Mar Biol (2013) 160:2437–2447
DOI 10.1007/s00227-013-2239-z

ORIGINAL PAPER

Coupled changes in oxygen concentration and pH caused by metabolism of benthic coral reef organisms

Jennifer E. Smith · Nichole N. Price · Craig E. Nelson · Andreas F. Haas

Received: 28 December 2012 / Accepted: 9 April 2013 / Published online: 25 April 2013

Abstract Benthic marine primary producers affect the chemistry of their surrounding environment through metabolic processes. Photosynthesis and respiration will elevate or depress the concentration of oxygen in the diffusive boundary layer. Likewise, acid–base regulation and biomineralization/dissolution for calcifying species can alter the relative concentration of inorganic carbon species and thus pH. Here, we measured the relative ability of several common benthic primary producers from coral reef systems of the central Pacific and the Caribbean to simultaneously affect seawater oxygen concentration and pH values. Repeated measurements over a diel cycle confirmed that several primary producers substantially alter surrounding seawater chemistry over time. The majority of fleshy algae exhibited a stoichiometric ratio of oxygen to hydrogen ions not significantly different from one during daylight hours. In contrast, calcifiers exhibited significantly lower oxygen to hydrogen ion ratios that were unique for each species and were inversely correlated with known rates of calcification. These data provide the first quantitative estimates of the simultaneous influence of several species of benthic primary producers on water column oxygen concentrations and pH across different tropical reef systems. Finally, because more productive fleshy taxa have the potential to raise both oxygen and pH during the day to a greater extent than calcified species, our results suggest that some fleshy taxa may provide a buffering capacity to future ocean acidification scenarios.

Communicated by R. Hill.

Electronic supplementary material The online version of this article (doi:10.1007/s00227-013-2239-z) contains supplementary material, which is available to authorized users.

J. E. Smith (✉) · N. N. Price · A. F. Haas
Scripps Institution of Oceanography, University of California, San Diego, CA 92093, USA
e-mail: smithj@ucsd.edu

C. E. Nelson
Marine Science Institute, University of California, Santa Barbara, CA 93106, USA

Introduction

Coral reefs are subjected to local anthropogenic stressors [e.g. overfishing, sedimentation; (Nyström et al. 2000; Bellwood et al. 2004)] as well as global warming and seawater acidification due to excessive CO_2 emissions that threaten marine ecosystems (Hughes et al. 2003; Bruno and Selig 2007; Hoegh-Guldberg et al. 2007). Recently, many studies have focused on the effects of changing pH or CO_2 concentrations on different, primarily calcifying, organisms in highly controlled mesocosm studies and have shown variable but negative results (Hendriks et al. 2010; Kroeker et al. 2010). However, information on the reciprocal effects (i.e. influence of benthic species on CO_2 or pH) is sparse (but see Hurd et al. 2011), despite the potential for these effects to be ecologically relevant due to variable rates of metabolic CO_2 uptake or release by a variety of organisms (Lindahl 1963; Axelsson 1988; Anthony et al. 2011).

Net community metabolism (NCM), or carbon and oxygen biogeochemical cycling, on a coral reef is a combination of net community calcification and net photosynthesis. The corals and algae dominating the benthos of these complex ecosystems have the potential to change the chemistry of the water column, despite global oceanographic and atmospheric influences (Kleypas et al. 2011). Metabolic processes can deplete or replenish oxygen, carbon, and nutrient concentrations either within hydrodynamic boundary layers

over time (Shashar et al. 1993; Zeebe et al. 1999; Anthony et al. 2011; Shamberger et al. 2011) or in larger water masses as they move across a given reef (Barnes 1983; Barnes and Lazar 1993; Frankignoulle et al. 1996; Gattuso et al. 1996a; Niggel et al. 2010; Wild et al. 2010). Understanding the degree to which benthic assemblages can alter local environmental chemical conditions of the seawater will allow us to better predict how climate change and ocean acidification will impact these important ecosystems in the future.

Historically, researchers have used discrete water sampling to estimate calcification and productivity rates of reef communities (Johannes et al. 1972; Barnes 1983; Barnes and Devereux 1984). Depletion in total alkalinity and total dissolved inorganic carbon from these samples over time (Eulerian method) or across space (Langrangian drift surveys) indicates the relative balance of productivity and calcification (e.g. Shamberger et al. 2011). Spatial variability in rates of NCM has been used to describe relative 'health' of a reef (net calcifying or autotrophic) or whether a reef is a sink or source of CO_2 (a by-product of calcification and released during respiration, but consumed during photosynthesis). Rarely do these studies report basic ecological descriptors of the benthic community (i.e. species relative or absolute abundances or distributions). However, the degree to which a benthic coral reef community affects the surrounding seawater chemistry will be determined by the intrinsic metabolic rates of community members, their relative abundance (or biomass), and the oceanographic conditions and circulation patterns over the reef (see Anthony et al. 2011). Thus, the 'health' of a reef and the local biogeochemical environment (e.g. pH and oxygen content of the water column) may depend on the daily or seasonal balance of productivity and calcification rates of the dominant members of the benthic community assemblage (Bates et al. 2009).

Primary producers affect the availability of dissolved inorganic carbon (CO_2 or bicarbonate) and oxygen in the surrounding water through their photosynthetic and respiratory metabolism (Roffman 1968; Marsh 1970; McCloskey and Muscatine 1984; Jokiel and Morrissey 1986; Ohde and van Woesik 1999). The fixation of inorganic carbon during photosynthesis, or release during respiration, indirectly affects the pH of the surrounding water (Murru and Sandgren 2004). The uptake of CO_2 during photosynthesis consequently results in a reduction of hydronium ions (H^+; Lucas 1983; Cook et al. 1988; Israel and Beer 1992; Raven 1997), thereby increasing pH values (i.e. the negative logarithm of hydronium ions) in the water surrounding primary producers (Allen and Spence 1981; Maberly and Spence 1983; Prins and Elzenga 1989). During respiration, CO_2 is released and pH values concurrently decline. Oxygen is released in the water column as a result of photosynthesis during the day, but consumed at night via respiration. The rate at which oxygen, inorganic carbon, and H^+ concentrations change in an enclosed body of water is therefore dependent upon photosynthetic activity (and biomass) of participant species.

Photosynthetic rates can further be influenced by a number of other physical and biological factors. Next to the availability of photosynthetically active radiation (PAR), which is likely the dominant external parameter controlling photosynthetic performance and therefore NCM, other variables such as temperature, salinity, nutrient availability, and/or flow regimes can affect photosynthetic performance of aquatic primary producers (Coles and Jokiel 1977; Dennison and Barnes 1988). While the effects of many of these factors on photophysiology are variable and species specific, increased flow regimes (to a point) have been shown to enhance photosynthetic rates by reducing boundary layer thickness and thus enhancing uptake of carbon and nutrients. More recent studies have shown that increased flow can increase the ability for photosynthetic carbon fixation owing to a flow-driven enhancement of oxygen efflux from the organism to the surrounding water body thereby increasing the affinity of RuBisCO to CO_2 (Mass et al. 2010).

Calcification processes, in addition to photosynthesis and respiration, change the biogeochemistry in the surrounding waters (Ohde and van Woesik 1999). Although dissolved inorganic carbon is used by organisms to deposit $CaCO_3$ during calcification, CO_2 and H^+ ions are released as by-products (Jokiel 2011), thereby decreasing the pH values in the water column. Thus, the ability of photosynthetic carbon fixation by primary producers to raise pH values can be tempered by simultaneously occurring calcification processes, either within a coral holobiont (Gattuso et al. 1999a), calcifying macroalgae or numerous other invertebrates present in a given reef community (Gattuso et al. 1999b; Anthony et al. 2011). The energetic costs associated with maintaining internal aragonite saturation state favorable for calcification may exacerbate oxygen depletion due to elevated daytime respiration.

It is difficult to predict how organisms that simultaneously calcify and photosynthesize (e.g. coral holobionts, calcifying algae) will affect water column chemistry (Muller et al. 2009; Edmunds et al. 2011). From a limited number of studies, hermatypic corals tend to drive down pH and oxygen availability in mesocosms, despite photosynthetic activity from the intercellular symbiotic dinoflagellates (Gattuso et al. 1999a), while benthic calcifying macroalgae raise pH and oxygen concentrations during the daytime (Borowitzka and Larkum 1976). During the night, when respiration predominates, both corals and fleshy macrophytes reduce oxygen concentrations and pH (Anthony et al. 2011), but the magnitude of change is

species specific and unknown for most reef species. The effects of metabolic rates of calcifying and fleshy algae and corals on seawater chemistry in mesocosms are rarely compared within the same study. Thus, there is a lack of knowledge of the relative contribution of some of the most important calcifiers and reef builders (many species of coral, coralline algae and *Halimeda*) to NCM and biogeochemistry of coral reefs.

Conversely, the relationship between oxygen production/consumption and hydrogen ion evolution is fairly predictable for non-calcifying photoautotrophs due to the C:O Redfield ratio (Anderson and Sarmiento 1994). Equal mole fractions of CO_2 and O_2 are exchanged during photosynthesis, and assuming that the resultant change in alkalinity is negligible, pH also changes equivalently. But how predictably does this relationship between oxygen and pH change for photoautotrophic calcifiers? The goal of this study was to compare species-specific rates of change in pH and oxygen concentrations over a diel cycle for several species of common benthic coral reef organisms including corals, turf algae, and fleshy and calcifying macroalgae. We conducted similar studies in the Caribbean and Pacific to assess the generality of the results across divergent reefs.

Materials and methods

Study sites

From 9 to 13 September 2010, consecutive experiments were conducted at the Richard B. Gump South Pacific Research Station located on the north shore of Moorea (17°30′S:149°50′W). Research at this location was performed under annual research permits issued by the French Polynesian Ministry of Research to the Moorea Coral Reef Long-Term Ecological Research program (MCR-LTER). Moorea, a high island in French Polynesia is surrounded by both fringing and barrier reefs separated by an expansive shallow (2–5 m depth, 1,300 wide) lagoon (Galzin and Pointier 1985) with current velocities of 0.05–0.20 m s^{-1} (Hench et al. 2008). The second set of consecutive experiments was conducted from 4 to 8 May 2011 at the Caribbean Research and Management of Biodiversity (CARMABI) station on Curaçao (12°07′N:68°58′W). Research on Curacao was conducted in collaboration with the Carmabi Foundation which holds permission by the Curacaoan government to conduct scientific experiments on its coral reefs and collect specimens where necessary. Curaçao is an island situated in the southern Caribbean about 80 km off the coast of Venezuela. Leeward southwest reefs are characterized by a shallow terrace (50–100 m wide) that averages ~3 m depth before reaching the reef slope at 8–12 m. Water current velocities in this system range from 0.01 to 0.40 m s^{-1} (van Duyl et al. 2006).

Sample collection

Replicates of common reef species of coral and macroalgae were collected from the back- and fringing reefs of Moorea and on the shallow terrace of Curaçao on snorkel or using SCUBA at 1–3 m depth. Individual live specimens of comparable surface areas (average surface area of the samples was 219 ± 24 and 183 ± 35 cm^2, for Moorea and Curaçao, respectively) were collected from the benthos and stored in Ziploc bags submerged in ambient seawater in 5 gallon buckets for immediate transport to cultivation tanks at the respective study sites (<30 min boat ride). In Moorea, a hermatypic coral (*Porites lobata*), three non-calcifying algae (the brown alga *Turbinaria ornata*, the red alga *Amansia rhodantha*, and a typical mixed consortium of turf algae), and two calcifying macroalgae (the green alga *Halimeda opuntia* and the red crustose coralline alga (CCA) *Hydrolithon* sp.) were collected from water depths of 1.0–1.5 m at back- and fringing-reef locations. In Curaçao, the hermatypic coral *Madracis mirabilis*, four non-calcifying algae (the green algae *Ulva lactuca* and *Caulerpa serrulata*, the brown alga *Dictyota cervicornis*, and a typical mixed consortium of turf algae), and one calcifying macroalga (the green alga *Halimeda tuna*) were all collected from the fringing reef. The complete thallus and holdfast or rhizoids were collected for fleshy algal samples and *Halimeda*. For corals, CCA, and turf algae free-living colonies, rhodoliths or pieces of reef rubble colonized by turf algae of comparable surface area were collected, respectively. Studies were not conducted on privately owned or protected locations and did not include endangered species.

Experimental design

Each sample was placed in an independent respiration chamber (1 L beaker) containing freshly collected seawater ($n = 5$); control incubations ($n = 5$) contained seawater alone. The volume of the biological sample was always <5 % of volume of the incubation water. At the start of each experimental day (08:00), initial oxygen concentrations and pH values were measured using a Hach Lange HQ40 multiparameter handheld meter (oxygen: precision 0.01 mg l^{-1}, accuracy ±0.05 %; pH_{NBS}: precision 0.001, calibrated with Tris buffer; pH 8.001); multiple readings were taken per replicate to ensure consistency for 2–5 min. Chambers were then sealed airtight with no headspace using low-density polyethylene film (Saran^{TM}) bound with rubber bands. Both study sites exhibit varying, but predominately low water velocity regimes. Water velocities will also decrease significantly in the vicinity of benthic

organisms as result of different boundary layers over the benthos (i.e. the diffusive- and momentum boundary layer, 1–2 mm or 5–10 cm, respectively, above the organisms, with undetectable water movement up to ~0.5 m above the reef, see [see Shashar et al. 1996)]. In order to provide the most conservative physiological estimates of how benthic primary producers may affect the surrounding water chemistry, our experiments were intentionally conducted in closed, non-mixed incubation chambers. This also allows for comparability with previous incubation studies (e.g. Haas et al. 2011) and ensures higher measurement accuracy, as water movement may cause noticeable and variable, effects on gas transfer velocities across the surface boundary of the incubation chambers (Murphy and Gardner 1975; Wu et al. 1997). As in other similar studies, the water was gently swirled with the handheld sensors and measurements of oxygen concentrations and pH were made once values stabilized (usually after ~10–30 s). While flow is certainly known to affect rates of photosynthesis and respiration, our goals were to compare the relationship between oxygen release and pH changes among taxa under controlled conditions, not the absolute metabolic rates or impacts on the water column, as flow will on one hand increase metabolic rates, but on the other will dilute the effects on oxygen concentrations and pH on the surrounding seawater chemistry. Thus, the lack of constant flow in these incubations may not represent realistic conditions experienced in the field and should be interpreted accordingly.

Chambers were kept outside in a flow-through water bath to ensure in situ temperature conditions and natural light conditions over the entire daylight cycle. Repeated oxygen and pH readings were taken hourly (during daylight hours) by carefully threading sensor tips through the tightened lids and gently stirring the enclosed water body before every reading, to ensure a homogeneous distribution of analytes in the sample chambers; readings were recorded once values of oxygen concentrations and/or pH stabilized in each chamber. Final daylight readings were taken just before sunset (18:00) to determine the daily net oxygen production and change in pH for each beaker. Incubations were then left for ~12 h in the dark, and final oxygen and pH measurements were taken the next morning (08:00) to complete the diurnal cycle. Diel patterns in oxygen consumption/evolution and in pH increases/decreases were quantified for each species by calculating the average difference from initial to sunset readings for daylight periods and the difference from sunset to final readings for nighttime incubation periods, respectively. We standardized the changes in oxygen concentrations and pH to an hourly rate, and average net fluxes of oxygen or change in pH for each species were calculated by summing the average daytime and nighttime rates for each sample. Rates were also standardized to the surface area for each of the individual species (see below).

To simultaneously monitor in situ and experimental light (lux) and temperature (°C) conditions, these parameters were measured and recorded at 5-min intervals for the duration of the respective study periods both at the sites of specimen collection and in the incubation chambers using Onset HOBO® Pendant UA-002-64 light and temperature loggers. Light intensities, measured in lux, were then converted to availability of photosynthetically active radiation (PAR) using the following conversion: 1 µmol quanta (400–700 nm) m^{-2} s^{-1} = 51.2 lux (Valiela 1984). These conversions were validated by additional in situ PAR measurements made at the collection site on Moorea, using the light sensor on a WALZ diving-PAM underwater fluorometer (Fig. S3).

Surface area normalization

Surface area was chosen for standardization because of its functional importance as a metabolic interface for light and nutrient absorption. Surface area normalized rates of oxygen concentration and pH changes were calculated by first subtracting changes of the respective controls and then by dividing resultant rates by the surface area of the organism incubated in the respective replicate beaker. For *Porites*, *Madracis*, turf algae and CCA, the surface area was measured directly (Naumann et al. 2009); for turf algae, the surface area of individual algal taxa was not measured but the substratum on which the consortium was growing. Surface area of the remaining specimens was estimated by measuring the dry weight and then applying conversion factors derived from the slopes of linear regression of plant surface area versus plant biomass measurements conducted by Russo (1990) and Haas and Wild (2010).

Statistical analysis

Hourly rates of change in oxygen concentration and pH were calculated by dividing the measured changes in seawater chemistry for each respiration chamber by the incubation duration. For subsequent statistical analyses, all rates were log-transformed to approximate a Gaussian distribution. Relative changes in organism incubations as compared to seawater controls were examined using ANOVA followed by Dunnet's post hoc test. We subtracted changes in control chambers from experimental chambers and then normalized changes to the surface area of each organism in each chamber to derive area-specific rates of change for oxygen and pH. We compared control-corrected and area-normalized rates of change among treatments on each island using ANOVA followed by Tukey's *post hoc* tests at $\alpha = 0.05$.

Molar ratios of oxygen and pH were examined by building log-linear regressions between the two parameters over the course of daylight incubations, with oxygen change as the independent and pH change as the dependent variable. We calculated the significance of each regression and derived estimates and 95 % confidence intervals for the slope of each line from pooled daily measurements from replicated chambers ($n = 5$) and hourly samples ($3 < n < 9$) for each species on each island. Regressions were deemed non-significant if $p > 0.05$ and treatment slopes were deemed not significantly different from each other or target values (1 or 0) if 95 % confidence intervals overlapped the target.

Results

Experimental and field conditions

Sites of sample collection in both Curaçao and Moorea had comparable light and temperature regimes. At Moorea, average backreef in situ daytime (09:00–17:00 h) PAR at ~1 m water depth was 580.6 ± 6.4 μmol quanta m^{-2} s^{-1} over the entire study period. Average in situ daytime PAR at sampling sites in Curaçao was 703.1 ± 43.8 μmol quanta m^{-2} s^{-1}. Average backreef water temperature was 26.06 °C with diurnal fluctuations of 2.51 ± 0.40 °C in Moorea and 28.7 °C with diurnal fluctuations of 2.35 ± 0.12 °C in Curaçao.

Light and temperature regimes in the incubation chambers were representative of in situ conditions on either reef and were similar at each research station. Light loggers deployed in incubation chambers recorded an average PAR of 622.1 ± 8.0 and 732.0 ± 35.0 μmol quanta m^{-2} s^{-1} during daylight hours on Moorea and Curaçao, respectively. Corresponding water temperatures in incubation chambers were 26.46 °C with diurnal fluctuations of 3.21 ± 0.51 °C and 29.28 °C with diurnal fluctuations of 1.74 ± 0.12 °C (Fig S1) on Moorea and Curaçao, respectively.

Changes in oxygen and pH during light and dark incubations

The magnitude of change in dissolved oxygen and pH depended on taxon and the direction of change (+/−) depended on time of day. Relative to the seawater controls, oxygen and pH changes in organismal incubations were significantly greater in both the light and dark (Dunnet's $p < 0.003$) with one exception: the pH increase in the coral *M. mirabilis* in the light did not differ significantly from the control (Dunnet's $p = 0.145$). Mean oxygen concentrations declined in dark incubations (ranging from −32.7 to −17.3 μmol L^{-1} h^{-1} for organisms and averaging −0.82 μmol L^{-1} h^{-1} for controls) and increased significantly in light incubations (ranging from 10.2 to 114.1 μmol L^{-1} h^{-1} for organisms and 1.23 μmol L^{-1} h^{-1} for controls). Over all, oxygen concentrations varied from a minimum of 83 % to a maximum of 243 % of oxygen saturation. In light incubations, mean pH generally increased (ranging from 0.024 to 0.12 h^{-1} for algae and averaging <0.01 h^{-1} for corals and controls), but decreased in incubations containing the calcified alga *H. tuna* (−0.019 h^{-1}). In dark incubations, mean pH decreased for all taxa (ranging from −0.011 to −0.060 h^{-1} for corals and algae and averaging −0.001 h^{-1} for controls).

We used ANOVA with Tukey's post hoc tests to assess significant differences ($\alpha = 0.05$) in control-corrected surface area standardized dark and light oxygen and pH change among organisms and functional groups both within and among islands. When normalized, the diel patterns of change in oxygen and pH remained taxon specific (Fig. 1). Turf algae had the highest oxygen release rate during daylight hours in both systems (Fig. 1a) and together with *Porites* the highest oxygen consumption rates during the night (Fig. 1c). Turf algae caused the greatest increase in pH values during daylight incubations on both Moorea and Curaçao (Fig. 1b). During the night, *P. lobata* caused the greatest decrease in pH relative to other taxa (Fig. 1d).

Net diel changes in oxygen and pH

Daytime and nighttime surface area normalized metabolic activities were summed to create a cumulative effect for each taxon on the chemistry of the seawater in the respiration chambers. Only for turf algae on Curaçao did productivity and respiration create a zero sum change in oxygen concentrations in the chambers (Fig. 1e). All other algae, whether calcified or not, significantly increased oxygen content of the chamber over the course of the assay. The magnitude of increase in oxygen over the diurnal cycle was not significantly different across various algal species within an island. Neither coral species evolved enough oxygen via photosynthesis during the daytime to counter balance nighttime respiration, creating a net loss of oxygen in the chambers (Fig. 1e).

The direction of the cumulative change in pH over the course of the 24 h assay was positive (or no net change for turf on Curaçao) for all non-calcified algae, although the magnitude of the effect was different across species on each island (Fig. 1f). Turf algae on Moorea raised pH to the greatest degree from an initial 8.18 ± 0.003 pH units to 8.78 ± 0.065 pH units 24 h later. Calcifying algae on Moorea had no net effect on pH, but *H. tuna* on Curaçao significantly reduced pH over 24 h. On both islands, the

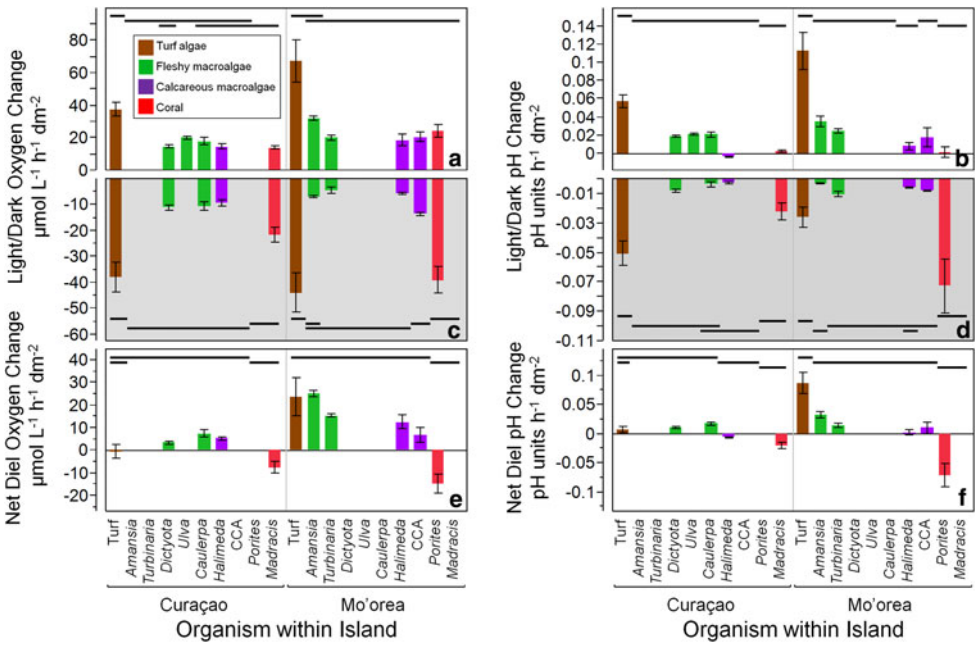

Fig. 1 Surface area normalized mean rates of change in dissolved oxygen (**a**, **c**, **e**) and pH (**b**, **d**, **f**) caused by metabolism of common benthic organisms from Curaçao and Moorea. *Top panels* (**a**, **b**) are mean daytime change, *middle panels* (**c**, **d**) are mean nighttime change, and *bottom panels* (**e**, **f**) are mean net diel change ($n = 5$–9). *Bars* are colored according to functional group; *error bars* correspond to one standard error above and below the mean. *Lines* across each graph connect organisms with rates which do not differ significantly within each reef system (Tukey's post hoc test $\alpha = 0.05$)

corals caused the most precipitous cumulative drop in pH by 0.16 ± 0.03 pH units.

Relationship between oxygen and pH during light incubations

Relative changes in oxygen concentrations and pH during the daytime within a chamber were also species specific, but were generally positive (increasing over time) on both islands (Fig. 2). Seawater controls exhibited no significant relationship between oxygen and pH over the course of the incubations ($p > 0.48$, $R^2 < 0.01$). We found strongly significant positive relationships between oxygen concentrations and pH (Table S1) in all of the fleshy algae studied, with coefficients of determination (R^2) ranging from 0.91 to 0.99. For all but two non-calcifying algae, molar ratios of pH:oxygen change did not differ significantly from one (Fig. 2c, d). Slopes for the non-calcifying algae *C. serrulata* and turf algae on Curacao were significantly <1 (0.74 and 0.77, respectively).

Among calcifying organisms, we found considerably more variation in molar ratios of oxygen and pH. On Moorea, the coral *P. lobata* and CCA showed highly significant positive relationships between oxygen and pH (Table S1) with slope estimates much <1 (0.35 and 0.58, respectively). *H. tuna*, a calcifying green alga, exhibited a significant negative relationship on Curaçao (slope estimate −0.27 with confidence range of −0.14 to −0.40), but *H. opuntia* had a weakly positive relationship on Moorea (slope estimate 0.11 with confidence range of 0.01–0.21; Fig. 2). The coral *M. mirabilis* showed no significant relationship between oxygen and pH (Fig. 2).

Discussion

The goals of this study were to examine how different coral reef primary producers affect surrounding seawater chemistry as a result of metabolic processes. Specifically, we were interested in determining if consistent relationships exist between metabolically driven changes in oxygen and pH for a variety of calcifying and non-calcifying taxa from the Caribbean and Pacific oceans. Historically, organismal productivity and respiration rates have been examined to quantify metabolic physiological processes, but not in the context of how these rates may affect seawater chemistry (Littler and Littler 1980; Gates and Edmunds 1999; Anthony et al. 2008). More recent work has focused on the influence of coral reef benthic primary producers on organic carbon dynamics (Naumann et al. 2010; Wild et al. 2010; Haas et al. 2011), but the effects of macroalgae on ambient inorganic carbon concentrations and concomitant pH values have rarely been studied in an ecological context (Smith 1973; Gattuso et al. 1997; but see Hurd et al. 2011 for coral examples). Our study shows for the first time that several primary producers cause species-specific ratios of oxygen and pH change in seawater associated with metabolism across different tropical reef systems regardless of the absolute magnitude of these processes.

Metabolic rates of primary producers are clearly influenced by a multitude of factors including hydrodynamics, irradiance, and nutrient availability but in order to understand how oxygen and pH are related as a result of metabolic activity, we held flow (and everything else) constant across our incubations. Because we found such compelling and strong relationships between these parameters and

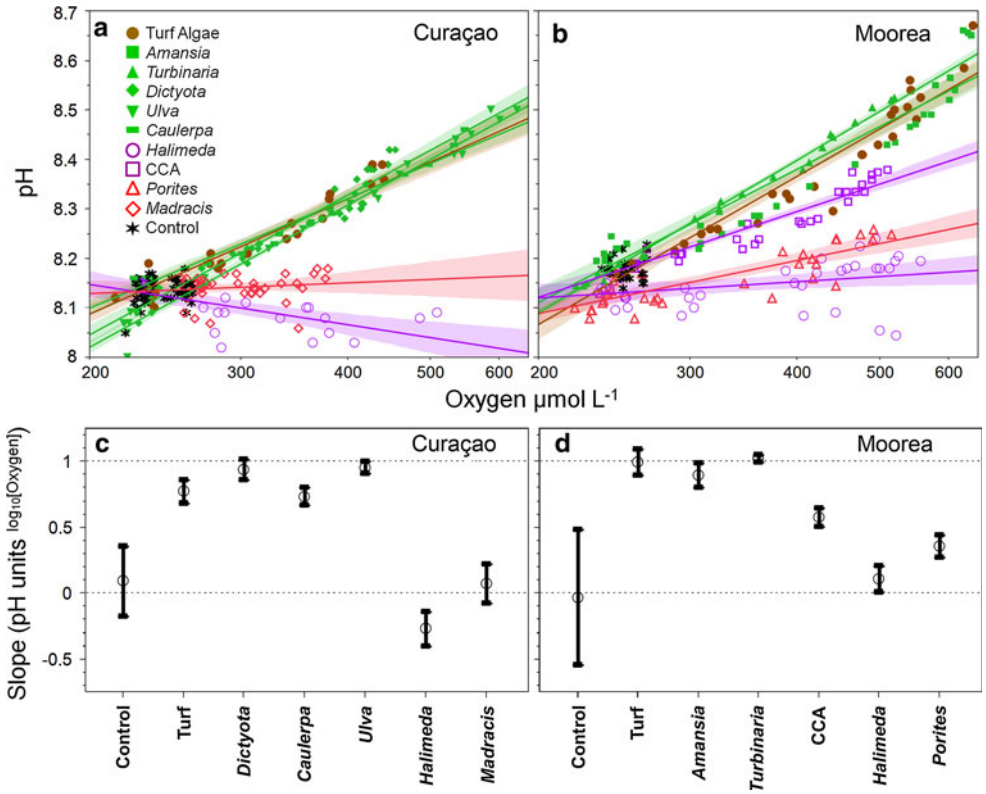

Fig. 2 Differential rates of change in pH with photosynthetic oxygen evolution among different benthic primary producers from Moorea and Curaçao. Axes are simultaneous point measurements of dissolved oxygen and pH made 30–50 times among 5–9 replicate incubations over the course of daylight incubations. *Top panels* (**a**, **b**) show results of least squares (Model I) regressions of pH on $\log_{10}$ (oxygen) for each organism with 95 % confidence interval shading around each model. *Bottom panels* (**c**, **d**) show regression slopes and 95 % confidence intervals among incubations in each reef system. *Symbols* are color coded according to functional group as in Fig. 1. Different species within a functional group are shown with *different shaped symbols*. Note that the non-calcifying algae (*Amansia*, *Turbinaria*, and turf in Moorea and *Ulva* and *Dictyota* in Curaçao) exhibit identical slopes (confidence intervals overlap each slope and 1) while calcifiers show significantly different degrees of attenuation of pH increase

showed evidence that relationships differed between calcified and fleshy algae, our results have significant implications for future ocean acidification scenarios. However, it is important to note that because our experiments were conducted in no-flow chambers, our results may not be representative of the absolute values of how these benthic organisms affect water chemistry in natural reef environments. While it is likely that metabolic rates would be higher under natural flow conditions (Carpenter et al. 1991; Lesser et al. 1994; Bruno and Edmunds 1998; Mass et al. 2010), the effects of benthic metabolism on surrounding seawater chemistry may be dampened due to dilution (Anthony et al. 2011). Ultimately, more research is needed to understand precisely how benthic metabolic rates feedback to affect diurnal patterns in water chemistry on reefs but our results do suggest that calcified and fleshy taxa may have differential effects.

As expected, all of the organisms investigated here significantly increased oxygen concentration during daylight and decreased it in the dark, as a result of photosynthesis and respiration, respectively (Fig. 1a). Previous studies have shown that benthic macroalgae elevate surrounding oxygen concentrations during daylight hours (Littler and Arnold 1982; Miller et al. 2009), but oxygen efflux rate depends on species-specific productivity rates (Littler and Arnold 1982; Kaspar 1992) and on flow (Mass et al. 2010). Accordingly, in our study, the consortia of turf algae contributed to the greatest changes in oxygen concentration while the other fleshy and calcified macroalgae had similar, but lower fluxes (Fig. 1a). All algae had positive or balanced (turf algae, Curaçao) net oxygen fluxes over the course of a day, despite nighttime respiration (Fig. 1b). For the coral species, the comparably low oxygen concentration increase rates during daylight periods coupled with relatively high respiration rates during the night created a net negative oxygen flux on each island (Fig. 1c). This suggests that the coral holobionts investigated here were net heterotrophic in both systems.

Our study does not allow for the separation of the effects of net community metabolism (productivity/respiration) from calcification/dissolution on seawater pH. However, the resulting changes in pH during the daylight and

nighttime incubations were consistent with respect to coarse benthic categories (e.g. calcifiers vs. non-calcifiers). Incubations containing any non-calcifying or 'fleshy' benthic macroalgae became more alkaline during the day as productivity peaked, but more acidic (to a lesser degree, if at all) during the night as respiration increased (Fig. 1c); the net effect on seawater pH was positive for almost all fleshy species, other than for turf algae on Curacao (Fig. 1d). The degree to which pH was elevated was species specific and reflected relative productivity rates, as inferred by oxygen evolution. To our knowledge, there is only one other study examining the degree to which a particular species of marine benthic macroalgae affects seawater pH. Anthony et al. (2011) also found that metabolic activity of the fleshy brown macroalga *Chnoospora* sp. caused similar diel patterns in seawater pH in experimental flumes, but the influence on the pH profile was dampened by increasing flow.

In the absence of productivity/respiration, calcifying benthic organisms should decrease seawater pH near their surfaces as CO_2 and H^+ ions are released and carbonate ions fixed during biomineralization (Gattuso et al. 1996b; Jokiel 2011). But, for calcifying autotrophs, CO_2 fixation via photosynthesis can potentially counteract the effects of biomineralization on seawater pH within the boundary layer. In this study, a coralline alga was the only calcifier to cause any increase in daytime seawater pH (Fig. 1b), albeit less substantial than the feedback from any of the fleshy algae. Our results suggest that productivity rates of this CCA are sufficient to offset changes to carbonate chemistry caused by calcification, at least during these short incubations. Likewise, another study conducted on temperate shallow reefs showed that *Sporolithon durum*, a cold-water CCA, also raised pH within the diffusion boundary layer above its thallus relative to upstream seawater, despite substantial water circulation (Hurd et al. 2011). However, neither coral species (*P. lobata* from Moorea and *M. mirabilis* from Curaçao), nor the calcifying green alga *H. opuntia* (Moorea) changed daytime seawater pH in our study. In fact, *H. tuna* on Curaçao caused a decrease in daytime pH (Fig. 1b), likely because the calcification rate for this species is substantially greater than its productivity rate (Barnes and Devereux 1984). All calcifying organisms decreased pH in their respective chambers overnight, but not necessarily to a greater degree than the fleshy species, as would be expected due to the combination of respiration and calcification. Over the entire diel cycle, calcifying organisms had no (CCA, *H. opuntia*) or net negative (*Porites*, *Madracis*, *H. tuna*) effects on pH (Fig. 1d). Thus, the relative influence of any autotrophic reef-building organism (corals, CCA, *Halimeda*) on its surrounding seawater chemistry appears to be highly dependent on a species-specific balance of productivity and calcification.

As our experiments were conducted in small enclosed mesocosms, it is not surprising that we were able to detect substantial diurnal changes in water chemistry due to metabolic rates. In a more turbulent or dynamic environment, the effect of metabolism on water chemistry is expected to dissipate downstream (Anthony et al. 2011). However, metabolic rates also increase with flow rates or flux as corals and algae are released from diffusive boundary layer limitation (Carpenter et al. 1991; Lesser et al. 1994; Bruno and Edmunds 1998; Mass et al. 2010). Thus, our measurements are conservative values and likely represent the lower range of potential effects that these reef organisms have on surrounding water chemistry, which will ultimately be the combined result of taxonomy, intrinsic rates of calcification and productivity, water residence time, and boundary layer hydrodynamics. Alternatively, our results are likely reflective of how these benthic organisms affect water chemistry in low-flow backreef or lagoonal habitats.

The specific relationship between oxygen evolution/consumption and pH, which is likely unaffected by alterations in water movement, was linear for both calcifying and non-calcifying species, although the slope of the relationship depended on species (Fig. 2). For each fleshy alga, there was a near perfect 1:1 stoichiometric equivalency of increased oxygen and decreased hydrogen ions (or increased pH) during the day (Fig. 2). However, incubation waters containing the calcifiers (CCA, *Porites*, *Madracis*, and the two species of *Halimeda*) showed a smaller increase in pH relative to oxygen production. Accordingly, the relationship of log oxygen concentrations to pH was significantly <1 (0.58, 0.35, 0.07, 0.11, and -0.27 for CCA, *Porites, H. opuntia*, *M. mirabilis*, and *H. tuna*, respectively), which likely reflects the balance between productivity and calcification in these species. Although we could not measure calcification rates in this study, *Halimeda* is known to have calcification rates as high as 13.5 mg cm^{-2} d^{-1} (Borowitzka and Larkum 1987; Price et al. 2011), considerably higher than estimates for *Porites* (4.5–5.4 mg cm^{-2} d^{-1}; Lough and Barnes 2000; Cooper et al. 2008) or CCA ($\sim$0.1 mg cm^{-2} d^{-1}: Jokiel et al. 2008). The slopes of the relationships between oxygen and pH correspond to these reported calcification rates: the slope is nearest to one for the CCA that calcify the slowest and is even negative for the species of *Halimeda* that calcify the fastest.

Turf algae and hermatypic corals from both Caribbean and Pacific reefs caused the largest fluctuations in oxygen concentrations and pH over a diurnal cycle and generally had the largest impact on net daily changes. These taxonomic functional groups are common components of most benthic reef communities (McCook et al. 2001; Wilkinson 2008) and thus have the potential to contribute

considerably to the natural diurnal variability in pH recorded from coral reefs (Hofmann et al. 2011). However, turf algae showed the greatest inconsistency between islands in terms of nighttime effects on pH, but because the consortia of filamentous algae that comprise turfs can vary greatly and because the turfs also host diverse assemblages of epi- and infauna, it is not surprising that the cumulative effects of turf algae on seawater chemistry are vast and variable. Contrastingly, the calcified macroalgae had little influence on the surrounding seawater pH, likely either because CO_2 fixation (photosynthesis) offset both the carbonate fixation and CO_2 release (during calcification and respiration) or because these rates are all lower for this algal group.

While particular species of macroalgae can negatively affect corals in a variety of ways (e.g. allelopathy, disease transmission, microbial feedbacks, abrasion, shading, etc.) (McCook et al. 2001), this study suggests that the presence of certain fleshy algal taxa might support growth of nearby calcifying organisms by elevating pH in the benthic boundary layer. Ongoing research indicates that especially the maximum pH values and/or time span above given pH thresholds may be essential for calcification processes in various organisms (Bates et al. 2009; Price et al. 2012). This study and other modeling efforts (Anthony et al. 2011; Kleypas et al. 2011) suggest that non-calcifying primary producers, especially those driving large amplitudes in diurnal pH fluctuations, may be important "buffer organisms" against potential ocean acidification on coral reefs. So, while many types of anthropogenic disturbances directly or indirectly enhance fleshy algal abundance and contribute to phase shifts from coral dominance to algal dominance on tropical reefs, the presence of fleshy algae may actually help to facilitate coral calcification. Of course the presence of algae will not make corals immune to anthropogenic disturbances and many factors than enhance fleshy algal abundance on reefs also negatively affect coral abundance. Nonetheless, these data highlight the complexity of biogeochemical cycles on reefs and show that macroalgae may not always have negative or neutral effects on corals. Finally, without also understanding the direct outcomes of species-specific coral–algal interactions, it remains to be seen how productivity and calcification rates indirectly influence the battle for limited space and the potential response to ocean acidification in these ecosystems.

Acknowledgments We thank the entire staff of the Richard B. Gump South Pacific Research Station in Moorea. The Moorea Coral Reef Long-Term Ecological Research (MCR-LTER) project (US NSF OCE-0417412) provided field and laboratory logistical support. We further thank the entire staff of the CARMABI research station in Curaçao and especially Dr. M. Vermeij for logistical support. We would like to specifically thank A. Gregg, F. L Rohwer and L. Wegley Kelly for their help during the field research and the Smith and Sandin laboratories at SIO for comments on the manuscript. This research was supported by the United States National Science Foundation (NSF) awards OCE-0927415 to F. Rohwer, OCE-0927411 to C. A. Carlson, and OCE-0927448 to J. E. Smith and J. J. Leichter and grants from the Gordon and Betty Moore Foundation to J. E. Smith, T. R. Martz, and R. Dunbar.

References

Allen ED, Spence DHN (1981) The differential ability of aquatic plants to utilize the inorganic carbon supply in fresh waters. New Phytol 87:269–283

Anderson LA, Sarmiento JL (1994) Redfield ratios of remineralization determined by nutrient data analysis. Global Biogeochem Cycles 8:65–80. doi:10.1029/93gb03318

Anthony KRN, Kline DI, Diaz-Pulido G, Dove S, Hoegh-Guldberg O (2008) Ocean acidification causes bleaching and productivity loss in coral reef builders. Proc Natl Acad Sci USA 105:17442–17446. doi:10.1073/pnas.0804478105

Anthony KRN, Kleypas JA, Gattuso JP (2011) Coral reefs modify their seawater carbon chemistry—implications for impacts of ocean acidification. Global Change Biol 17:3655–3666. doi:10.1111/j.1365-2486.2011.02510.x

Axelsson L (1988) Changes in pH as a measure of photosynthesis by marine macroalgae. Mar Biol 97:287–294

Barnes DJ (1983) Profiling coral reef productivity and calcification using pH and oxygen electrodes. J Exp Mar Biol Ecol 66:149–161. doi:10.1016/0022-0981(83)90036-9

Barnes DJ, Devereux MJ (1984) Productivity and calcification on a coral reef: a survey using pH and oxygen electrode techniques. J Exp Mar Biol Ecol 79:213–231. doi:10.1016/0022-0981(84)90196-5

Barnes DJ, Lazar B (1993) Metabolic performance of a shallow reef patch near Eilat on the Red sea. J Exp Mar Biol Ecol 174:1–13

Bates NR, Amat A, Andersson AJ (2009) The interaction of ocean acidification and carbonate chemistry on coral reef calcification: evaluating the carbonate chemistry coral reef ecosystem feedback (CREF) hypothesis on the Bermuda coral reef. Biogeosci Discuss 6:7627–7672

Bellwood DR, Hughes TP, Folke C, Nystrom M (2004) Confronting the coral reef crisis. Nature 429:827–833

Borowitzka MA, Larkum AWD (1976) Calcification in the green alga *Halimeda* IV: action of metabolic inhibitors on photosynthesis and calcification. J Exp Bot 27:894–907

Borowitzka MA, Larkum AWD (1987) Calcification in algae: mechanisms and the role of metabolism. Crit Rev Plant Sci 6:1–45

Bruno JF, Edmunds PJ (1998) Metabolic consequences of phenotypic plasticity in the coral *Madracis mirabilis*: the effect of morphology and water flow on aggregate respiration. J Exp Mar Biol Ecol 229:187–195. doi:10.1016/s0022-0981(98)00050-1

Bruno JF, Selig ER (2007) Regional decline of coral cover in the Indo-Pacific: timing, extent, and subregional comparisons. PLoS ONE 2:e711

Carpenter RC, Hackney JM, Adey WH (1991) Measurements of primary productivity and nitrogenase activity of coral reef algae in a chamber incorporating oscillatory flow. Limnol Oceanogr 36:40–49

Coles SL, Jokiel P (1977) Effects of temperature on photosynthesis and respiration in hermatypic corals. Mar Biol (Berl) 43:209–216

Cook CM, Lanaras T, Roubelakis-Angelakis KA (1988) Bicarbonate transport and alkalization of the medium by four species of *Rhodophyta*. J Exp Bot 39:1185–1198

Cooper TF, De'Ath G, Fabricius KE, Lough JM (2008) Declining coral calcification in massive *Porites* in two nearshore regions of the northern great barrier reef. Global Change Biol 14:529–538. doi:10.1111/j.1365-2486.2007.01520.x

Dennison WC, Barnes DJ (1988) Effect of water motion on coral photosynthesis and calcification. J Exp Mar Biol Ecol 115:167–177

Edmunds PJ, Putnam HM, Nisbet RM, Muller EB (2011) Benchmarks in organism performance and their use in comparative analyses. Oecologia 167:379–390. doi:10.1007/s00442-011-2004-2

Frankignoulle M, Gattuso JP, Biondo R, Bourge I, CopinMontegut G, Pichon M (1996) Carbon fluxes in coral reefs II: eulerian study of inorganic carbon dynamics and measurement of air-sea CO_2 exchanges. Mar Ecol Prog Ser 145:123–132. doi:10.3354/meps145123

Galzin R, Pointier JP (1985) Moorea Island, society archipelago 5th int coral reef congress. Tahiti, pp 73–101

Gates RD, Edmunds PJ (1999) The physiological mechanisms of acclimatization in tropical reef corals. Am Zool 39:30–43

Gattuso JP, Pichon M, Delesalle B, Canon C, Frankignoulle M (1996) Carbon fluxes in coral reefs I: lagrangian measurement of community metabolism and resulting air-sea CO_2 disequilibrium. Mar Ecol Prog Ser 145:109–121. doi:10.3354/meps145109

Gattuso JP, Payri CE, Pichon M, Delesalle B, Frankignoulle M (1997) Primary production, calcification, and air-sea CO_2 fluxes of a macroalgal-dominated coral reef community (Moorea, French Polynesia). J Phycol 33:729–738

Gattuso JP, Allemand D, Frankignoulle M (1999a) Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry. Am Zool 39:160–183

Gattuso JP, Frankignoulle M, Smith SV (1999b) Measurement of community metabolism and significance in the coral reef CO_2 source-sink debate. Proc Natl Acad Sci USA 96:13017–13022. doi:10.1073/pnas.96.23.13017

Gattuso JP, Pichon M, Jaubert J, Marchioretti M, Frankignoulle M (1996b) Primary production, calcification and air-sea CO_2 fluxes in coral reefs: organism, ecosystem and global scales. Bull Inst Oceanogr (Monaco) 14(4):39–46

Haas AF, Wild C (2010) Composition analysis of organic matter released by cosmopolitan coral reef-associated green algae. Aquat Biol 10:131–138. doi:10.3354/ab00271

Haas AF, Nelson CE, Wegley Kelly L, Carlson CA, Rohwer F, Leichter JJ, Wyatt A, Smith JE (2011) Effects of coral reef benthic primary producers on dissolved organic carbon and microbial activity. PLoS One 6:e27973. doi:10.1371/journal.pone.0027973

Hench JL, Leichter JJ, Monismith SG (2008) Episodic circulation and exchange in a wave-driven coral reef and lagoon system. Limnol Oceanogr 53:2681–2694

Hendriks IE, Duarte CM, Alvarez M (2010) Vulnerability of marine biodiversity to ocean acidification: a meta-analysis. Estuar Coast Shelf Sci 86:157–164. doi:10.1016/j.ecss.2009.11.022

Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS, Greenfield P, Gomez E, Harvell CD, Sale PF, Edwards AJ, Caldeira K, Knowlton N, Eakin CM, Iglesias-Prieto R, Muthiga N, Bradbury RH, Dubi A, Hatziolos ME (2007) Coral reefs under rapid climate change and ocean acidification. Science 318:1737–1742

Hofmann GE, Smith JE, Johnson KS, Send U, Levin LA, Micheli F, Paytan A, Price NN, Peterson B, Takeshita Y, Matson PG, Crook ED, Kroeker KJ, Gambi MC, Rivest EB, Frieder CA, Yu PC, Martz T (2011) High-frequency dynamics of ocean pH: a multi-ecosystem comparison. PLoS ONE 6:e28983. doi:10.1371/journal.pone.0028983

Hughes TP, Baird AH, Bellwood DR, Card M, Connolly SR, Folke C, Grosberg R, Hoegh-Guldberg O, Jackson JB, Kleypas J, Lough JM, Marshall P, Nystrom M, Palumbi SR, Pandolfi JM, Rosen B, Roughgarden J (2003) Climate change, human impacts, and the resilience of coral reefs. Science 301:929–933

Hurd CL, Cornwall CE, Currie K, Hepburn CD, McGraw CM, Hunter KA, Boyd PW (2011) Metabolically induced pH fluctuations by some coastal calcifiers exceed projected 22nd century ocean acidification: a mechanism for differential susceptibility? Global Change Biol 17:3254–3262. doi:10.1111/j.1365-2486.2011.02473.x

Israel A, Beer S (1992) Photosynthetic carbon acquisition in the red alga *Gracilaria conferta*. Mar Biol 112:697–700. doi:10.1007/bf00346189

Johannes RE, Alberts J, D'Elia C, Kinzie RA, Pomeroy LR, Sottile W, Wiebe W, Marsh JA Jr, Helfrich P, Maragos J, Meyer J, Smith S, Crabtree D, Roth A, McCloskey LR, Betzer S, Marshall N, Pilson MEQ, Telek G, Clutter RI, DuPaul WD, Webb KL, Wells JM Jr (1972) The metabolism of some coral reef communities: a team study of nutrient and energy flux at Eniwetok. Bioscience 22:541–543

Jokiel PL (2011) Ocean acidification and control of reef coral calcification by boundary layer limitation of proton flux. Bull Mar Sci 87:639–657. doi:10.5343/bms.2010.1107

Jokiel PL, Morrissey JI (1986) Influence of size on primary production in the reef coral *Pocillopora damicornis* and the macroalga *Acanthophora spicifera*. Mar Biol 91:15–26. doi:10.1007/bf00397566

Jokiel P, Rodgers K, Kuffner I, Andersson A, Cox E, Mackenzie F (2008) Ocean acidification and calcifying reef organisms: a mesocosm investigation. Coral Reefs 27:473–483. doi:10.1007/s00338-008-0380-9

Kaspar HF (1992) Oxygen conditions on surfaces of coralline red algae. Mar Ecol Prog Ser 81:97–100

Kleypas JA, Anthony KRN, Gattuso JP (2011) Coral reefs modify their seawater carbon chemistry—case study from a barrier reef (Moorea, French Polynesia). Global Change Biol 17:3667–3678

Kroeker KJ, Kordas RL, Crim RN, Singh GG (2010) Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. Ecol Lett 13:1419–1434. doi:10.1111/j.1461-0248.2010.01518.x

Lesser MP, Weis VM, Patterson MR, Jokiel PL (1994) Effects of morphology and water motion on carbon delivery and productivity in the reef coral, *Pocillopora damicornis*: diffusion barriers, inorganic carbon limitation, and biochemical plasticity. J Exp Mar Biol Ecol 178:153–179. doi:10.1016/0022-0981(94)90034-5

Lindahl PEB (1963) The inhibition of the photosynthesis of aquatic plants by tetramethylthiuram disulphide. Symbolae Botanicae Upsaliensis 17:1–47

Littler MM, Arnold KE (1982) Primary productivity of marine macroalgal functional-form groups from southwestern North America. J Phycol 18:307–311. doi:10.1111/j.1529-8817.1982.tb03188.x

Littler MM, Littler DS (1980) The evolution of thallus form and survival strategies in benthic marine macroalgae: field and laboratory tests of a functional form model. Am Nat 116:25–44

Lough JM, Barnes DJ (2000) Environmental controls on growth of the massive coral *Porites*. J Exp Mar Biol Ecol 245:225–243. doi:10.1016/s0022-0981(99)00168-9

Lucas WJ (1983) Photosynthetic assimilation of exogenous HCO_3 by aquatic plants. Annu Rev of Plant Physiol 34:71–104. doi:10.1146/annurev.pp.34.060183.000443

Maberly SC, Spence DHN (1983) Photosynthetic inorganic carbon use by freshwater plants. J Ecol 71:705–724

Marsh JA Jr (1970) Primary productivity of reef-building calcareous red algae. Ecology 51:255–263

Mass T, Genin A, Shavit U, Grinstein M, Tchernov D (2010) Flow enhances photosynthesis in marine benthic autotrophs by increasing the efflux of oxygen from the organism to the water. Proc Natl Acad Sci USA 107:2527–2531. doi:10.1073/pnas.0912348107

McCloskey LR, Muscatine L (1984) Production and respiration in the Red Sea coral *Stylophora pistillata* as a function of depth. Proc R Soc Lond B Biol 222:215–230. doi:10.1098/rspb.1984.0060

McCook LJ, Jompa J, Diaz-Pulido G (2001) Competition between corals and algae on coral reefs: a review of evidence and mechanisms. Coral Reefs 19:400–417

Miller RJ, Reed DC, Brzezinski MA (2009) Community structure and productivity of subtidal turf and foliose algal assemblages. Mar Ecol Prog Ser 388:1–11. doi:10.3354/meps08131

Muller EB, Kooijman S, Edmunds PJ, Doyle FJ, Nisbet RM (2009) Dynamic energy budgets in syntrophic symbiotic relationships between heterotrophic hosts and photoautotrophic symbionts. J Theor Biol 259:44–57. doi:10.1016/j.jtbi.2009.03.004

Murphy S, Gardner FH (1975) Platelet storage at 22 degrees C: role of gas transport across plastic containers in maintenance of viability. Blood 46:209–218

Murru M, Sandgren CD (2004) Habitat matters for inorganic carbon acquisition in 38 species of red macroalgae (*Rhodophyta*) from Puget Sound, Washingto, USA. J Phycol 40:837–845. doi:10.1111/j.1529-8817.2004.03182.x

Naumann M, Niggl W, Laforsch C, Glaser C, Wild C (2009) Coral surface area quantification–evaluation of established techniques by comparison with computer tomography. Coral Reefs 28:109–117. doi:10.1007/s00338-008-0459-3

Naumann M, Haas A, Struck U, Mayr C, el-Zibdah M, Wild C (2010) Organic matter release by dominant hermatypic corals of the Northern Red Sea. Coral Reefs 29:649–659. doi:10.1007/s00338-010-0612-7

Niggel W, Haas AF, Wild C (2010) Benthic community composition affects O_2 availability and variability in a Northern Red Sea fringing reef. Hydrobiologia 644:401–405

Nyström M, Folke C, Moberg F (2000) Coral reef disturbance and resilience in a human-dominated environment. Trends Ecol Evol 15:413–417. doi:10.1016/s0169-5347(00)01948-0

Ohde S, van Woesik R (1999) Carbon dioxide flux and metabolic processes of a coral reef, Okinawa. Bull Mar Sci 65:559–576

Price NN, Hamilton SL, Tootell JS, Smith JE (2011) Species-specific consequences of ocean acidification for the calcareous tropical green algae *Halimeda*. Mar Ecol Prog Ser 440:67–78. doi:10.3354/meps09309

Price NN, Martz TR, Brainard RE, Smith JE (2012) Diel variability in seawater pH relates to calcification and benthic community structure on coral reefs. PLoS One 7. doi:10.1371/journal.pone.0043843

Prins HBA, Elzenga JTM (1989) Bicarbonate utilization: function and mechanism. Aquat Bot 34:59–83. doi:10.1016/0304-3770(89)90050-8

Raven JA (1997) Inorganic carbon acquisition by marine autotrophs. In: Callow JA (ed) Advances in botanical research. Academic Press, New York, pp 85–209

Roffman B (1968) Patterns of oxygen exchange in some Pacific corals. Comp Biochem Physiol 27:405–418. doi:10.1016/0010-406x(68)90239-9

Russo AR (1990) The role of seaweed complexity in structuring Hawaiian epiphytal amphipod communities. Hydrobiologia 194:1–12. doi:10.1007/bf00012107

Shamberger KEF, Feely RA, Sabine CL, Atkinson MJ, DeCarlo EH, Mackenzie FT, Drupp PS, Butterfield DA (2011) Calcification and organic production on a Hawaiian coral reef. Mar Chem 127:64–75. doi:10.1016/j.marchem.2011.08.003

Shashar N, Cohen Y, Loya Y (1993) Extreme diel fluctuations of oxygen in diffusive boundary layers surrounding stony corals. Biol Bull 185:455–461

Shashar N, Kinane S, Jokiel PJ, Patterson MR (1996) Hydromechanical boundary layers over a coral reef. J Exp Mar Biol Ecol 199:17–28

Smith SV (1973) Carbon dioxide dynamics: a record of organic carbon production, respiration, and calcification in the Eniwetok reef flat community. Limnol Oceanogr 18:106–120

Valiela I (1984) Marine ecological processes. Springer, New York

van Duyl FC, Scheffers SR, Thomas FIM, Driscoll M (2006) The effect of water exchange on bacterioplankton depletion and inorganic nutrient dynamics in coral reef cavities. Coral Reefs 25:23–36

Wild C, Niggel W, Naumann MS, Haas AF (2010) Organic matter release by Red Sea coral reef organisms—potential effects on microbial activity and in situ O_2 availability. Mar Ecol Prog Ser 411:61–71. doi:10.3354/meps08653

Wilkinson C (2008) Status of coral reefs of the world: 2008. In: Wilkinson C (ed) Coral reefs. Global Coral Reef Monitoring Network and Reef and Rainforest Research Centre, Townsville, Australia p 296

Wu EY, Barazanji KW, Johnson RLJ (1997) Sources of error in A-aD-O_2 calculated from blood stored in plastic and glass syringes. J Appl Physiol 82:196–202

Zeebe RE, Wolf-Gladrow DA, Jansen H (1999) On the time required to establish chemical and isotopic equilibrium in the carbon dioxide system in seawater. Mar Chem 65:135–153