (Fig 6.2b). Concentrations of phosphate peaked at $\sim 1 \mu\text{mol/L}$ during the third month (Fig 6.2b).

Settlement succession of calcifying organisms

The calcifying community that developed inside and on the coral substrates consisted of phototrophic and organotrophic organisms. From μCT scans, photographs, and thin-sections the following calcifying genera were identified (Figs 6.3-6.5; S6.5-S6.9 Figs): crustose coralline red algae (CCA), biomineralizing polychaetes (serpulid worms), encrusting bryozoans, encrusting benthic foraminifers (*Homotrema rubrum*), lithophagine bivalves (S6.11 Fig, *Lithophaga* (*Leiosolenus*) cf. *aristata* (Dillwyn, 1817); (Kleemann, 2013), Leon Hoffmann, pers. comm.), and balanids (acorn barnacles). The settlement of the calcifiers followed a temporal trend. Crustose coralline red algae (CCA) and serpulid worms were primary settlers (present after one month; Figs 6.3c and 6.5b). Bryozoans and balanids were observed after two months, increasing in

abundance with time of exposure (Figs 6.3c, d, e, 6.5b, c, d). Likewise, lithophagine bivalves were first observed after two months (Figs 6.3d and 6.4b). The number and size of the bivalves increased rapidly after three and four months of exposure (Fig 6.4d, e). However, reaching only 2 to 3 mm in size, the bivalves were still in a juvenile stage at the end of the experiment. The benthic foraminifer species *H. rubrum* was present from the second month onward (Fig 6.3d), encrusting the surface of the coral substrate between corallites (i.e. coenosteum) (Fig 6.3d, f, h, k).

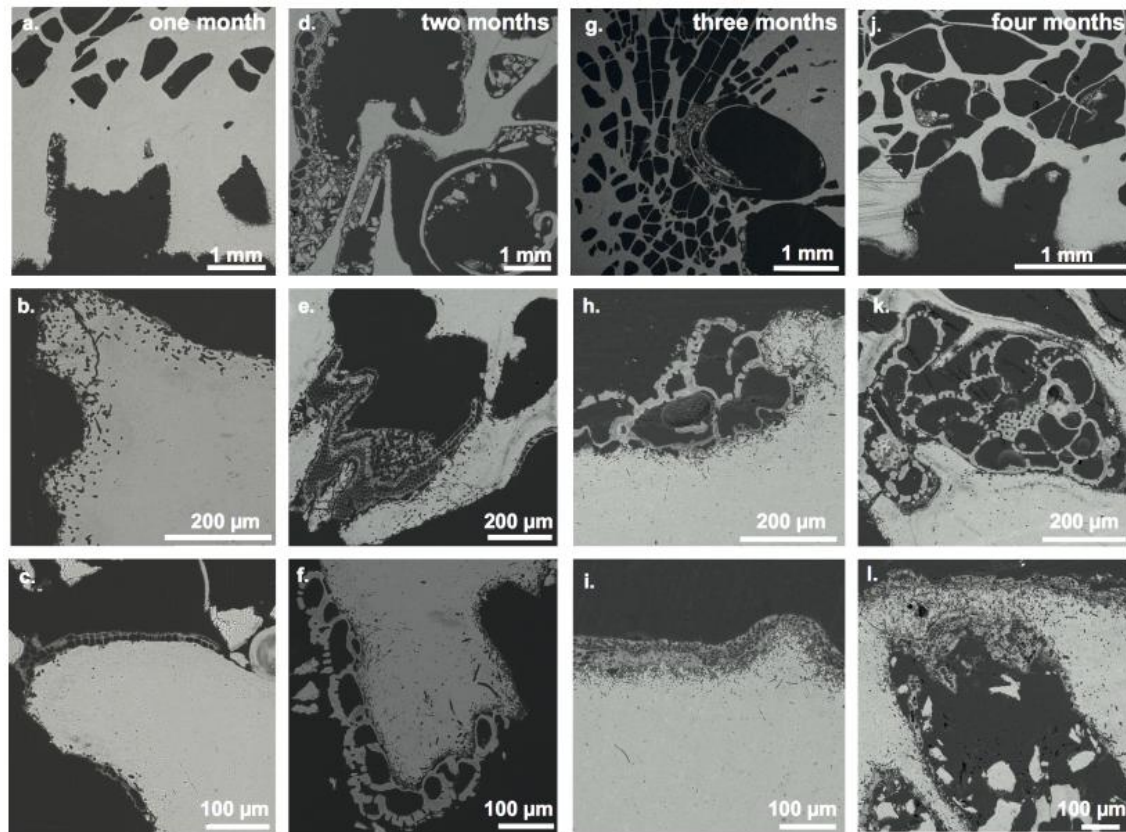


Figure 6.3. Time-series BSE images of thin-sections from coral substrates throughout the experiment. Shown are representative areas of thin-sections of coral substrates after a-c) one month, d-f) two months, g-i) three months, and j-l) four months of exposure. Encrusting species shown are c) crustose coralline red alga (CCA), d) lithophagine bivalve (genus *Lithophaga/Leiosolenus*), encrusting benthic foraminifer (*Homotrema rubrum*), e) encrusting bryozoan f) encrusting benthic foraminifer, g) lithophagine bivalve, h) encrusting benthic foraminifer, i) CCA, J) CCA (lower left) k) encrusting benthic foraminifer, and l) CCA. Note in k) darker thin bands indicate CaCO_3 mineralogy change of the original coral skeleton (i.e. aragonite to calcite) due to microbioerosion. Also note the change in surface morphology and the increase in microbioerosion through time.

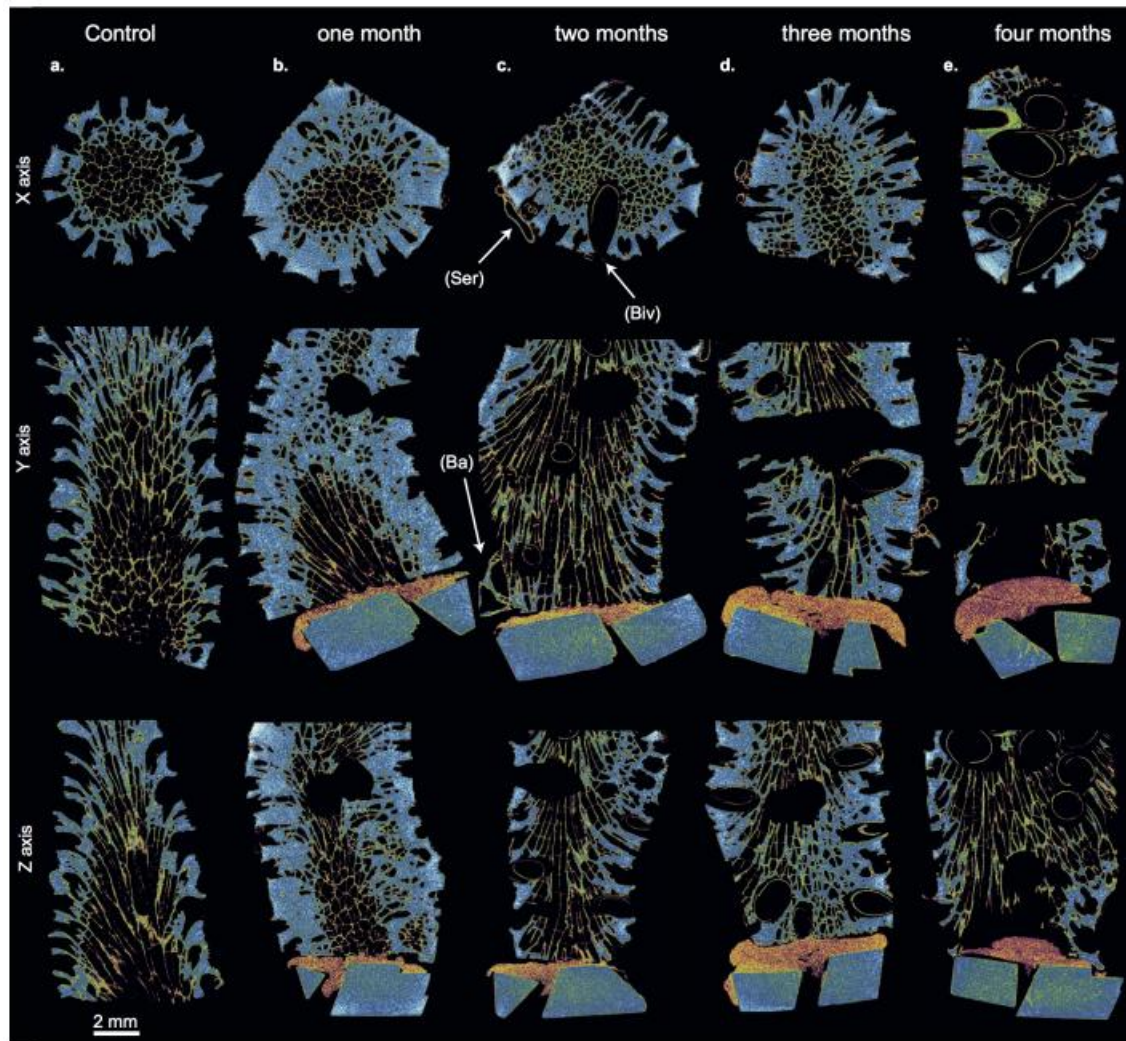


Figure 6.4. Cross sections from modeled μ CT scans of substrates per exposure period, which indicate the settlement succession of the bioeroder community and the internal change in morphology. Shown are cross sections through the X-, Y- and Z-axis of coral substrates of a) control, and after b) one month, c) two months, d) three months, and e) four months of exposure. The hole in the middle part was pre-experimentally drilled to fix the substrates in the reef (cf. S6.1 Fig). Genera depicted in the μ CT scan cross-sections are in c-e) serpulids (Ser), lithophagine bivalves (Biv), and balanids (Ba). Note the increase in abundance and size of lithophagine bivalves through time.

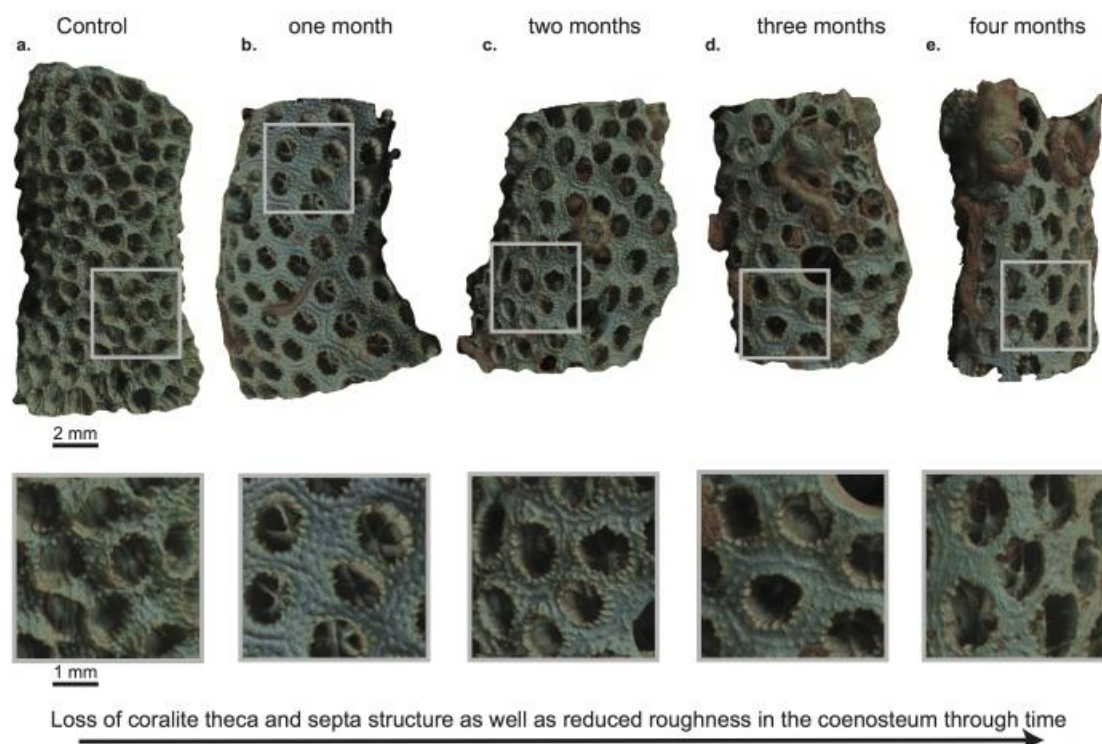


Figure 6.5. Modeled μ CT scans showing the surface morphological change and the settlement succession of bioeroders on the coral substrates. Smaller quadrates at the bottom indicate the alteration of surface roughness per substrate and month. Shown are coral substrates of a) control, and after b) one month, c) two months, d) three months, and e) four months of exposure. Settled genera depicted are in b) serpulids and small CCA (lower left side), c) balanids and serpulids, d) balanids, serpulids and CCA (encrusting on right side, brownish color), and e) balanids and serpulids. Also see supplementary video files in S6.4-S6.8 Figs.

Macrobioerosion

The main macrobioeroder observed was the lithophagine bivalve, genus *Lithophaga/Leiosolenus* (S6.11 Fig). After two months of exposure, shells of these bivalves were identified in μ CT scans inside the coral substrates (Figs 6.4 and 6.5; S6.6-6.8 Figs). With increasing size and numbers of individuals through time, a substantial part of the internal CaCO_3 coral substrate was bioeroded after the exposure period (Table 6.2; Figs 6.4 and 6.5; S6.8 Fig).

Table 6.2. Coral substrates deployed on December 3rd 2013 at Matapalo Reef with date of collection, pre- and post-experimental weight, CaCO_3 loss and indication, which individual substrates per exposure time are presented in Figures.

ID / Exposure	Collection date (d/m/y)	Pre-weight (mg)	Post-weight (mg)	CaCO_3 loss (mg)	CaCO_3 loss (%)	CaCO_3 loss after months (mean %)	μ CT and thin-section
37 / one month	06/01/2014	1474.5	1457.5	-17.0	1.15	0.87	
38 / one	06/01/2014	2461.5	2445.5	-16.0	0.65		X

month							
39 / one month	06/01/2014	1273.5	1266.3	-7.2	0.57		
40 / one month	06/01/2014	1875.6	1854.9	-20.7	1.10		
41 / two months	10.02.2014	2130.3	2116.2	-14.1	0.66		
42 / two months	10/02/2014	2257.9	1898.2	-359.7	15.93	6.90	
43 / two months	not recovered*	1491.7	-	-			
44 / two months	10/02/2014	1652.4	1584.5	-67.9	4.11		X
45 / three months	10/03/2014	1666.8	1593.2	-73.6	4.41		
46 / three months	10/03/2014	1510.0	1319.9	-190.1	12.58	8.40	
47 / three months	not recovered*	1520.2	-	-			
48 / three months	10/03/2014	2699.5	2478.1	-221.4	8.20		X
77 / four months	07/04/2014	1531.2	1048.9	-482.3	31.50		X
78 / four months	07/04/2014	1931.0	1278.5	-652.5	33.79	32.65	
79 / four months	not recovered*	1288.4	-	-			
80 / four months	not recovered*	1257.9	-	-			

*eroded by bioerosion, lost to the substratum

Microbioerosion

By investigating microbioerosion traces in the epoxy resin casts of the control and exposed substrates, an increase in the diversity of microbioerosion became evident. SEM images of the surface of the control substrate show a comparatively intact original substrate structure (i.e. fine detail of coral fibers are visible; S6.3 Fig). Nevertheless, some degree of syn-vivo microbioerosion, mainly by the ubiquitous symbiotic chlorophyte algae *Ostreobium quekettii*, was present before the deployment of the substrates (Fig 6.6a). Traces of microbioeroders in the control substrate were predominantly located at the surface of the coenosteum, where polyp tissue cover is generally thinner in living specimens. Throughout the experiment the coral substrates became progressively altered by microbioeroders with an overall increase in average penetration depth (Fig 6.6, S6.3 Fig). Deep skeletal microbioerosion is typically enhanced when live polyp tissue is damaged or removed and active re-calcification of the coral ceases. The observed microbioerosion traces identify endolithic cyanobacteria as the main agents of microbioerosion during the experiment (complemented by some chlorophyte algae and marine fungi), while they were absent

in the pre-experiment control sample (Fig 6.6). Since cyanobacteria and chlorophytes are phototrophs, the density of their bioerosion traces in the experimental substrates was governed by the orientation of the substrates, and hence light exposure, resulting in a heterogeneous distribution evident around the circumference of substrate cross sections. Traces of microborers reach the inner parts of the coral skeleton only in substrates retrieved after three and four months (Fig 6.6d, e).

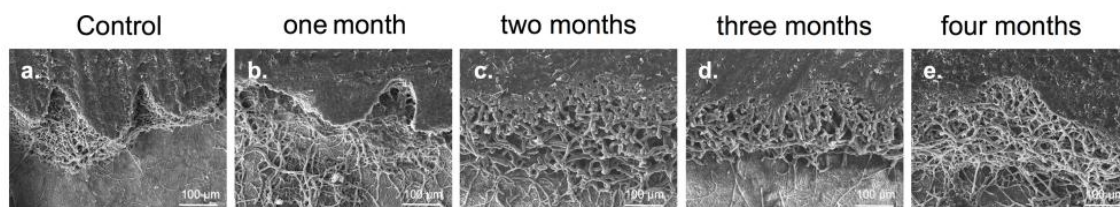


Figure 6.6 SEM images of cast-embedded and partially etched cross sections of coral substrates with positive infills of microbioerosion traces on the skeletal surface. Shown are coral substrates of a) control, and after b) one month, c) two months, d) three months, and e) four months of exposure. Most of the observed bioerosion traces were produced by euendolithic cyanobacteria complemented by some traces formed by chlorophyte algae and marine fungi. Note the increase in boring density over time and the increase in the depth of penetration into the skeletal structure.

Abiotic CaCO_3 cementation and mineralogy

BSE analyses of thin-sections from coral substrates did not show signs of early internal cementation of the skeletal structure (e.g. crystals of aragonite needles) after the four months exposure period (Fig 6.3a, j). No gross diagenetic alteration of the original aragonite coral skeleton was observed (i.e. coral fibers of the substrate preserved). BSE images show uniform mineralogy of the original coral skeleton (gray-scale value). However some local mineral recrystallization of the CaCO_3 from aragonite to calcite adjacent to bioerosion traces was observed (cf. Fig 6.3k; areas with darker grey level within the coral skeleton), indicating micritization of the original coral skeleton.

Changes in net bioerosion CaCO_3 substrate budget

The time-series analysis of the net bioerosion CaCO_3 substrate budget (accretion minus bioerosion) shows an overall negative trend with a mean loss of $0.5 \pm 0.2 \text{ mg CaCO}_3 \text{ d}^{-1}$ over the four months period of the experiment, which over the exposure period equates to a mean $\sim 9\%$ CaCO_3 substrate loss per month (Fig 6.2c; Table 6.2). The one-way ANOVA results and post-hoc Tukey HSD indicate a highly significant loss of CaCO_3 during the final month of exposure, after the onset of upwelling ($p < 0.01$; Table 6.3, S6.1 Table). However, the statistical tests are based on very low replication and therefore demand cautious interpretation. The net CaCO_3 loss per day increased from a rate of $< 0.5 \text{ mg d}^{-1}$, for substrates exposed from one to three months, to a rate of $> 1 \text{ mg d}^{-1}$, after the upwelling pulse. The mean net CaCO_3 loss rate of the substrates that

were sampled after the fourth month of exposure was $\sim 1.5 \text{ mg CaCO}_3 \text{ d}^{-1}$, which equates to a $\sim 36\%$ total CaCO_3 loss of these substrates (Table 6.2). The substrate's CaCO_3 budget change (i.e. the strong increase in CaCO_3 loss for substrates of four months of exposure) also correlates with a shift in settlement community. The community shift is represented by a change from phototrophic (e.g. CCA) to larger organotrophic calcifying genera (bivalves and barnacles) that settled especially during the last two months. Primarily, bioerosion from bivalves (genus *Lithophaga/Leiosolenus*) and microbioerosion caused net CaCO_3 loss of original coral substrate (Figs 6.2c, 6.3l and 6.4d, e). However concerning the net bioerosion CaCO_3 budget of the substrates this has to be viewed in the context that the calcifying organisms of the settlement community produce CaCO_3 shells (i.e. may be reworked to consolidated carbonate sediment after death and thereby contribute to accretion of the reef platform). Thus, these calcifying settlers biased the total CaCO_3 loss of the coral substrates, which in this study was not investigated separately.

Table 6.3. Analysis of Variance from the exponential loss rate of $\text{CaCO}_3 \text{ mg d}^{-1}$. Post-hoc Tukey HSD identified a significantly different rate of CaCO_3 loss only in the final month of exposure, after the onset of upwelling (S6.1 Table). Note that statistical results base on low replication.

Source of Variance	DF	SS	Mean Square	F Ratio	Prob > F
Month	3	2.355	0.785	13.341	0.002
Error	8	0.471	0.059		
Total	11	2.826			

6.4 Discussion

Seawater characteristics at Matapalo Reef

Low seawater temperature, low dissolved oxygen concentration and enhanced nutrient concentrations provide evidence that several cold water intrusions (i.e. upwelling event) influenced the study site at Matapalo Reef during the period from December 2013 to April 2014 (Stuhldreier et al., 2015b, 2015a). Data from Marina Papagayo (a field site within $\sim 200 \text{ m}$ distance to a coral reef) showed that increased intrusions of cold and nutrient-enriched subsurface water rised seawater $p\text{CO}_2$, lowered pH and decreased Ω_{arag} (Rixen et al., 2012; Sánchez-Noguera et al., 2018b). As indicated by these data, pH and Ω_{arag} generally decreased concordantly with lower seawater temperatures, reflecting a strong influence of the corrosive subsurface (i.e. upwelled) waters on the seawater carbon chemistry at Marina Papagayo (S6.12 a, b Fig). Compared to these trends the mean $\text{pH}_{\text{VINDTA}}$ and Ω_{arag} derived from the A_{T} and DIC measurements at Matapalo Reef are enhanced during upwelling. This means that at the measured seawater temperatures one would expect a much lower pH and Ω_{arag} , given the fact that A_{T}/DIC ratio controls pH and Ω_{arag} and an increasing A_{T}/DIC ratio raises both the pH and Ω_{arag} (S6.12 c Fig). Photosynthesis production of organic matter,

and the dissolution of CaCO_3 are two processes increasing the A_T/DIC ratio. The elevated pH and Ω_{arag} at Matapalo Reef (i.e. when compared to the seawater temperature, and to measurements at Marina Papagayo) could accordingly be explained by a stronger response of photoautotrophic organisms and bioeroders to the intrusion of corrosive and nutrient-enriched seawater. Such an amplified response to the intrusion of cold subsurface water could also explain why the pH did not drop during the main upwelling event in February 2014. The reason why CaCO_3 dissolution can occur despite CaCO_3 over-saturation is that the conditions measured in the water column likely differ from conditions at the substrate-seawater interface (i.e. diffusive boundary layer effect; e.g. Cornwall et al., 2013). Seawater within the boundary layer of the substrate-seawater interface may well be CaCO_3 under-saturated due to activity of the settlement community creating erosive conditions. By dissolution of CaCO_3 substrate, bioerosive activity may have caused a carbonate buffer effect of the surrounding seawater covering the reef benthos (i.e. assumingly a phenomenon ranging few meters in the water column, depending on currents), which is reflected in the measured seawater parameters (i.e. elevated seawater pH and Ω_{arag}).

Successive calcareous macrobioeroder community settlement

Due to the specific environmental conditions in the ETP reefs, it is known that the temporal succession of macroborer communities differs from trends observed in reefs less influenced by upwelling (Londoño-Cruz et al., 2003). The rapid development of the settlement community indicates high larvae abundance in the reef during the upwelling period, with environmental conditions beneficial for macrobioeroders. Serpulids and bryozoans are considered to be opportunistic colonizers in the initial stage of substrate infestation (Davies and Hutchings, 1983; Hutchings, 2008), whereas for lithophagine bivalves such an early succession is unusual (Kleemann, 2013). In typical tropical reef settings, lithophagine bivalves are first observed after one year or even longer time periods, thus in a much later successional stage (Chazottes et al., 1995; Kiene and Hutchings, 1994; Osorno et al., 2005; Tribollet et al., 2002). In our experiment, the bivalves represent the most prominent group of macrobioeroders. The use of natural coral substrate likely benefited the rapid settlement observed, compared to the use of CaCO_3 blocks, and thus may represent a realistic scenario of sedimentary infestation. The skeletal morphology of the coral substrate used is comparable with the *Pocillopora* coral rubble at the study site (e.g. corallite size; Baird and Babcock, 2000). Bivalve veliger larvae likely entered the coral substrate through calices and between septae, as other lithophagines do also in live corals (Scott, 1986). No boreholes from bivalves were found at the coenosteum. However, lithophagine bivalves boring into live coral tissue may not be this rapid when polyps are present (i.e. defense mechanisms of the coral; Scott, 1988). Infestation and fragmentation of living coral branches by lithophagine bivalves can support coral dispersal (Scott et al., 1988; Scott and Risk, 1988). In reefs off Panama, intense settlement of lithophagine bivalves

was observed during upwelling conditions. During the non-upwelling season almost no recruitment of bivalve larvae was observed (Kleemann, 2013).

CaCO₃ cementation

Abiotic precipitation of secondary CaCO₃ cements was not observed during the four months exposure period. Although Matapalo Reef is a relatively sheltered near-shore environment, it does experience a relatively low seawater CaCO₃ saturation state ($\Omega_{\text{arag}} < 3$; (Fiedler and Lavín, 2017; Maas et al., 2012; Rixen et al., 2012). This may suggest that the low Ω_{arag} is a cause for the lack of secondary CaCO₃ cements (Manzello et al., 2008). Moreover, the settlement community likely lowers Ω_{arag} further at the substrate-seawater interface. In marginal reef environments with comparatively poorly developed reef framework, similar to the present study site, an envelope of encrusting calcifiers (e.g. CCA, encrusting benthic foraminifers, serpulids, and barnacles) fills the role of stabilizing the reef framework (Perry and Larcombe, 2003; Rasser and Riegl, 2002). Despite bio-corrosive alteration of the skeletal substrate structure, a gross change in mineralogy (e.g. aragonite to calcite, or crystal structure alteration) was not observed. However, minor CaCO₃ recrystallization (from aragonite to calcite) and micritization of the original coral skeleton was present in close vicinity to microborings (cf. Fig 6.3k). This was likely caused by the metabolism, exudates and acidic substances of the (micro) bioeroder community.

CaCO₃ erosion and dissolution

When considering the whole exposure period, bivalves of the genus *Lithophaga/Leiosolenus* are the main macrobioeroders of CaCO₃ coral substrate. Bivalve boreholes increased in size and abundance with increased exposure time, which resulted in a marked increase in CaCO₃ substrate loss especially during the upwelling months (Feb/Mar). Another important cause for the rapid CaCO₃ substrate loss through time is endolithic microbioerosion. Number and penetration depth of microbioerosion traces also increased considerably with exposure time (cf. Figs 6.3 and 6.6; S6.3 Fig). Substrates of the last two months (Feb/Mar) show a gradual morphological degradation of the corallite microstructure and the coenosteum (including the papillae), which consequently may be a further result of the progressive increase of microbioerosion on the exposed surface (Figs 6.5 and 6.6; S6.3 Fig).

The observed CaCO₃ recrystallization associated with the bioeroder community indicates that CaCO₃ dissolution likely is biologically mediated. Besides chemically-based CaCO₃ bioerosion by some species of bioeroders, the dissolution of coral substrate skeleton may also originate from physiologically mediated alteration of the diffusive boundary layer conditions through the settling organisms, which may have created seawater CaCO₃ under-saturation ($\Omega_{\text{arag}} < 1$) at the substrate-seawater interface. This assumption is supported by the fact that the onset of intense CaCO₃ substrate loss correlates with enhanced settlement of organotrophic species such as

serpulids, bryozoans, barnacles, lithophagine bivalves (i.e. metabolic respiration) from the second month onward, favored by elevated nutrient conditions with the onset of upwelling. To a minor part bioerosive grazing and predation (e.g. of mollusks, crustaceans, echinoderms, reef fish) may have contributed to the observed erosion pattern. The complete loss of some substrates, especially for the substrates exposed for four months, may well be complete crumbling due to external and internal bioerosion, the lack of intragranular cementation and sufficient external encrustation.

Net bioerosion CaCO_3 budget change

The coral substrates underwent a significant CaCO_3 loss of ~36% total dry weight after four months of exposure. This resembles a mean loss of $>1 \text{ mg CaCO}_3 \text{ d}^{-1}$ in coral substrates that were exposed in the reef for the whole experimental period (Fig 6.2c, Table 6.2). However, the mean CaCO_3 loss per day was significantly higher in the substrates exposed for four months compared to the substrates exposed only up to three months ($<0.5 \text{ mg CaCO}_3 \text{ d}^{-1}$), which indicates an enhancement of the bioerosive activity during the fourth month and after the onset of upwelling ($p < 0.01$; Fig 6.2, Table 6.2; S6.1 Table). When additionally considering the possibility of crumbling of the lost substrates exposed for four months, total CaCO_3 loss even exceeded 50%. It has to be noted that these time-series results on the bioerosion of the substrate CaCO_3 budget are based on low replication, i.e. local representatives in a patchy reef environment. Spatially larger-scaled studies are needed to validate the observed trend for the influence of bioerosion on the CaCO_3 budget in ETP reefs.

The organisms of the encruster and macrobioeroder community build CaCO_3 skeletons and shells that contribute to the carbonate sediments. In addition to corals, these organisms are also an important source of CaCO_3 for the reef ecosystem and thus both negatively and positively contribute to the CaCO_3 budget of the reef. The production of CaCO_3 by these organisms may be especially important for the reef's CaCO_3 budget during periods with disruptive environmental events, when coral growth may cease (cf. Fig 6.7, eutrophic condition; (Stuhldreier et al., 2015a). Interestingly, the observed loss in CaCO_3 substrate may explain the elevated pH and Ω_{arag} at Matapalo Reef (i.e. when correlated to the seawater temperature). This indicates an effect of bioerosion on the carbonate buffer capacity of the seawater (Table 6.1, Figs 6.2a, S6.12 Fig). If so, bioerosion causing CaCO_3 dissolution (e.g. of coral rubble substrate; cf. S6.2 Fig) may on the one hand thrive under the high $p\text{CO}_2$ conditions associated with upwelling. On the other hand however, bioerosion-driven CaCO_3 dissolution may aid to mitigate effects of the upwelled corrosive seawater on reef health (i.e. local carbonate buffer against abiotic dissolution of the living reef framework).

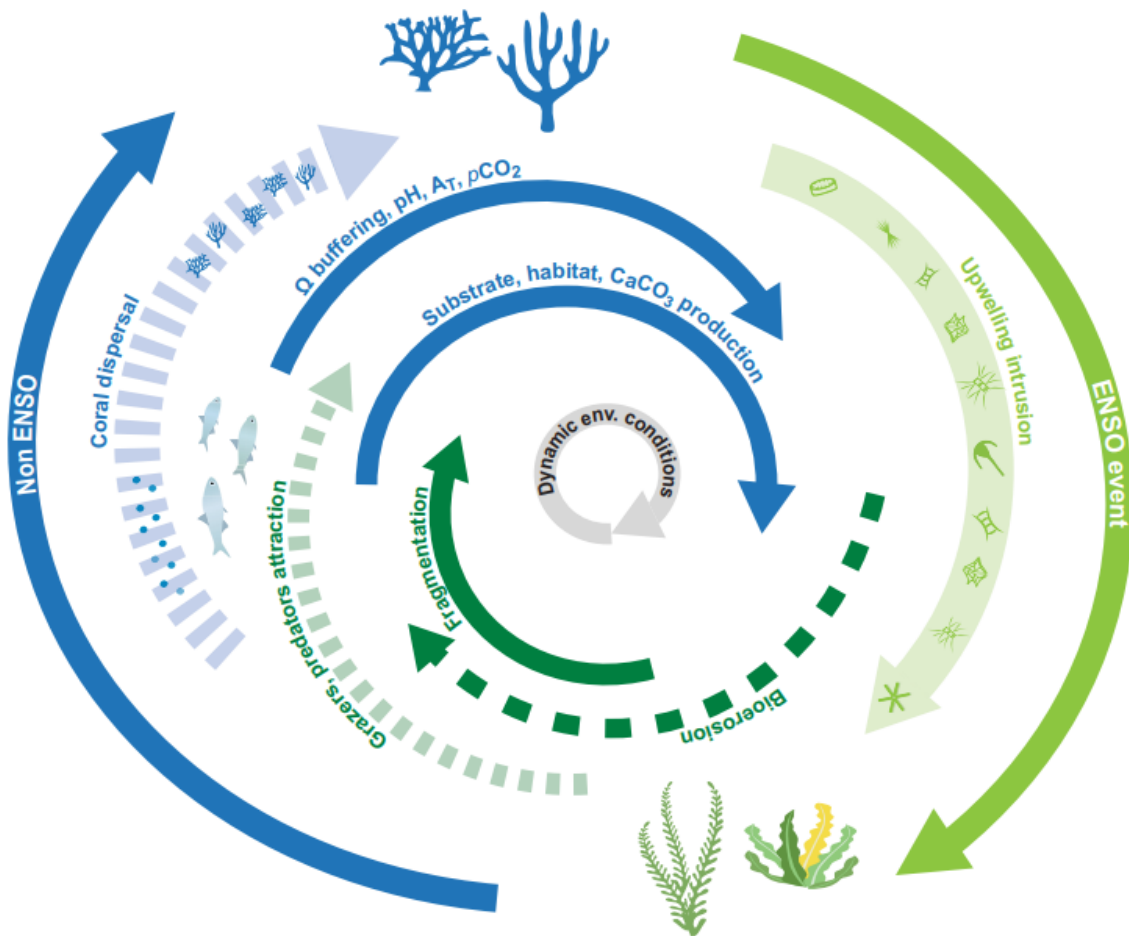


Figure 6.7. Graphical concept of the role of bioerosion in ETP coral reef community transitions. Short-term transitions between coral and algal dominance can occur due to changes in environmental boundary conditions. Coral growth may cease during ENSO events or during periods of intensive upwelling. Eutrophic conditions in the reef favor organotrophic settlers, in particular detritus and filter feeders, including many calcifying encrusting and bioeroding species. Enhanced activity of bioeroders, as an ecological response, supports the re-transition of the reef into an oligotrophic condition by the uptake of nutrients and buffering seawater carbon chemistry (carbonate sediment production and dissolution; influence seawater Ω , pH, A_T , pCO_2). Additionally, grazers and predators are attracted due to the increase in food or prey abundance. New substrate is formed by predation (reef fish, echinoderms, mollusks) and macrobioerosion, which allows coral dispersal (fragmentation) and formation of rhodolitic substrate serving as larvae settling grounds. The ecological effects benefit the growth of phototrophic calcifiers (i.e. corals, crustose coralline algae). Dashed lines indicate ecological responses to environmental processes (solid lines). Green lines indicate an effect on the reef community towards algal growth and blue lines indicate effects towards coral growth.

Bioerosion and encrustation under dynamic environmental conditions and their role for ecosystem functioning in ETP coral reefs

Bioerosion rates in ETP reefs are among the highest recorded in the world (Alvarado et al., 2017; Eakin, 1996; Reaka-Kudla et al., 1996). The rapid macro- and microbioerosion observed at Matapalo Reef confirms previous investigations. Variable boundary conditions and ENSO events can cause ETP reefs to experience environmental transitions with temporary die-off and re-growth of corals (Fig 6.7) (Glynn et al., 2017b). During periods of intense upwelling with high nutrient concentrations, reef ecosystems may become algal dominated (which at Matapalo Reef is the fleshy green algae of the genus *Caulerpa*; S6.2 Fig) that negatively affects coral growth (Stuhldreier et al., 2015b, 2015a; Wild et al., 2014). Additionally, with the onset of upwelling, bioerosion on corals increases. This facilitates the creation of unique habitats besides the coral reef community, like the cryptic coral rubble habitat (Fong et al., 2017). The species that live within this habitat originate from different environmental and oceanographic regimes and form “historically-developed” communities in ETP reefs (Cortés et al., 2017). These communities that consist primarily of eroders and encrusters influence the reef’s resilience by triggering various environmental responses, e.g. the attraction of predators and grazers, coral dispersal and the formation of new substrate. Consequently, the evoked effects may allow the reef ecosystem to regain oligotrophic conditions that benefit coral growth (Fig 6.7) (Scheffer and Carpenter, 2003). It is a well-known ecological principle that in ecosystems under (temporal) environmental stress, biological processes promoting regeneration capacity gain momentum (Gunderson, 2000; Hughes et al., 2010; Peterson et al., 1998).

Especially in marginal reefs of the ETP, such transitions may occur frequently due to disruptive environmental events, resulting in periods of stagnation and (re-)commencement of coral growth (Stuhldreier et al., 2015b, 2015a). The main parameters known to steer the cyclicity of coral die-off events are varying oceanic boundary conditions (e.g. El Niño/La Niña events) (Glynn, 1984; Glynn and D’Croz, 1990). Other possible synergistic causes include predator/prey relationships, grazer abundance or diseases, and climate change (Stuhldreier et al., 2015b, 2015a; Wild et al., 2014). While influences from the land or human made pollution are not yet a major factor, they may become more prominent in the future (Cortés and Reyes-Bonilla, 2017). The question is, how resilient these reefs will be under future climate change scenarios? However, “historically-developed” and interconnected community structures in ETP reefs may still enable them to recover after temporal environmental stress.

6.5 Conclusion

In this study, we present the rapid development and alternate succession of an encruster and bioeroder community on coral substrate in an ETP coral reef. Foremost the rapid settlement of lithophagine bivalves as the main macrobioeroders of the substrates is particular to coral reefs in the ETP. CaCO_3 erosion of the substrate by

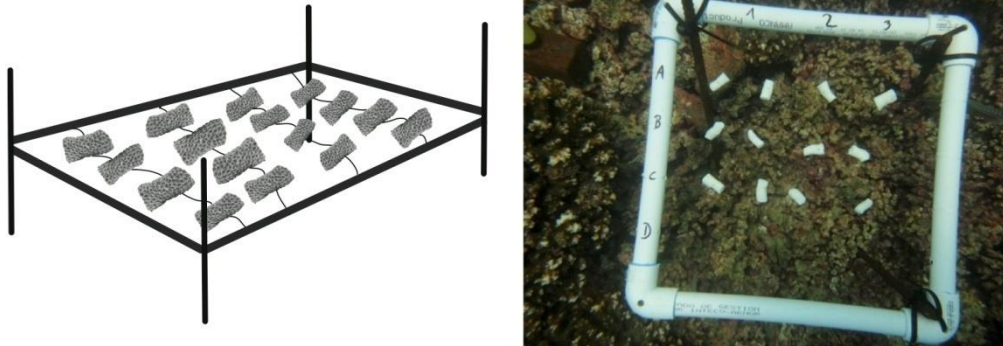
bioeroders increased markedly with the onset of upwelling. Derived from our time-series experiment, bioerosion caused a negative CaCO_3 substrate budget. Dissolution of CaCO_3 agrees with the elevated Ω_{arag} and pH observed at Matapalo Reef, when compared to the site at Marina Papagayo, which is located in ~200 m distance to a reef. The resulting local carbonate buffer effect favored an influx of atmospheric CO_2 into reef waters. This may suggest that even in upwelling influenced reef zones, ocean waters are still capable to take up atmospheric CO_2 , and presently mitigate and conceal the global concentration rise caused by anthropogenic sources.

For the ecosystem scope, the settlement community provides important functions, such as habitat formation, and substrate consolidation. The community may even have an effect on the reef's seawater carbon chemistry, enhancing the carbonate buffer capacity. With these functions settlement communities give plasticity to marginal coral reefs where dynamic environmental conditions, such as upwelling, can temporarily impair coral growth. The rapid bioerosion observed in ETP reefs thus provides a possible future scenario for tropical coral reefs affected by ocean acidification and eutrophication. Up to now, encrusting and bioeroding organisms complement the resilience potential of marginal reefs as an important part of their "historically-developed" community structures. However, these communities will likely become altered due to climate change, and marginal reef ecosystems may become locked in eutrophic, bioerosive conditions. The resulting negative CaCO_3 substrate budget due to enhanced bioerosion, paired with the absence of secondary cementation, may have negative consequences for net reef accretion. However, if marginal reef ecosystems are protected from further and upcoming anthropogenic impacts and are granted sufficient time to recover, natural regeneration processes stimulated by settlement communities of encrusting and bioeroding organisms may still assist in the remediation of such temporarily stressed coral reefs.

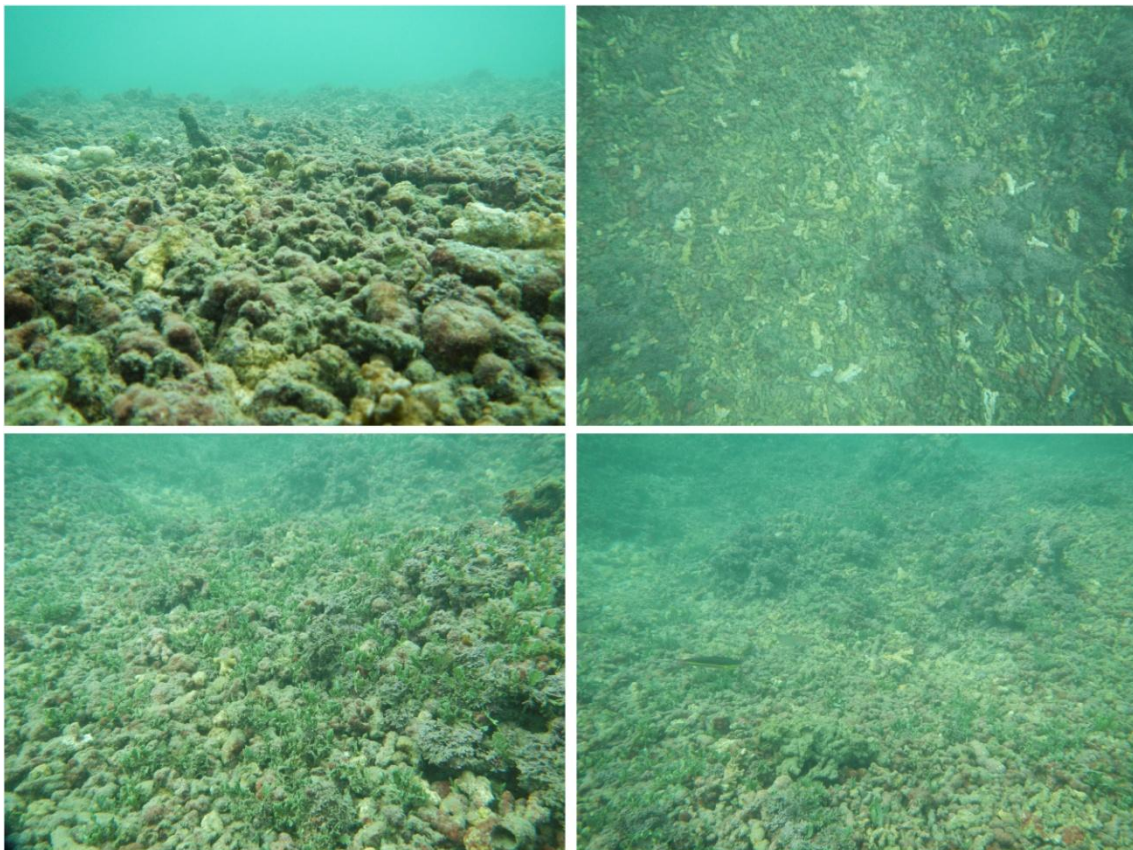
Acknowledgments

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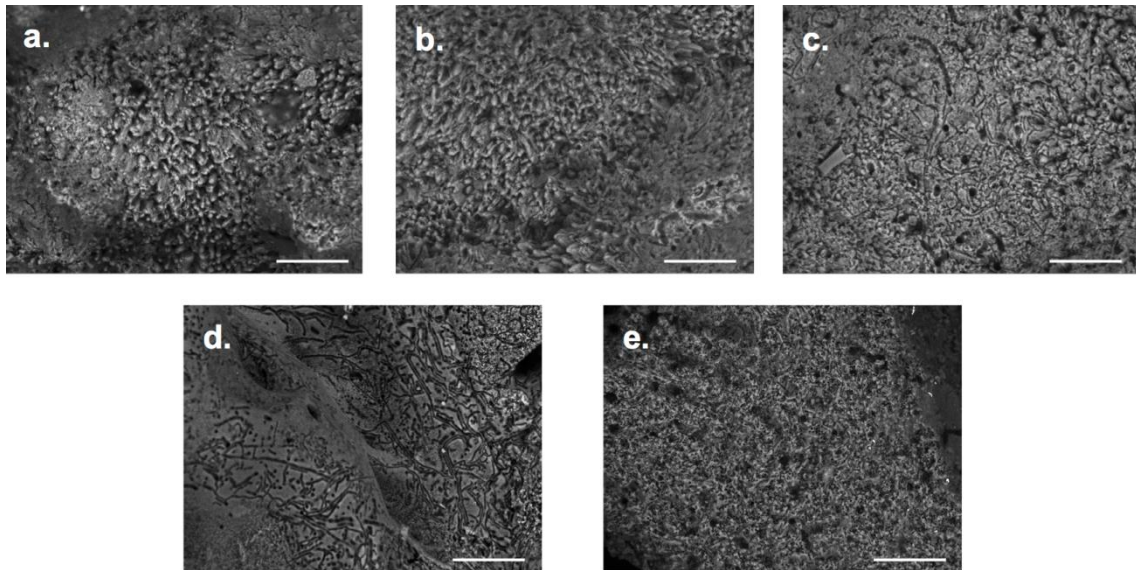
6.6 Supplementary Figures



S6.1 Fig. Experimental setup deployed in the reef (schematic drawing and photograph).



S6.2 Fig. Photographs of typical benthic seafloor cover and sediment at the Matapalo Reef site. Crustose coralline red algae (CCA) encrusting the coral rubble substrate forming rhodoliths, and growth of the green macro-alga genus *Caulerpa*. Water depth ~5 m bsl.



S6.3 Fig. SEM images from microbioerosion traces on the surface of the coral substrates. a) control, and after b) one month, c) two months, d) three months, and e) four month of exposure. Note the increase in borings and the loss of skeletal structure (e.g. coral fibers) over time. Scale bar 50 μm .

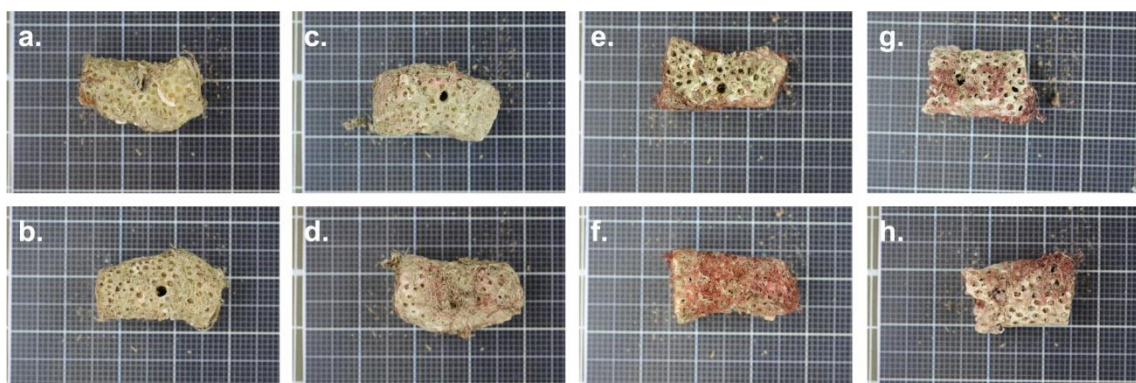
S6.4 Fig. μCT scan video of control coral substrate (pre-experiment). Link to video: <https://doi.org/10.1371/journal.pone.0202887.s006>.

S6.5 Fig. μCT scan video of coral substrate exposed for one month at Matapalo Reef. Link to video: <https://doi.org/10.1371/journal.pone.0202887.s007>.

S6.6 Fig. μCT scan video of coral substrate exposed for two months at Matapalo Reef. Link to video: <https://doi.org/10.1371/journal.pone.0202887.s008>.

S6.7 Fig. μCT scan video of coral substrate exposed for three months at Matapalo Reef. Link to video: <https://doi.org/10.1371/journal.pone.0202887.s009>.

S6.8 Fig. μCT scan video of coral substrate exposed for four months at Matapalo Reef. Link to video: <https://doi.org/10.1371/journal.pone.0202887.s010>.

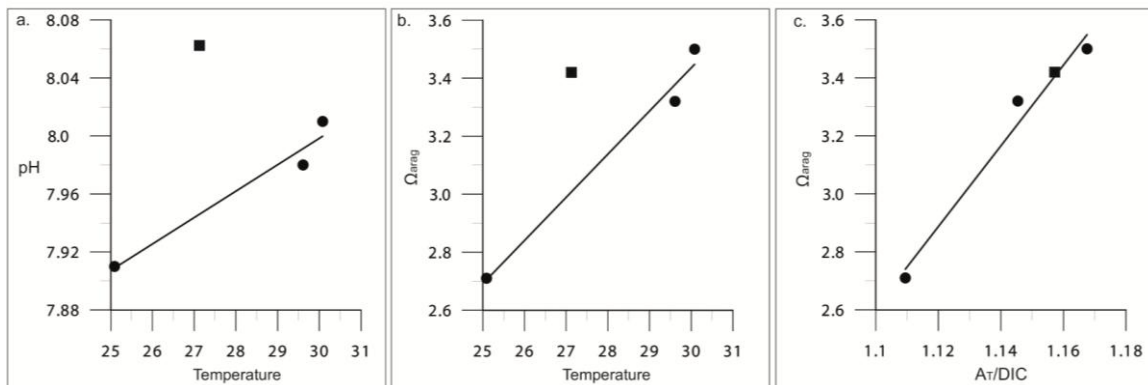


S6.9 Fig. Photographs of retrieved coral substrates from the Matapalo Reef site, before bleaching (30% H_2O_2). After a, b) one month; c, d) two months; e, f) three months; g, h) four months of exposure.

S6.10 Fig. Video showing the reconstructed μ CT scan of one coral substrate (example) retrieved after two months of exposure from the field site Bahía Santa Elena. Note the enhanced settlement of balanids (acorn barnacles), i.e. competition for space, and the presence of lithophagine bivalves. Link to video: <https://doi.org/10.1371/journal.pone.0202887.s012>.



S6.11 Fig. SEM images of the internal and external valve from one lithophagine bivalve, juvenile stage, identified as *Lithophaga (Leiosolenus) cf. aristata* (Dillwyn, 1817). Scale bar 500 μ m.



S6.12 Fig. Graphs showing the correlation between measurement period means of a) pH and temperature, b) Ω_{arag} and temperature, and c) Ω_{arag} and A_T/DIC at Marina Papagayo (black dots; 2009, 2012, and 2013; data from (Rixen et al., 2012; Sánchez-Noguera et al., 2018b) compared to the study site at Matapalo Reef (black squares; 2013/2014; data from (Stuhldreier et al., 2015b), this study). Regression lines exclude data from Matapalo Reef. At Matapalo Reef, seawater pH and Ω_{arag} are elevated.

Supplementary Tables

S6.1 Table Post-hoc Tukey HSD, Ordered differences report

Level	- Level	Difference	Std Err Dif	Lower CL	Upper CL	p-Value
1m	4m	1,307603	0,2100823	0,634847	1,980359	0,0011*
2m	4m	1,038740	0,2214462	0,329593	1,747887	0,0068*
3m	4m	1,020994	0,2214462	0,311848	1,730141	0,0075*
1m	3m	0,286608	0,1852752	-0,306707	0,879923	0,4562
1m	2m	0,268863	0,1852752	-0,324452	0,862178	0,5056
2m	3m	0,017745	0,1980675	-0,616535	0,652025	0,9997

S6.2 Table Data comparison of measured and calculated seawater parameters from bottle samples (VINDTA) and Manta multiprobe.

Date _{VINDTA}	Time	Depth (m)	A _T (μmol/kg)	DIC (μmol/kg)	SST (°C)	SSS	pH-cal tot	fCO ₂ -cal (μatm)	Omega _a -rag-cal
02/12/2013	16:10	6,00	2211,18	1971,99	25,63	32,52	7,97	479,48	2,81
09/12/2013	15:30	6,00	2106,38	1805,37	27,87	31,08	8,09	330,82	3,49
16/12/2013	15:30	6,00	2093,72	1822,51	28,20	31,00	8,03	385,15	3,18
23/12/2013	15:30	6,00	2072,18	1785,09	28,16	30,68	8,07	343,27	3,35
30/12/2013	15:30	6,00	2078,75	1783,16	28,53	30,70	8,08	335,76	3,45
06/01/2014	14:30	5,00	2086,62	1789,08	28,51	31,19	8,07	339,57	3,45
20/01/2014	13:13	3,25	2213,52	1890,27	26,41	31,92	8,12	318,66	3,73
21/01/2014	08:30	3,25	2218,88	1918,48	26,41	30,54	8,10	345,66	3,55
23/01/2014	11:23	3,25	2209,45	1917,96	26,64	33,31	8,04	391,36	3,34
24/01/2014	13:00	3,25	2224,72	1938,93	25,98	32,02	8,06	381,87	3,33
25/01/2014	11:45	3,25	2207,52	1903,20	26,80	30,50	8,10	340,08	3,59
26/01/2014	12:15	3,25	2169,64	1864,63	27,46	32,98	8,06	360,27	3,49
27/01/2014	12:30	3,25	2185,60	1874,89	27,19	33,13	8,07	353,02	3,55
28/01/2014	08:50	3,25	2198,65	1915,50	27,00	33,90	8,02	412,88	3,24
03/02/2014	12:30	5,50	2179,02	1889,40	27,00	33,65	8,03	390,48	3,30
31/03/2014	12:28	3,00	2256,14	1924,72	25,40	33,67	8,11	337,41	3,75
17/04/2014	10:02	2,25	2263,01	1956,66	27,95	33,64	8,03	404,54	3,55

Date _{Manta}	start	end	Temp (°C)	pH (tot)	Salinity
02/12/2013	09:15	15:30	25,40	8,07	32,55
09/12/2013	09:15	15:00	27,97	8,09	31,03
16/12/2013	15:45	17:30	28,40	8,06	30,86
23/12/2013	09:30	15:00	28,45	8,09	30,60
30/12/2013	15:30	18:00	28,63	8,11	30,69
06/01/2014	09:00	15:00	28,85	8,12	31,07
14/01/2014	13:15	17:00	28,00	8,13	32,97
20/01/2014	09:00	16:00	26,55	8,12	33,31
27/01/2014	09:00	14:15	27,17	8,10	33,20
03/02/2014	11:12	15:12	27,14	8,12	32,97
10/02/2014	14:00	17:00	23,64	8,30	33,83
17/02/2014	09:00	15:30	21,62	8,26	34,19
24/02/2014	15:30	17:00	25,03	8,29	33,58
03/03/2014	11:00	16:00	24,07	8,26	33,60

10/03/2014	09:00	15:00	28,17	8,16	32,87
17/03/2014	09:00	15:00	27,44	8,14	33,57
24/03/2014	09:00	14:30	26,62	8,05	33,52
31/03/2014	11:00	15:45	25,67	8,13	33,65
07/04/2014	09:00	14:00	28,11	8,03	33,70
14/04/2014	13:30	17:00	28,23	8,07	33,59
17/04/2014	08:00	10:30	28,23	8,07	33,62

7. GENERAL DISCUSSION AND CONCLUSIONS

The overarching goal of this thesis was to characterize the carbonate chemistry and its influence on the reef development along the Pacific coast of Costa Rica. It was the first study during which the carbonate chemistry was measured in different locations along the coast. The obtained data represent baseline knowledge for the general understanding of the carbonate chemistry in the coastal areas, which are threatened by global warming and ocean acidification in synergy with local stressors. In the following section key findings of this thesis and their significance are summarized and discussed in broader context.

7.1 High local seawater variability in tropical coastal waters

Globally, coastal areas show a high variability when compared to open ocean (Gattuso et al., 1998). In the Pacific Ocean the Costa Rican coastline extends to > 1100 km and holds a variety of ecosystems, including coral reefs (Cortés and Jiménez, 2003). These ecosystems are influenced by a seasonal upwelling system and a vast number of incoming rivers. In the past several studies have described the seasonal changes promoted by the upwelling of Papagayo regarding fluctuations in seawater temperature, salinity, oxygen and nutrient concentrations (Alfaro et al., 2012; Fernández-García et al., 2012; Jiménez, 2001c; Lavín et al., 2006; Legeckis, 1988); however, most of them lack a description of the carbonate chemistry. Our data showed that coastal waters from northernmost locations (Santa Elena) are more corrosive than coastal waters at the central (Matapalo) and southern (Marino Ballena) location, with annual mean pH values of < 8.0 (Sánchez-Noguera et al., 2018b; Stuhldreier et al., 2015b). During the upwelling season the pH dropped down to values of 7.85 ± 0.26 (Sánchez-Noguera et al., 2018b). During the non-upwelling season in June 2012 we witnessed for the first time an upwelling-like event. It was characterized by slightly increased wind speeds, which promoted the inflow of acidic offshore waters, with values of pH as low as 7.81 (Sánchez-Noguera et al., 2018b).

Towards the south the influence of upwelling diminishes and river discharges become a dominant factor controlling the carbonate chemistry in southern locations (Section 5). This section of the Pacific coast holds an important watershed that includes the largest river in the country, the Térraba River, located 10 km southwest from Marino Ballena.

In section 6, we discovered that enhanced bioerosion during the upwelling season influenced the carbonate chemistry in the proximity of Matapalo reef, as the dissolution of carbonates increased the buffer capacity of seawater against the inflow of acidic subsurface waters (Wizemann et al., 2018). Upwelling-driven nutrient inputs caused the enhanced bioerosion by raising productivity, sustaining the growth of larger and more effective bioeroders.

In summary, our results evidenced that coastal waters from the Pacific coast of Costa Rica exhibit a high local variability in seawater chemistry, due to the occurrence of seasonal upwelling events and the inflow of open ocean waters in the north and river discharges in the south. These results largely support previous studies in other regions focusing on the impact of upwelling and fresh water discharge on the seawater chemistry in coastal areas (Carstensen and Duarte, 2019; Hauri et al., 2009; Vargas et al., 2016). The pH at our study sites ranged between 7.85 ± 0.26 and 8.04 ± 0.08 and is therewith at the lower range of those measured in world's surface ocean (Rhein et al., 2013). The associated carbonate saturation states were also low but the water remained oversaturated with respect to aragonite and calcite. Enhanced nutrient inputs in turn reduced the effects of the incoming acidic waters on the carbonate system as it favored productivity and bioerosion. In addition to strong coastal currents, this increased the vulnerability of the entire reef structure to physical erosion and explains the low reef accretion in the ETP in comparison to Western Tropical Pacific. This sheds new light on the future vulnerability of coral reefs to combined effects of stressors such as ocean acidification and eutrophication.

7.2 Can be the upwelling of Papagayo considered a real window to the future?

There is an open discussion in the scientific community studying the impacts of climate change in the ocean and the adaptation capacity of marine species to the ongoing environmental perturbations (IPCC, 2018). The geological record showed that global environmental perturbations are not restricted to this century, and that previous warming and ocean acidification events took place over the last 300 million of years (Hönisch et al., 2012). However, what makes a striking difference between the past and the present is the rate of change, as the current change of the ocean carbonate chemistry is going so fast that has no analog on the geological record except perhaps at the Paleocene-Eocene Thermal Maximum (PETM) (Zachos et al., 2008; Zeebe et al., 2016). This raises the concern that some species might not be able to adapt to the current rate of global environmental changes, as they are already close to their physiological limits (Hoffmann and Sgró, 2011).

In an attempt to address this issue, scientists around the world have started to study species that are currently living in locations, which are naturally exposed to extreme conditions, as CO₂ vents and upwelling areas. The northern section of the Pacific coast of Costa Rica is exposed to a seasonal upwelling system forced by trade winds, which produce marked changes in the seawater chemistry between December and April (Section 5, Rixen et al., 2012; Stuhldreier et al., 2015b, 2015c). The environmental conditions promoted by the upwelling of Papagayo resemble those expected under ocean acidification scenarios (IPCC, 2018), with measured values of pH as low as 7.81 and $p\text{CO}_2$ as high as 658.32 μatm (Section 4). Consequently, the Gulf of Papagayo can be considered as a remarkable location to investigate of low-pH conditions on coral reefs, which in turn might help to predict the response of these

organisms in the future under global change scenarios. However, such studies are biased by upwelling-driven shifts in the pelagic and benthic community.

Organisms living on locations regularly exposed to extreme conditions are subject to a strong selection process and therefore a high local adaptation (Gaitán-Espitia et al., 2017). This was shown in one of the complementary studies of this thesis for a reef in the Gulf of Papagayo, where it was reported that corals and algae increased their primary production during upwelling season (Stuhldreier et al., 2015c) which in turn favored development of larger and more effective bioeroders (Wizemann et al., 2018). Considering such shifts, we assume that corals growing under the influence of the Papagayo upwelling system are adapted to the regular exposition of cold nutrient-enriched and acidic waters, and therefore must have developed particular features to thrive under these conditions. On the other hand, this could also mean that they are not ready to cope with another set of stressful factors such as global warming or local stresses such as siltation or HAB.

At the ecosystem level, an annual benthic survey showed that Matapalo reef is highly dynamic (Stuhldreier et al., 2015a) and in comparison to other study sites along the Costa Rican coast the environmental parameters in this reef are relatively stable throughout the year (Section 5). This suggests that ecological buffer-effects such as the upwelling-driven enhanced bioerosion counteract externally driven environmental changes. Such feedback loops are still poorly studied and will vary due to shifts in the ecosystem structure caused by invasive species and environmental changes exceeding the tolerance level of individual organisms.

To summarize, the Gulf of Papagayo is not necessarily a suitable window to the future due to the specific adaptation of reefs to seasonal changes (Stuhldreier et al., 2015c). Our results showed that coral reef development in this region is likely to be threatened in the future by anthropogenic ocean acidification, as some of these corals are currently living in conditions close to their growing thresholds (Sánchez-Noguera et al., 2018b). However, the best way to use the Gulf of Papagayo as a natural laboratory for studying the physiological response of organisms to future global change scenarios would be to restrict this location as “laboratory facilities”, and “import” organisms from other Costa Rican locations, which are not exposed to the seasonal upwelling. This would provide a more realistic scenario, with a complex set up of extreme natural environmental conditions and non-acclimated organisms being exposed to a rapid rate of change. Consequently, additional studies including cross transplants between locations are needed in order to disclose whether the selection of these specific traits in corals from the Gulf of Papagayo represents a real case of strong selection (adaptation) or plasticity (acclimation) (Calosi et al., 2016; Sunday et al., 2014).

7.3 Costa Rican coral reefs in the face of climate change and ocean acidification scenarios

Marine ecosystems in tropical areas are at high risk under “business-as-usual” emission scenarios (IPCC, 2018), when environmental conditions will not only drive a loss of biodiversity but also phase shifts at the ecosystem level. For example, field-based studies in locations exposed to natural ocean acidification conditions revealed shifts from coral-dominated to macroalgae-dominated communities when moving through a low-pH gradient (Enochs et al., 2015). These studies investigating the potential impacts of ocean acidification at the ecosystem level provide a good broad picture, especially considering that responses of calcifying organisms to changes in seawater chemistry are sometimes contrasting (Ries et al., 2009). Despite the broad set of responses documented through experiments, there is a general consensus that human-driven ocean acidification will produce changes in the carbonate chemistry that will challenge the survival of coral reefs around the world (Dove et al., 2013; Eyre et al., 2018), albeit specific mechanisms of these impacts are still under debate.

The results presented in this thesis contribute to elucidate some responses under low-pH conditions, at both, the species and ecosystem level. Benthic organisms from the Gulf of Papagayo showed diverse responses to high-fluctuations and natural acidic waters, which might also be dependent on the level of exposition to extreme conditions. For example, in the location highly-exposed to the upwelling (Santa Elena) a negative effect was documented during upwelling season, when intrusion of low-pH waters promote a significant loss of carbonates (30%) (Wizemann et al., 2018). On the other hand, in the location with a lower exposition to the upwelling (Matapalo) a positive effect was documented, with corals and algae showing an enhanced primary production during upwelling season (Stuhldreier et al., 2015c). Two complementing studies of this thesis also showed that colonial ascidians are active competitors for settlement substrates in Matapalo reef (Roth et al., 2015). The significant advantage of this benthic organism over key reef calcifiers resulted in a reduced accumulation of carbonates, which implies a direct impact on the carbonate budgets and the integrity of the reef frameworks in the Gulf of Papagayo (Roth et al., 2017). A similar variety of responses to changing seawater chemistry has been globally reported in diverse studies (Kroeker et al., 2011, 2013), confirming that more research is needed on the species and community level, in order to improve the accuracy of predictions under global change scenarios.

Several studies suggest that coral reefs will be threatened in the future by ocean acidification and global warming (Albright et al., 2016; Doney et al., 2012; Hoegh-Guldberg et al., 2007). These ecosystems hold a boundless biodiversity but are also subject to the impact of multiple stressors, both on the global and local scale (Barlow et al., 2018). Even it has been stated that tropics will be the first regions around the world to experience extreme high temperature conditions (Mahlstein et al., 2011), in addition to intense and frequent climate oscillations as ENSO. The fact that global

stressors act on top of local ones poses a major threat for these tropical coastal ecosystems, because local stressors will diminish the resilience and increase the vulnerability of coral reef against global stressors.

Considering that natural bioerosion is a key local stressor for reef resilience (Schönberg et al., 2017), studying this natural process and its relationship with the natural variability of the carbonate chemistry might provide a good impression of future ecological changes in coral reefs under climate change scenarios.

In Section 6 we showed a close link between the occurrence of the upwelling of Papagayo and the carbonate loss due to bioerosion (Wizemann et al., 2018). The succession of calcifying organisms followed a temporal trend, with bioeroders such as the lithophagine bivalves dominating over smaller bioeroders during upwelling season. A more detailed study of bioeroders in locations highly-exposed to the seasonal upwelling, such as Santa Elena, will also provide insights into the adaptation mechanisms of these organisms in addition to their potential impact on seawater chemistry and coral reef development. For example, a recent study unveiled the mechanism by which boring sponges uses the excess of protons in the seawater to reduce their energy investment for the dissolution of carbonates (Webb et al., 2019). This study helped to disclosed how bioeroders benefited from high-CO₂ conditions. This stands as a very convincing explanation for the skeletal disconformities and abundant boreholes observed in massive coral from Santa Elena (Toth et al., 2017).

One of the most relevant results of this thesis is that it helped to explain the factors responsible for the observed differences in coral species composition in reefs, between northern and southern sections of the Costa Rican Pacific coast. Nevertheless, mass mortalities from recent years (Sánchez-Noguera et al., 2018b) and from the geological record (Cortés et al., 1994; Glynn et al., 1983) suggest that despite these corals have wider environmental thresholds, their tolerance to extreme conditions has limits with respect to e.g. changes in the upwelling intensity (Toth et al., 2015) and ocean acidification. Furthermore, a decreasing pressure from local stressors such as pollution, siltation, eutrophication and overexploitation will increase their resilience capability towards global stressors (Barlow et al., 2018; Hughes et al., 2003). Conservation actions such as the creation and/or expansion of Marine Protected Areas (MPAs) in addition to reduction of greenhouse gas emissions as claimed by the United Nations Framework Convention on Climate Change on its 21st Conference of the Parties, in Paris 2015, are key elements to safeguard coral reef ecosystems.

8. OUTLOOK AND FUTURE RESEARCH

What is to come for future studies?

This thesis fills knowledge gaps regarding the carbonate chemistry and the influence of also other environmental factors on the reef development along the Costa Rican coast in the ETP. Nevertheless, there are still knowledge gaps to fill. According to my opinion the most urgent ones are described below:

Additional drivers explaining the variability of the carbonate chemistry: A higher resolution of measurements in upwelling and non-upwelling locations is required, to unveil interactions between local wind-driven upwelling systems and ocean currents. This also will allow to disclose the frequency of sporadic upwelling-like events during the non-upwelling season as seen in June 2012 (Sánchez-Noguera et al., 2018b, Section 4) and to improve the understanding of processes causing such events.

Identify “winners and losers”: Organisms exposed to natural extreme conditions are subject to strong selection processes (Gaitán-Espitia et al., 2017), which leads to local adaptation by selection of specific traits. The research performed by Suthldreier et al. (2015c) in Matapalo reef suggests that benthic species from this location are acclimatized to local conditions. However, our results also revealed that upwelling conditions in Matapalo are less extreme than in northern locations (Santa Elena, Section 5). Therefore, it is necessary to measure in situ metabolic rates (through incubations) in species from upwelling and non-upwelling locations, in order to disclose if adaptation of metabolic strategies differ between locations and is dependent of the level of exposition to upwelling conditions. Furthermore, it is crucial to better understand regime shifts in response to environmental changes and their feedback to the carbonate chemistry; because this might help to better predict the development of reefs in a high-CO₂ world. Following this line, we also recommend repeating the experimental transplant of massive coral species between locations, to investigate the vulnerability of *P. lobata* to acidic conditions. Studies carried out in Papua New Guinea suggested that this massive coral can outcompete other species under low-pH conditions (Fabricius et al., 2011). Unfortunately, this could not be confirmed during our study because colonies of this species were systematically stolen from the study sites. However, transplantation experiments will also help to identify the “fittest corals”, to be used as donors in an ongoing local coral restoration project (“Raising coral: a human-coral symbiosis”, www.raisingcoral.org).

Expand the studies including carbonate chemistry along the Costa Rican coasts: E.g. the Golfo Dulce, located in the southern Pacific of Costa Rica, is an outstanding site where important coral reefs built by *P. lobata*, *Pavona* sp. and *Psammocora* sp. are exposed to high river discharges. Coral communities associated to methane seeps have also been documented in this gulf (Wild et al., 2015). Therefore, due to its particular

features this location should be included in future research projects as well as sites at the Costa Rican Caribbean coast.

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Figure 5.4. Dissolved inorganic carbon versus total alkalinity measured in three locations at the Pacific coast of Costa Rica. A_T and C_T were normalized to a salinity of 35 ($nA_T = A_T \times 35/S$, $nC_T = C_T \times 35/S$; S corresponds to the salinity measured in situ). The slope of the C_T - A_T relationship indicates the balance between the organic (photosynthesis-respiration) and inorganic (calcification-dissolution) metabolism. The ratio between organic carbon production:inorganic carbon production is given by the equation $(2/m)-1$.

Figure 5.5. Benthic cover along the Pacific coast of Costa Rica. (A) Percentages of benthic cover in coral reefs from three locations; CA = coralline algae. (B) Contribution (%) of coral species to benthic community.

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Figure 6.2. Graphs showing a) daytime means of seawater temperature, pHManta (total scale) and pHVINDTA (total scale), b) nutrient concentrations of nitrate, ammonia and phosphate, and c) bioerosion $CaCO_3$ budget of the experimental coral

substrate through time (with standard deviation, black bars). Temperature, pH_{Manta} and nutrient data modified after Stuhldreier et al. (2015b).

Figure 6.3. Time-series BSE images of thin-sections from coral substrates throughout the experiment. Shown are representative areas of thin-sections of coral substrates after a-c) one month, d-f) two months, g-i) three months, and j-l) four months of exposure. Encrusting species shown are c) crustose coralline red alga (CCA), d) lithophagine bivalve (genus *Lithophaga/Leiosolenus*), encrusting benthic foraminifer (*Homotrema rubrum*), e) encrusting bryozoan f) encrusting benthic foraminifer, g) lithophagine bivalve, h) encrusting benthic foraminifer, i) CCA, J) CCA (lower left) k) encrusting benthic foraminifer, and l) CCA. Note in k) darker thin bands indicate CaCO₃ mineralogy change of the original coral skeleton (i.e. aragonite to calcite) due to microbioerosion. Also note the change in surface morphology and the increase in microbioerosion through time.

Figure 6.4. Cross sections from modeled μ CT scans of substrates per exposure period, which indicate the settlement succession of the bioeroder community and the internal change in morphology. Shown are cross sections through the X-, Y- and Z-axis of coral substrates of a) control, and after b) one month, c) two months, d) three months, and e) four months of exposure. The hole in the middle part was pre-experimentally drilled to fix the substrates in the reef (cf. S6.1 Fig). Genera depicted in the μ CT scan cross-sections are in c-e) serpulids (Ser), lithophagine bivalves (Biv), and balanids (Ba). Note the increase in abundance and size of lithophagine bivalves through time.

Figure 6.5. Modeled μ CT scans showing the surface morphological change and the settlement succession of bioeroders on the coral substrates. Smaller quadrates at the bottom indicate the alteration of surface roughness per substrate and month. Shown are coral substrates of a) control, and after b) one month, c) two months, d) three months, and e) four months of exposure. Settled genera depicted are in b) serpulids and small CCA (lower left side), c) balanids and serpulids, d) balanids, serpulids and CCA (encrusting on right side, brownish color), and e) balanids and serpulids. Also see supplementary video files in S6.4-S6.8 Figs.

Figure 6.6 SEM images of cast-embedded and partially etched cross sections of coral substrates with positive infills of microbioerosion traces on the skeletal surface. Shown are coral substrates of a) control, and after b) one month, c) two months, d) three months, and e) four months of exposure. Most of the observed bioerosion traces were produced by euendolithic cyanobacteria complemented by some traces formed by chlorophyte algae and marine fungi. Note the increase in boring density over time and the increase in the depth of penetration into the skeletal structure.

Figure 6.7. Graphical concept of the role of bioerosion in ETP coral reef community transitions. Short-term transitions between coral and algal dominance can occur due

to changes in environmental boundary conditions. Coral growth may cease during ENSO events or during periods of intensive upwelling. Eutrophic conditions in the reef favor organotrophic settlers, in particular detritus and filter feeders, including many calcifying encrusting and bioeroding species. Enhanced activity of bioeroders, as an ecological response, supports the re-transition of the reef into an oligotrophic condition by the uptake of nutrients and buffering seawater carbon chemistry (carbonate sediment production and dissolution; influence seawater Ω , pH, A_T , pCO_2). Additionally, grazers and predators are attracted due to the increase in food or prey abundance. New substrate is formed by predation (reef fish, echinoderms, mollusks) and macrobioerosion, which allows coral dispersal (fragmentation) and formation of rhodolithic substrate serving as larvae settling grounds. The ecological effects benefit the growth of phototrophic calcifiers (i.e. corals, crustose coralline algae). Dashed lines indicate ecological responses to environmental processes (solid lines). Green lines indicate an effect on the reef community towards algal growth and blue lines indicate effects towards coral growth.

S6.1 Fig. Experimental setup deployed in the reef (schematic drawing and photograph).

S6.2 Fig. Photographs of typical benthic seafloor cover and sediment at the Matapalo Reef site. Crustose coralline red algae (CCA) encrusting the coral rubble substrate forming rhodoliths, and growth of the green macro-alga genus *Caulerpa*. Water depth ~5 m bsl.

S6.3 Fig. SEM images from microbioerosion traces on the surface of the coral substrates. a) control, and after b) one month, c) two months, d) three months, and e) four month of exposure. Note the increase in borings and the loss of skeletal structure (e.g. coral fibers) over time. Scale bar 50 μm . (TIFF File, <https://doi.org/10.1371/journal.pone.0202887.s005>)

S6.4 Fig. μ CT scan video of control coral substrate (pre-experiment).

S6.5 Fig. μ CT scan video of coral substrate exposed for one month at Matapalo Reef.

S6.6 Fig. μ CT scan video of coral substrate exposed for two months at Matapalo Reef.

S6.7 Fig. μ CT scan video of coral substrate exposed for three months at Matapalo Reef.

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S6.9 Fig. Photographs of retrieved coral substrates from the Matapalo Reef site, before bleaching (30% H_2O_2). After a, b) one month; c, d) two months; e, f) three months; g, h) four months of exposure.

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DECLARATION IN LIEU OF OATH

Hiermit versichere ich an Eides statt, dass ich die vorliegende Dissertation mit dem Titel: "Carbonate chemistry and coral reefs in the Pacific coast of Costa Rica" selbstständig verfasst und keine anderen als die angegebenen Hilfsmittel – insbesondere keine im Quellenverzeichnis nicht benannten Internet-Quellen – benutzt habe. Alle Stellen, die wörtlich oder sinngemäß aus Veröffentlichungen entnommen wurden, sind als solche kenntlich gemacht. Ich versichere weiterhin, dass ich die Dissertation oder Teile davon vorher weder im In- noch im Ausland in einem anderen Prüfungsverfahren eingereicht habe und die eingereichte schriftliche Fassung der auf dem elektronischen Speichermedium entspricht.

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San José, 30.10.2019

Celeste Sánchez Noguera