Carbon turnover rates in the One Tree Island reef: A 40-year perspective

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[1] During November–December 2009 community rates of gross photosynthesis (Pg), respiration (R) and net calcification (Gnet) were estimated from low-tide slack water measurements of dissolved oxygen, dissolved inorganic carbon and total alkalinity at the historical station DK13 One Tree Island reef, Great Barrier Reef, Australia. Compared to measurements made during the 1960s–1970s at DK13 in the same season, Pg increased from 833 to 914 mmol O2m−2d−1 and Pn−R increased from 1.14 to 1.30, indicating that the reef has become more autotrophic. In contrast, Gnet decreased from 133 mmol Cm−2d−1 to 74 ± 24 mmol Cm−2d−1. This decrease stems primarily from the threefold increase in nighttime CaCO3 dissolution from −2.5 mmolm−2h−1 to −7.5 mmolm−2h−1. Comparison of the benthic community survey results from DK13 and its vicinity conducted during this study and in studies from the 1970s, 1980s and 1990s suggest that there have been no significant changes in the live coral coverage during the past 40 years. The reduced Gnet most likely reflects the almost threefold increase in dissolution rates, possibly resulting from increased bioerosion due to changes in the biota (e.g., sea cucumbers, boring organisms) and/or from greater chemical dissolution produced by changing abiotic conditions over the past 40 years associated with climate change, such as increased temperatures and ocean acidification. However, at this stage of research on One Tree Island the effects of these changes are not entirely understood.


1. Introduction

[2] Calcification, photosynthesis and respiration are three major metabolic processes dominating the carbon turnover of coral reef ecosystems [Hatcher, 1997]. It has been proposed that quantification of these rates at the community level, i.e., for the whole reef, will shed light on the development and geographical distribution of coral reefs [e.g., Kinsey, 1979]. More recent studies have shown that reef metabolism monitoring can provide insight into the trophic balance between benthic heterotrophs (e.g., corals) and autotrophs (e.g., macro algae), and the “health” status of the coral reef ecosystem [Silverman et al., 2004; Silverman et al., 2006; Silverman et al., 2007a]. In addition, it has been shown that the rates of inorganic carbon uptake, i.e., deposition of CaCO3, in coral reefs is positively correlated with the aragonite degree of saturation (Ωarag) and temperature of ambient seawater [Ohde and van-Woesik, 1999; Silverman et al., 2007b].

[3] The metabolic rates of gross production or photosynthesis (Pp), respiration (R) and net calcification (Gnet) can be evaluated at the community level by following changes in the dissolved oxygen (DO), total dissolved inorganic carbon (CT) and total alkalinity (AT) of reef water [Kinsey, 1978a; Marsh and Smith, 1978; Gattuso et al., 1999]. These changes are relatively large due to: (1) shallow water flowing over a biologically active surface; (2) intense biological activity due to prevalence of optimal environmental conditions in reef water (e.g., light penetration, warm temperatures, relatively high nutrient levels and high Ωarag facilitated by excess photosynthesis over respiration during the daytime); and (3) extended residence time of water in isolated zones of the reef, such as the lagoons of fringing reefs or atolls.
In coral reef ecosystems, $P_g$ and $R$ are generally very high and almost equal. Hence, net production ($P_{net}$), which is the difference between the two, is often close to zero [e.g., Kinsey, 1983, 1985; Pichon, 1997]. Accordingly, the ratio $P_g:R$ is close to unity, indicating the reef is in trophic balance. When $P_g:R > 1$, the reef is autotrophic and requires an increased external supply of dissolved nutrients to support its growth [Marsh and Smith, 1978; Erez, 1990; Silverman et al., 2007a]. When $P_g:R < 1$ the reef is heterotrophic and requires an increased supply of particulate and dissolved organic matter from the open sea to support its growth [Erez, 1990; Yahel et al., 2003].

During 1967–1975 detailed measurements of reef metabolism were conducted at DK13 and other sites in the One Tree Island reef using the low-tide slack water method [Kinsey, 1978b; Kinsey, 1979]. Based on a statistical compilation of these measurements it was shown that reef metabolism at DK13 varied seasonally [Kinsey, 1979]. The basic premise of this analytical approach was that reef metabolism varied diurnally in a consistent manner over extended periods of time. This assumption was supported by taking rigorous slack water measurements at different times of the day and night over an extended period of time (a month to a few months) and compiling them into a standard day representing that period [Kinsey, 1978b]. As proposed, this compilation resulted in a coherent diel cycle. This type of long-term behavior has been shown to exist also in a Red Sea reef [Silverman et al., 2006] and is also apparent in the results of this study as shown in Figures 11–14. These findings show that under normal climatic conditions (light, sea state, wind and current direction and speed, water chemistry and temperature, etc) measurements made on different days as well as different years during the same period (month or season) on the same reef at the same location are comparable. This proposition has been indisputably demonstrated for DK13 in a compilation of measurements made in different years by Kinsey [1977]. In light of the emerging worldwide coral reef crisis [Veron et al., 2009], the primary goal of this study was to repeat the measurements done by Kinsey at DK13 to see if there have been any significant
changes in reef metabolism, which could be symptomatic of this crisis.

2. Material and Methods

2.1. Study Site

One Tree Reef is a lagoonal platform reef in the Capricorn-Bunker Group near the southern end of the Great Barrier Reef (23°30′S 152°06′E), Australia. The reef is an irregularly shaped pseudo atoll, 2.7 km in length from north to south and 4.7 km in length from east to west (Figure 1). The reef flat, which is mostly a ca. 100–300 m-wide algal ridge, encompasses three shallow lagoons (2–10 m deep) and a coral cay in the SE corner off the extreme weather side of the reef. Approximately 3 h before and after low tide the reef flat is higher than the surrounding open water and the water in the lagoon is trapped.

2.2. Chemical Sampling and Analysis

During November–December 2009, water samples were taken from the inner rim of the reef flat on the south side of the One Tree Reef (Figure 1) at a single station (DK13, 23°30.6384′S 152°05.1300′E) during the low-tide slack water periods occurring twice a day (Figure 2). Our sampling station is approximately 50 m south of the original DK13 station (Donald Kinsey personal communication), which was sampled intensively throughout the latter half of the 1960s and early half of the 1970s. Water samples were analyzed for dissolved oxygen (DO), pH, total alkalinity (AT), total dissolved inorganic carbon (CT), nutrients (NH3tot = NH3 + NH4+, TON = NO3− + NO2− and PO43−) and chlorophyll a. Immediately after sampling, duplicate samples of DO were measured using the modified Winkler method [Strickland and Parsons, 1972] with a Metrohm burette to a precision of ±1 µmol/L. Water samples for pH analysis were immediately sampled into 60 ml sealed brown glass bottles with screw on cap and Teflon sealing ring, refrigerated and measured every 3–4 days using a Radiometer PHM220 pH meter with a combined glass electrode pHC-2401 (Radiometer analytical) calibrated with Radiometer commercial buffers at room temperature to a precision of ±0.001–0.003. Water samples for AT analysis were immediately sampled into 100 ml brown glass bottles with screw cap and Teflon sealing ring refrigerated and measured within 3–4 days after sampling in replicate sub samples that were filtered with a 0.45 µm Sartorius filter and weighed with an analytical scale (±0.001 g). Samples were then titrated in an open Teflon cup with 0.05 N HCl using an automated Radiometer Copenhagen ABU91 Autoburette to below the inflexion point and down to pH = 3. The AT values were calculated according to the method outlined by Sass and Ben-Yaakov [1977] and had a precision of better than ±2 µmol/kg. The concentration of HCl used to titrate seawater samples was calibrated with a seawater certified reference material (CRM) from A. Dickson’s laboratory.

Water samples for CT analysis were sampled into 30 ml glass bottles sealed with rubber stoppers that were crimped close with external tin caps (Wheaton, USA). Before sealing the bottles, samples were poisoned with 15 µl (0.05% v/v) saturated HgCl2 solution with some crystals [Dickson et al., 2007]. The samples were measured about 2 months after sampling. Dissolved inorganic carbon...
was extracted from the samples by acidifying them with phosphoric acid (H₃PO₄, 5%) using a custom, automated CO₂ extractor and delivery system (D. Mucciaroni, EESS, Stanford) using high grade N₂ as a carrier gas based on the Bandstra et al. [2006] design connected on line with a LiCor 7000 CO₂/H₂O analyzer. C₇ measurements were calibrated using seawater CRMs from A. Dickson’s lab. A new CRM was used to verify the accuracy of the measurements at the beginning of each measuring day and every sample was measured in triplicate. In order to check for drift, 2 CRMs were run after every 4 sample measurements. The repeatability (mean ±SD) of the measurements was 1.3 ± 0.9 μmol/L.

Chlorophyll a was measured using the fluorometric method described by Parsons et al. [1984] using a Turner Designs Aquafluor fluorometer. Nitrite (NO₂⁻) was measured with a colorimetric method described by Grasshoff et al. [1999] using a Flow Injection Autoanalyzer (Lachat Instruments Model QuickChem 8000). Nitrate (NO₃⁻) was measured by reducing it to nitrite using a copperized cadmium column (precision of nitrite and nitrate measurements was ±0.02 μmol/L). Nitrite and nitrate in this study are reported as total oxidized nitrogen \( TON = NO_3^- + NO_2^- \). Total ammonium concentrations \( NH_3 + NH_4^+ \) were determined by a fluorometric method modified from protocol A of Holmes et al. [1999]. The precision of ammonium measurements was ±0.05 μmol/L.

2.3. Continuous Measurements

Seawater temperature, salinity, depth, dissolved oxygen (DO) concentration and PAR were logged every 10 min at DK13 using a SBE-19 CTD data logger (Sea-Bird Electronics, USA) fitted with a DO sensor (SBE23Y) and a PAR sensor (LI-COR LI192SA). Data were not recorded from 28 November until 3 December due to loss of battery power. Air temperature, relative humidity, wind speed, air pressure, global radiation and precipitation were measured with a Vaisala weather transmitter WXT520 connected to a Campbell CR200 data logger. The weather station was deployed at the research station on One Tree Island on the wet lab roof ca. 10 m above the water surface.

2.4. Calculating Reef Metabolism

During the slack water period at low tide, water in the lagoon is ponded and barely moves. Under the assumption that the water is stagnant the metabolic rates are easily calculated as a function of the temporal change in the relevant chemical constituent and water depth, which is assumed to be constant. Thus, net production \( P_{net} \), net deposition rate of CaCO₃ \( G_{net} \), and the fluxes of nutrients \( J_{net(TON)} \) and \( J_{net(NH₃-tox)} \) of the reef at DK13 per m² are calculated according to equations (1)–(5):

\[
P_{net(DO)} = \frac{(DO_f - DO_i) \cdot Z_{SW}}{\Delta t} - k_{PV-DO} \cdot \left(\frac{DO_f - DO_{sat}}{SW} \right)
\]

\[
P_{net(C₇)} = \frac{\left(\left[C_{T-f} - C_{T-i}\right] - 0.5 \cdot (A_{T-f} - A_{T-i})\right] \cdot Z_{SW}}{\Delta t} - k_{PV-CO_2} \cdot K_H \cdot \left(\frac{PCO_2 - PCO_2_{sat}}{SW} \right)
\]

\[
G_{net} = \frac{0.5 \cdot (A_{T-f} - A_{T-i}) \cdot Z_{SW}}{\Delta t}
\]

\[
J_{net(TON)} = \frac{(TON_f - TON_i) \cdot Z_{SW}}{\Delta t}
\]

\[
J_{net(NH₃-tox)} = \frac{(NH₃_{sat-f} - NH₃_{sat-i}) \cdot Z_{SW}}{\Delta t}
\]

In equations (1)–(5) the subscripts \( f \) and \( i \) denote the final and initial concentrations of consecutive measurements made at DK13 during a low-tide slack water period. \( Z_{SW} \) is the water depth during the slack water period, which is the same for all calculations (0.8 ± 0.01 m). \( DO \) bar is the average of \( DO_f \) and \( DO_i \). \( DO_{sat} \) bar is the average of the oxygen saturation concentrations \( DO_{sat-f} \) and \( DO_{sat-i} \) calculated as a function of temperature \( (T_f \) and \( T_i) \) and salinity \( (S_f \) and \( S_i) \) according to García and Gordon [1992]. The piston velocity \( K_{PV-DO} \) is calculated using the average wind speed and seawater temperature between consecutive measurements according to Ho et al. [2006]. Uptake and production of \( C_T \) (equation 2) is adjusted for precipitation and dissolution of CaCO₃ by subtracting the difference between the consecutive measurements of \( A_T \), which is multiplied by 0.5 to convert it to moles carbon. The gas transfer flux is calculated using the difference between the average \( PCO₂ \) of two consecutive measurements in seawater and atmospheric \( PCO₂ \) with Henry’s constant \( (K_H) \) and the piston velocity for \( CO₂ \) \( (K_{PV-CO₂}) \). Atmospheric \( PCO₂ \) was taken to be 390 μatm. \( K_H \) was calculated as a function of the average temperature and salinity between consecutive measurements according to Weiss [1974]. The piston velocity \( (K_{PV-CO₂}) \) was calculated as a function of the average wind speed, seawater temperature and salinity according to Wanninkhof [1992]. In equation 3, \( G_{net} \) is determined in units of mmol carbon or CaCO₃ per m² per day and therefore the difference in \( A_T \) is multiplied by a factor of 0.5. Here, the conversion of \( A_T \) and \( C_T \) concentrations from units of μmol/kg to μmol/L is crucial due to the relatively large changes in seawater density at DK13 between consecutive measurements. The water density at the time of sampling was calculated as a function of temperature and salinity measured by the CTD deployed at DK13 [Millero and Poisson, 1981; Fofonoff and Millard, 1983]. Note that \( A_T \) values in equations 2 and 3 are not corrected for salinity changes, nitrate and ammonium even though these changes are quite large (see results section below). This is in keeping with the calculation methodology of Kinsey who determined as we have also (see results section below) that the total effect of these changes is negligible compared to the changes in \( A_T \) [Kinsey, 1978a].

2.5. Carbonate Chemistry

Aragonite saturation state \( (\Omega_{arag}) \) and \( PCO₂ \) values are calculated as a function of the measured salinity, temperature, \( A_T \) and \( C_T \) using the CO2sys program [Lewis and Wallace, 1998]. We used the carbonate chemistry dissociation constants of Roy et al. [1993] and the apparent aragonite solubility constant of Mucci [1983] for calculating \( \Omega_{arag} \).

2.6. Benthic Community Structure

Benthic community surveys were conducted at DK13 using a linear point-intercept method along 50 m transects following Aronson and Precht [1997]. The benthic community surveys were designed to make the results most
comparable to the measurements made in previous studies from 1967 to 1975 [Kinsey, 1972, 1978b, 1979]. Three replicate zones were surveyed with 3–5 replicate 50 m transects analyzed in each zone (Figure 1c). Along each 50 m transect, the benthic type underneath the transect tape was determined every 50 cm, with the benthos assigned to one of 7 categories (sand, soft coral, algae, hard corals, dead coral, rock and other). The transect tape was laid down haphazardly along the bottom moving from the inner reef flat toward the algal flat at 50 m intervals. This process was repeated 3–5 times in each of the 3 replicate reef flat zones that were surveyed along its inner rim and were separated by 50–100 m.

3. Results

[14] During November–December 2009 the wind blew 61% of the time from the SE quadrant at speeds ranging between 1 and 10 m s−1 (average wind speed ±1SD = 4.5 ± 1.6 m s−1). During the same period there were 12 light rain events (precipitation rate < 2.5 mm h−1) and two moderate rain events (2.5 < precipitation rate < 7.6 mm h−1). In the early morning hours of 2 December and from 05:00 to 14:00 LT on 3 December it rained a total of 55 mm. The daily integrated solar radiation (GR) varied between 21 and 33 MJ m−2 while precipitation events and lower GR values were not well correlated. Air temperature during the study period varied between 21°C and 29°C with an average value of 25.8 ± 1.3°C (±1SD). During the first 11 days of the study period the air temperature was 1.7°C lower on average than in the last 14 days.

[15] During the ebb tide, the water level at DK13 leveled out at ca. 0.8 m once the receding water level outside the reef fell beneath the level of the algal ridge flat surrounding the entire OTR lagoon (Figure 2) as observed in previous studies [Kinsey, 1979; Ludington, 1979]. Below the 0.8 m threshold the water level seems to level off asymptotically but only on very few occasions does it obtain a constant level. The reason for this is not known and may have been caused by continued flow of water out of the reef in areas where the rim of the reef is slightly lower than the 0.8 m level (relative to DK13 datum) such as the northern and southern passages “Gutter” and “Shark Alley” (Figure 1), or through the reef framework, or due to piling of water by the wind. Regardless of the reason, the continued decrease in water levels indicates that there is a limited amount of water movement around DK13 during the low-tide slack water period. This movement was observed on a number of occasions by injecting fluorescein dye into the water in the groove where the sampling station was located (Table 1).

[16] The speed of the dye patch that formed was measured by following its progress along a 12 ft. tape measure that was laid out along the bottom of the groove. In three of the measurements the dye patch did not move at all. The maximum observed speed of the dye patch was 1.8 cm s−1 and the overall average was 0.6 ± 0.7 cm s−1 (±1SD). It is possible that metabolic rates calculated at DK13 may represent a larger area of the reef in the vicinity of the sampling station, however for the sake of comparison with previous measurements [Kinsey, 1978b; Kinsey, 1979] an ideal slack water situation is assumed.

[17] The water temperature time series measured at DK13 is displayed in Figure 3. The average temperature for the entire study period was 26.5 ± 1.8°C (±1SD). During daytime slack water periods temperature rose by as much as ~7°C in 5–6 h, while during nighttime slack water periods water temperatures fell by as much as ~4°C. During the daytime colder water from the open ocean would cause water temperature to fall at DK13 by as much as ~8°C in less than 2 h from the beginning of the flood tide, while during nighttime relatively warmer water from the open ocean would cause water temperature to rise by as much as 3°C in <2 h from the time when water level rises above 0.8 m during the flood tide. A number of days before, after and during the neap tide, temperature rose after its initial decline with the rising tide by as much as ~5.7°C.

[18] Salinity at DK13 fluctuated similarly to temperature throughout the study period as a result of evaporation, precipitation and mixing of relatively fresh water from the open ocean during flood tide (Figure 4). This can be seen during slack water period, when salinity usually increased by as much as 0.2. Similarly, temperature and salinity would drop following the water level’s rise above the reef flat (0.8 m). Salinity would drop within a relatively short time (<2 h) by as much as 0.4 and then start to increase to its previous levels in the next 4 h until the end of slack water. These measurements indicate that the water inside the lagoon is well isolated from the water outside the reef during slack water period. Additionally, the increase of temperature and salinity following the water level rise above 0.8 m suggests that lagoon water is a reservoir for both heat and salt and therefore must also have a significant residence time, particularly around neap tide.

[19] During November–December 2009 water was sampled at DK13 109 times during 47 slack water periods. Samples were collected twice, three times and five times within 40, 3 and 4 of the sampling periods, respectively. All daytime and nighttime slack water values of measured and calculated parameters from DK13 were plotted together with

### Table 1. Average Water Speed and Direction Measured at DK13 During the Low-Tide Slack Water Period Using Fluorescein

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Direction</th>
<th>Speed (cm s⁻¹)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/29/2009</td>
<td>11:42</td>
<td>—</td>
<td>0.0</td>
<td>Patch dispersed and did not move</td>
</tr>
<tr>
<td>11/29/2009</td>
<td>11:49</td>
<td>Toward lagoon</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>12/1/2009</td>
<td>13:25</td>
<td>—</td>
<td>0.0</td>
<td>Patch dispersed and did not move</td>
</tr>
<tr>
<td>12/1/2009</td>
<td>13:35</td>
<td>Toward lagoon</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>12/1/2009</td>
<td>15:18</td>
<td>—</td>
<td>0.0</td>
<td>Patch dispersed and did not move</td>
</tr>
<tr>
<td>12/2/2009</td>
<td>05:40</td>
<td>Toward lagoon</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>12/2/2009</td>
<td>05:50</td>
<td>Toward lagoon</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

[14] [15] [16] [17] [18] [19]
their corresponding open water values in Figures 5–9. Average and extreme values of all measured and calculated parameters from DK13 and the open water are presented in Table 2.

During the study period daytime $A_T$ values varied with a long period (Figure 5). This cyclical behavior, while less apparent, seems to have occurred in the nighttime $A_T$ measurements as well. The difference between consecutive measurements of $A_T$ was negative (decrease in $A_T$) during the daytime indicating net precipitation of CaCO$_3$ and positive (increase in $A_T$) during the nighttime indicating net dissolution of CaCO$_3$. The maximum observed decrease in daytime $A_T$ during a slack water period was 168 $\mu$mol/kg, while the maximum observed increase during the nighttime was 122 $\mu$mol/kg. Comparison of the daytime and nighttime averages of $A_T$ at DK13 to the average $A_T$ measured at Figure 4. Salinity (black line) and pressure (gray line) at DK13 during the period 11/20/2009–12/2/2009 (top) and 12/3/2009–12/15/2009 (bottom) measured at 10-min intervals.

Figure 3. Water temperature (black line) and pressure (gray line) at DK13 during the period 11/20/2009–12/2/2009 (top) and 12/3/2009–12/15/2009 (bottom) measured at 10-min intervals.
various stations in the open water around One Tree Reef (Table 2) suggests that the reef is a net sink for total alkalinity, i.e., there is net precipitation of CaCO$_3$ in the reef.

Daytime DO also varied with a long period (Figure 6). Similarly, the cyclical behavior of nighttime DO is less pronounced. Nighttime concentrations decreased between consecutive measurements on all but 2 occasions when the first sample of the slack water period was made during the dark and the second measurement was made after sunrise. The rest of the consecutive nighttime measurements decreased by as much as 136 $\mu$mol/L. Daytime concentrations increased between consecutive measurements on all but four occasions where the first sample of the slack water period was taken prior to sunset and the second after sunset. It is noted that these measurements displayed a larger decreases in DO (>100 $\mu$mol/L) relative to the nighttime
measurements. Relative to the average value for all DO measurements made at various stations in the open water around One Tree Reef (Table 2) the average daytime and nighttime concentrations of DO (Table 2) indicate that the reef is a net sink for DO, i.e., the nighttime uptake due to respiration is greater than the net daytime production of DO due to photosynthesis excess over respiration.

The long period variation observed in CT measurements over the monthlong sampling period at DK13 (Figure 7) is similar to that observed in AT (Figure 5). The difference between consecutive measurements of CT was negative (decrease in CT) during the daytime and positive (increase in CT) during the nighttime as expected. The maximum observed decrease in CT was 286 μmol/kg, while during the nighttime the maximum increase in CT was 291 μmol/kg. Comparison of the average CT measured at various stations in the open water around One Tree Reef (Table 2) to the daytime and nighttime averages at DK13 suggests that the reef is a small net source of dissolved inorganic carbon, i.e., the nighttime production of CT due

Figure 7. Total dissolved inorganic carbon (CT) measured at DK13 during the slack water period of November and December 2009. The solid gray circles indicate daytime measurements (after sunrise and before sunset). The white circles indicate the nighttime measurements (after sunset and before sunrise). The solid black triangles indicate measurements made outside the reef at various distances and directions away from the One Tree Reef.

Figure 8. Dissolved ammonia (NH₃) + ammonium (NH₄⁺) measured at DK13 during the slack water period of November and December 2009. The solid gray circles indicate daytime measurements (after sunrise and before sunset). The white circles indicate the nighttime measurements (after sunset and before sunrise). The solid black triangles indicate measurements made outside the reef at various distances and directions away from the One Tree Reef.
to respiration and CaCO$_3$ dissolution is greater than the net daytime uptake due to photosynthesis excess over respiration and calcification.

[23] The concentration of $NH_{3\text{-tot}}$ did not differ much between daytime and nighttime (Figure 8). Unlike, $A_T$ and $C_T$ the diurnal pattern is mixed, where out of 24 consecutive measurements during the nighttime $NH_{3\text{-tot}}$ increased in 14 of these measurements, while out of 21 consecutive daytime measurements $NH_{3\text{-tot}}$ increased 15 times. Thus, the majority of the measurements indicated that $NH_{3\text{-tot}}$ was being produced throughout the study period at DK13. Additionally, $NH_{3\text{-tot}}$ at DK13 was substantially higher than the open water concentration at all times (Table 2, Figure 8). These observations indicate that the reef is acting as a source of dissolved inorganic nitrogen to the surrounding open water outside the reef. Finally, the concentration of $TON$ measured at DK13 also displayed a long period behavior, however daytime values were not significantly different from nighttime values (Figure 9). Out of 53 consecutive measurements $TON$ increased 42 times, decreased 9 times and didn’t change twice. Out of the 9 times that $TON$ decreased 7 occurred during nighttime. As is the case with $NH_{3\text{-tot}}$, the average $TON$ at DK13 was significantly higher than in the open water surrounding the One Tree Reef (Table 2) indicating that the reef is a significant source of dissolved inorganic nitrogen supporting open water productivity.

[24] Out of the 60 daytime $\Omega_{\text{arag}}$ values 30 were greater than 4, while only 11 out of the total 106 $\Omega_{\text{arag}}$ values were less than 2 most of which, except for one, occurred between 01:00 and 07:00. In addition, the mean $\Omega_{\text{arag}}$ measured during the first half of the night (sunset to 24:00) is 2.78 ± 0.26 (±1SD, n = 28) and during the second half of the night (00:00 to sunrise) it is 2.21 ± 0.43 (±1SD, n = 21), which is significantly smaller than the first half of the night according to the Mann-Whitney test (p < 0.0001). The diel average $PCO_2$ at DK13 is substantially higher than the estimated $PCO_2$ in the open water around the reef (Table 2) indicating that the reef is acting as source for atmospheric $CO_2$ throughout the study period.

![Figure 9. Dissolved nitrite (NO$_2^-$) + nitrate (NO$_3^-$) measured at DK13 during the slack water period of November and December 2009. The solid gray circles indicate daytime measurements (after sunrise and before sunset). The white circles indicate the nighttime measurements (after sunset and before sunrise). The solid black triangles indicate measurements made outside the reef at various distances and directions away from the One Tree Reef.](image)

### Table 2. Daytime (05:03–18:31 LT) and Nighttime (18:31–05:03 LT) Averages ±1SD of the Water Chemistry Measurements Made at DK13 and on the Open Ocean, 11/20/2009–12/15/2009

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Diel Average$^a$</th>
<th>Daytime Average$^a$</th>
<th>Daytime Maximum</th>
<th>Nighttime Minimum</th>
<th>Nighttime Average$^a$</th>
<th>Nighttime Maximum</th>
<th>Nighttime Minimum</th>
<th>Open Water Average$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_T$ ($\mu$mol/kg)</td>
<td>2248 ± 80 (109)</td>
<td>2204 ± 76 (60)</td>
<td>2381</td>
<td>2058</td>
<td>2302 ± 44 (44)</td>
<td>2385</td>
<td>2210</td>
<td>2299 ± 4 (6)</td>
</tr>
<tr>
<td>$DO$ ($\mu$mol/l)</td>
<td>195 ± 111 (104)</td>
<td>275 ± 88 (56)</td>
<td>410</td>
<td>59</td>
<td>101 ± 36 (48)</td>
<td>191</td>
<td>48</td>
<td>207 ± 5 (4)</td>
</tr>
<tr>
<td>$C_T$ ($\mu$mol/kg)</td>
<td>1973 ± 175 (108)</td>
<td>1871 ± 165 (59)</td>
<td>2287</td>
<td>1579</td>
<td>2095 ± 86 (49)</td>
<td>2243</td>
<td>1895</td>
<td>1979 ± 4 (6)</td>
</tr>
<tr>
<td>$NH_{3\text{-tot}}$ ($\mu$mol/l)</td>
<td>1.20 ± 0.47 (87)</td>
<td>1.11 ± 0.41 (47)</td>
<td>2.26</td>
<td>0.53</td>
<td>1.31 ± 0.51 (40)</td>
<td>3.37</td>
<td>0.36</td>
<td>0.29 ± 0.12 (6)</td>
</tr>
<tr>
<td>$TON$ ($\mu$mol/l)</td>
<td>2.35 ± 0.65 (105)</td>
<td>2.15 ± 0.69 (57)</td>
<td>3.83</td>
<td>0.81</td>
<td>2.58 ± 0.49 (48)</td>
<td>3.49</td>
<td>1.60</td>
<td>0.23 ± 0.17 (6)</td>
</tr>
<tr>
<td>$pH$</td>
<td>7.911 ± 0.165 (106)</td>
<td>8.006 ± 0.155 (57)</td>
<td>8.230</td>
<td>7.490</td>
<td>7.801 ± 0.091 (49)</td>
<td>7.649</td>
<td>8.018</td>
<td></td>
</tr>
<tr>
<td>$PCO_2$ ($\mu$atm)</td>
<td>591 ± 288 (106)</td>
<td>443 ± 275 (57)</td>
<td>1697</td>
<td>188</td>
<td>763 ± 193 (49)</td>
<td>1140</td>
<td>391</td>
<td>387$^b$</td>
</tr>
<tr>
<td>$\Omega_{\text{arag}}$</td>
<td>3.22 ± 0.99 (106)</td>
<td>3.80 ± 0.95 (57)</td>
<td>5.30</td>
<td>1.27</td>
<td>2.53 ± 0.46 (49)</td>
<td>3.56</td>
<td>1.80</td>
<td>3.65$^b$</td>
</tr>
</tbody>
</table>

$^a$Numbers in parentheses indicate the number of measurements made.

$^b$Calculated with open water average $A_T$ and $C_T$ and assuming salinity = 35 and temperature = 26°C.
Table 3. Diel Averages, Daytime (05:00–18:31 LT) and Nightime (18:31–06:00 LT) Metabolic Rates Calculated According to Equations (1)–(5) Based on Water Chemistry Measurements Made at DK13, 11/20/2009–12/15/2009.

<table>
<thead>
<tr>
<th>Metabolic Parameter</th>
<th>Daytime Average</th>
<th>Nighttime Average</th>
<th>Daytime Minimum</th>
<th>Nighttime Minimum</th>
<th>SD</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta P_{\text{net(DO)}} )</td>
<td>74 ± 24</td>
<td>269 ± 59</td>
<td>62 ± 14</td>
<td>751 ± 58</td>
<td>614 ± 24</td>
<td>504 ± 38</td>
</tr>
<tr>
<td>( \Delta P_{\text{net(CT)}} )</td>
<td>74 ± 24</td>
<td>269 ± 59</td>
<td>62 ± 14</td>
<td>751 ± 58</td>
<td>614 ± 24</td>
<td>504 ± 38</td>
</tr>
<tr>
<td>( \Delta P_{\text{net(NH}_3\text{-tot)}} )</td>
<td>5.72 ± 0.61</td>
<td>4.84 ± 0.46</td>
<td>5.72 ± 0.61</td>
<td>4.84 ± 0.46</td>
<td>5.72 ± 0.61</td>
<td>4.84 ± 0.46</td>
</tr>
<tr>
<td>( \Delta J_{\text{net(TON)}} )</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>( \Delta J_{\text{net(NH}_3\text{-tot)}} )</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Reported errors are the average values of the first differential (equation (1)) using the analytical error of each parameter used in equations (1)–(5) following Topping [1972]. Numbers in parentheses indicate the number of measurements made.

3.1. Metabolic Rates

[25] Changes in salinity, \( \text{NH}_3\text{-tot} \) and \( \text{TON} \) between consecutive measurements and compared to surrounding open water appear to be quite large compared to other reef systems where these parameters have been measured in a similar fashion as well as in comparison to their surrounding open water values [Silverman et al., 2007a]. Therefore, as suggested by Chisholm and Barnes [1998] the effect of these changes on \( A_T \), which is used for estimating rates of CaCO₃ precipitation/dissolution, may be significant. Linear regression analysis with 0 intercept of the changes in measured \( A_T \) between consecutive slack water measurements at DK13 in this study compared to the corresponding changes in \( A_T \) that were adjusted for changes in salinity, \( \text{NH}_3\text{-tot} \) and \( \text{TON} \) yielded a slope = 1.05 with \( R^2 = 1.00 \) (n = 48; data not shown). This finding conclusively supports the use of unadjusted changes in \( A_T \) to calculate rates of net calcification at DK13 as originally determined by Kinsey [1978a, 1979].

[26] Rates of net calcification (\( G_{\text{net}} \)), net production (\( P_{\text{net(DO)}} \) and \( P_{\text{net(CT)}} \)), net \( \text{TON} \) and net \( \text{NH}_3\text{-tot} \) production (\( J_{\text{net(TON)}} \) and \( J_{\text{net(NH}_3\text{-tot)}} \)) were calculated using equations (1)–(5) and are presented in Table 3 and Figures 11–17. The reported errors represent averages of daytime, nighttime and diel first differential values calculated for equations (1)–(5) using the analytical error of the measured quantities following Topping [1972]. Where, \( \Delta \text{DO} = \pm 1 \mu\text{mol/L}, \Delta \text{CT} = \pm 1.3 \mu\text{mol/L}, \Delta \text{AT} = \pm 2 \mu\text{mol/L}, \Delta \text{TON} = \pm 0.02 \mu\text{mol/L}, \Delta \text{NH}_3\text{-tot} = \pm 0.05 \mu\text{mol/L}, \) and calculated \( \Delta \text{PCO}_2 = \pm 5 \mu\text{atm}, \Delta K_{\text{pw-DO}} = 7\% \).

[27] Negative and positive values of \( G_{\text{net}} \) indicate net dissolution and precipitation of CaCO₃, respectively. The mean \( G_{\text{net}} \) during the first half of the night (18:31–24:00 LT) is \(-169 \pm 80 \) mmol C·m⁻²·d⁻¹ (±1SD, n = 16) and during the second half of the night (00:00–05:03 LT) is \(-199 \pm 84 \) mmol C·m⁻²·d⁻¹ (±1SD, n = 11). Although \( G_{\text{net}} \) is higher the second half of the night, it is not significantly different from the first half of the night according to a 2 tailed t-test (p = 0.376).

[28] In the calculations of \( P_{\text{net(DO)}} \) the gas transfer component in equation 1 accounted for 27% (SD = 23%) on
average of the values (maximum 81%), while in equation 2, the gas transfer component of \( P_{\text{net} (CT)} \) accounted for only 3% on average of the values (maximum 18%). Adding the average nighttime net production rates, which are actually respiration rates (\( R \)), to the average daytime net production rates following Marsh and Smith [1978], and taking into account the average day length for the period of the study (13 h 28 m), the average daytime gross production rate (\( P_g \)) was 678 ± 14 mmol \( \text{O}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1} \) and 788 ± 6 mmol \( C \cdot \text{m}^{-2} \cdot \text{d}^{-1} \) according to the \( DO \) and \( C_T \) measurements made at DK13, respectively. Thus, the respective \( P_g : R \) ratios are 1.14 ± 0.02 and 1.01 ± 0.01.

3.2. Benthic Populations Survey

[29] Live hard coral cover at DK13 was 13.7% ± 3.2% and dead coral coverage was 34.5% ± 8.2% (Figure 10). Coraline algae coverage was 5.2% ± 2.2% with the other living bottom cover was predominately made up of \( Palthyoa \) spp. (zooanthids). Macro algae, soft coral, and Tridacna cover was less than 1%. Branching corals accounted for 68.2% of

![Figure 11](image1.png)

**Figure 11.** Standard day compilation of all \( G_{\text{net}} \) slack water values measured at DK13 during 11/20/2009–12/15/2009 (gray markers). The black line is the cubic spline fit to the \( G_{\text{net}} \) values calculated using the csaps.m Matlab function with a smoothing parameter of \( P = 0.99996 \). The vertical dashed black lines indicate the range of the sunrise and sunset times during 11/20/2009–12/15/2009 at One Tree Island.

![Figure 12](image2.png)

**Figure 12.** Standard day compilation of all \( P_{\text{net} (DO)} \) (black diamonds), \( P_{\text{net} (CT)} \) (gray triangles) and dissolved oxygen (\( DO \), open circles) slack water values measured at DK13 during 11/20/2009–12/15/2009. The \( DO \) values presented were measured at the end of each slack water period. The black lines are the cubic spline fits to the \( P_{\text{net} (DO)} \), \( P_{\text{net} (CT)} \) and \( DO \) values calculated using the csaps.m Matlab function with a smoothing parameter of \( P = 0.99996 \). The vertical dashed black lines indicate the range of the sunrise and sunset times during 11/20/2009–12/15/2009 at One Tree Island.
the hard coral cover and were a mix of Acropora spp. (18.1%), Pocillopora damicornis (25.3%), and branching Porites (24.8%). Massive corals were dominated by Porites spp.

4. Discussion

[30] According to Kinsey [1979], during 1967–1975 $P_g$, $R$ and $G_{net}$ at DK13 varied annually with high values during the summer and low values during the winter similar to observed variations in other Indo-Pacific reefs [Kinsey, 1985] and Red Sea reefs [Pichon, 1997; Silverman et al., 2006; Silverman et al., 2007a]. Therefore, it is appropriate to compare the measurements made in this study with corresponding seasonal values reported by Kinsey, i.e., the average values for the period November–January (summer).

[31] During 1967–1975, the seasonal average for the period November–January is $G_{net} = 133 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ [Kinsey, 1979], which is an average value of 19 daytime and 17 nighttime calcification rate measurements made at DK13. This value is nearly twice the value measured in our study $G_{net} = 74 \pm 24 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, which is an average of 33 daytime and 26 nighttime measurements. The difference between both values appears to stem primarily from the average nighttime calcification rate in this study $G_{net} = -7.5 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, which is three times greater than the value reported by Kinsey. It has been suggested that nearly 50% of this relatively high community rate of CaCO$_3$ dissolution at DK13 was caused by the activity of sea cucumbers that dissolve CaCO$_3$ in their guts as part of their digestive process [Schneider et al., 2011]. Additionally, it is reasonable to assume that decreased nighttime $\Omega_{arag}$ in the reef would result in increased inorganic dissolution rate. While it is noted that all calculated $\Omega_{arag}$ values for the water at DK13 during our study are substantially $>1$ it is very likely that chemical conditions for inorganic dissolution of CaCO$_3$, i.e., $\Omega_{arag} < 1$, exist within the reef framework and sediments. However, the case for a substantial component of inorganic dissolution of CaCO$_3$ in this study is not supported as the significantly lower $\Omega_{arag}$ values observed during the second half of the night compared to the first half of the night are associated with insignificantly higher rates of dissolution measured during the corresponding periods. This suggests that most of the observed dissolution at DK13 may be biologically mediated.

[32] The average daytime (sunrise to sunset) net calcification in this study is $275 \pm 178 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ ($n = 33$) or $11.4 \pm 7.4 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, which is 14% lower than the corresponding value from the 1967–1975 (13.3 $\pm 7.5 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, $n = 19$). Thus, both the daytime and diel average reductions in $G_{net}$ compared to the 1960–1970s are consistent with the predicted reduction in community calcification due to ocean acidification for this period [Silverman et al., 2009] as well as the observed reduction in coral growth records from the Great Barrier Reef over the past few decades [De’ath et al., 2009].

[33] The 1967–1975 $P_g$ value was estimated using measurements of dissolved oxygen only. Rates of oxygen consumption and production were converted to rates of carbon consumption and production due to respiration and photosynthesis using a respiratory quotient ($RQ = \Delta \text{CO}_2/\Delta \text{O}_2$) of 1.05 and a photosynthetic quotient ($PQ = \Delta \text{O}_2/\Delta \text{CO}_2$) of 1.11 [Kinsey, 1978b]. Both $RQ$ and $PQ$ values were determined by comparing a small number of measured changes in DO to their corresponding changes in $C_T$ (calculated from $pH$ and $A_T$ measurements) after removing the effect of net calcification (see equation 2). Thus, given that the reported $P_g$ was 750 mmol $\cdot$ m$^{-2} \cdot$ d$^{-1}$ [Kinsey, 1979] and taking into account the $PQ$ used by Kinsey we calculate a $P_g$ of 833 mmol $\text{O}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, which is significantly greater than
the current value of \( P_g = 678 \pm 14 \text{ mmol O}_2\text{m}^{-2}\text{d}^{-1} \).

However, if we use the standardized curve method developed by Kinsey [1978b], where the maximum diurnal hourly rate of gross production \( P_{\text{max}} \), which is equal to the maximum hourly rate of net production (in this study \( P_{\text{net-max}} = 48 \text{ mmol O}_2\text{m}^{-2}\text{h}^{-1} \)) plus the average hourly respiration rate measured during the nighttime (in this study \( r = 25 \text{ mmol O}_2\text{m}^{-2}\text{h}^{-1} \)), is multiplied by a factor of 11 used for this time of year then \( P_g = 803 \text{ mmol O}_2\text{m}^{-2}\text{d}^{-1} \) [Kinsey, 1978b]. This value is not significantly different from the one reported for November–January during 1967–1975. Nonetheless, it is evident that for the current study is smaller than the one measured during the 1960s–1970s (\( r = 27 \text{ mmol O}_2\text{m}^{-2}\text{h}^{-1} \)) and the \( P_{\text{net-max}} \) in this study is correspondingly higher than that reported for the 1960s–1970s study (\( P_{\text{net-max}} = 43 \text{ mmol O}_2\text{m}^{-2}\text{h}^{-1} \)). Calculating \( P_g \) using a standardized curve method, yields a \( P_g:R \) ratio of 1.34, which is significantly higher than the value reported by Kinsey (\( P_g:R = 1.14 \)), indicating the reef is much more autotrophic now relative to 1967–1975.

[34] As shown in the results, the gas transfer flux can account for up to 81% of the \( P_{\text{net(DO)}} \) Therefore, applying an inappropriate gas transfer coefficient may lead to significant error in estimates of \( P_{\text{net(DO)}} \), \( R \) and \( P_g \). In this study, we chose to use an updated equation for calculating the gas transfer coefficient in an open ocean setting. This equation is recommended in the CO2sys software and is based on results of an in situ experiment [Ho et al., 2006]. In this experiment changes in the ratios of \( SF_6 \) to \(^{3}He \) that were injected into the mixed layer, which was 60–80 m deep at the study site, were followed over time. At One Tree Island, Kinsey [1978b] showed the dependence of gas transfer on wind speed for shallow (1 m deep) and deeper (2–3 m deep) areas in the lagoon. Using a third-order polynomial fit to Kinsey’s data, the gas transfer coefficient for shallow water (\( \sim 1 \text{ m deep} \)) is expressed as \( K = 0.0837 \cdot u^3 - 0.6594 \cdot u^2 + 2.421 \cdot u + 15.583 \) \( (R^2 = 0.9987, n = 8) \), where \( u \) is the wind velocity in m/sec (height above sea surface was unspecified) and \( K \) has units of mmol \text{O}_2\text{m}^{-2}\text{h}^{-1} \). The units used for \( K \) are the same as the flux units because Kinsey used the % difference from saturation to calculate the rate of \( O_2 \) transfer between the sea and the atmosphere. Note that according to Kinsey’s observations, in contrast to the formulations of Wanninkhof [1992] and Ho et al. [2006], the gas transfer coefficient at 0 wind speed is not 0.

[35] Comparison of \( P_{\text{net(DO)}} \) curves calculated using the formulations of Kinsey, Wanninkhof and Ho et al. (Figure 14) show that these estimates are strongly affected by the choice of gas transfer coefficient. Therefore, we conclude that estimates of \( P_{\text{net}} \) using measurements of DO in situations where it is likely that the gas transfer flux is large should be treated carefully due to the large degree of uncertainty associated with them. For the sake of comparison to the rates reported by Kinsey [1979], we recalculate the oxygen fluxes associated with photosynthesis and respiration using Kinsey’s gas transfer coefficient and the standard curve method. Thus, \( P_{\text{net(DO)}} = 12 \text{ mmol O}_2\text{m}^{-2}\text{d}^{-1} \), \( P_{\text{net-max}} = 54 \text{ mmol O}_2\text{m}^{-2}\text{h}^{-1} \), \( r = 29 \text{ mmol O}_2\text{m}^{-2}\text{h}^{-1} \), \( P_g = 914 \text{ mmol O}_2\text{m}^{-2}\text{d}^{-1} \) and \( P_g:R = 1.30 \).

[36] Unlike our estimate of \( P_g \) using DO measurements, the \( P_g \) estimated from \( C_T \) measurements in this study is somewhat similar (788 ± 6 mmol \text{C}\text{m}^{-2}\text{d}^{-1} \) to that reported by Kinsey [1979], although his measurements were based on DO. However, \( r \) in this study (32 mmol \text{C}\text{m}^{-2}\text{d}^{-1} \) is nearly 20% greater than that reported by Kinsey and the daytime \( P_{\text{net-max}} \) (45 mmol \text{C}\text{m}^{-2}\text{d}^{-1} \) is ca. 15% greater than the corresponding value. Therefore, assuming that the standard curve method is applicable, \( P_g \) is 847 mmol \text{C}\text{m}^{-2}\text{d}^{-1} \) and \( P_g:R = 1.10 \). The application of the standard curve, which was developed for DO measurements, is questionable and the use of \( C_T \) measurements for calculating productivity is more appropriate. A comparison
of $P_{\text{net(DO)}}$ values (calculated using Kinsey’s gas transfer coefficient) to their corresponding $P_{\text{net(CT)}}$ values (Figure 15) shows that they are well correlated ($R^2 = 0.92$) with a slope of $-1.02$. After removing obvious outliers, which are found in the transition from day to night and night to day where rates are relatively small (Figure 12), the average $P_{\text{g(DO)}}$/$P_{\text{g(CT)}}$ ($PQ$), is $0.95 \pm 0.26$ ($\pm$1SD, Min = 0.45, Max = 1.58). The average value is somewhat smaller than the value used by Kinsey in his estimates of $P_g$. Interestingly, from $\sim$11:00 until $\sim$14:00 $P_{\text{net(CT)}}$ remains constant at $\sim$1000 mmol C m$^{-2}$ d$^{-1}$ (net uptake of carbon) while $P_{\text{net(DO)}}$ decreases from $\sim$1300 mmol O$_2$ m$^{-2}$ d$^{-1}$ to $\sim$740 mmol O$_2$ m$^{-2}$ d$^{-1}$ (net production of oxygen) indicating that $PQ$ has decreased from 0.9 to 0.6 (Figure 12). This decrease in $PQ$ coincided with the relatively high and constant levels of DO = 340–360 $\mu$mol/L measured near the end of the slack water period (Figure 12) suggesting that the gas transfer flux may still be underestimated. During the nighttime the average $RQ = -(\Delta CO_2/\Delta t)/(\Delta DO/\Delta t) = -(P_{\text{net(CT)}}/P_{\text{net(DO)}})$ is $1.3 \pm 0.4$ ($\pm$1SD) with a minimum value of 0.7 and maximum value of 2.1. This average value is somewhat larger than the value used by Kinsey in 1967–1975. Correlation analysis of the $RQ$ values versus time yields a positive trend from sunset to sunrise ($p < 0.05$) and versus oxygen levels measured at the end of the slack water period yields a negative trend ($p < 0.05$). Again, as in the observed variation in $PQ$, this analysis suggests that the gas transfer flux may also be underestimated for exceptionally low levels of DO (50–60 $\mu$mol/L).

[37] Using the same method to compile a standard day for the $J_{\text{net-TON}}$ and $J_{\text{net-NH3}}$ values (Figure 13) yields a coherent diurnal cycle for $J_{\text{net-TON}}$ while $J_{\text{net-NH3}}$ varies greatly at low positive levels, i.e., during daytime where net production was positive, relative to $J_{\text{net-TON}}$ values. This behavior of $J_{\text{net-NH3}}$ suggests that the production of NH$_3$-tot is likely kept low by uptake in primary production during the daytime and bacterially mediated nitrification during the day and night. Daytime nitrification is supported by the relatively high production rate of TON and at relatively high levels (Figure 8) considering that NH$_3$-tot is the preferable form of dissolved nitrogen for primary producers [e.g., Fong and Paul, 2011].

[38] During the nighttime the low to negative (consumption) values of $J_{\text{net-TON}}$ that coincide with low levels of DO suggest that at least part of the nitrate uptake is due to anaerobic respiration (de-nitrification), which is an additional source of $C_T$ and may be a contributing factor to the relatively high $RQ$. Considering that daytime nitrate production peaks at 15:00 ($J_{\text{net(TON)}} = 16.6 \pm 1.92$ mmol NO$_3$-m$^{-2}$ d$^{-1}$, Figure 13) when DO peaks as well at 363 $\mu$mol/L (Figure 6), and adjusting $P_{\text{g(DO)}}$ and $P_{\text{g(CT)}}$ at this time for O$_2$ uptake ($3 \cdot J_{\text{net(TON)}}$) and CO$_2$ uptake ($2 \cdot J_{\text{net(TON)}}$), which are at the time of peak $J_{\text{net(TON)}} \sim 1300$ mmol O$_2$ m$^{-2}$ d$^{-1}$ and is $\sim$1550 mmol C m$^{-2}$ d$^{-1}$, respectively, then $PQ = 0.9$. This value is only slightly higher than calculated without adjusting for nitrification. $PQ = 0.84$. From these measurements it is difficult to say what the gross rates of nitrification during the daytime and denitrification during the night actually are and therefore it is difficult to determine what their total effect on $PQ$ and $RQ$ is. However, using the same method for estimating the contribution of sea cucumber activity to the community level dissolution rate of CaCO$_3$ [Schneider et al., 2011] it is estimated that sea cumbers are responsible for producing ca. 30 mmol NH$_3$-tot m$^{-2}$ d$^{-1}$. This rate is substantially higher than the maximum measured $J_{\text{net-NH3}} = 12.3$ mmol NH$_3$-tot m$^{-2}$ d$^{-1}$ and is nearly twice the combined maximum $J_{\text{net(TON)}} + J_{\text{net-NH3}}$, which occurred during the daytime. Considering that the measurements of NH$_3$-tot production by sea cumbers were conducted during the daytime when these nocturnal feeders are less active it is likely that the rates of nitrification/de-nitrification processes are much higher during the night. Regardless of the rate it is clear that the reef is a net exporter of dissolved inorganic nitrogen to the adjacent open water even though the reef is autotrophic according to the DO measurements. This is somewhat
peculiar given that autotrophic reefs are supposed to be a sink for dissolved inorganic nutrients from the adjacent open water [Erez, 1990] as seen in Silverman et al. [2007a]. Additionally, the sum of spline curves of $J_{\text{net(TON)}}$ and $J_{\text{net(NH3)}}$ (Figure 13) yields a diel curve with a peak constant level of production between 15:00 and 20:00 at an average rate of $15.5 \pm 0.9 \text{ mmol C m}^{-2} \text{d}^{-1}$. In Figure 14, $P_{\text{net(C)}}$ starts to increase dramatically from $\sim 1000 \text{ mmol C m}^{-2} \text{d}^{-1}$ ca. 15:00 to a maximum value of $+1000 \text{ mmol C m}^{-2} \text{d}^{-1}$ at ca. 20:00. $P_{\text{net(DO)}}$ starts declining much earlier relative to $P_{\text{net(C)}}$ at around 11:00 as described above, but attains a minimum negative net production rate of $-970 \text{ mmol O}_2 \text{m}^{-2} \text{d}^{-1}$ at ca. 19:00. This behavior suggests daytime respiration is much higher than previously considered and at least as high as the maximum value attained at the beginning of the night. Individual coral in situ incubations also suggested that respiration has a strong control on diel net primary production [Schneider et al., 2009]. As a result the use of the average nighttime $P_{\text{net}}$ or $R$ according to Marsh and Smith [1978] may be leading to a gross underestimate of $P_{\text{R}}$. Using the maximum value of $P_{\text{net(C)}} = 1046 \text{ mmol C m}^{-2} \text{d}^{-1}$ (from the spline curve) as the daytime respiration value yields a $P_{\text{R}}$ of $1623 \text{ mmol C m}^{-2} \text{d}^{-1}$, which is slightly more than twice our previous estimate. The resulting $P_{\text{R}}:R$ taking into account the daytime respiration and average nighttime respiration from the spline curve of $P_{\text{net(C)}}$ is 1.75. This result clearly indicates that the reef at DK13 is substantially autotrophic.

[39] The diel curve of $P_{\text{net(DO)}}$ appearing in Kinsey [1978b] does not display a similar behavior to diel curve in this study and the nighttime rates are constant with no variation at the beginning of the night. However, the diel cycle of $P_{\text{net(DO)}}$ measured during March 1980 (late summer) on a coral reef in the Houtman Abrolhos Islands, Western Australia show a substantial increase in respiration just after sunrise and sunset relative to the average nighttime rate [Smith, 1981]. These features were not apparent in the smoothed curve going through the measurements and the nighttime part of the curve is kept constant. Similar behaviors were also observed in two Red Sea reefs (J. Silverman, unpublished data).

[40] During the 1960s–1970s the benthic community structure of the back reef zone of the One Tree Island atoll, where DK13 is situated, was described a number of times [Kinsey, 1972, 1978b, 1979]. According to Kinsey [1978b] the coral coverage in the vicinity of DK13 was 40%. Considering that most of the corals in the back reef zone at DK13 are found on pie crust formations, which covered 35% of the back reef area on average [Kinsey, 1979], it is possible to get a reasonable estimate of the live coral cover for the entire back reef zone area (0.4 · 35% = 14%), which is similar to the value we measured. Therefore, in accordance with Anthony et al. [2011] and Kleypas et al. [2011], the apparent significant changes in reef metabolism must result from other forcing factors.

[41] In summary, the live coral coverage during the 1960s–1970s seems to have been not much different than it is in the current study. The average $G_{\text{net}}$ at DK13 in our study is nearly half the rate measured in the same season during the 1960s–1970s. This reduction appears to stem primarily from the threefold increase in nighttime dissolution of CaCO$_3$, while the daytime calcification rate decreased from 320 mmol C m$^{-2}$d$^{-1}$ during the 1960s–1970s to 275 ± 25 mmol C m$^{-2}$d$^{-1}$. Increased dissolution rates may have resulted from increased bioerosion due to changes in the biota (e.g., sea cucumbers, boring organisms), which may be associated with the significant shift in the trophic balance of the reef toward autotrophy [Glynn, 1997]. The greater dissolution may have also resulted from changing abiotic conditions over the last 40 years associated with global warming and ocean acidification [Tribollet et al., 2009]. Either way, the reduction in diel average and average daytime $G_{\text{net}}$ is consistent with predicted decline in community calcification and observed declining trends in coral growth records from the Great Barrier Reef over the past few decades [De'ath et al., 2009]. Finally, it has been shown that estimates of productivity and respiration based on DO at DK13 do not agree with the rates derived from measurements of dissolved inorganic carbon. Therefore, it is suggested that future studies of photosynthesis and respiration on coral reefs should not rely solely on dissolved oxygen measurements as a proxy for carbon turnover.

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References


Silverman ET AL.: CARBON TURNOVER RATES AT ONE TREE REEF


