Characterizing Reef Net Metabolism Via the Diel Co-Variation of pH and Dissolved Oxygen From High Resolution in Situ Sensors

Sarah E. Cryer[1,2] , Claire Evans[2] , Sara E. Fowell[2] , Gilbert Andrews[3], Peter Brown[2] , Filipa Carvalho[2] , Diana Degallerie[4] , Jake Ludgate[2], Samir Rosado[3], Richard Sanders[2,5], James A. Strong[2], Derrick Theophille[4], Arlene Young[3], and Socratis Loucaides[2]

[1]Ocean and Earth Science, University of Southampton, Southampton, UK, [2]National Oceanography Centre, Southampton, UK, [3]Coastal Zone Marine Authority and Institute, Belize City, Belize, [4]Dominica Fisheries Division, Roseau, Commonwealth of Dominica, [5]NORCE Norwegian Research Centre, Bergen, Norway

Abstract Coral reefs are subject to degradation by multiple environmental stressors which are predicted to intensify. Stress can alter ecosystem composition, with shifts from hard coral to macroalgae dominated reefs often accompanied by an increase in soft corals and sponges. Such changes may alter net ecosystem metabolism and biogeochemistry by shifting the balance between photosynthesis, respiration, calcification and dissolution. We deployed high temporal resolution pH and dissolved oxygen (DO) sensors at four Caribbean reef sites with varying covers of hard and soft corals, sponges and macroalgae. The resultant data indicated that the strength of the "metabolic pulse", specifically the co-variation in daily pH and DO oscillations, was driven by the net balance of light -dependent and -independent metabolism. pH and DO were positively correlated over the diel cycle at coral dominated sites, suggesting that photosynthesis and respiration were the major controlling processes, and further indicated by agreement with a simple production:respiration model. Whereas, at a site with high macroalgal cover, pH and DO decoupling was observed during daylight hours. This indicates that an unidentified light-driven process altered the expected pH:DO relationship. We hypothesize that this could be mediated by the higher levels of macroalgae, which either stimulated bacterial-mediated carbonate dissolution via the production and release of allelopathic compounds or retained oxygen, evolved during photosynthesis, in the gaseous form in seawater (ebullition). Our work demonstrates that high resolution monitoring of pH and DO provides insight into coral reef biogeochemical functioning and can be key for understanding long-term changes in coral reef metabolism.

Plain Language Summary Coral reefs are regarded as the rainforests of the sea, supporting 25% of marine species and millions of people worldwide. Yet, they are facing a number of threats including rising sea surface temperature, decreasing ocean pH, overfishing and increased competition with algae. As coral reefs experience stress, the relative abundance of hard coral, algae, soft corals and sponges can change. A healthy reef is generally thought of as one with a high proportion of hard coral as their skeletons form the backbone of the reef environment. Under stress, however, a reef can transition from hard coral to algae dominated with significant implications for the entire reef ecosystem. In this paper, we suggest that the reef metabolism, which is driven by benthic composition, drives the natural variability and the relationship between pH and dissolved oxygen (DO) over a 24-hr cycle. Our data suggest that the daily range in pH and DO is larger at sites with more hard coral and less algae, and the relationship between pH and DO is stronger. High resolution measurements of pH and DO using autonomous sensors could potentially reveal vital information on ecosystem functioning and may be valuable tools in monitoring changes in coral reefs.

1. Introduction

Coral reefs are subject to numerous intensifying environmental stressors, including rising sea surface temperatures and ocean acidification, and anthropogenic activities, such as overfishing and nutrient loading (Bove et al., 2020; Bozec et al., 2016; Pendleton et al., 2016; Romanó de Orte et al., 2021; Silbiger et al., 2014, 2018). This has resulted in a global decline of coral reef health, with an approximate 50% reduction in coral cover from 1957 to 2007 (Eddy et al., 2021). A key indicator of declining reef health is changes to ecosystem community composition, which frequently results in phase shifts. Phase shifts are often characterized by a change in

Methodology: Sarah E. Cryer, Sara E. Fowell, Gilbert Andrews, Diana Degallerie, Jake Ludgate, Samir Rosado, James A. Strong, Derrick Theophille, Arlene Young, Socratis Loucaides
Project Administration: Claire Evans, Sara E. Fowell, Diana Degallerie, Richard Sanders, James A. Strong, Derrick Theophille, Arlene Young, Socratis Loucaides
Resources: Claire Evans, Sara E. Fowell, Gilbert Andrews, Diana Degallerie, Jake Ludgate, Samir Rosado, James A. Strong, Derrick Theophille, Arlene Young, Socratis Loucaides
Software: Sara E. Fowell, Jake Ludgate, Socratis Loucaides
Supervision: Claire Evans, Peter Brown, Filipa Carvalho, Richard Sanders, Socratis Loucaides
Validation: Jake Ludgate, Socratis Loucaides
Visualization: Sarah E. Cryer, Filipa Carvalho
Writing – original draft: Sarah E. Cryer, Claire Evans
Writing – review & editing: Sarah E. Cryer, Sara E. Fowell, Peter Brown, Filipa Carvalho, Richard Sanders, James A. Strong, Derrick Theophille, Socratis Loucaides

dominance from hard coral to macroalgae (Hughes, 1994; Nyström et al., 2008). Healthier reefs are generally associated with higher hard coral cover and lower macroalgae presence (Mumby et al., 2007). Following coral mortality, algal assemblages are usually the first colonizers of the bare substrate (Romanó de Orte et al., 2021), and once established, macroalgae can damage adult corals and suppress coral recruitment (Brooker et al., 2016). Phase shifts to the dominance of other life forms, including soft corals and sponges, can also occur following a disturbance to a reef (Norström et al., 2009). Sponge abundance on reefs, for example, has risen globally (Bennett et al., 2017), with an increase in bioeroding clionid sponges reported in the Caribbean (Antonius & Ballesteros, 1998; López-Victoria & Zea, 2005). Coral loss is particularly acute in the Caribbean where hard coral cover has declined by 80% on average since the 1970s (Gardner, 2003). Hard corals form aragonite skeletons, which typically provide the physical framework for a reef; therefore, their loss can have profound consequences, not only for the coral (Nyström et al., 2008) but also for the entire reef ecosystem and local biogeochemistry (Webb et al., 2021).

Calcification is the key process responsible for constructing the physical reef (Erez et al., 2011), and to maintain their habitat, reefs need to calcify at a rate greater than the combined rates of erosion, dissolution (Andersson & Gledhill, 2013; Erez et al., 2011; Kleypas et al., 1999) and sea-level rise (Perry et al., 2018). It may, therefore, be more appropriate to define a healthy reef as one that is actively growing and accreting net calcium carbonate ($CaCO_3$), as opposed to the proportions of different benthos (Smith et al., 2016). Reductions in rates of calcification as a result of anthropogenic stressors such as ocean acidification (Erez et al., 2011), rising sea surface temperatures (D'Olivo & McCulloch, 2017), or eutrophication (Steiner et al., 2018) could result in reef-wide consequences due to alteration of reef structure (Hoegh-Guildberg et al., 2007; Kleypas et al., 1999). Ocean acidification, caused by the air-to-sea flux of atmospheric carbon dioxide (CO_2), is of particular concern for marine calcifiers due to the consequent decrease in carbonate ion concentrations $[CO_3^{2-}]$ (Shamberger et al., 2018) and therefore calcite and aragonite saturation states. As calcification at the organism level responds mainly to $[CO_3^{2-}]$ (Erez et al., 2011), community calcification is expected to decline as the ocean becomes more acidic (e.g., Bove et al., 2019; Shamberger et al., 2018).

The extent to which biology affects seawater chemistry in shallow reef waters is determined by the coral reef community metabolism (Langdon et al., 2003; Price et al., 2012; Smith et al., 2013), topography (depth, open water connectivity, etc.) and a number of physical processes (i.e., mixing, currents, etc) (Falter et al., 2013). During daylight, photosynthesis by autotrophs produces oxygen (O_2), while consuming CO_2, increasing seawater pH and shifting carbonate speciation toward higher $[CO_3^{2-}]$ (Suzuki et al., 1995). In the absence of light, respiration dominates and, therefore, dissolved oxygen (DO) is consumed and CO_2 released, reducing pH and $[CO_3^{2-}]$. In non-calcifying photoautotrophs such as algae, the relationship between DO production/consumption and pH is reasonably predictable from the stoichiometric "Redfield Ratio", assuming the change in total alkalinity (TA) is negligible (Smith et al., 2013). Corals, however, have a more complex pH to DO relationship given that they calcify, photosynthesize (by zooxanthellae symbionts) and respire, thereby altering seawater dissolved inorganic carbon (DIC) and TA. During calcification TA and DIC are removed from seawater at a 2:1 ratio and hydrogen ions (H^+) are released causing an overall decline in pH (Jokiel et al., 2014; Wolf-Gladrow et al., 2007). $CaCO_3$ dissolution releases TA and DIC at a 2:1 ratio, therefore increasing pH (Wolf-Gladrow et al., 2007). Deviations from a "Redfield" pH:DO covariation could, therefore, be evidence of $CaCO_3$ calcification or dissolution, as neither process is directly related to O_2 metabolism. Calcification occurs during both day and night, however its rates are higher during daylight when photosynthesizing coral symbionts can enhance calcification rates through light-enhanced calcification (Gattuso et al., 1999; Moya et al., 2006). This algal-coral symbiosis is also referred to as the "biological engine producing the reef" (Roth, 2014). Dissolution typically happens at night (e.g., Moav-Barzel et al., 2023; Page et al., 2016; Romanó de Orte et al., 2021) as a consequence of decreasing pH and $[CO_3^{2-}]$, which results from CO_2 generated by respiration no longer being consumed by photosynthesis. Net reef dissolution can be an indicator of reef ecosystem health decline, and has been associated with vulnerability to environmental stress (Hoegh-Guildberg et al., 2007). Carbonate chemistry speciation in reef ecosystems is, therefore, dependent on the community-specific balance between calcification, dissolution, respiration and photosynthesis, which is a product of the relative abundance of calcifying, non-calcifying (Anthony et al., 2011), autotrophic and heterotrophic organisms.

Biogeochemical monitoring can shed light on marine ecosystem functioning by revealing natural environmental variability and providing baselines against which long-term changes can be assessed. Typically, ecosystems exhibit threshold responses to stress, rather than responding linearly to environmental change (Hughes et al., 2010); this
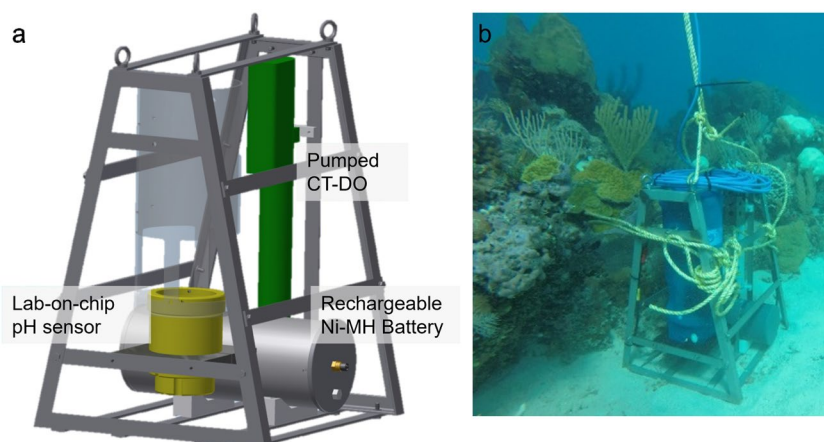
Figure 1. (a) Technical drawing of the fixed-point observing platform with lab-on-chip pH sensor, rechargeable Ni-MH battery pack and Seabird CT-DO sensor labeled. (b) Platform deployed on the Goff's Caye fore reef site.

could lead to changes in seawater biogeochemistry being detecatable before changes are identifiable by visual ecosystem assessments. High temporal resolution biogeochemical observations from coral reefs are lacking. The shallow bathymetry and inaccessibility of coral reefs make it difficult to collect high resolution data through the traditional means of discrete water sampling. These barriers can be overcome by autonomous sensors and technological advances (e.g., Cryer et al., 2020; Schaap et al., 2021; Takeshita et al., 2018; Yin et al., 2021), which enable sustained high-temporal resolution and robust measurement. Over the last decade or so, as sensor technology has advanced, more high-resolution reef pH data sets have become available (e.g., Cyronak et al., 2020; Kline et al., 2015; McMahon et al., 2018; Santos et al., 2011; Silbiger et al., 2014). The availability of carbonate sensors (particularly TA and DIC) capable of high-quality measurements in dynamic environments, such as coral reefs, remains limited. Therefore, data from reefs, especially coupled pH and DO measurements (e.g., Gray et al., 2012; Pezner et al., 2021; Takeshita et al., 2018), remain scarce.

Stress induced disturbances to the balance of metabolic processes on reefs and the resultant phase shifts, are likely to be evident in the diel cycles of biogeochemical parameters such as pH and DO concentrations. In this work we investigated the relationship between biogeochemical parameters and benthic composition on four Caribbean reef sites, via high-resolution, simultaneous measurements of pH and DO and their co-variation. We propose that the magnitude of the diel cycle of pH and DO and the relationship between them can be indicative of the reef's "metabolic pulse" analogous to that described by Cyronak et al. (2018) for DIC and TA.

2. Materials and Methods

2.1. Data Collection

Custom-built fixed-point observing platforms (Figure 1) were deployed at four sites on Caribbean coral reefs (see Section 2.3). The fixed-point observatories were developed at the National Oceanography Centre, UK (Ocean Technology and Engineering group) to enable high performance, user friendly and low-cost ocean acidification observations in coastal waters as part of the Commonwealth Marine Economies Program (https://cmeprogramme.org). Their relatively small size and low weight in air (<50 kg) enable deployment and recovery by hand in coastal and shallow waters without the need of a winch or a large vessel. Each platform includes a microfluidic lab-on-chip (LOC) pH sensor (Yin et al., 2021) and a pumped conductivity, temperature and dissolved oxygen (CT-DO) sensor (SBE 37 SMP ODO MicroCAT; Seabird Scientific, Bellevue WA, USA). The technology used was designed to assist developing nations to monitor their coastal waters in response to the UN Sustainable Development Goals. Communication between the two sensors and power supply are enabled through a custom-built communications hub. The hub enabled the pH sensor to operate the CT-DO sensor on demand and use its temperature and reference salinity (psu) measurements to calculate total scale pH (pH_T) as per Liu et al. (2011), at in situ conditions. From here onward quoted pH values are on the total scale. Power was provided by a custom-made rechargeable Ni-MH battery pack enclosed within a polyvinyl chloride (PVC) 100 m depth rated housing. The battery provides enough power for hourly meas-

Table 1
Characteristics of Deployment Locations

Site	Country	Latitude	Longitude	Site description	Depth (m)
Goff's Caye Fore Reef	Belize	17.35229°N	88.03381°W	Dominated by hard and soft corals	6
Goff's Caye Back Reef	Belize	17.35401°N	88.03789°W	Dominated by rubble, sand and soft coral	4.5
English Caye	Belize	17.326094°N	88.04933°W	Dominated by macroalgae, soft coals and sponges. Back reef environment	6.5
Soufrière	Dominica	15.236866°N	61.370282°W	Mostly dead coral and rock with encrusting species (corals, sponges and algae) beginning to grow. Back reef environment	9

urements over a 1-month deployment. The sensors and battery pack were contained within a stainless-steel frame designed for seabed or moored deployments. Data generated were stored on-board the pH sensor, while optional near-real time data telemetry was enabled by Trident Sensors Iridium data and tracking beacon fixed to a surface buoy and connected to the data hub by a 25 m cable. The LOC pH sensor (now manufactured and sold by ClearWater Sensors Ltd.) measures pH on the total scale using purified meta-Cresol Purple indicator dye as described in Clayton and Byrne (1993). It has a combined standard measurement uncertainty of <0.010 at pH 8.0 (<0.009 at pH 8.5 and <0.014 at pH 7.5) and measurement reproducibility of <0.001 pH units (Yin et al., 2021). Measurement frequency can be adjusted to a maximum of 1 measurement every 8 min.

2.2. Collection and Analysis of DIC and TA

Two DIC and TA samples were collected at the Belize Goff's Caye sites (Section 2.3) using a 5 L Niskin bottle deployed to sensor depth on 4 November 2019. Samples were then collected in 250 ml borosilicate glass bottles, poisoned with 50 µL saturated mercuric chloride solution, sealed with Apiezon L silicone grease on ground-glass stoppers and stored in the dark at room temperature before transport to, and analysis in, the UK. TA was determined using a two-stage potentiometric open-cell titration using a Scripps TA Titration System (Dickson et al., 2003). The titration acid was calibrated each day using CRMs (Certified Reference Material, Dickson Lab Batches 180 and 191; Dickson, 2010), with an average uncertainty on CRMs of ±1.7 µmol/kg. DIC was measured by coulometry using a MARIANDA VINDTA 3C system (Mintrop, 2004). CRMs (Batches 180 and 191; Dickson, 2010) were run every ~12 samples, with an average uncertainty of ±3.0 µmol/kg.

2.3. Study Sites

Observing platforms were deployed on the Meso-American Barrier Reef (Belize) and the fringing reef of Dominica (Table 1). We collected high resolution time series data from four different sites: three sites in Belize (fore reef and back reef at Goff's Caye, back reef at English Caye, Figure 2) and a single back reef site in Dominica (5 separate deployments near Coral Gardens; Figure 2).

2.3.1. Belize

Two observing platforms were deployed simultaneously for 10 days at two sites on the Belize Barrier Reef by Goff's Caye (Figure 2a) in October–November 2019, around 20 km offshore of Belize City. Wet season is typically June–November; however, during our deployment Belize was experiencing a prolonged dry season. Coral cover in Belize is estimated to have declined from 26.3% to 10.7% from 1997 to 2016, while macroalgal cover increased from 12.9% to 39.7% (Alves et al., 2022). Despite Belize putting measures in place to tackle reef degradation, such as the implementation of Marine Protected Areas and a ban on herbivorous fishing, coral cover is yet to show signs of recovery (Alves et al., 2022; Cox et al., 2017). However, recent studies suggest coral cover has not decreased further in the last decade (Mumby et al., 2021). Extensive seagrass beds characterized the seabed between the mainland and the Belize Barrier Reef.

One platform was deployed on the fore reef (6 m depth) and the other on the back reef (4.5 m depth) in order to compare short-term pH and DO variability between the two sites simultaneously. Prior to the deployment, the two observing platforms were placed on the seabed adjacent to each other for two hours at a 20-min measurement frequency in order to determine any measurement offsets between the sensors. The pH difference was calculated at 0.016, which is within the cumulative uncertainty of the two sensors (each sensor has an estimated measure-
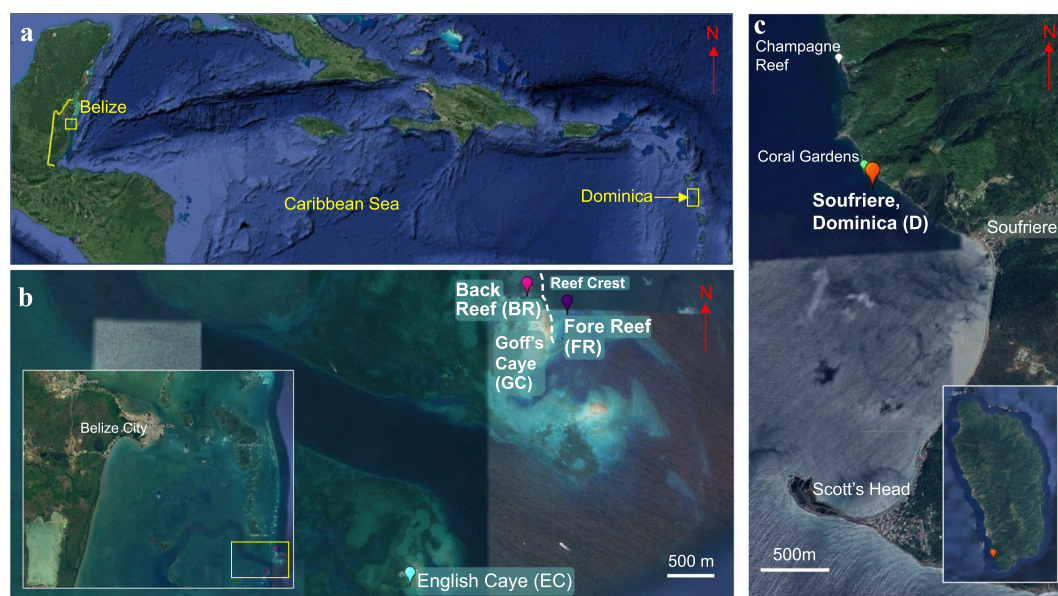
Figure 2. Locations of fixed-point observing sites on a true color Google Map—(a) Location of Belize and Dominica in the Caribbean with location of (b) and (c) shown by yellow box, (b) Belizean sites—fore and back reef at Goff's Caye and a site at English Caye; inset, sites are ~20–25 km off shore of Belize City. (c) Dominica site within the Soufrière-Scott's Head Marine reserve, north of the village of Soufrière, ~100 m offshore; inset: site located in SW Dominica (Google Earth Pro, 2011, 2015a, 2015b, 2015c, 2019).

ment uncertainty of ~0.01), DO difference was 2.95 μmol/L (sensor accuracy ±3 μmol/L), 0.003°C difference in temperature (accuracy ±0.002°C) and a 0.008 g/kg difference in salinity (accuracy ±1 × 10^{-4} g/kg at 25°C). One of the two platforms was redeployed afterward at a back reef site adjacent to English Caye for long-term monitoring. The English Caye site, 3.3 km south of Goff's Caye, was chosen mainly due to the safety provided by the continuous presence of the caye's lighthouse keeper.

2.3.2. Dominica

An observing platform was deployed at a back reef site within the Soufriere-Scott's Head Marine Reserve, around 100 m offshore (Figure 2c). The platform was deployed five times for 11–16 days in 2018 (March, April, June) and in 2019 (March and July), covering both wet and dry seasons. Wet season occurs between June and October, with heaviest rainfall typically between late summer and fall and peak hurricane season late August–early September. Coral reefs in Dominica are comparatively isolated (Steiner, 2015), consisting of a rock base and are predominately sponge-dominated reefs (Madisetti, 2018). In September 2017 Hurricane Maria, a Category 5 hurricane, hit Dominica and destroyed an estimated 20%–40% of the reefs across the island (Madisetti, 2018). Coral Gardens, the closest site surveyed to the platform's deployment, was extensively damaged, with trees, rocks and silt from the associated landslides smothering the reef (Madisetti, 2018). At Champagne Reef, everything shallower than 3 m water depth was completely destroyed, while the reef wall was damaged to a depth of 15 m and many large sponges were destroyed (Madisetti, 2018).

2.4. Characterization of Benthos

Benthic ecosystem assemblages around each observatory were characterized from photographs of the seabed. In Belize, photos were taken using a GoPro Hero 3+ by scuba divers or snorkelers immediately after platform deployment. These photos were within 10 m of the sensor frame. In Dominica, a GoPro mounted on a mini Remotely Operated Vehicle (DeepTrecker) was deployed over the side of the boat and screengrabs were taken from recorded video. The photos from Dominica were taken on 10 March 2019, 1 year after the first deployment but before deployments 4 and 5.

Benthos and substrate were determined using Coral Point Count (CPC) with Excel Extensions (Kohler & Gill, 2006). Photos, representative of the reef environment, were loaded into CPC, 4 for each of the Belize sites and 13 screengrabs for Dominica. For each photo an 8 × 8 grid was constructed and within each cell a point was randomly distributed. The marine benthos or substratum for each point was then identified manually.

2.5. Statistical Analysis & Production Respiration (P:R) Model

A two-sample t-test (Matlab, 2018) was used to determine if pH, DO, salinity and temperature differences between Belize fore reef and back reef sites were statistically significant, with significance determined if $\rho < 0.05$. Pearson's Correlation (Matlab, 2022) was used to test the relationship between pH and DO or between salinity and temperature, at each site. A one-way anlaysis of variance (ANOVA) was used to test the differences in pH or DO between Dominica deployments.

pH and DO observations were compared against theoretical Photosynthesis: Respiration (P:R) model, following Frieder et al. (2012). This model describes the expected relationship between pH and DO in systems when photosynthesis and respiration are assumed to be the dominant controlling processes. For a given change in DO (ΔDO, in mol kg^{-1}), proportional changes in dissolved CO_2 (ΔCO_2, equal to ΔDIC, also in mol kg^{-1}) are expected according to the stoichiometric "Redfield" ratio $\Delta CO_2 = \frac{\Delta O_2}{-150/106}$ (Anderson, 1995). The model assumes limited contributions from air-sea gas fluxes, which is a reasonable approximation given that maximum flux estimates around Belize are ~5 mol m^{-2} yr^{-1} (Wanninkhof et al., 2020) and calcification or carbonate dissolution if prevalent would be observed through pH divergence without an accompanying oxygen change.

ΔDIC was converted to changes in pH (ΔpH) using internal inorganic carbon thermodynamic constants in CO2SYS (Lewis & Wallace, 1998; Sharp et al., 2020). For this we use TA (TA = TA$_i$ + ΔTA; where i indicates initial concentrations, ΔTA = change in TA) and DIC (DIC = DIC$_i$ + ΔDIC) as input parameters, and dissociation constants for carbonic acid from Mehrbach et al. (1973) refitted by Dickson and Millero (1987), for KSO$_4$ from Dickson (1990), for total Boron concentration from Lee et al. (2010), KH$_F$ from Perez and Fraga (1987) and median temperature (°C) and salinity (psu) from each site (Table 2). Initial TA (TA$_i$) for each site was calculated from salinity using a TA-salinity parameterization for the North Atlantic and Caribbean region (TA = 57.3 × salinity +296.4; Cai et al., 2010). ΔTA was calculated using ΔTA = $\frac{\Delta CO_2}{-18/106}$ (Frieder et al., 2012; Stumm & Morgan, 1996), which accounts for changes in seawater proton concentration [H$^+$] during photosynthesis/respiration. Initial DIC (DIC$_i$) was adjusted to match as much as possible the P:R model to our observations. Adjusted DIC$_i$ values were 2,075.9 µmol/kg (Goff's Caye fore reef), 2,052.5 µmol/kg (Goff's Caye back reef), 2,078.6 µmol/kg (English Caye), and 2,041.2 µmol/kg (Dominican site). Measured DIC and TA from samples collected at Goff's Caye fore reef (DIC: 2,020 µmol/kg; TA: 2,352 µmol/kg) and back reefs (DIC: 2,026 µmol/kg; TA: 2,345 µmol/kg) on 4 November 2019, were within the DIC and TA ranges used for the Goff's Caye fore reef (DIC: 1,822–2,133 µmol/kg, TA: 2,344–2,397 µmol/kg) and back reef (DIC: 1,798–2,109 µmol/kg, TA: 2,344–2,396 µmol/kg) P:R models. We tested the validity of our choice of TA$_i$ and DIC$_i$ by varying it across typical oceanic ranges (Figure S3 in Supporting Information S1, P:R model calculated using a range of TA$_i$ and DIC$_i$). We found that it did not affect our data interpretation due to it primarily affecting only the model's y intercept and not the relationship calculated between pH and DO.

3. Results

3.1. Diel Cycle in pH and DO

The amplitude of the diel cycle in both pH and DO varied between sites (Figures 3–6), with the minimum and maximum measurements recorded summarized in Table 2. Within a 24-hr period, the maximum diel range in pH at each site was 0.116 (Goff's Caye fore reef), 0.137 (Goff's Caye back reef), 0.164 (English Caye), and 0.097 (Dominica—March 2018 deployment). Minimum pH was observed around dawn (04:00–06:00, local time) at all sites with maximum pH between 11:00–14:00. Minimum DO was observed between 05:00 and 07:00 with maximum DO between 13:00–15:00 and maximum DO either coincided with maximum pH (Goff's Caye fore reef and back reef) or was observed shortly after (English Caye and Dominica). The median range in pH and DO was calculated using the median of the daily minimum and median of the daily maximum. The largest median range in both pH and DO was observed at the Goff's Caye back reef site (Table 2, Figures 3c and 3d), with the minimum range recorded at the Dominica site (Table 2, Figures 3g and 3h). In Dominica, median DO and pH varied significantly between the five deployments (DO; one way ANOVA, $p = 0.0422$ and pH; one way ANOVA, $p < 0.0001$).

3.2. Intra-Reef Comparison (Goff's Caye, Belize)

Figure 4 shows pH, DO, temperature and absolute salinity over the 9.5-day deployment at the fore and back reef sites (Goff's Caye). The variability in all parameters was similar between the back and fore reef sites, although

Table 2
Maximum, Minimum, Median and Range of pH, DO, Absolute Salinity and Temperature Measurements From Each Deployment

| Site	Date	No. days	Sampling interval (hour)	Max pH_T	Min pH_T	Median pH_T range	Median pH_T	Max DO (µmol/L)	Min DO (µmol/L)	Median DO range (µmol/L)	Median DO (µmol/L)	Salinity range (g/kg)	Median salinity (g/kg)	Temperature range (°C)	Median temperature (°C)
Fore Reef, Belize	25 October 2019–4 November 2019	9.5	1	7.991	7.849	0.066	7.937	206.7	131.3	30.7	176.1	0.53	36.08	0.69	29.61
Back Reef, Belize	25 October 2019–4 November 2019	9.5	1	8.024	7.8820	0.070	7.968	217.4	144.5	32.0	180.8	0.66	36.06	0.97	29.59
English Caye, Belize	06 November 2019–2023 December 2019	47	2	8.090	7.866	0.047	7.965	196.5	137.5	11.9	174.6	1.29	36.42	4.20	28.71
Soufrière, Dominica	15 March 2018–2029 March 2018	14	2	8.066	7.969	0.022	8.021	209.2	194.2	5.6	202.0	0.99	35.80	1.02	27.13
Soufrière, Dominica	9 April 2018–2020 April 2018	11	2	8.035	7.963	0.026	8.007	210.5	194.2	7.6	202.3	1.45	35.39	0.65	27.52
Soufrière, Dominica	08 June 2018–2024 June 2018	16	2	8.029	7.95	0.032	8.006	208.8	190.9	9.4	200.0	1.72	34.40	0.19	27.87
Soufrière, Dominica	27 March 2019–07 April 2019	11	2	8.059	8.004	0.024	8.034	208.5	194.6	7.5	202.6	0.35	36.40	0.71	26.77
Soufrière, Dominica	03 July 2019–14 July 2019	11	2	8.081	7.973	0.03	8.023	206.7	191.2	8.1	201.1	0.56	34.53	0.46	28.35
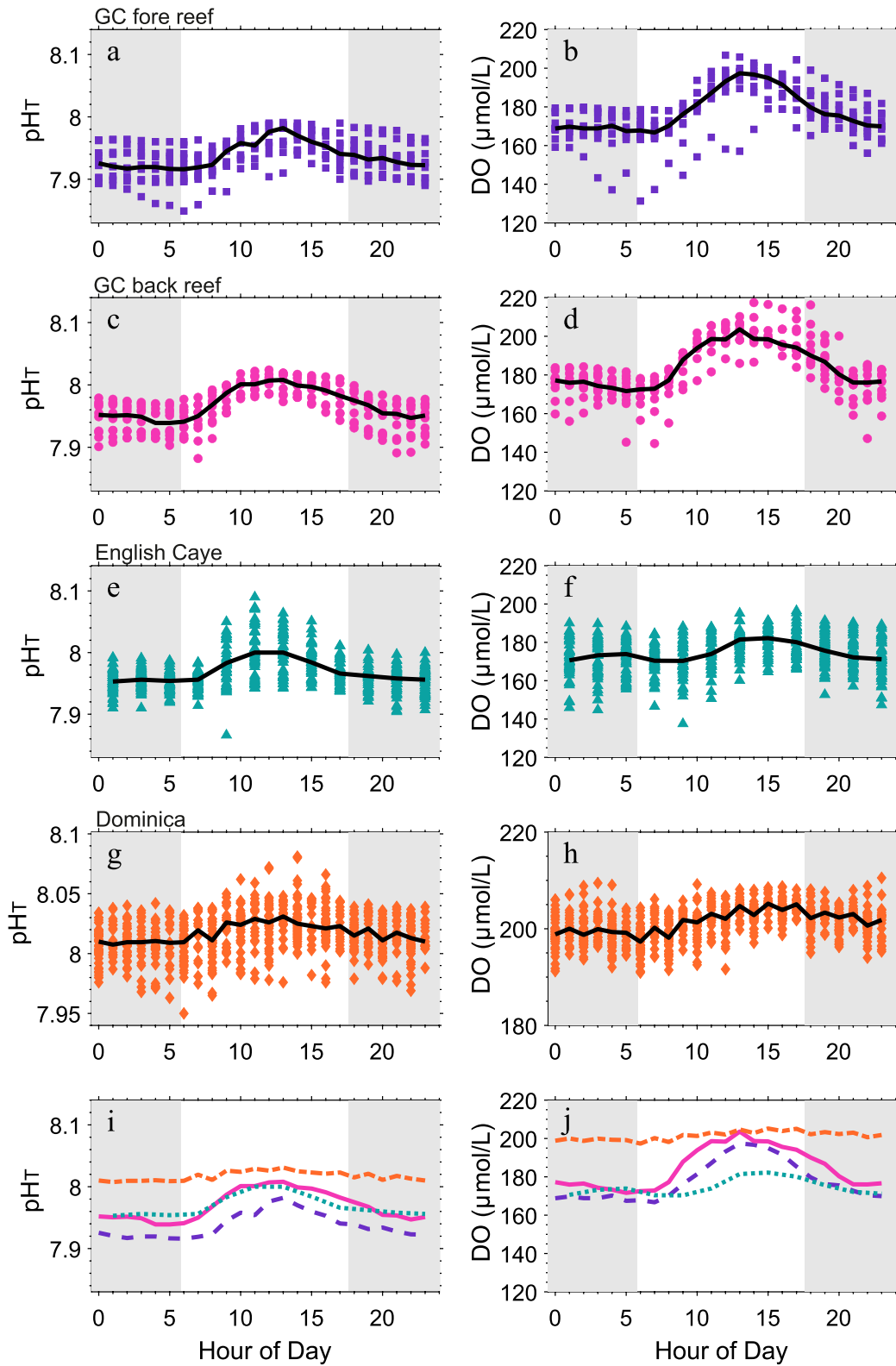
Figure 3.
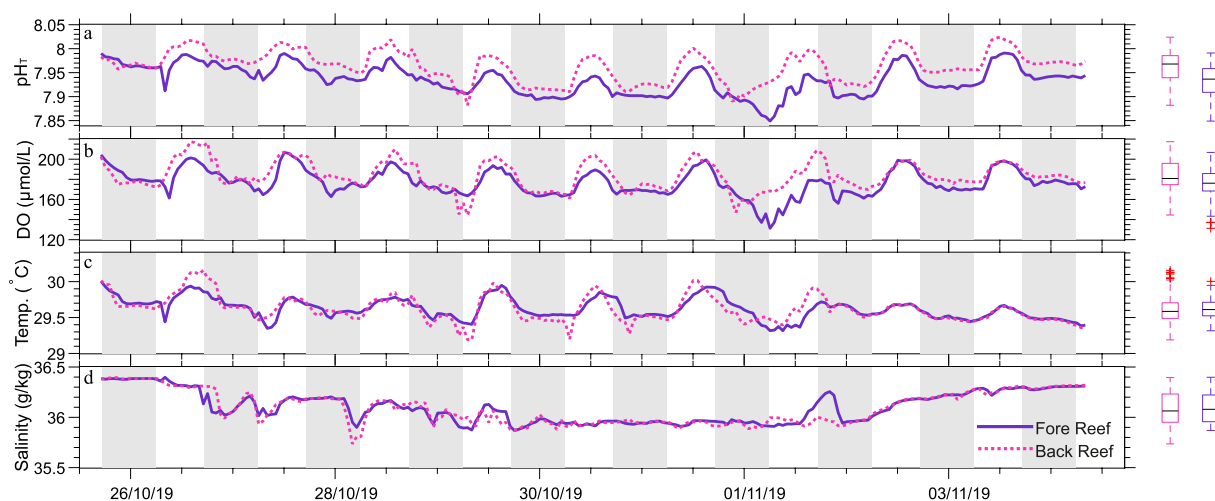
Figure 4. Time series for a 9.5 days deployment showing (a) pH_T, (b) DO, (c) temperature and (d) absolute salinity for the Goff's Caye fore reef site (purple, solid line) and back reef (pink, dashed line). Nighttime is shown by gray shading. The corresponding box plots for each site are also plotted in purple for fore reef and pink for back reef.

pH and DO values recorded at the back reef were significantly higher (two sample t-test, pH $p < 0.0001$, DO $p < 0.0001$) with medians 0.029 and 6.23 μmol/L higher respectively. The larger amplitudes in pH and DO were observed when salinity was 35.9–36 g/kg. Temperature and salinity values at the two sites were similar (median difference 0.014°C and 0.001 g/kg respectively; two sample t-test, temperature $p = 0.85$, salinity $p = 0.64$).

3.3. Relationship Between pH and DO

pH and DO values correlated positively across all sites (Figure 7, Table 3), with distinct differences in regression characteristics between sites (Table 3). In Dominica, data from all five deployments were grouped together as there was no significant difference in pH:DO relationships between the deployments. There was a stronger correlation between pH and DO at Goff's Caye fore ($R^2 = 0.78$, $p < 0.001$) and back reef ($R^2 = 0.73$, $p < 0.001$) sites where the diel signal was also strongest (Figure 3, Table 3). At English Caye pH and DO correlation was weak ($R^2 = 0.30$, $p < 0.001$) but stronger when only the nighttime data were included ($R^2 = 0.58$, $p < 0.001$). Both the pH:DO correlation ($R^2 = 0.20$, $p < 0.001$) and diel signal were weakest at the Dominica site.

Classifying the data according to whether it was collected during daylight or in darkness highlighted distinctions in the pH:DO relationship, particularly at English Caye (Figure 7c, Table 3). At both Goff's Caye sites the pH:DO relationship was very similar between night and day and closely agreed with the theoretical P:R Model. Observations from English Caye agreed well with the theoretical P:R model during the night but not during daytime. At the Dominica site, there was no significant distinction between observations made during day or night.

3.4. Benthic Coverage

The four sites exhibited different benthic community compositions (Figure 8). Hard coral cover was highest at Goff's Caye fore reef and was significantly lower at the other sites. Goff's Caye fore reef was dominated by hard and soft corals and the back reef by sand, rubble and soft coral. English Caye's main benthos was macroalgae and soft coral, and Soufriere was dominated by rock and encrusting sponge, coral, or coralline crustose algae (CCA). Differentiating between encrusting organisms (sponges, coral or CCA) was not always obvious; therefore, they have been grouped together to avoid misclassification.

Figure 3. Diel cycles in pH_T (left hand side) and DO (right hand side). pH is reported on the total scale. All deployments for each site are included. The solid black line shows the median pH/DO and nighttime is shown with gray shading. Measurements throughout the day for the four sites (a + b, purple squares) Goff's Caye fore reef, Belize; (c + d, pink circles) Goff's Caye back reef, Belize; (e + f, turquoise triangles) English Caye, Belize; (g + h, orange diamonds) Soufriere, Dominica (five deployments). The pH and DO data from Dominica are on a smaller scale to better illustrate the diel signal. The bottom two panels compare the pH_T (i) and DO (j) median lines for each site: Goff's Caye fore reef is dashed purple; Goff's Caye back reef is solid pink; English Caye is dotted turquoise; and Dominica is dotted dashed orange.

4. Discussion

Measuring pH at high temporal resolution is recommended by the global ocean acidification community for monitoring both long-term changes in average seawater acidity and its temporal variability (range). Examining the short-term variability in pH (over hours, days, seasons) is most relevant in establishing ocean acidification impacts on marine ecosystems (Widdicombe et al., 2023). This is because it reveals the range in pH and the extreme organisms are exposed to. Such information can be generated effectively using the autonomous observing platforms described in this study, which in addition to pH record DO, salinity and temperature, enabling a more comprehensive characterization of biogeochemical processes. The pH values recorded during our study (7.849–8.090; Table 2) across all sites in Belize and Dominica were generally below the global seawater average at the time of sampling (8.07 between 60°N and 60°S; Jiang et al., 2019). Minimum pH was measured at Goff's Caye fore reef site (7.849), similar to that reported for other Caribbean reefs (e.g., ~7.9 on reefs in Bermuda, Panama and Puerto Rico; Cyronak et al., 2020; Gray et al., 2012; Pezner et al., 2021), but higher than some reported Pacific reef minimums (e.g., Palmyra atoll < 7.85; Price et al., 2012 and Great Barrier Reef < 7.7; Shaw et al., 2012). Minimum pH values from high-resolution studies on coral reefs are rarely reported and therefore, it remains difficult to make comparisons across space and time. While the pH minimums we recorded were not unusually low, they will continue to decline as the ocean CO_2 content increases, with lower pH minimums across the diel cycle due to the reduced buffering capacity of seawater (Cai et al., 2011; Page et al., 2016).

The diel ranges in pH recorded (0.070 Goff's Caye fore reef, 0.066 Goff's Caye back reef, 0.047 English Caye and 0.027 Dominica) are similar to those recorded at other Caribbean reefs—for example, 0.08 mean in Puerto Rico (Gray et al., 2012), and 0.03–0.07 at Hog Reef, Bermuda (Cyronak et al., 2020; Pezner et al., 2021; Takeshita et al., 2018). However, diel pH ranges recorded at Pacific reefs are around an order of magnitude larger than those recorded at our sites or elsewhere in the Caribbean—for example, 0.24 at Line Islands, Pacific (Price et al., 2012), 0.6 on Molokai Reef, Hawaii (Yates & Halley, 2006) and 0.7 at Heron Island, Australia (Santos et al., 2011). Higher diel pH variability has previously been associated with increased probability of coral recruit survival (Dufault et al., 2012) and higher coral calcification rates (Chan & Connolly, 2013; Chan & Eggins, 2017; Enochs et al., 2018), factors often used as indicators of reef health (Smith et al., 2016). Therefore, declining pH diel ranges, due to phase shifts and changes in ecosystem composition in general, may further exacerbate coral decline by reducing recruitment and calcification through a positive feedback loop. The lower diel pH ranges reported here and by previous studies may reflect the vulnerability of Caribbean reefs to environmental change and their higher susceptibility to phase shifts (Mumby et al., 2021).

The DO ranges recorded at our sites 30.7 μmol/L at Goff's Caye fore reef (30.0 μmol/kg), 32.0 μmol/L at Goff's Caye back reef (31.3 μmol/kg), 11.9 μmol/L at English Caye (11.6 μmol/kg), and 7.6 μmol/L in Dominica (7.4 μmol/kg) are generally lower than those reported in other studies (e.g., 22–54 μmol/kg in Bermuda (Pezner et al., 2021; Takeshita et al., 2018) and in Puerto Rico 60 μmol/L (fall) and 120 μmol/L (winter) (Gray et al., 2012)). More recently, mean daily DO concentrations and ranges from 32 reefs around the globe have been reported as 173 ± 28 μmol/kg and 81 ± 52 μmol/kg respectively (Pezner et al., 2023). The greater DO amplitudes reported in the literature do not always correspond to greater pH ranges (0.067 (winter) and 0.093 (fall) in Puerto Rico (Gray et al., 2012) and 0.07 at Hog Reef (Pezner et al., 2021; Takeshita et al., 2018)) and could imply different biogeochemical and metabolic regimes, reflecting variations in benthic ecosystem compositions. Minimum DO values recorded at English Caye and Goff's Caye (both fore reef and back reef sites) were on occasion below 156 μmol/L, a threshold below which reef ecosystems are considered "weakly hypoxic" and therefore under stress (Vaquer-Sunyer & Duarte, 2008). Climate change scenarios predict that warming oceans will further decrease minimum DO concentrations and lengthen the duration reefs are exposed to hypoxic conditions (Pezner et al., 2023).

The Goff's Caye observations illustrate how small-scale variability in pH within a single reef system can be determined using high-quality, high-resolution sensor measurements. Our measurements suggest that the back reef environment may be more biologically active, as evident by the higher median pH and DO concentrations (Table 2). This could be driven by closer proximity to terrestrial influence (e.g., nutrient inputs), as it has been suggested further south on the Mesoamerican Reef in Belize (Sapodilla Cayes) based on coral core isotopic data (Fowell et al., 2018). Fowell et al. (2018) data suggested that net ecosystem production and pH were higher in the part of the reef more exposed to terrestrial inputs (i.e., nutrients and sediments). The closer proximity of seagrass beds to the back reef site may also have been responsible for the higher pH and DO concentrations. Seagrass beds can significantly elevate seawater pH (>0.1) through the efficient consumption of seawater CO_2 (Ricart et al., 2021), release of TA from sediments (Burdige & Zimmerman, 2002; Palacios & Zimmerman, 2007) and

amplifying metabolic signals by increasing water residence time (Hendriks et al., 2015). Our data suggest that benthic community composition may have an effect on the amplitude of biogeochemical signals. Specifically, pH and DO diel ranges appear to correlate positively with hard coral cover with the fore reef site at Goff's Caye having the highest percentage of hard coral cover and the Dominica site the lowest. The diel DO and pH range recorded at English Caye were lower than those recorded at the Goff's Cayes sites (Figure 3), potentially reflecting the lower hard coral cover and higher macroalgae abundance (Figure 8). Despite the higher macroalgae abundance, median pH and DO diel ranges were lower than those at the Goff's Caye sites, in line with what has been observed during phase shifts from calcifying to fleshy species (e.g., Price et al., 2012). Price et al. (2012) found that declining median pH values measured in reefs of Palmyra Atoll corresponded with an increase in fleshy algae. In Dominica, the small amplitudes of pH and DO (Figures 3g and 3h) may be evidence of the relatively low biomass and live coral abundance (only 5% of each hard and soft coral) and the relatively high abundance of rock.

Although our data suggest a link between diel ranges (pH and DO) and benthic community composition and metabolism, the effect of topography and hydrology cannot be dismissed. The magnitude of biogeochemical signals can be a function of reef morphology (width, depth and wave/current characteristics (e.g., Cyronak et al., 2020; Falter et al., 2013; Pezner et al., 2023; Takeshita et al., 2018)). Therefore, it cannot be ruled out that some of the pH and DO diel range variability between our sites, and others reported in the literature, is due to factors additional to ecosystem metabolism. It is possible that the smaller diel cycles, observed at the Dominica site (2.5–4.5 m deeper) compared to those in Belize, may be driven in part by higher levels of mixing and dilution driven by the deeper and steeper topography. Significantly higher diel rages in pH and DO, however, have been recorded in reefs much deeper than our site in Dominica (depth (d) = 9 m, range = 0.027 pH and 7.4 μmol/kg DO); in Bermuda, for example, (d = 18.5 m, range = 0.056 pH and 42 μmol/kg DO; Takeshita et al., 2018) and in American Samoa (d = 15.2 m, range = 23 μmol/kg DO range; Pezner et al., 2023). Consequently, using diel ranges as a proxy of benthic composition and metabolism may not be as meaningful if topography and hydrology are not taken into consideration.

The theoretical P:R model used here provides a means for interpreting the observed relationship between pH and DO measurements. In marine systems where photosynthesis and respiration dominate the control of DO, and dissolved CO_2 can be expressed by $C_6H_{12}O_6 + 6O_2 \leftrightarrow 6CO_2 + 6H_2O$. At a fixed TA, pH correlates negatively with dissolved CO_2 according to the speciation of carbonic acid in seawater (Zeebe & Wolf-Gladrow, 2003). Therefore, a positive correlation between DO and pH can be expected in productive marine habitats such as kelp forests (Frieder et al., 2012), seagrass beds (Hendriks et al., 2014), and coral reef systems (Gray et al., 2012; Pezner et al., 2021). Divergence from
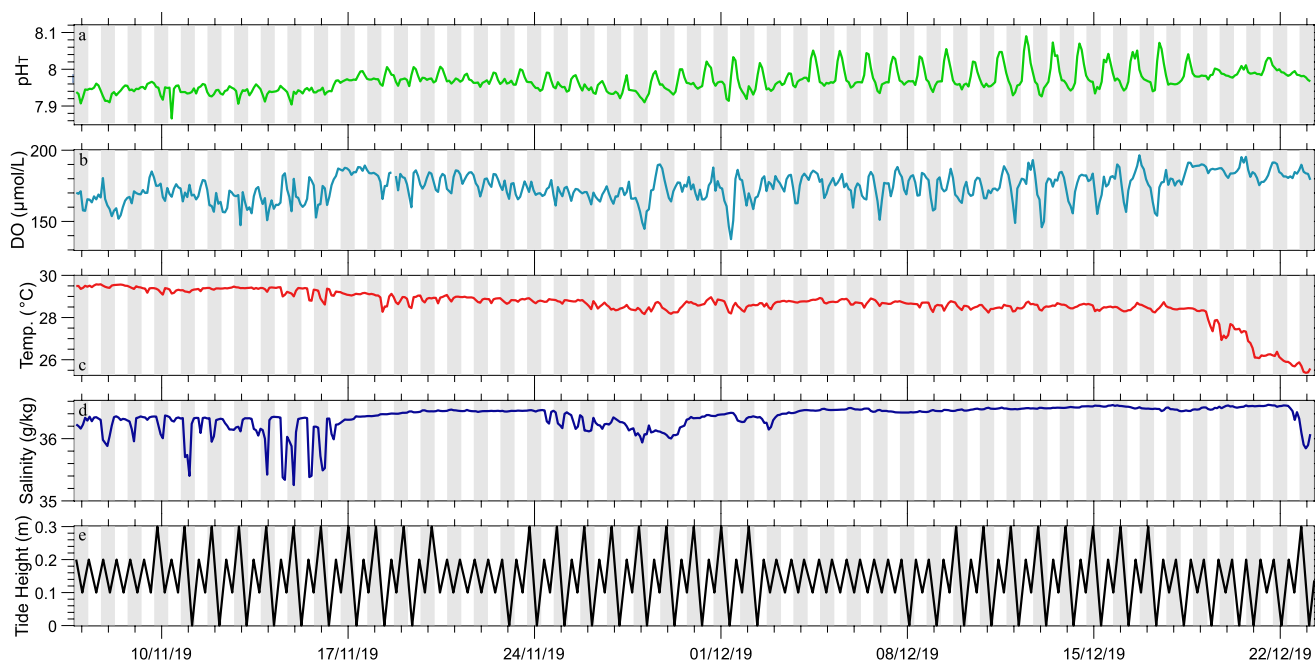

Figure 5. Time series of English Caye of (a) pH_T, (b) DO, (c) temperature, (d) absolute salinity and (e) predicted tides over 6.5 weeks. Nighttime is shown by gray shading.
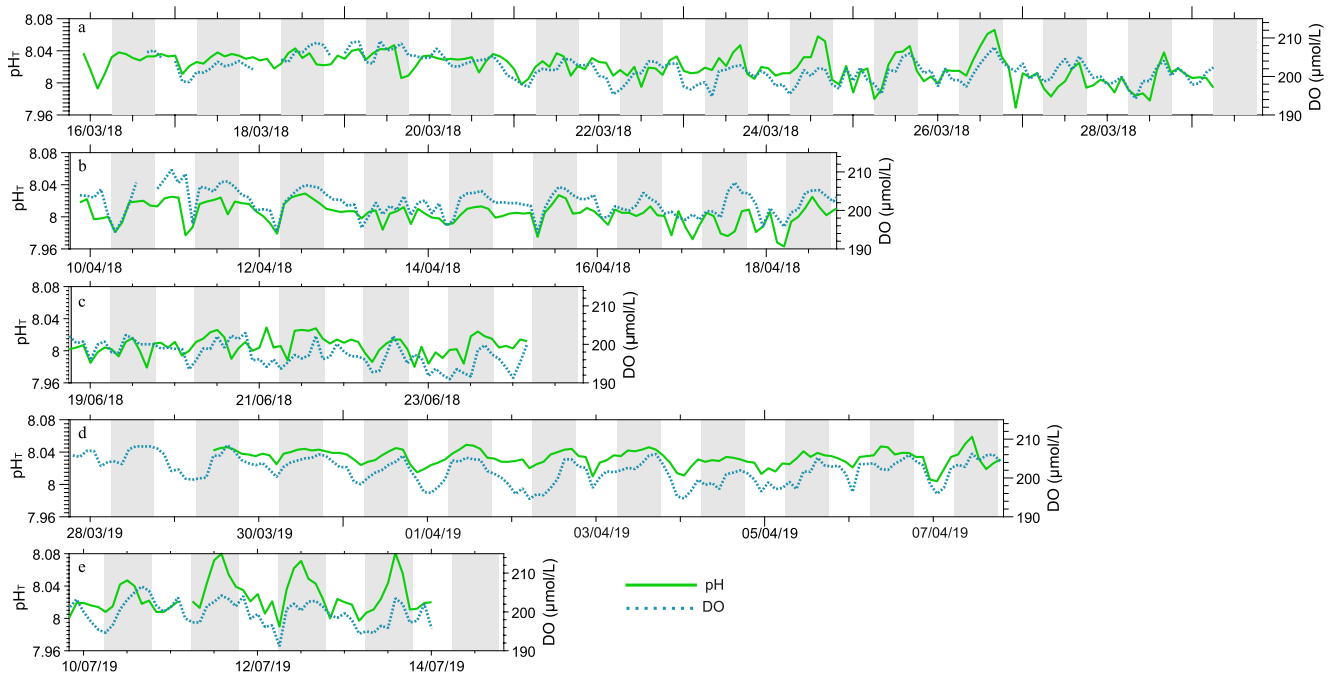
Figure 6. Time series of five deployments in Dominica, with night shown in gray shading; (a–c) are deployments in 2018 and (d–e) in 2019. pH$_T$ is the solid green line and DO is the dotted blue line. Salinity and temperature data are in Supporting Information S1 (Figure S1).

the predicted P:R model could indicate that other physical, chemical, or biological processes may be at play (besides photosynthesis and respiration). In coral reef environments, for example, calcification or dissolution would result in a pH decrease or increase, respectively, without any effect on the DO concentration. The pH and DO observations at both Goff's Caye sites correlated well and were generally in good agreement with the theoretical P:R relationship throughout a 24 hr cycle. This suggests that significant biological activity (i.e., photosynthesis and respiration) was mainly responsible for the observed diel signals (Figure 7, Table 3). In contrast, the weaker pH:DO relationship and the relatively small observed pH and DO diel range (0.027 and 7.6 μmol/L, respectively, Figures 3 and 6) at the Dominica site likely reflect the relatively low ecosystem biomass (Figure 8) and therefore weak biological activity.
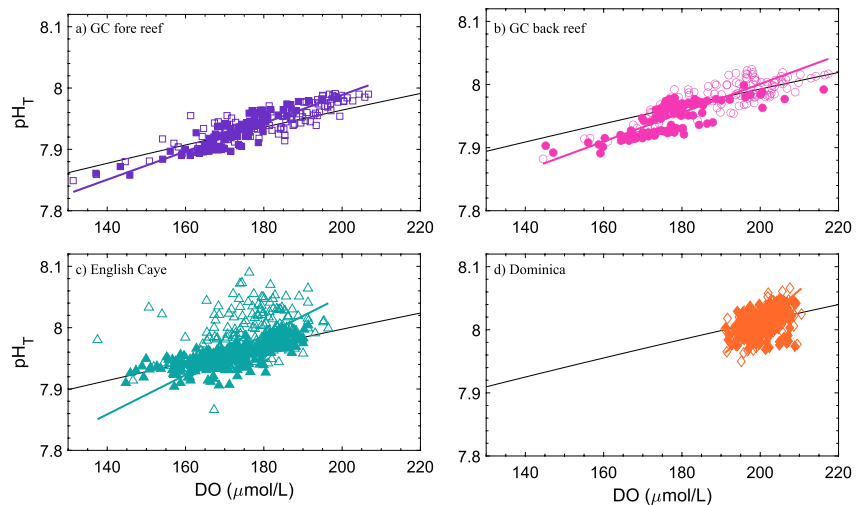

Figure 7. Relationship between pH and DO at all monitoring sites, with nighttime measurements represented by filled symbols and daytime by empty symbols. The solid black line represents the theoretical pH:DO relationship based on the PR model described in Section 2.5. The solid colored line is the linear fit of all data points at that site. (a) Goff's Caye Fore Reef, Belize, (b) Goff's Caye Back Reef, Belize, (c) English Caye, Belize and (d) Soufriere, Dominica.

Table 3
Statistical Relationships Between DO and pH at the Four Sites, All Data and Then Separated Into Night and Day Time Data

Site	Equation of best fit line	Pearson's correlation coefficient	Night equation of best fit line	Day equation of best fit line	Day Pearson's correlation coefficient
Goff's Caye Fore Reef, Belize	$y = 0.00230x + 7.53$	$0.8841\ p < 0.0001$	$y = 0.00293x + 7.42$	$y = 0.00203x + 7.58$	$0.8789\ p < 0.0001$
Goff's Caye Back Reef, Belize	$y = 0.00228x + 7.54$	$0.8542\ p < 0.0001$	$y = 0.00245x + 7.51$	$y = 0.00203x + 7.59$	$0.8275\ p < 0.0001$
English Caye, Belize	$y = 0.00321x + 7.41$	$0.5439\ p < 0.0001$	$y = 0.00195x + 7.62$	$y = 0.00372x + 7.33$	$0.4301\ p < 0.0001$
Soufrière, Dominica	$y = 0.00522x + 6.97$	$0.4525\ p < 0.0001$	$y = 0.00475x + 7.06$	$y = 0.00538x + 6.94$	$0.4967\ p < 0.0001$

Note. Best fit lines of all data are plotted on equivalent plots in Figure 7.

Decoupling between pH and DO at English Caye during daylight hours suggests that, unlike the other sites, photosynthesis was not always the primary control on the pH:DO relationship (Figure 7c). This is also evident in Figure 5, where pH and DO variability often appears to be decoupled. The disproportional increase in pH observed could potentially be caused by an increase in TA through water mass mixing or dissolution of carbonates. Water mass mixing can likely be ruled out, as there was no discernible correlation between temperature and salinity as one would expect from a two-endmember mixing scenario (Pearson's Correlation = −0.4, $p < 0.0001$). Similarly, lack of correlation between tidal cycles or tidal amplitude (predicted estimates for Belize City as illustrated on Figure 5; Tides4Fishing, 2019) and the relationship between pH and DO suggest that is unlikely that tide-induced TA release from porewaters (e.g., Faber et al., 2014) was significant or responsible for the disproportional daytime increase in pH. The exclusive occurrence of the pH:DO decoupling during daylight hours may point toward a light-dependent process.

The English Caye site had the largest relative distribution of macroalgae (Figure 8). Macroalgae are efficient photosynthesizers that can often outcompete corals for space and reduce coral recruitment (Birrell et al., 2008) leading to coral-to-algae phase shifts. Macroalgae have also been known to have allelopathic relationships with corals, either directly (Del Monaco et al., 2017; Rasher & Hay, 2010; Slattery & Lesser, 2014) or indirectly, via their associated microbial communities (Smith et al., 2006). Concentrations of allelopathic compounds and their affects are likely a function of macroalgae abundance. Allelopathic compounds released from macroalgae (such as lipid metabolites) have been shown to adversely affect corals through direct contact with coral surfaces, often leading to bleaching (Rasher & Hay, 2010; Rasher et al., 2011). Their release during photosynthesis (Paul & Ritson-Williams, 2008; Shalaby, 2011) can also indirectly affect corals by acting as a substrate to microbial communities and thereby influencing their growth and functioning. Macroalgae are efficient consumers of CO_2 maintaining high pH in the water column during the day (Smith et al., 2013). However, allelopathic effects on the microbial communities can enhance daytime respiration, which may lower the pH in microenvironments on coral or rubble surfaces and crevices promoting dissolution (Islam et al., 2016; Romanó de Orte et al., 2021). Although we have no direct evidence of such processes taking place at English Caye, allelopathy-mediated coral dissolution could potentially explain the observed daytime decoupling of pH:DO. Daytime dissolution is unusual as coral dissolution usually occurs at night when the absence of photosynthesis allows respiration to drive down pH and aragonite saturation state (e.g., Cyronak et al., 2018; Romanó de Orte et al., 2021; Webb et al., 2021). However, the dissolution of dead corals at seawater aragonite saturation states of >1 have been observed, proposed to be mediated by microbial respiration (Romanó de Orte et al., 2021), indicating that daytime dissolution is possible.

The pH:DO decoupling observed at English Caye could also be explained if oxygen ebullition was at play. Oxygen ebullition, the production of oxygen bubbles (Koschorreck et al., 2017), can occur as water in contact with algal surfaces becomes supersaturated with respect to O_2 (Howard et al., 2018). Macroalgal surfaces have been known to promote oxygen ebullition through heterogenous nucleation on algae surfaces (Silveira et al., 2019). Oxygen ebullition can lead to an underestimation of the seawater DO concentration by up to 20%, as most of the produced oxygen remains in gaseous form (Howard et al., 2018; Koschorreck et al., 2017). A 20% increase in the English Caye DO data (Figure 7c) would account for the observed pH:DO decoupling as illustrated in Supporting Information S1 (Figure S4).

To better understand what drives the pH:DO decoupling observed at English Caye, the seawater carbonate system would have to be fully constrained at high resolution. This would only be possible by measuring another carbonate system parameter such as TA or DIC. Doing so, dissolution and calcification could be estimated and changes in pH could be directly attributed to biotic or non-biotic processes. Although autonomous pH sensors are commercially available, sensors for measurements of TA or DIC are still in development (e.g., Schaap et al., 2021). Autonomous characterization of the carbonate system at high resolution would allow us to understand, quantify and compare key metabolic processes across different reefs such as net ecosystem dissolution and calcification and can enable long-term baseline monitoring of the coral reefs "metabolic pulse" (Cyronak et al., 2018).

High resolution reef monitoring over several diel and seasonal cycles is only possible using autonomous sensors. We have demonstrated that monitoring pH and DO (along with temperature and salinity) can offer insight into reef metabolism. A more holistic understanding of coral reef biogeochemistry and reef ecosystem functioning could be ascertained by constraining the carbonate system by measuring an addi-
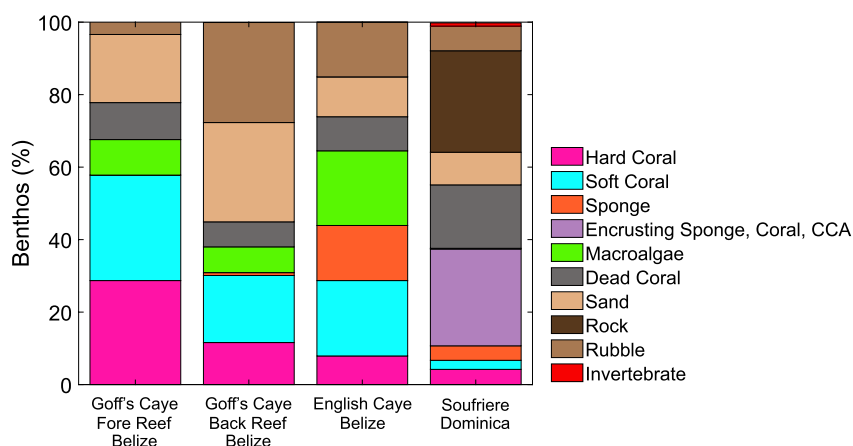
Figure 8. Benthic coverage of Goff's Caye fore reef, Goff's Caye back reef, and English Caye and Soufriere sites.

tional carbonate chemistry parameter such as TA or DIC, and including sensors for constraining primary production such as photosynthetically active radiation meters and fluorometers (for chlorophyll estimations), and constraining hydrodynamics such as acoustic Doppler current profilers. Practical considerations however, related to power availability, cost and site accessibility may be the determining factors on the number of parameters that can be monitored.

4.1. Conclusions

The loss and deterioration of coral reef ecosystems globally threaten global biodiversity, ecosystem function and the blue economy of coastal regions. In the Caribbean, over half of the population live within 1.5 km of the coastline (Schnitter et al., 2019), making reef decline an urgent and critical problem. Here we demonstrate that high resolution data of pH and DO offer insight into the functioning of coral reef ecosystems. Specifically, our data suggest a correlation between the strength and amplitude of the pH:DO relationship "the metabolic pulse" and benthic ecosystem composition. The strength of the metabolic pulse appeared to be a function of the balance between hard and soft corals, macroalgae and sponge abundance as well as proximity to other ecosystems such as seagrass beds. This was illustrated by comparisons of adjacent reef sites with different benthic community compositions (Goff's Caye and English Caye) which exhibited distinctly different DO and pH relationships and diel ranges. The weakest "metabolic pulse" as indicated by small pH and DO diel ranges and poor pH:DO correlation was recorded at the Dominica reef site where the ecosystem was heavily affected by Hurricane Maria. The high-resolution data also revealed unexpected biogeochemical functioning such as the decoupling of pH and DO during the day (at English Caye) which could be attributed to physical (oxygen ebullition) or geochemical (carbonate dissolution) processes which are still not well understood within the context of coral reef ecology and biogeochemistry.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All sensor data are available from The University of Southampton Data Repository https://doi.org/10.5258/SOTON/D2346. This data set includes pH_T, dissolved O_2, temperature and salinity data from all four sites. At the same DOI, benthos data is included—the proportions of each benthos and substrate from the four sites, determined using Coral Point Count.

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