Coral Reefs on the Edge? Carbon Chemistry on Inshore Reefs of the Great Barrier Reef

Sven Uthicke*, Miles Furnas, Christian Lønborg
Australian Institute of Marine Science, PMB No 3, Townsville, Queensland, Australia

Abstract
While increasing atmospheric carbon dioxide (CO2) concentration alters global water chemistry (Ocean Acidification; OA), the degree of changes vary on local and regional spatial scales. Inshore fringing coral reefs of the Great Barrier Reef (GBR) are subjected to a variety of local pressures, and some sites may already be marginal habitats for corals. The spatial and temporal variation in directly measured parameters: Total Alkalinity (TA) and dissolved inorganic carbon (DIC) concentration, and derived parameters: partial pressure of CO2 (pCO2), pH and aragonite saturation state (Ωar) were measured at 14 inshore reefs over a two year period in the GBR region. Total Alkalinity varied between 2069 and 2364 µmol kg⁻¹ and DIC concentrations ranged from 1846 to 2099 µmol kg⁻¹. This resulted in pCO2 concentrations from 340 to 554 µatm, with higher values during the wet seasons and pCO2 on inshore reefs distinctly above atmospheric values. However, due to temperature effects, Ωar was not further reduced in the wet season. Aragonite saturation on inshore reefs was consistently lower and pCO2 higher than on GBR reefs further offshore. Thermodynamic effects contribute to this, and anthropogenic runoff may also contribute by altering productivity (P), respiration (R) and P/R ratios. Compared to surveys 18 and 30 years ago, pCO2 on GBR mid- and outer-shelf reefs has risen at the same rate as atmospheric values (~1.7 µatm yr⁻¹) over 30 years. By contrast, values on inshore reefs have increased at 2.5 to 3 times higher rates. Thus, pCO2 levels on inshore reefs have disproportionately increased compared to atmospheric levels. Our study suggests that inshore GBR reefs are more vulnerable to OA and have less buffering capacity compared to offshore reefs. This may be caused by anthropogenically induced trophic changes in the water column and benthos of inshore reefs subjected to land runoff.

Introduction
Present day atmospheric carbon dioxide (CO2) concentrations are now over 30% higher than the maximum observed in the previous 2 million years [1]. Approximately 28% of this additional CO2 is absorbed by the world’s oceans [2,3], leading to lower seawater pH (Ocean Acidification; OA) with reduced carbonate ion concentrations ([CO3²⁻]) and a reduced saturation state (Ω) of calcium carbonate minerals (CaCO3). Surface seawater pH has decreased by 0.1 units since pre-industrial times and is predicted to fall by a further 0.3–0.5 units in the next 100 years [4]. Large-scale spatial and temporal variations (seasonal, inter-annual) in surface seawater CO2 concentrations are known to be caused by biogeochemical and air-sea exchange processes. Knowledge of this variability is critical to understand the current state of the carbon cycle and to predict how the ocean will react to future increases in atmospheric CO2 concentration. A recent review indicated that the partial pressure of CO2 (pCO2) in coral reef waters is increasing more rapidly than in the atmosphere, most likely due to other anthropogenic impacts on water quality [5]. Coral reefs in tropical and subtropical regions contribute to the ocean carbon cycle through the processes of photosynthesis, respiration, CaCO3 production and dissolution [6,7]. Coral reef ecosystems are vulnerable to OA and climate change induced ocean warming [8] with a range of effects on the ecosystem and associated biota e.g., [9–12]. In particular, increases in oceanic CO2 will reduce the aragonite saturation state (Ωar), which decreases the ability of many coral species to produce their carbonate skeletons [10,13,14]. As a consequence, future coral reefs may exhibit net-carbonate dissolution as opposed to the net-accretion witnessed today [15].

Because many coral reefs are net-autotrophic, these reefs may have an increased buffering capacity towards OA [16,17]. Shallow reef flat areas are dominated by respiratory processes at night (increasing CO2 in the water) and autotrophic processes during the day (decreasing CO2 and thus increasing pH). This can lead to considerable fluctuations of pH, Ωar and pCO2 [13,18,19].

The Great Barrier Reef (GBR), situated on the NE Australia continental shelf between 9 and 24°S, is the largest contiguous coral reef system in the world. The GBR contains approximately 3,700 individual coral reefs on a shallow shelf with an area close to 250,000 km². Reefs occupy approximately 10% of the shelf area, while most of the remaining shelf is covered with carbonate sediments. The majority of the coral reefs are located on the outer half of the shelf, which is primarily under oceanic influence; however, approximately 20% of reefs lie within 10 km of the coast.
and are under direct terrestrial influence from freshwater, sediment, nutrient and organic carbon runoff.

Research to date on reef calcification and inorganic carbon dynamics within the GBR system has largely focused upon on-reef processes on mid- and outer-shelf reefs [6,7,15,20]. Relatively little work has been done on the shelf-scale dynamics of inorganic carbon in the GBR system [21,22] and almost no consideration has been given to the many inshore reefs close to the coast that are under the greatest threat from increases in runoff of sediment, nutrients and pesticides [23–25]. The ratio of primary productivity and respiration (P/R) of inshore reefs are often lower than on reefs further from the coast due to decreased light availability associated with greater turbidity inshore [26–29]. Because of this, inshore reefs may be less able to buffer rising dissolved inorganic carbon (DIC) by photosynthesis.

Here, we present broad-scale carbon chemistry data from inshore reefs of the GBR, collected six times over two years covering a comprehensive latitudinal range. We tested if there were any persistent regional and seasonal differences between inorganic carbon system parameters in the coastal waters of the GBR. In addition, we compared the carbon chemistry on inshore reefs to a smaller sample set from mid- and outer-shelf reefs and to historical data collected 18 and 30 years ago.

Materials and Methods

Sampling design

All work described was covered under a permit obtained from the Great Barrier Reef Marine Park Authority (G12/35236.1).

Water sampling for inshore chemical characteristics was carried out at 14 nearshore fringing reefs at islands between 16 and 23° S (Fig. 1). Twelve of the 14 core sites are within 15 km of the mainland and all are directly affected on a seasonal or episodic basis by terrestrial runoff. Sampling at the inshore core reef sites (Visits, n = 6) was conducted at four-monthly intervals over two years (September 2011–June 2013) in the late dry season (September–October), wet season (February) and early dry season (June). The GBR region has a monsoonal climate with most (ca. 60–80%) rainfall falling in the January to March period. All samples were collected during the day time. In order to test if values differed between times of the day all samples were grouped into four time brackets (0600–0900, 0901–1200, 1201–1500, and 1501–1800) and an overall one factor analysis of variance (ANOVA) was conducted to test if average Total Alkalinity (TA) and dissolved inorganic carbon (DIC) were different between sampling times. This analysis illustrated that there was no significant difference in TA (F1, 165 = 0.55, p = 0.6462) or DIC (F1, 165 = 1.41, p = 0.2418) values between the four time brackets. The majority (~65%) of the samples were collected between 0900 and 1500. We therefore concluded that the time of sampling did not bias our spatial or long-term temporal comparisons.

To provide comparison with mid- and outer-shelf reef water we collected additional samples in two GBR regions (the Northern section and the Swains region) on five occasions. Samples from the Northern section were collected in November 2011 (Wreck Bay, Tydeman Reef, and Arlington Reef), June 2012 (Mantis Reef [7 samples] and Lizard Island), and November 2013 (Teydeman Reef and Fairway Channel). Samples from the Swains region were collected in April 2012 (Elusive Reef, Twin Cays Mooring Site, Swains Reefs, and Inner Swains) and September 2013 (Elusive Reef and Swains Reefs). All locations are shown in Fig. 1. Water masses at the outer-shelf sites are primarily influenced by mixing with the oceanic waters of the Coral Sea. For most of its length, the outer-shelf reef matrix is separated from the mainland (and inshore reefs) by an open water body known as the GBR lagoon. South of 15° S, the dominant (non-tidal) water movement on the outer-shelf is to the south under the forcing of the geostrophic pressure gradient of the East Australian Current. Northward surface flows on the shelf may occur during periods of strong SE trade winds. On the inner-shelf, this northward flow driven by SE trade winds is stronger and more persistent. To the north of 15° S, shelf flows are primarily wind-driven.

Sample collection and analysis

Water samples for analysis of TA and DIC were collected at the 14 core reefs in conjunction with a range of standard oceanographic (temperature and salinity) and water quality (nitrate/nitrite (NO3/NO2), ammonium (NH4+), phosphate (PO43−), and chlorophyll a (Chl a)) parameters. The latter parameters are only summarised here to provide a background on the biogeochemical setting of the sites; a more detailed description of these parameters is given elsewhere [30]. At each of the inshore locations, surface (~1 m water depth) and near-bottom (average depth 9.4 m, 1 SD = 3.1 m) water samples were collected from the R/V Cape Ferguson using 10 L Niskin bottles. These open water stations were 0.5–2 km from the neighbouring reef. In addition, divers collected water near-bottom (average depth 6.5 m) on the reef slopes of the coral reef at each inshore site.

Duplicate aliquots (250 ml) were carefully drawn from the Niskin bottles for TA and DIC analysis, taking care to avoid bubble formation and minimize headspace. Samples were fixed with 125 μl of saturated HgCl2. Samples for TA and DIC were analysed using a VINDTA 3C titrator (Marianda, Germany) at the Australian Institute of Marine Science (AIMS). Alkalinity was determined by acid titration [31] and DIC by acidification and coulometric detection (UIC 5105 Coulometer) of the evolved CO2. The VINDTA titrator was calibrated with Certified Reference seawaters [A. G. Dickson, Scripps Institute of Oceanography, Dixon, Batch 106]. Raw-data for TA and DIC samples are given in Table S1 in File S1.

Historical data

Our data collected in 2011 to 2013 were compared to data collected by Kawahata et al. [22] which were only collected during the dry season (May 1996) and on locations further from the reef than those obtained here. In addition, we obtained historical data from 1982/83 from the AIMS data archive. These were collected by Dr Dave Barnes and colleagues following detailed methods described in [6,7]. The carbon chemistry calculations from the 1982/83 dataset were based on precision measurements of pH and TA, and those from 1996 on CO2 measurements in equilibrator chambers and TA measurements. Although individual methods may vary in their measuring certainty, all are still accepted methods [32] and there is therefore no reason to assume that these data are not comparable. See Table S2 in File S1 for more detailed descriptions and a transcript of the raw data used.

Data analysis

Carbon chemistry parameters (the partial pressure of CO2 [pCO2], pH on the total scale [pHTotal], and the saturation state for aragonite [Ωar]) were calculated using the Excel macro CO2SYS [33], taking salinity and temperature into consideration.

Salinity normalization to a constant salinity is commonly used to correct for differences between source water masses and local effects from evaporation and precipitation on the marine carbon chemistry [34,35]. We used the method proposed by Friis et al. [34] for TA and DIC, using the annual average salinity during the
sampling period of 34.5 and a non-zero freshwater end member 
\( \text{TAS}_S=0 = 309.13 \; \text{mmol Kg}^{-1}; \text{DIC}_S=0 = 288.48 \; \text{mmol Kg}^{-1} \).

To separate the seasonal effect of biological processes (B) and 
temperature (T) on the \( pCO_2 \) dynamics, we used the method 
developed by Takahashi et al. [36] and calculated the effect as:

\[
1. \quad pCO_{2,\text{bio}} = pCO_{2,\text{obs}} \times e^{0.0423 \times (T_{\text{mean}} - T_{\text{obs}})}
\]

\[
2. \quad pCO_{2,\text{Temp}} = pCO_{2,\text{mean}} \times e^{0.0423 \times (T_{\text{obs}} - T_{\text{mean}})}
\]

where \( T \) is temperature (°C) and the subscripts “mean” and “obs” 
indicate the annual mean temperatures (reported in Table 1) or 
\( pCO_2 \) for each region and the observed values, respectively. The 
relative importance of each effect is expressed as the ratio between 
\( pCO_2, \text{Temp} \) and \( pCO_2, \text{bio} \) \( (T/B) \). A ratio >1 suggests a dominance 
of temperature effects over biological processes on the \( pCO_2 \) dynamics.

Salinity-normalized data for TA (TAS) and DIC (DIC_S) were 
also used to create TAS vs DIC_S plots to examine the impact of 
calcification on the annual changes in the carbon system. This 
approach follows on from the assumption that net primary 
production of one mole of organic C reduces DIC by one mole, 
while calcification reduces TA by two moles and DIC by one mole 
for each mole of CaCO_3 precipitated [37]. In systems where 
calcification is dominating, there should therefore be a linear 
relationship between DIC and TA with a slope approaching 2.0. 
The slope of this relationship can be used to calculate the net 
ecosystem production (NEP) to net ecosystem calcification (NEC) 
ratio, which is given by the function: \( (2/\text{slope})-1 \) [37].

We used mixed model ANOVAs to examine sources of 
variation in observed levels of TA, DIC, \( pCO_2 \), pH_{Total} and
Table 1. Biological, chemical and physical properties of water samples at the time of collection between 2011 and 2013.

| Area         | Season      | N  | Sal. °C | Temp. °C | Chl a μg l⁻¹ | NH₄⁺ μmol kg⁻¹ | NO₃⁻ /NO₂⁻ μmol kg⁻¹ | PO₄³⁻ μmol kg⁻¹ |
|--------------|-------------|----|---------|-----------|---------------|-----------------|-----------------------|-----------------|
| Wet-tropics  | Early dry   | 20 | 33.7    | 23.2      | 0.33±0.11     | 0.07±0.04       | 0.17±0.14             | 0.11±0.05       |
|              | Late dry    | 20 | 35.2    | 25.3      | 0.28±0.02     | 0.06±0.05       | 0.20±0.19             | 0.11±0.02       |
|              | Wet         | 20 | 33.7    | 29.9      | 0.38±0.17     | 0.11±0.10       | 0.18±0.17             | 0.05±0.02       |
|              | All year    | 34.2| 26.1    | 0.33±0.15 | 0.08±0.07     | 0.18±0.16       | 0.11±0.04             |                 |
|              | Amplitude   | 3.6 | 8.0     | 0.75      | 0.37          | 0.80            | 0.22                  |                 |
| Burdekin     | Early dry   | 12 | 34.6    | 22.5      | 0.25±0.06     | 0.07±0.07       | 0.14±0.09             | 0.11±0.02       |
|              | Late dry    | 12 | 35.3    | 24.7      | 0.48±0.27     | 0.11±0.12       | 0.24±0.22             | 0.11±0.03       |
|              | Wet         | 12 | 33.9    | 30.0      | 0.34±0.13     | 0.11±0.07       | 0.16±0.18             | 0.05±0.02       |
|              | All year    | 34.6| 25.7    | 0.38±0.22 | 0.10±0.09     | 0.18±0.17       | 0.09±0.04             |                 |
|              | Amplitude   | 3.2 | 10.0    | 0.75      | 0.37          | 0.76            | 0.16                  |                 |
| Whitsundays  | Early dry   | 12 | 34.3    | 22.2      | 0.45±0.16     | 0.10±0.05       | 0.25±0.13             | 0.15±0.04       |
|              | Late dry    | 12 | 35.2    | 23.0      | 0.41±0.17     | 0.06±0.04       | 0.11±0.05             | 0.14±0.03       |
|              | Wet         | 12 | 34.8    | 29.0      | 0.58±0.11     | 0.19±0.15       | 0.26±0.22             | 0.09±0.03       |
|              | All year    | 34.8| 24.7    | 0.48±0.17 | 0.13±0.12     | 0.21±0.16       | 0.12±0.04             |                 |
|              | Amplitude   | 1.6 | 8.4     | 0.59      | 0.41          | 0.56            | 0.16                  |                 |
| Fitzroy      | Early dry   | 12 | 35.1    | 21.0      | 0.46±0.28     | 0.03±0.02       | 0.11±0.06             | 0.10±0.06       |
|              | Late dry    | 12 | 35.6    | 22.0      | 0.36±0.42     | 0.05±0.05       | 0.16±0.13             | 0.13±0.05       |
|              | Wet         | 12 | 33.5    | 28.0      | 0.59±0.18     | 0.11±0.11       | 0.18±0.22             | 0.11±0.07       |
|              | All year    | 34.7| 23.7    | 0.47±0.31 | 0.07±0.08     | 0.15±0.15       | 0.12±0.06             |                 |
|              | Amplitude   | 4.6 | 10.4    | 1.17      | 0.28          | 0.64            | 0.28                  |                 |
| Offshore     | Early dry   | 18 | 34.9    | 25.8      | 0.39±0.18     | 0.03±0.05       | 0.12±0.07             | 0.09±0.04       |
|              | Late dry    | 23 | 35.4    | 26.7      | 0.29±0.23     | 0.03±0.05       | 0.13±0.06             | 0.06±0.02       |
|              | Wet         | nd | nd      | nd        | nd            | nd              | nd                    | nd              |
|              | All year    | nd | nd      | nd        | nd            | nd              | nd                    | nd              |
|              | Amplitude   | 1.7 | 7.2     | 1.02      | 0.18          | 0.31            | 0.21                  |                 |

Average values for salinity (Sal.), temperature (Temp.), chlorophyll a (Chl a), ammonium (NH₄⁺), Nitrate/Nitrite (NO₃⁻/NO₂⁻) and phosphate (PO₄³⁻) and their amplitude (maximum minus minimum level) are shown. Standard deviations are shown for chlorophyll a and nutrient data; N: number of samples used to calculate the average. doi:10.1371/journal.pone.0109092.t001
The fixed main factor “Region” was used to test for differences between the five regions (Wet-tropics, Burdekin, Whitsundays, Fitzroy and offshore). We considered replicate “Islands” as a random nested factor within Regions. To evaluate if samples taken from the reef slopes were different from those collected from the research vessel “Location” was included in the model as a second fixed factor. The main factor “Visit” tested for differences between the six sample periods. With the exception of pH (that is already on a log-scale) all data were log-transformed prior to analysis. Boxplot and residual plots indicated no deviation from ANOVA assumptions for the transformed variables. We tested for correlations between several parameters using Pearson’s product moment correlations. To further investigate differences between seasons and inshore vs offshore reefs, we conducted a principal component analysis (PCA) with TA, DIC, pCO2 and \( \Omega_{ar} \) as carbon chemistry parameters. pH was omitted from this analysis as it is highly correlated with pCO2. For the comparison of the historical data, we calculated a Bayesian 95% confidence

Figure 2. Total Alkalinity (TA) and dissolved inorganic carbon (DIC) data for each island station, sorted from north to south, during each Visit and for each of the three Locations. Regions are colour coded as per Fig. 1. Note that duplicates are plotted but in most cases cannot be distinguished because of the low between-duplicate variance.

doi:10.1371/journal.pone.0109092.g002

\( \Omega_{ar} \) The fixed main factor “Region” was used to test for differences between the five regions (Wet-tropics, Burdekin, Whitsundays, Fitzroy and offshore). We considered replicate “Islands” as a random nested factor within Regions. To evaluate if samples taken from the reef slopes were different from those collected from the research vessel “Location” was included in the model as a second fixed factor. The main factor “Visit” tested for differences between the six sample periods. With the exception of pH (that is already on a log-scale) all data were log-transformed prior to analysis. Boxplot and residual plots indicated no deviation from ANOVA assumptions for the transformed variables. We tested for correlations between several parameters using Pearson’s product moment correlations. To further investigate differences between seasons and inshore vs offshore reefs, we conducted a principal component analysis (PCA) with TA, DIC, pCO2 and \( \Omega_{ar} \) as carbon chemistry parameters. pH was omitted from this analysis as it is highly correlated with pCO2. For the comparison of the historical data, we calculated a Bayesian 95% confidence
Table 2. Mixed model ANOVA for measured parameters Total Alkalinity (TA) and dissolved inorganic carbon (DIC).

| Region       | DF   | TA       | F      | P      | DF   | DIC      | F      | P      |
|--------------|------|----------|--------|--------|------|----------|--------|--------|
| Island (R)   | 5    | 1.63     | 1.11   | 0.358  | 5    | 1.32     | 0.1    | 0.974  |
| Location     | 15   | 2.38     | 1.94   | 0.096  | 15   | 2.45     | 0.538  | 0.041  |
| LX           | R    | 2.45     | 0.538  | 0.041  | R    | 2.09     | 0.494  | 0.0001 |
| R x L x V    | 110  | 1.99     | 0.0001 | <0.0001| 110  | 2.09     | 0.494  | 0.0001 |

The model tests for differences between four Regions of the Great Barrier Reef (factor ‘Region’), the vessel’s anchorage (0 m) and dive site (‘Location’) and six visits over two years of monitoring (‘Visit’). ‘Island’ is nested as a random factor and significant (p<0.05) fixed factors are highlighted in bold. All data are log-transformed for analysis. DF: degrees of freedom; MS: mean square; F: F-value for F test.

Elevated pCO₂ on Great Barrier Reef Inshore Reefs

Results

Environmental conditions

Salinity at the core reef sites ranged from 31.4 to 36.0, being highest at the end of the dry season (September 2011, October 2012) and lowest during the two wet seasons (Table 1). This pattern is most distinct in the two northern regions (Wet-tropics and Burdekin) that had the highest levels of terrestrial runoff. During most seasons, salinities in the southern-most region (Fitzroy) were slightly higher compared to other regions. The one exception was during the 2013 wet season when major flooding in the Fitzroy River catchment resulted in low (ca. 31) and variable salinities. Temperatures were highest during the summer wet season and lowest in June and declined from the north to the south, regardless of season (Table 1).

Measured Chl a concentrations varied between 0.11 and 1.3 μg l⁻¹. Inorganic nitrogen and phosphorus concentrations were of the order of 0.1 μmol kg⁻¹, with elevated NH₄⁺ and NO₃⁻/NO₂⁻ concentrations during the wet season. The highest wet season NO₃⁻/NO₂⁻ levels were generally found in the more freshwater influenced geographic regions (Wet-tropics and Fitzroy). In contrast, the highest PO₄³⁻ concentrations were measured during the dry season (Table 1).

Inorganic carbon dynamics

With few exceptions, there was no appreciable or consistent difference between data derived from samples collected from the research vessel (near-surface, near-bottom) and by diver on the adjacent coral reef slope (diver collected; Fig. 2). Exceptions were observed during the wet seasons, where the surface sample differed from the two near-bottom samples (e.g. Snapper Island February 2012, Dunk Island February 2013). These samples were characterized as having lower salinity than the contemporaneous near-bottom samples, so the most likely cause was either recent rainfall or freshwater runoff affecting these sites. To facilitate interpretation, we restricted further analyses and statistical tests to samples from the reef slope and the surface samples from the research vessel’s anchorage and averaged replicate sub-samples.

Total Alkalinity values ranged between 2069 and 2315 μmol kg⁻¹. Higher TA levels were generally measured during the late dry season (September–October) and in the regions more influenced by freshwater (Wet-tropics and Fitzroy). There was a general increase from north to south, with the exception of low values in the Fitzroy region in February 2013 (Fig. 2). The ANOVA for inshore TA values showed significant effects of geographic regions and amongst visits (Table 2) with a significant interaction between these factors, indicating that regional trends were dependent on the season sampled (Fig. 3). In general, TA values were closely correlated with salinity (r² = 0.94, p<0.0001; Fig. 2). Thus, salinity normalization (TAS) removed a large part of the seasonal variability in TA at the inshore stations; particularly in the Wet-tropics (198 μmol kg⁻¹) and Fitzroy (106 μmol kg⁻¹) regions where freshwater inputs from rivers were largest (Table 3). In contrast, no salinity related variation was found for the outer shelf reefs (Table 3).
Regional averages of DIC concentrations at inshore reefs ranged between 1930 and 2050 µmol kg$^{-1}$. The within-region variation in DIC concentrations was between 340 and 554 µmol kg$^{-1}$, with the highest concentrations and variation measured in September 2011 and October 2012. Again, there was a distinct north to south DIC gradient during most sampling campaigns (Table 3; Fig. 3). The DIC ANOVA was similar to that for TA, with a strong interaction between Region and Visit (Table 2). As evident in the raw-data plots (Fig 2), there was no effect of Location (surface water at the anchorage and the reef slope sites) or interactions of this factor with other fixed factors for either TA or DIC (Table 2). Dissolved inorganic carbon was also strongly correlated with salinity ($r^2 = 0.88$, $p < 0.0001$) and TA ($r^2 = 0.95$, $p < 0.0001$). Salinity normalization of the DIC data (DIC$_S$) removed a large part of the seasonal variation, especially in the Wet-tropics (130 µmol kg$^{-1}$) and Fitzroy (87 µmol kg$^{-1}$) region, leaving a residual seasonal variability of 123 and 155 µmol kg$^{-1}$ in those areas (Table 3). The linear relationships between DIC$_S$ and TA$_S$ had the steepest slopes in the offshore and Fitzroy regions and flattest in the Whitsunday region (Fig 4). In all cases, the slope value was <2, which resulted in NEP/NEC ratios varying between 7.3 (Whitsundays) and 0.4 (Offshore). This suggests that the importance of calcification in controlling the carbon cycle varies regionally with decreasing importance and larger influence of primary production/respiration in the sequence Offshore (NEP/NEC = 0.4) > Fitzroy (1.2) > Burdekin (1.7) > Wet-tropics (3.0) > Whitsundays (7.5).

Based on the observed patterns of variability for the measured parameters (DIC, TA), the derived parameters $p$CO$_2$, pH and $\Omega_m$ also exhibited significant interactions between Region and Visit (Table 4). $p$CO$_2$ reached concentrations between 340 and 554 µatm, with a decline from north to south during three of the visits (Table 3; Fig. 5). The most distinct temporal pattern in the $p$CO$_2$ data (Fig. 5) was an elevation during the wet seasons (total average February 2012: 460 µatm, 1 SD = 19 µatm; February 2013: 460 µatm, 1 SD = 33 µatm), compared to the early dry seasons (June 2012: 383 µatm, 1 SD = 21; June 2013: 410 µatm, 1 SD = 25 µatm) and late dry seasons (September 2011: 416 µatm, 1 SD = 35 µatm; October 2012: 440 µatm, 1 SD = 29 µatm) (Table 3; Fig. 5). Dry season $p$CO$_2$ concentrations were slightly elevated relative to present atmospheric values, whereas wet season concentrations were distinctively (~15%) above atmospheric values. The seasonal fluctuation of $p$CO$_2$ concentrations was highest in the Wet-tropics (198 µmol kg$^{-1}$) and Fitzroy (175 µmol kg$^{-1}$) regions (Table 3). Derived pH values varied significantly among trips and a Region x Visit interaction was also significant (Table 4). As expected, seasonal and spatial variations for pH were reversed compared to those of $p$CO$_2$.
Table 3. A summary of carbon chemistry of water samples collected during 2011 to 2013 in the Great Barrier Reef region.

| Area       | Season        | N  | TA  | TA<sub>S</sub> | DIC | DIC<sub>S</sub> | pCO<sub>2</sub> | pCO<sub>2</sub> Bio | pCO<sub>2</sub> Temp |
|------------|---------------|----|-----|---------------|-----|----------------|-------------|------------------|------------------|
| Wet-tropics| Early dry     | 20 | 2196±40 | 2244±6     | 1936±32 | 1978±12     | 398±24    | 478±26           | 380±8            |
|            | Late dry      | 20 | 2302±10 | 2262±9    | 2021±20    | 1986±19   | 445±35    | 490±37           | 415±12           |
|            | Wet           | 20 | 2195±40 | 2239±8    | 1916±30    | 1955±11   | 470±29    | 401±27           | 513±5            |
|            | All year      | 20 | 2231±60 | 2249±13   | 1957±53    | 1973±20   | 437±42    | 437±39           | 441±54           |
| Amplitude  |               | 269| 71     | 253        | 123        | 198       | 220       | 150              |
| Burdekin   | Early dry     | 12 | 2262±9  | 2256±8    | 1991±12    | 1986±19   | 399±25    | 489±29           | 367±12           |
|            | Late dry      | 12 | 2320±11 | 2274±9    | 2038±23    | 1998±20   | 442±35    | 493±37           | 403±6            |
|            | Wet           | 12 | 2234±15 | 2270±31   | 1941±17    | 1972±31   | 458±14    | 383±15           | 518±15           |
|            | All year      | 2272±38 | 2266±20 | 1990±44   | 1985±26   | 433±36  | 434±44  | 437±51           |
| Amplitude  |               | 131| 100   | 164        | 106        | 134      | 162       | 186              |
| Whitsundays| Early dry     | 12 | 2248±23 | 2258±8    | 1991±16    | 2000±13   | 414±26    | 487±23           | 367±12           |
|            | Late dry      | 12 | 2300±14 | 2261±10   | 2022±11    | 1988±13   | 411±14    | 467±15           | 380±13           |
|            | Wet           | 12 | 2271±18 | 2252±7    | 1971±7    | 1954±5    | 451±8     | 377±15           | 509±15           |
|            | All year      | 2273±28 | 2257±9  | 1995±25   | 1981±22   | 425±25    | 427±0    | 429±59           |
| Amplitude  |               | 107| 34    | 80         | 68         | 90       | 162       | 157              |
| Fitzroy    | Early dry     | 12 | 2303±4  | 2268±27   | 2023±13    | 1993±33   | 376±23    | 446±22           | 363±20           |
|            | Late dry      | 12 | 2332±15 | 2271±14   | 2052±21    | 1998±25   | 406±31    | 461±29           | 379±6            |
|            | Wet           | 12 | 2214±70 | 2271±40   | 1940±62   | 1900±35   | 454±39    | 377±24           | 496±19           |
|            | All year      | 2283±65 | 2270±28 | 2005±61   | 1994±31   | 412±45    | 411±34   | 416±60           |
| Amplitude  |               | 257| 151   | 242        | 155        | 175      | 145       | 187              |
| Offshore   | Early dry     | 18 | 2290±16 | 2267±19   | 1969±11   | 1950±14   | 368±15    | 377±22           | 374±24           |
|            | Late dry      | 23 | 2308±14 | 2257±12   | 1986±12   | 1943±8    | 392±27    | 385±10           | 389±24           |
|            | Wet           |     | n.d     | n.d        | n.d       | n.d      | n.d       | n.d              |
|            | All year      |     | n.d     | n.d        | n.d       | n.d      | n.d       | n.d              |
| Amplitude  |               | 79 | 86     | 51         | 55         | 103      | 73        | 111              |

The average values (± standard deviation) and amplitude (maximum minus minimum level) for Total Alkalinity (TA), dissolved inorganic carbon (DIC) and salinity normalized TA and DIC (TA<sub>S</sub>, DIC<sub>S</sub>) values are shown, together with partial pressure of carbon dioxide (pCO<sub>2</sub>) and effect of biological processes (pCO<sub>2</sub> Bio) and temperature (pCO<sub>2</sub> Temp) on pCO<sub>2</sub> dynamics. N: number of samples used to calculate the average. doi:10.1371/journal.pone.0109092.t003
Derived pH values were lowest during the wet seasons (February 2012: 7.97, SD = 0.01; February 2013: 7.97, SD = 0.03) and slightly higher in both the early dry seasons (June 2012: 8.04, 1 SD = 0.02; June 2013: 8.02, 1 SD = 0.02) and the late dry seasons (September 2011: 8.02, 1 SD = 0.03, October 2012: 8.00, 1 SD = 0.02). With one exception (February 2012), there was a slight increase in pH from north to south (Fig. 5).

Aragonite saturation state ($\Omega_{ar}$) varied between 2.6 and 3.8, with highly significant differences between sampling trips and a significant Region x Visit interaction (Table 4; Fig. 5). Average $\Omega_{ar}$ values in the wet seasons (February 2012: 3.39, 1 SD = 0.15; February 2013: 3.25, 1 SD = 0.16) were higher than in the early dry seasons (June 2012: 2.99, 1 SD = 0.13; June 2013: 2.98, 1 SD = 0.16) or in the late dry seasons (September 2011: 3.17, 1 SD = 0.14; October 2012: 3.16, 1 SD = 0.10). Thus, despite higher $pCO_2$ and lower pH values during the summer wet season, $\Omega_{ar}$ were not reduced, but actually increased. This is likely due to higher water temperatures; resulting in lower aragonite solubility in the summer wet season.

In contrast to TA and DIC, the derived parameters $pCO_2$ and pH exhibited small but significant differences between sampling locations at individual sites (Table 4). The average $pCO_2$ for reef slope and adjacent open water samples were 432 (1 SD = 42) and 424 (1 SD = 36) mbar, respectively. The overall average pH for the reef slope sites (8.00, 1 SD = 0.04) was slightly lower than the mean for the anchorage sites (8.01, 1 SD = 0.04).

Water samples taken at the mid- to outer-shelf reefs over the same study period were less variable than those collected on inshore reefs (Table 3) and the $pCO_2$ was always closer to atmospheric equilibrium, with resulting higher pH values. The mid- to outer-shelf $\Omega_{ar}$ was also clearly higher than most inshore values. A principal component analysis of measured and derived parameters (Fig. 6) separates inshore and mid – to outer-shelf sites, with the main distinguishing factors being $\Omega_{ar}$ and $pCO_2$. In addition, samples taken within the three defined ‘seasons’ (wet, early dry, late dry) clearly group together, with wet season samples distinguished by lower DIC and TA values.

In order to determine whether temperature (T) or biological (B) processes (T/B ratio) primarily controlled $pCO_2$ dynamics, we used the method proposed by Takahashi et al. [36]. The T/B ratios showed that over an annual cycle, biological effects primarily control $pCO_2$ dynamics in the Wet-tropics (T/B ratio = 0.7). In the Whitsundays region, temperature and biology contributed equally (1.0), while in the Burdekin (1.2), Fitzroy (1.3) and at the offshore reefs (1.5) the $pCO_2$ concentrations appear to be primarily controlled by temperature. Thus, for the largest part of the GBR, seasonal $pCO_2$ changes are most likely controlled by temperature.

**Discussion**

Like other coastal areas [40], OA is part of a suite of factors that influence the coral reefs found on the GBR. We analyzed a two
Table 4. Mixed model ANOVA for derived parameters partial pressure of carbon dioxide (pCO2), pH_{Total} and aragonite saturation state (Ω_ar). The model tests for differences between four Regions of the Great Barrier Reef (factor "Region"), the vessel’s anchorage (0 m) and dive site ("Location"), and six visits over two years of monitoring ("Visit"). "Island" is nested as a random factor in "Region". Significant (p < 0.05) fixed factors are highlighted in bold. With the exception of pH, all data are log-transformed for analysis. DF: degrees of freedom; MS: mean square; F: F-value for F test.

| Factor          | MS   | F     | p     | MS   | F     | p     |
|-----------------|------|-------|-------|------|-------|-------|
| Region          |      |       |       |      |       |       |
| DF              | 3.95 | 0.0057|       |      |       |       |
| Island (DF)     | 3.36 | 0.0001|       |      |       |       |
| Location (DF)   | 0.81 | 0.0001|       |      |       |       |
| Visit (DF)      | 1.91 | 0.0001|       |      |       |       |
| R x L x V        | 9.84 | 0.0001|       |      |       |       |
| Residual        | 10.95| 0.0001|       |      |       |       |

The model tests for differences between four Regions of the Great Barrier Reef (factor "Region"), the vessel’s anchorage (0 m) and dive site ("Location"), and six visits over two years of monitoring ("Visit"). "Island" is nested as a random factor in "Region". Significant (p < 0.05) fixed factors are highlighted in bold. With the exception of pH, all data are log-transformed for analysis. DF: degrees of freedom; MS: mean square; F: F-value for F test.

Elevated pCO2 on Great Barrier Reef Inshore Reefs

year data set collected over a large portion of the GBR to describe seasonal and broad-scale spatial changes in carbon chemistry and contrast those to outer reef areas. Overall, regional variability in carbon system parameters is relatively small. Within the inshore reefs, the largest amount of variation occurred seasonally. In addition, pCO2 was distinctly higher on inshore compared to offshore reefs.

pCO2 in the GBR and other coastal waters is influenced by a number of processes, including thermodynamics; air-sea exchange; biological metabolism (photosynthesis, respiration, calcification); and freshwater inputs. Reasons for elevated pCO2 in the GBR inshore waters especially during the wet season are not fully resolved. In European estuaries, high DIC levels in freshwater can elevate pCO2 in inshore areas [41]. Although salinity normalization removed a large part of the seasonal amplitude in DIC and TA fluctuations, there is no significant correlation between salinity and pCO2 in our dataset (r² = 0.02, p = 0.0940). Thus, it is unlikely that freshwater inflow resulted in the elevated pCO2 in the inshore GBR.

It is also possible that pCO2 increase is a consequence of higher calcification (benthic – e.g., corals, foraminifera; or pelagic – e.g., coccolithophorids), resulting from elevated temperatures during the wet seasons [22,42]. It is difficult to judge the net effect of this on the areas studied, because it would also require more detailed knowledge on accompanying respiration (CO2 source) and primary production (CO2 sink). The expected slope of the linear regression between DIC3 and TA in systems where calcification is dominating is close to 2.0 e.g., [22,37]. We found slopes <2 and high (1.2 to 7.3) NEP/NEC ratios for all the inshore regions investigated (Fig. 5), suggesting that processes other than calcification (e.g., photosynthesis, respiration) are largely controlling the carbon cycle on inshore GBR reefs.

Changing pCO2 outside the equilibrium may also be caused by thermodynamic effects. A seasonal increase at a similar range as observed here (albeit from a lower baseline) was observed near Lady Elliot Island in the southern GBR [20]. Based on the slope of the pCO2 – temperature relationship, the authors of that study suggested thermodynamic effects as the most likely explanation for elevated pCO2 values in summer. There was a significant correlation between temperature and pCO2 in our dataset (r² = 0.53, p < 0.0001, pCO2 = 2.07% [1 SE = 0.1%] * Temp (°C)+5.53), but our value was lower than that found at Lady Elliot Island [3.8 [1 SE = 0.4%], 20], and only about 50% of the expected slope of 4.2% pCO2 [43]. However, the regression clearly levels off at >26°C. If data >26°C were excluded, the slope of the regression (r² = 0.42, p < 0.0001, pCO2 = 3.6% [1 SE = 0.4%] * Temp (°C)+5.19) is closer to the theoretical value for temperature controlled systems.

We applied the method proposed by Takahashi et al. [36] to distinguish if seasonal changes in pCO2 concentrations were controlled by temperature or biological processes. The definition of “biology effect” applied includes biogeochemical processes (e.g., primary production, respiration, calcification), and other processes influencing the CO2 such as air-sea exchange and lateral vertical mixing processes [44]. The application of this method suggested a strong temperature control in the southern GBR, as was also proposed by Shaw and McNeil [20]. Northern GBR reefs were impacted more by biological processes. In addition, temporal difference in the controlling factor also existed, with stronger biological and temperature control during wet and dry seasons, respectively (Table 3).

Analysis and modelling of historical trends in coral reef pCO2 levels worldwide [5] suggests that pCO2 is sensitive to the P/R ratio of the system and also to overall increases in production and
respiration. Sediment and nutrient loads through riverine input into the GBR lagoon have increased several fold since European settlement [45]. Thus, the inshore reefs studied here are characterized by elevated chlorophyll and nutrient values and increased turbidity, especially during the summer months [46]. Higher near-shore turbidity associated with enhanced wet season runoff on the GBR [24] may reduce in situ light availability and thus restrain benthic primary production and favour heterotrophic processes. Although coastal waters in the GBR system are net-autotrophic throughout the year [47], pelagic and benthic heterotrophic processes may also be seasonally enhanced by greater inputs of organic carbon in terrestrial runoff, thus shifting the P/R ratio and increasing the $pCO_2$ levels in coastal GBR waters.

Dissolved inorganic carbon and TA levels in samples taken during the daytime directly over the coral reef slopes on inshore reefs did not vary greatly from levels taken at the water surface or at $\sim 9$ m depth in nearby open water at the research vessel’s anchorages. We consider the small differences in pH and $pCO_2$ measured as biologically insignificant. This casts some doubt on whether inshore reefs (or at least reef slope areas investigated) on the GBR can take up sufficient DIC during light periods to alter carbon chemistry and buffer increased DIC, as has been suggested for larger offshore reefs [15–18]. We assume that currents and wave induced mixing are too high on inshore reefs for the benthos to affect the water carbon chemistry. On reef flats of Lady Elliot Island (southern GBR) $pCO_2$ can vary between 89 and 1325 µatm and pH between 7.59 and 8.56 depending on time of day and season. pH and $pCO_2$ in similar ranges were measured on the reef flat of One Tree Island, southern GBR [19] and in lagoonal waters of Heron Island for pH [48,49]. Diurnal and seasonal changes on a mid-shelf reef flat in the central GBR were also distinct, albeit somewhat less than reported in the latter studies [15]. Compared to that, changes at a back-reef area of another mid-shelf reef were rather small [19]. Thus, it is possible that highly fluctuating values on reef flats reported are extremes and not representative for all habitats, even on mid-shelf reefs. However, further studies including finer scale temporal (i.e., sampling during day and night) and spatial (i.e., comparing different reef habitats) investigations are required to further investigate these dynamics.

Although we did not sample mid- and outer-shelf reefs contemporaneously with the inshore reefs, outer-shelf carbon parameters were less variable than encountered near to the coast. From these data there is clear evidence that inshore reefs at present are subjected to higher $pCO_2$ and lower $\Omega_{AR}$ than on the outer-shelf. Recent measurements at Lady Elliot Island and Davies Reef [15,18] are in a similar range as observed for mid-shelf reefs here. Both these studies indicated that, even on mid-shelf reefs, night time $\Omega_{AR}$ values on reef flats can fall below 3, but all day time values were above the value of the surrounding water, and often above 4. Similarly, carbon chemistry analyses from samples collected in surface waters near mid- and outer-shelf reefs of the

---

**Figure 5.** Derived parameters at 14 inshore reefs during six research trips in four geographic regions along the length of the Great Barrier Reef. $\Omega_{AR} =$ Aragonite saturation state. The box denotes the inter-quartile range, whiskers denote 1.5 x the inter-quartile range, the black line indicates the mean, and circles are outliers >1.5 x the inter-quartile range.

doi:10.1371/journal.pone.0109092.g005
Figure 6. Principal component analysis of carbonate chemistry data for four inshore regions of the Great Barrier Reef (GBR) over three different seasons. Data are contrasted to those from the mid- and outer-shelf reefs of the GBR. Inshore data were pooled over regions per sampling visit.

doi:10.1371/journal.pone.0109092.g006

Table 5. Summary table of historic (1982/83; 1996) and present (2011 to 2013) data from inshore, mid-and outer-shelf reefs for partial pressure of carbon dioxide in the water ($pCO_2$ water), aragonite saturation state ($\Omega_{ar}$) and partial pressure of carbon dioxide in the atmosphere ($pCO_2$ atmosphere).

| Shelf position          | Season | $pCO_2$ water (µ atm) | $\Omega_{ar}$ | $pCO_2$ atmosphere** (µ atm) |
|------------------------|--------|-----------------------|---------------|----------------------------|
| 1982/83*               |        |                       |               |                            |
| Mid-/Outer-shelf reefs | Wet    | 350 (13)              | 4.1 (0.2)     | Mauna Loa: 343 (2)         |
|                        | Dry    | 329 (29)              | 3.7 (0.9)     |                            |
| Inshore                | Wet    | 324 (24)              | 4.0 (0.1)     |                            |
|                        | Dry    | 309 (7)               | 3.7 (0.3)     |                            |
| 1996†                  |        |                       |               |                            |
| All lagoonal samples   | Dry    | 332 (13)              | 3.8 (0.1)     | Cape Ferguson: 361 (1)     |
| Inshore                | Dry    | 325 (1)               | 3.8 (0.1)     | Mauna Loa: 363 (2)         |
| 2011 - 13‡             |        |                       |               |                            |
| Mid-/Outer-shelf reefs | Dry    | 380 (15)              | 3.6 (0.1)     | Cape Ferguson: 394 (1)     |
|                        |        |                       |               | Mauna Loa: 396 (2)         |
| Inshore                | Wet    | 411 (23)              | 3.1 (0.1)     |                            |
|                        | Dry    | 458 (9)               | 3.3 (0.2)     |                            |
| Rate of increase:      | $pCO_2$ (µ atm yr$^{-1}$) | Atmospheric: 1.7 (1.6–2.0) |
|                        |        | Outer Dry: 1.6 (–0.4–3.8) |
|                        |        | Inshore Dry: 3.4 (1.8–5.0) |
|                        |        | Inshore Wet: 4.5 (2.8–6.1) |

Standard deviations are given in brackets. Average annual rates of increase of atmospheric $pCO_2$ and water $pCO_2$ values are calculated from present and 1982/83 data; ranges are 95% Bayesian confidence intervals.

*1982/83: Barnes et al. unpublished, for raw data see Table S2 in File S1, N = number of reefs surveyed.

†1996: Kawahata et al. [22].

‡2011 - 13: present study, data are averages of the annual regional averages.

**Atmospheric data are given as annual averages from Mauna Loa, Hawaii (available at: http://www.esrl.noaa.gov/gmd/ccgg/trends/#mlo_data) and data for inshore GBR areas at AIMS Townsville (Cape Ferguson: available at: http://ds.data.jma.go.jp/gmd/wdcgg/cgi-bin/wdcgg/accessdata.cgi?index=CFAS19500-CSIRO&select=inventory; only available from 1991 onwards); based on raw data averaged over months (N = 12).

doi:10.1371/journal.pone.0109092.t005
GBR showed little spatial or temporal variation (Table 3). $\rho CO_2$ values on these reefs were generally at or slightly below equilibrium with the atmosphere, and thus somewhat lower than on inshore reefs in the wet-season (~20%) and the late dry season (~10%). Aragonite saturation state on mid- and outer-shelf reefs was in the range of 3.6–3.8, also higher than on the inshore reefs studied (~10–20%, depending on the season). The PCA analysis clearly separated data from inshore and mid- and outer-shelf reefs, primarily based on their $\Omega_w$ and $\rho CO_2$ values.

In general, DIC was lower and less variable on mid- and outer-shelf reefs. As discussed above for seasonal differences, possible sources for CO2 are calcification, respiration or input through runoff, but it remains unresolved which factor(s) elevate DIC and $\rho CO_2$ inshore. It has been shown from a global dataset that reefs closer to the shore generally have elevated $\rho CO_2$ levels [5]. The latter authors suggested that human induced changes in productivity and P/R ratios are the most likely explanation for this, $\rho CO_2$ measurements conducted in the GBR lagoon in 1996 [21,22] showed that all samples had $\rho CO_2$ concentrations below atmospheric values. Offshore $\rho CO_2$ data collected in the present study were also lower than atmospheric levels, although the difference between atmospheric and near-surface $\rho CO_2$ is smaller (Table 5). Kawahata et al. [22] also included data from two inshore stations in the Burdekin and Whitsunday regions, which had $\rho CO_2$ close to 325 ppm and $\Omega_w$ of ~3.8. Data collected in the GBR 30 years ago also showed no indication of elevated $\rho CO_2$ compared with the atmospheric values (Table 5, Table S2 in File S1) [6,7]. The rate of increase of $\rho CO_2$ on outer reefs measured in this study was on a similar level to that in the atmosphere (1.7 and 1.6 ppm yr $^{-1}$, respectively, based on dry season data only), which is distinctly below that reported for global reefs based on changes over the last 20 years [5]. The rate of increase in $\rho CO_2$ measured on inshore reefs was much closer to the latter estimates. According to the Bayesian modelling there was a 91% and 98% probability that the increase inshore is higher than offshore for the dry and wet seasons, respectively. This comparison suggests that elevated $\rho CO_2$ levels on inshore reefs are a relatively recent phenomenon, and it is possible that these are caused by anthropogenically increased sediment and nutrient runoff.

In conclusion, further investigation of the differences between inshore and offshore carbon chemistry and the trophic status of the surrounding waters are crucial for our understanding of the vulnerability of inshore GBR reefs to climate change and OA. However, given the two year dataset presented here and data from offshore reefs it is apparent that, in addition to sporadically enhanced nutrient levels, decreased light and increased sedimentation [24,25,30,51], inshore reefs are subjected to elevated $\rho CO_2$ values similar to those expected in the near future under OA scenarios [52]. The present study also confirms that the rate of increase on inshore reefs is faster than for offshore reefs and atmospheric values [5]. Increased $\rho CO_2$ can be beneficial for primary producers such as benthic algae, seagrasses and phytoplankton [53,54] but might decrease coral calcification due to reduced aragonite saturation states. Thus, there is a potential for a further shift from coral reefs to algal-dominated areas. However, it should also be acknowledged that at least to some extent corals on inshore reefs can grow under conditions previously predicted as detrimental for coral reef existence $\rho CO_2 >1450$, $\Omega_w < 3.3$ [5,53]. To disentangle what controls these processes, further water quality and community studies, as well as detailed measurements of calcification and growth of corals and other coral reefs organisms, are needed.

Supporting Information

File S1 Table S1. Raw data of all inshore samples analyzed in the present publications. Station: a unique station code from the Australian Institute of Marine Science (AIMS) database; Island: sample location; Code: a depth related code; Depth (in m): actual sampling depth, 0 m = surface sample, assumed to be on average from 1 m depth; Dup.: duplicate number; Temp.: temperature (°C); Sal.: salinity; DIC: dissolved inorganic carbon (μmol kg $^{-1}$); TA: Total Alkalinity (μmol kg $^{-1}$); Date: collection date; pH: calculated pH on total scale; $\rho CO_2$: calculated partial pressure of CO2 (μatm); $\Omega_w$: aragonite saturation state; Time: time of sample collection.

Table S2, Historic water chemistry data from inshore (Bowling Green Bay, Pandora Reef), mid-shelf (Rib Reef, Davies Reef) and outer-shelf (Myrvidon Reef) reefs of the Great Barrier Reef. Samples are the first sample from the cross-reef transects, and are thus close to the windward reef edge and presumed under little influence of reef metabolism. Samples in Cape Bowling Green are not associated with reefs, but represent inshore water close to the coastline. Methods are the same as described in [6,7]. (DOCX)

Acknowledgments

We are indebted to all team members of the marine monitoring program group, especially Irena Zagorski and Johnstone Davidson for their help in collecting water samples. We also thank Stephen Boyle for water chemistry analysis, Dr. Murray Logan for help with statistical analysis and Samantha Talbot for editorial comments on the manuscript.

Author Contributions

Conceived and designed the experiments: SU. Performed the experiments: SU MF CL. Analyzed the data: SU MF CL. Contributed reagents/materials/analysis tools: SU MF. Wrote the paper: SU MF CL.

References

1. Honisch B, Hemming NG, Archer D, Siddall M, McManus JF (2009) Atmospheric carbon dioxide concentration across the mid-Pleistocene transition. Science 324: 1551.
2. Tyrrell T (2011) Anthropogenic modification of the oceans. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 369: 887-908.
3. Khattawala S, Tanhua T, Mikoloff Fletcher S, Gerber M, Doney S, et al. (2013) Global ocean storage of anthropogenic carbon. Biogeosciences 10: 2169-2191.
4. Caldeira K, Wickett ME (2005) Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. J Geophys Res 110: 12.
5. Goyranak T, Schulz KG, Santos IR, Eyer BD (2014) Enhanced acidification of global coral reefs driven by regional biogeochemical feedbacks. Geophysical Research Letters.
6. Barnes D, Deverux M (1984) Productivity and calcification on a coral reef: a survey using pH and oxygen electrode techniques. Journal of Experimental Marine Biology and Ecology 79: 213-231.
7. Barnes D (1983) Profiling coral reef productivity and calcification using pH and oxygen electrodes. Journal of Experimental Marine Biology and Ecology 79: 213-231.
8. Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS, Greenfield P, et al. (2007) Coral reefs under rapid climate change and ocean acidification. Science 318: 1737-1742.
9. Fabricus KE, Langdon C, Uthicke S, Humphrey C, Noonan S, et al. (2011) Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations. Nature Climate Change 1: 165-169.
10. Anthony KRN, Kline DI, Diaz-Pulido G, Dove S, Hoegh-Guldberg O (2008) Ocean acidification causes bleaching and productivity loss in coral reef builders. Proceedings of the National Academy of Sciences 105: 17442.
11. Munday PL, Dixson DL, Donelson JM, Jones GP, Pratchett MS, et al. (2009) Ocean acidification impairs olfactory discrimination and homing ability of a marine fish. PNAS 106: 10480–10483.

12. Uthicke S, Momigliano F, Fabricius KE (2013) High risk of extinction of benthic foraminifera in this century due to ocean acidification. Sci Rep 3.

13. De’ath G, Lough JM, Fabricius KE (2009) Declining coral calcification on the Great Barrier Reef. Science 323: 116.

14. Reynaud S, Leclercq N, Romaine-Louid S, Ferrier-Pagès C, Jaubert J, et al. (2003) Interacting effects of CO2 partial pressure and temperature on photosynthesis and calcification in a scleractinian coral. Global Change Biology 9: 1660–1668.

15. Albright R, Langdon C, Anthony K (2013) Dynamics of seawater carbonate chemistry, production, and calcification of a coral reef flat, central Great Barrier Reef. Biogeosciences 10.

16. Anthony K, A Kleypas J, Gattuso JP (2011) Coral reefs modify their seawater carbon chemistry - implications for impacts of ocean acidification. Global Change Biology.

17. Kleypas JA, Anthony K, Gattuso JP (2011) Coral reefs modify their seawater carbon chemistry - case study from a barrier reef (Moorea, French Polynesia). Global Change Biology.

18. Shaw EC, McNeil BI, Tilbrook B (2012) Impacts of ocean acidification in naturally variable coral reef flat ecosystems. Journal of Geophysical Research 117: C03038.

19. Uthicke S, Laddy M, Nguyen HD, Byrne M (2014) Interactive effects of near-future temperature increase and ocean acidification on physiology and gonad development in adult Pacific sea urchin, Echinometra sp. a. Coral Reefs 33: 831–845.

20. Shaw EC, McNeil BI (2014) Seasonal variability in carbonate chemistry and air-sea CO2 fluxes in the southern Great Barrier Reef. Marine Chemistry 158: 49–58.

21. Suzuki A, Kawahata H, Ayukai T, Goto K (2001) The oceanic CO2 system and carbon budget in the Great Barrier Reef, Australia. Geophysical Research Letters 28: 1243–1246.

22. Kawahata H, Suzuki A, Ayukai T, Goto K (2000) Distribution of the fugacity of carbon dioxide in the surface seawater of the Great Barrier Reef. Marine Chemistry 72: 257–272.

23. Fabricius KE (2005) Effects of terrestrial runoff on the ecology of corals and coral reefs: review and synthesis. Mar Pollut Bull 50: 125–146.

24. Cooper T, Uthicke S, Humphrey C, Fabricius K (2007) Gradients in water column nutrients, sediments, irradiance and coral reef development in the Whitsunday Region, central Great Barrier Reef. Estuar Coast Shelf Sci 74: 458–470.

25. Fabricius KE, Cooper TF, Humphrey C, Uthicke S, De’ath G, et al. (2012) A bioindicator system for water quality on inshore coral reefs of the Great Barrier Reef. Marine Pollution Bulletin 65: 320–332.

26. Fabricius KE, De’ath G (2008) Photosynthetic symbionts and energy supply determine octocoral biodiversity in coral reefs. Ecology 89: 3163–3175.

27. Nohes K, Uthicke S, Henderson R (2008) Is light the limiting factor for the determination of octocoral biodiversity in coral reefs. Ecology 89: 3163–3175.

28. Nohes K, Uthicke S, Henderson R (2008) Is light the limiting factor for the distribution of benthic symbiotic bearing foraminifera on the Great Barrier Reef? Journal of Experimental Marine Biology and Ecology 363: 48–57.

29. Uthicke S, Nohes K (2008) Benthic Foraminifera as ecological indicators for water quality of the Great Barrier Reef. Estuar Coast Shelf Sci 78: 763–773.

30. Uthicke S, Alterath C (2010) Water column nutrients control growth and C: N ratios of symbiotic-bearing benthic foraminifera on the Great Barrier Reef, Australia. Limnol Oceanogr 55: 1681–1696.

31. Schaffelke B, Carleton J, Deyle J, Fursan M, Gunn K, et al. (2011) Reef Rescue Marine Monitoring Program Final Report of AIMS Activities 2010/11 Inshore Water Quality Monitoring. Available: http://www.gbrmpa.gov.au/_data/assets/pdf_file/0011/167776/Inshore-Water-Quality-Monitoring-Report2011.pdf.

32. Dickson AG, Sabine CL, Christian JR (2007) Guide to best practices for ocean CO2 measurements. PCIES special publication 3.

33. Riebesell U, Fabry VJ, Hansson L, Gattuso J-P (2010) Guide to best practices for ocean acidification research and data reporting. Publications Office of the European Union Luxembourg.

34. Pierrot D, Fabricius KE, Russell BD, Connell SD, Uthicke S, Muehllehner N, et al. (2013) Future seaward birds: Can increased productivity lead to increased carbon storage? Marine Pollution Bulletin 73: 463–469.

35. Veron JEN, Hoegh-Guldberg O, Lenton TM, Lough JM, Obura DO, et al. (2009) The coral reef crisis: The critical importance of <350 ppm CO2. Marine Pollution Bulletin 58: 1429–1436.