CHAPTER 9

The Calcium Carbonate Cycle in Seagrass Ecosystems

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HIGHLIGHTS

- 1. Seagrass meadows provide an important habitat for a wide range of marine organisms, including those that form or secrete skeletal or non-skeletal calcium carbonate ($CaCO_3$), which is deposited on the soil surface along with organic remains.
- 2. The direction and magnitude of the air-sea CO₂ exchange potential in seagrass ecosystems depends on the relative rates of the organic and inorganic carbon cycles within the system.
- 3. In settings where there is potential for CO₂ evasion from seawater to the atmosphere, the soil still provides a long-term store for detrital organic and CaCO₃ carbon.

9.1 INTRODUCTION

Seagrass meadows are commonly associated with carbonate-rich soils in the sub-tropics and tropics (Alongi et al. 2008; Mazarrasa et al. 2015), where the functional traits of seagrasses and the ecosystem supported by seagrass meadows facilitate the growth of calcareous organisms (calcifiers) that contribute to the accumulation of detrital carbonate particles (CaCO₃) in the soil. The seagrass canopy provides structural complexity for the settlement and growth of calcifiers, and the high productivity of seagrasses, their epiphytes, and associated benthic algae attracts other infaunal and epifaunal sessile and mobile calcifying organisms that benefit from the meadow as an energy source, nursery ground, and a place to avoid predation (Heck et al. 2008). The CaCO₃ produced by these organisms is added to the underlying soil and is termed autochthonous. Allochthonous CaCO₃ particles can be transported from elsewhere and get trapped in the meadow via the reduction in hydrodynamic flow by the seagrass canopy, which enhances local particle deposition. The soil that accumulates is stabilized by the extensive belowground root and rhizome system of the seagrass beds (Figure 9.1).

Blue carbon is the organic carbon produced and/or trapped by the seagrass meadow and stored in the underlying soil; the ultimate source of the carbon is the atmosphere (Nellemann et al. 2009). This function is dependent on seagrass ecosystems being net autotrophic, that is, where gross primary production (GPP) exceeds respiration (R) and there is a net transfer of carbon dioxide (CO₂) from the atmosphere to seawater. Not all seagrass ecosystems are net autotrophic; Duarte et al. (2005) demonstrated that there is a threshold GPP, below which respiration dominates ecosystem metabolism and there is a net transfer of CO₂ from seawater to the atmosphere. It is now becoming clear that the CaCO₃ cycle also has a role to play in determining whether there is a net transfer of CO₂ from the atmosphere to seawater or vice versa in a seagrass ecosystem.

While the organic carbon cycle has been well studied in seagrass ecosystems, the $CaCO_3$ cycle has rarely been evaluated. Here, we outline the processes in seagrass ecosystems that contribute to



Figure 9.1 (See color insert following page 266.) Conceptual diagram illustrating the major processes affecting the CaCO₃ and organic carbon cycle in seagrass ecosystems.

 $CaCO_3$ production and accumulation in the underlying soils and how the relative rates of the organic carbon and the $CaCO_3$ cycles affect chemical changes in the water column that determine the direction of the air-sea CO_2 exchange (Figure 9.1). A better understanding of these processes form a basis from which to assess the role of seagrass ecosystems in storing carbon over the short and long time scales, and the vulnerability of the stored carbon to human disturbance and climate change.

9.2 BIOGENIC CaCO₃ PRODUCTION ASSOCIATED WITH SEAGRASS MEADOWS

Calcifying and non-calcifying epiphytic organisms are commonly present on seagrass leaves and stems (Borowitzka et al. 2006), while it has recently been demonstrated that seagrass can also make a direct contribution to CaCO₃ production and local CaCO₃ deposition by CaCO₃ precipitation internally and as coatings externally on their leaves (Enríquez and Schubert 2014). Coralline and articulated red algae, serpulid worms, foraminifera, and bivalves are all regularly observed epiphytic calcifiers (Figures 9.1 and 9.2). Coralline encrusting (non-geniculate) and articulated (geniculate) algae make up a large proportion and are the most prolific CaCO₃ producers of the epiphytic community (Land 1970; Patriquin 1972; Nelsen and Ginsberg 1986; Boscence 1989; Frankovich and Zieman 1994; Perry and Beavington–Penney 2005; Corlett and Jones 2007; James et al. 2009; Basso 2012). In southern Australia, for example, corallines made up 53.6% of the taxa, with benthic foraminifera contributing 17.4%, bryozoans 16.4%, spiroids 8%, and bivalves, serpulids, and ostracods each contributing < 0.3% to the epiphyte taxa (James et al. 2009). Many other different calcareous epiphytes have been documented but not quantified (Humm 1964; Wilson 1998).

The non-geniculate epiphytic calcifiers produce thin ($\leq 100 \,\mu$ m) layers of CaCO₃ that gradually spread over the leaf surface. The maximum contribution of these epiphytes to the CaCO₃ production depends on their growth rate, the surface area available for colonization, the time span of each leaf in a shoot, and the shoot density of the seagrass species (Walker and Woelkerling 1988; Borowitzka et al. 2006). Variation in the epiphyte community is also observed on different structural components of a seagrass. For example, a higher occurrence was observed of non-geniculate corallines on leaf blades and geniculate corallines on the stems of the seagrass *Amphibolis antarctica* in



Figure 9.2 (See color insert following page 266.) Calcium carbonate producing organisms: (a) coralline red algae (Rhodophyta), (b) the foraminifer *Cornuspiramia antillarum*, (c) the polychaete *Spirorbis* sp., and (d) the gastropod *Modulus*. Scale bars: (a, b) 1 mm, (c) 500 μm, and (d) 5mm. Photographs provided courtesy of Tom Frankovich, Marine Education and Research Center, Florida International University.

Australia (James et al. 2009). Species such as *Thalassia*, *Posidonia*, and *Amphibolis* have large, long-lived, strap-type leaves that facilitate epiphyte colonization and growth. It is these long-lived species that have been most intensively studied (Table 9.1), e.g., *Thalassia testudinum* in Florida Bay, USA, in the Bahamas Bank, and in the Caribbean, *Amphibolis antarctica* in Australia, and *Posidonia oceanica* in the Mediterranean (Walker and Woelkerling 1988; Corlett and Jones 2007; James et al. 2009). The more ephemeral seagrass species with a smaller leaf area available for colonization, such as *Halophila* and *Halodule*, will sustain lower amount of epiphytes and have rarely been studied (Borowitzka et al. 2006).

Beyond these sessile epiphytes, there are more mobile calcifying organisms, which do not always depend directly on the seagrass structural components but are still resident in the seagrass meadow and the surrounding area (Figure 9.2). Mobile gastropods graze on seagrass leaves for food, while ostracods and calcareous mobile and sessile bivalves are also commonly found on the seagrass structures. Fish, which utilize the meadows as nursery grounds and foraging areas, also contribute CaCO₃ as they produce and excrete various forms of non-skeletal CaCO₃ from their guts as very fine-grained (<2 μ m) CaCO₃ crystallites. Their overall contribution may be very low (<1%) compared to other calcifiers but they are still considered a measureable contributor to the accumulation of lime mud across the Bahamian archipelago (Perry et al. 2011).

Fish use the meadows as refugia from predation, but the meadows also have the potential to act as refugia for calcifying organisms that are vulnerable to ocean acidification (oceanic pH decrease via absorption of anthropogenically increasing atmospheric CO_2) (Semesi et al. 2009; Manzello et al. 2012; Hendricks et al. 2014). During photosynthesis seagrass removes CO_2 from seawater, which raises

Location	CARB _{prod} (g CaCO₂m ⁻² vear ⁻¹)	Species	Reference
Jamaica	min: 40 mean: 180	Thalassia testudinum	Land (1970)
Barbados	max: 5100	Thalassia testudinum	Patriquin (1972)
Barbados	134	Seagrass	Webster and Parnankap (1977) (in Brown 2005)
Florida Bay (USA)	30–303 (mean: 188 ± 44)	Thalassia testudinum	Nelsen and Ginsburgh (1986)
Florida Bay (USA)	55–1042 (site means: 81, 482)	Thalassia testudinum	Bosence (1989)
Florida Bay	60 ^a	Seagrass	Hallock et al. (1986)
Florida Bay (USA)	2–283 (mean: 120)	Thalassia testudinum	Frankovitch and Zieman (1994)
Bahamas	0–68 (mean: 28 ± 6)	Thalassia testudinum	Armstrong (1989) (in Brown 2005)
Inhaca Island, Mozambique	31–86 (mean: 44)	Thalassodendron ciliatum	Perry and Beavington-Penny (2005)
Inhaca Island, Mozambique	8–55 (mean: 33)	Thalassia hemprichii	Perry and Beavington-Penny (2005)
Mallorca-Menorca Shelf (NW Mediterranean)	60–70 (mean: 68)	Posidonia oceanica	Canals and Ballesteros (1997)
Spain (NW Mediterranean)	82–158	Posidonia oceanica	Romero (1988) (in Barrón et al. 2006)
Australia	49–661 (mean: 210 ± 26)	all species	James et al. (2009)
Shark bay (Australia)	50–526 36–313	Amphibolis antarctica	Walker and Woelkerling (1988)

Table 9.1 Seagrass Gross CaCO₃ Production Rates Using the Biological Approach

^a Only foraminifera.

seawater pH and increases the concentration of carbonate ions (CO_3^2) in seawater (Section 9.4.3). The CO_3^{-1} concentration is a strong driver of the CaCO₃ precipitation and dissolution reactions, and its effect can be assessed through the saturation state (Ω) of seawater with respect to a CaCO₃ mineral form (e.g., calcite, aragonite) as $\Omega(CaCO_3) = \left[Ca^{2+1}\right] \left[CO_3^{2-1}\right] / K_{sp}^*$, with brackets denoting concentration and K_{sp}^* = concentration-based (stoichiometric) equilibrium solubility product of the CaCO₃ mineral form, a function of salinity, solution composition, and temperature. Because Ca²⁺ is present at relatively constant concentrations in seawater, $\Omega(CaCO_3)$ depends strongly on the variation of CO_3^{-1} concentration. The variability of the CO_3^{2-} concentration is a major control on the ability of calcifying organisms to produce CaCO₃ (calcification). Calcification (CARB_{orod}) is favorable when the ambient water $\Omega(CaCO_3) > 1$ (CaCO₃ supersaturation), and CaCO₃ dissolution (CARB_{diss}), which destroys biogenic CaCO₃, is favorable when Ω (CaCO₃) < 1 (CaCO₃ undersaturation). As photosynthesis is highest during daytime and in spring-summer, net calcification ($CARB_{net} = CARB_{prod} - CARB_{diss} > 0$) is often observed during these periods (Yates and Halley 2006; Turk et al. 2015; Muehllehner et al. 2016). And so, by reducing the CO₂ concentration and increasing the pH of seawater, seagrass productivity may also ameliorate ocean acidification stress to calcifying organisms found in the same locality (Manzello et al. 2012).

The effect of $\Omega(\text{CaCO}_3)$ on calcifiers will vary as different calcifying organisms secrete a range of structurally and chemically different CaCO₃ mineral forms (Scholle 1978). The typical crystalline forms of biogenic CaCO₃ are aragonite and calcite, the latter having variable magnesium (Mg²⁺) content. Magnesium can replace some of the Ca²⁺ in the calcite lattice, and calcite containing > 4 wt% of MgCO₃ is conventionally defined as high Mg calcite, which is the dominant mineralogy found in the red coralline algae and benthic foraminifera. Bryozoans, foraminifera, echinoderms, arthropods, and brachiopods produce both calcite and high Mg calcite, while green calcareous algae produce aragonite. In tropical regions, aragonite is also a major component of the CaCO₃ produced by corals, serpulid worms, and molluscs, while tropical fish excreta consist of low Mg calcite, high Mg calcite, and aragonite. Each of these biogenic CaCO₃ mineral forms has a different solubility (K^{*}_{sp}) in seawater and, hence, a different set of conditions for which seawater favors CaCO₃ production or its dissolution. Solubility decreases from aragonite to Mg calcite to pure calcite (e.g., Burdige et al. 2010).

The conditions that lend themselves to CaCO₃ dissolution, i.e., seawater CO₂ increase and pH decrease (acidification) are the opposite of those that promote calcification. Organism respiration adds CO₂ to seawater; accumulation of respired CO₂ promotes the decrease of seawater pH, CO_3^{2-} concentration, and, consequently, Ω (CaCO₃) (Section 9.4.3). Seagrass ecosystem respiration occurs in the water column and underlying soils, and is dominant at night and during the winter months of senescence, thus net CaCO₃ dissolution (CARB_{net} = CARB_{prod} – CARB_{diss} < 0) is often observed during these times (Barrón et al. 2006; Yates and Halley 2006; Turk et al. 2015; Muehllehner et al. 2016). The overall balance (CARB_{net}) between calcification (CARB_{prod}) and CaCO₃ dissolution (CARB_{diss}) depends on a number of factors (Section 9.3).

Calcification has been reported for epiphytic communities, or the whole seagrass ecosystem using different methods, which, in general, divide into two approaches. The first approach (termed biological) uses the epiphytic CaCO₃ standing stock and the rates of leaf or shoot production and/or turnover (Table 9.1). Rates of calcification (CARB_{prod}) are provided for three seagrass species from six different countries and vary from 2 to 5,100 g CaCO₃m⁻²year⁻¹. These data are associated, generally, with large coefficients of variation due to the spatial variation in both the epiphytic standing crop and the annual mean rates of seagrass productivity/turnover (Perry and Beavington-Penney 2005). For example, Frankovitch and Zieman (1994) estimated coefficients of variation of epiphyte production between 40% and 136%. The most comprehensive study to date of calcareous epiphyte biomass and CARB_{prod} using the biological approach has been for seagrass species in southern Australia, with CARB_{prod} reported for different locations, seagrass species, epiphytic biota, and seagrass modules, as well as seasonal changes in CARB_{prod} (Brown 2005).

The second approach (termed chemical) uses the seawater alkalinity anomaly generated during calcification and CaCO₃ dissolution. This method entails the removal of water samples from an incubation chamber that is inserted into the soil (in situ) or removal of seagrass leaves and their incubation in seawater (ex situ). The in situ method includes changes due to processes occurring in the soil as well as on the seagrass leaves. As the soils are sites of CaCO₃ dissolution (Section 9.3.2) they can have a strong influence on the in situ method results. The measurements from the in situ method, therefore, represent net rates of combined calcification (CARB_{prod}) and CaCO₃ dissolution (CARB_{diss}). As mentioned earlier, when CARB_{prod} > CARB_{diss}, net ecosystem calcification occurs, with CARB_{net} = CARB_{prod} – CARB_{diss} reported as positive values (>0). In contrast, when CARB_{prod} < CARB_{diss}, net ecosystem CaCO₃ dissolution occurs, with CARB_{net} reported as negative values (<0).

The biological approach results in CaCO₃ production rates only (CARB_{prod}) and does not take into account soil CaCO₃ dissolution or soil transport (Stockman et al. 1967; Bosence 1989). The chemical method will measure both calcification and dissolution, and, depending on the relative rates of these two processes, can return both negative and positive values (Table 9.2). In the same meadow, CARB_{net} measured by the chemical method cannot only vary numerically, but also between negative and positive values depending on the time interval of measurement. On diurnal scales, Yates and Halley (2006) reported generally positive CARB_{net} during the day when the seagrass ecosystem is net photosynthetic, and negative CARB_{net} during the night when CaCO₃ dissolution dominates in the different compartments of the ecosystem (Table 9.2). Estimating annual rates of CARB_{net} by the chemical approach is time consuming and costly, and still only accounts for CaCO₃ production and soil CaCO₃ dissolution, but not for soil transport (Yates and Halley 2006). Only directly measured soil accumulation rates can account for all three processes.

9.3 THE FATE OF BIOGENIC CaCO₃ PRODUCTION

The biogenic production of $CaCO_3$ in seagrass ecosystems generally leads to local $CaCO_3$ deposition and accumulation of $CaCO_3$ stocks. Some part of the biogenic $CaCO_3$ production can be exported by waves and tides out of the meadow to adjacent regions, while some part of the detrital

Location	CARB _{net} (g CaCO ₃ m ⁻² year ⁻¹)	Species	Reference
Florida Bay Dense beds	31–805⁵ (mean: 244)	Thalassia testudinum	Yates and Halley (2006)
Florida Bay Intermediate beds	−1363−61.9⁵ (mean: −84)		
Florida Bay Sparse beds	–328–181⁵ (mean: –112)		
Mallorca (NW Mediterranean)	$51\pm110^{\mathrm{b}}$	Posidonia oceanica	Barrón et al. (2006)
Shark bay	117°	mixed species	Smith and Atkinson (1983)
Shark bay (Australia)	35–295 ^d	Amphibolis antarctica	Walker and Woelkerling (1988)
Caribbean Mexico	590–5,630 ^d	Thalassia testudinum	Enriquez and Schubert (2014)
Nagura Bay (Japan)	200 ^b		Fujita (2002)

Table 9.2 aCARB_{net} in Seagrass Meadows Determined by the Chemical Approach

^a $CARB_{net} > 0$ when $CARB_{prod} > CARB_{diss}$ and $CARB_{net} > 0$ when $CARB_{prod} < CARB_{diss}$.

^b In situ incubation chamber.

^c Carbon budget.

^d Ex situ estimate.

 $CaCO_3$ accumulated in the soil will be lost due to post-depositional CaCO₃ dissolution. The accumulating soils consist not only of CaCO₃ but also of the organic carbon produced (and trapped) by the meadow (Figure 9.1).

9.3.1 CaCO₃ Soil Stocks and Accumulation Rate

The production of CaCO₃ within seagrass meadows (autochthonous CaCO₃ production) results in CaCO₃ deposition on the soil surface, facilitated by the reduction in current speed within the meadows and the stabilization of the soils by roots and rhizomes (Koch et al. 2006). In quiescent environmental settings, these factors may contribute to the development of CaCO₃ mud mounds such as those found in Florida Bay, USA, the Great Bahamas Bank, and in Shark Bay, Australia (Ginsburg and Lowenstam 1958). The particle trapping and soil stability of seagrass beds are also instrumental in the accumulation of CaCO₃ transported from adjacent regions (allochthonous CaCO₃).

Carbonate soils are not equally distributed around the globe. They have much higher abundance in tropical and sub-tropical regions than in temperate and boreal zones (Mazarrasa et al. 2015). Because the concentration of dissolved CO_2 in waters in equilibrium with the atmosphere increases as temperature decreases, the seawater saturation state of carbonate minerals increases with increasing temperature or decreasing latitude (Zeebe and Wolf-Gladrow 2001). Thus, seagrass meadows inhabiting colder waters generally support lower rates of epiphytic CaCO₃ production and have lower CaCO₃ content in their soils. Reviewing CaCO₃ stocks in seagrass soils, Mazarrasa et al. (2015) found a discernible trend of decreasing CaCO₃ stocks in seagrass soils with increasing latitude and decreasing temperature, such that stocks tended to decrease polewards at a rate of -67 ± 17 Mg CaCO₃ ha⁻¹ per degree latitude. Similarly, smaller spatial scale differences in mean water temperature caused by oceanic upwelling can lead to much lower CaCO₃ contents of soil in the colder, upwelling-influenced regions of the coastal ocean (Howard et al. 2017). Overall, Mazarrasa et al. (2015) estimated that seagrass meadows store between 25 and 13,833 Mg CaCO₃ ha⁻¹ (average $\pm 1\sigma$: $5,480 \pm 200 \text{ Mg CaCO}_3 \text{ ha}^{-1}$ in the upper 1 m of their soils. Soil CaCO₃ stocks have also been found to vary across seagrass communities, with the highest stocks found underlying meadows dominated by Halodule, Thalassia, or Cymodocea species, while the soils with the lowest CaCO₃ stocks were colonized by Zostera and Halophila species (Mazarrasa et al. 2015). These observations are not in line with those observations on epiphyte CaCO₃ production rates, which are maximal on large, long-lived seagrass species. The lack of a clear effect of the seagrass traits on $CaCO_3$ stocks could be due to other controlling factors on the precipitation, preservation, and accumulation of $CaCO_3$ in the underlying soils. The seagrass species found in warmer seas (e.g., the Caribbean and Mediterranean Seas, and the tropical Indo-Pacific) are the ones associated with higher CaCO₃ stocks.

Under conditions of net calcification (CARB_{prod} > CARB_{diss}), CaCO₃ accumulates in the underlying soils (Yates and Halley 2006). However, the accumulation rate of CaCO₃ soils underlying seagrass meadows has rarely been directly measured, with most current estimates derived from calculated rates of epiphyte production or from soil stocks of CaCO₃ and soil accumulation rate, or from the alkalinity anomaly method from benthic incubations and seawater transects. Using soil CaCO₃ content and estimates of soil accretion in seagrass meadows, Mazarrasa et al. (2015) estimated a mean global CaCO₃ accumulation rate of $1,053 \pm 259$ g CaCO₃ m⁻² year⁻¹, while Serrano et al. (2012) measured a soil accretion rate of 483 ± 16 g CaCO₃ m⁻² year⁻¹ in a *Posidonia oceanica* meadow.

9.3.2 CaCO₃ Dissolution in Seagrass Soils

The detrital CaCO₃ that accumulates in the soil alongside the organic matter is subsequently subject to mixing by the infaunal organisms (bioturbation) and dissolution, bathed in the soil pore waters (overlying water buried with the deposited biogenic and lithogenic particles). The dissolution of soil $CaCO_3$ is driven by the intense modification of the chemical composition of soil pore waters by benthic bacterial oxidation of organic matter (benthic bacterial respiration), which adds CO_2 (metabolic CO_2) and other metabolites to the pore waters, such as ammonium and sulfide in the absence of dissolved oxygen (O_2). It is in the oxic metabolic zone of the surface of marine deposits where bacterial respiration majorly affects the dissolution of detrital $CaCO_3$ as outlined below for seagrass beds.

Seagrasses, rooted in the soil, contribute to CaCO₃ dissolution, which can be traced in measurable changes in the chemical composition and in the parameters of the carbonate system (Section 9.4.1) of the pore waters (Rude and Aller 1991; Jensen et al 1998; Ku et al. 1999; Burdige and Zimmerman 2002; Hu and Burdige 2007; Burdige et al. 2008; Jensen et al. 2009; Burdige et al. 2010). Oxic benthic respiration generates acidity in the pore waters via the production of CO₂ from the decomposition and remineralization of soil organic carbon by dissolved molecular oxygen (O₂). The accumulation of metabolic CO₂ in the soil pore waters, buffered by the ambient carbonate system (Section 9.4.1), results in the decline of the pH and Ω (CaCO₃) (Jensen et al. 1998; Burdige et al. 2010). In addition, at the boundary between the surface oxic metabolic zone and the deeper anoxic zone, where there is no O₂, benthic metabolism can result in conditions favorable to benthic CaCO₃ dissolution. The oxidation of anoxic metabolites (e.g., reduced iron and sulfur compounds) at the oxic/anoxic boundary releases acidity and consequently reduces pH and lowers Ω (CaCO₃) of the pore waters (Ku et al. 1999; Jensen et al. 2009).

The primary source of benthic O_2 is generally the overlying water column via molecular diffusion across the soil-water interface. In seagrass-colonized soils, belowground efflux of photosynthetic O_2 through the root-rhizome system can become the primary source, while, in high-permeability carbonate sands, tidally and wave-driven pore water advective exchange becomes equally important as a source of O_2 to the soil (Burdige et al. 2008; Cyronak et al. 2013). Seagrass metabolism thus supports rates of oxic organic matter remineralization by the benthic bacterial community that are much higher than those that could be supported solely on the O_2 supply to the surface soil pore waters by molecular diffusion alone from the overlying water (Burdige et al. 2008). Seagrass growth also directly adds to benthic metabolism by the net production of organic carbon and its accumulation in the soil, as well as the additional efflux of CO_2 from seagrass roots, both of which lead to a lowered pH in the soil pore waters, facilitating soil CaCO₃ dissolution.

In the soils, $CaCO_3$ dissolution is prominent and has been extensively determined in a few locations in the sub-tropics and tropics (Table 9.3). An increasing rate of benthic $CaCO_3$ dissolution with increasing seagrass cover as Leaf Area Index (LAI) has been documented in the most extensively studied carbonate platform, the Bahamas Bank, and was deemed an important loss mechanism for $CaCO_3$ from these ecosystems, equivalent to $CaCO_3$ export by physical transport (Burdige et al. 2010).

The effects of benthic metabolic respiration and $CaCO_3$ dissolution in the soil are large enough to be traceable in the chemistry of the surface waters via solute fluxes across the soil-water interface (Figure 9.1) (Ku et al. 1999; Yates and Halley 2006; Cyronak et al. 2013; Muellehner et al. 2016).

Location	^a CARB _{diss} (g CaCO ₃ m ⁻² year ⁻¹)	Species	Reference
Florida Keys (USA)	292–876 ^b	T. testudinum	Turk et al. (2015)
Indonesia	511–3,979°	mixed species	Alongi et al. (2008)
Bahamas Bank	51–2,935 ^d	T. testudinum	Burdige et al. (2010)
Bahamas Bank	281–942 ^d	T. testudinum	Burdige et al. (2008)

Table 9.3 Benthic CARB_{diss} in Seagrass Soils

^a Annual rates estimated as $365 \times \text{daily rate}$.

^b Maximum night rates, benthic chambers, TA anomaly.

^c Benthic chambers, Ca²⁺ anomaly.

^d Transport-reaction modeling of pore water solutes (metabolites).

Benthic metabolism results in accumulation of the end products in the pore waters of the surface soils, such as dissolved inorganic carbon (DIC) and total alkalinity (TA), with TA representing the proton (H⁺) buffering capacity of the aquatic system (Zeebe and Wolf-Gladrow 2001; Dickson et al. 2007), and their transport to the overlying water column via molecular diffusion, bioturbation, and, in the case of highly permeable CaCO₃ sands, advective exchange by wave action and tidal pumping (Cyronak et al. 2013; Drupp et al. 2016). In seagrass meadows, therefore, the magnitude of changes in seawater chemistry caused by the organisms that produce CaCO₃ (i.e., DIC removal and TA increase; Section 9.4.2) can be reduced by the chemically distinct fluxes across the sediment-water interface. The benthic TA flux becomes more influential the shallower the water column, the longer the water residence time, and the higher the CaCO₃ dissolution rate. The dissolution rate itself depends on the magnitude of benthic bacterial respiration and the solubility of the deposited CaCO₃ mineral, with high Mg calcite being the most soluble. On an even larger scale, the benthic metabolic CaCO₃ dissolution rates documented in the Bahamas Bank by Burdige et al. (2010) generated TA fluxes that were an important component of the TA budget of the surface ocean, comparable in this respect to major TA sources to the global ocean such as the riverine TA source.

9.4 EFFECT OF THE CaCO₃ CYCLE ON THE AIR-SEA CO₂ EXCHANGE IN SEAGRASS ECOSYSTEMS

Calcification and CaCO₃ dissolution modify the chemistry of seawater in and around seagrass meadows. These changes do not occur in isolation but add to, and modify, those associated with organic matter production and respiration. The seawater is intimately connected to the underlying soils and overlying atmosphere, and fluxes of CO₂ and other relevant dissolved constituents from these distinct reservoirs further modify the seawater chemistry (Figure 9.1). Finally, any net change observed depends on the residence time of the water, i.e., when residence time is long, water mass movement is slow and expressions of chemical change maximal, and vice versa (Frankignoulle and Distèche 1984; Yates and Halley 2006; Tokoro et al. 2014; Turk et al. 2015). Overall, the modification of the seawater chemistry depends on the relative magnitude and rates of hydrodynamic and biogeochemical processes.

9.4.1 The Carbonate System of Seawater

To understand the role of the biogenic $CaCO_3$ reactions (calcification, dissolution) in the exchange of CO_2 across the air-sea interface, first, the dissolved constituents of the seawater carbonate system and the processes that affect them must be outlined. The largest component of the seawater carbonate system consists of the three species of DIC, CO_{2}° , HCO_{3}° (bicarbonate ion), and CO_3^{2-} (carbonate ion). By definition, CO_2^{2-} includes both the dissolved CO_2 and the trace concentrations of carbonic acid (H_2CO_3), and is proportional to the fugacity of CO_2 (fCO_2) in ambient water as $\left[CO_{2}^{*}\right] = K_{0}fCO_{2}$, with $K_{0} = CO_{2}$ solubility (in mol kg⁻¹ atm⁻¹ or mol L⁻¹ atm⁻¹), a function of salinity, temperature, and pressure (Zeebe and Wolf-Gladrow 2001). The (measurable) fCO_2 is related to the partial pressure of CO_2 (p CO_2) via the activity coefficient of gaseous CO_2 as the proportionality factor (Plummer and Busenberg 1982). The concentrations of the DIC species (CO_{2}^{*} , HCO_3^- , and CO_3^{--}) in seawater are typically determined by knowledge of the temperature and salinity (and pressure in deep waters) of seawater, the boron, sulfate, fluorine, phosphate, and silicate concentrations, the acid-base dissociation constants (pK) of water, bisulphate, HF, and the carbonic, boric, phosphoric, and silicic acids, and the measurement of two of the four directly measurable parameters of the seawater carbonate system, pH, fCO₂, TA, and DIC (Dickson et al. 2007; Zeebe and Wolf-Gladrow 2001). These calculations are aided now by the availability of software such as CO2SYS (Lewis and Wallace 1998). Given any two of the four measurable carbonate system parameters, the software calculates the other two, together with the inorganic carbon speciation and the saturation state of seawater with respect to calcite and aragonite. The program also allows the user to select from four different pH scales and several empirical sets of dissociation constants suitable for oceanographic conditions and widely cited in the literature. The changes that photosynthesis, respiration, calcification, and CaCO₃ dissolution have on the seawater carbonate system and CO_2 air-sea exchange potential are outlined in Sections 9.4.2–9.4.4.

9.4.2 The Effect of Calcification and CaCO₃ Dissolution on the Seawater Carbonate System

Calcification (CARB_{prod}) and CaCO₃ dissolution (CARB_{diss}) affect the aquatic carbonate system. Through the precipitation of CO₃²⁻ as solid CaCO₃ by calcifying organisms, calcification leads to a decrease in DIC and the largest relative TA decrease in natural waters in a molar Δ TA: Δ DIC = 2:1 in a closed system, with consequent decrease in pH and increase in *f*CO₂ (Figure 9.3). The dissolution of CaCO₃, which can be strongly influenced by benthic metabolism results in the opposite DIC, TA, pH, and *f*CO₂ changes but at the same molar Δ TA: Δ DIC in a closed system as calcification (Figure 9.3).

9.4.3 The Effect of Photosynthesis and Respiration on the Seawater Carbonate System

As mentioned in Section 9.2, the biogenic $CaCO_3$ cycle does not occur in isolation but rather occurs in association with the organic carbon cycle of photosynthesis and respiration in seagrass ecosystems with its planktonic and benthic communities. Ecosystem-wide photosynthesis and respiration also modify the parameters of the aquatic carbonate system of ambient waters through the uptake of CO_2 and HCO_3^- by primary producers and the concurrent uptake of inorganic nutrients, such as nitrate and phosphate, and the release of CO_2 via respiration (R) by all organisms, including benthic bacterial decomposition of organic matter. For example, net photosynthesis (net ecosystem production, NEP = GPP – R > 0) results in a decrease in DIC and a relatively weak change in TA due to the biological uptake of inorganic nutrients, depending on the fixed nitrogen species (nitrate, nitrite, ammonium) supporting nitrogen metabolism (Wolf-Gladrow et al. 2007). At constant salinity and temperature in a closed aquatic system, the chemical changes due to net photosynthesis



Figure 9.3 Changes in the measurable parameters of the aquatic carbonate system during individual biogeochemical reactions in seawater of salinity 35 at 25°C. The initial conditions for the seawater are equilibrium with the current atmosphere (400 ppmv mol CO₂ fraction in dry air at 1 atm total pressure) and TA = 2,370 µmol kg⁻¹, with derived initial pH_{SWS} = 8.055, fCO₂ = 386 µatm, and DIC = 2049 µmol kg⁻¹. All changes are relative to the initial values and were derived assuming no air-sea exchange during biogeochemical reaction, with photosynthesis and respiration Δ TA and Δ DIC illustrated for nitrate-based metabolism and the mean pelagic phytoplankton C:N:P = 106:16:1 (Redfield C:N:P ratio) (Wolf-Gladrow et al. 2007). alone lead to an increase in pH and a decrease in fCO_2 , while net ecosystem respiration (NEP < 0) results in opposite changes in these parameters (Figure 9.3).

9.4.4 Air-Sea CO₂ Exchange

As outlined above (Sections 9.4.2 and 9.4.3), the changes in DIC and TA associated with photosynthesis, respiration, calcification, and CaCO₃ dissolution result in either an increase or decrease in the seawater pCO₂. If the pCO₂ of seawater is higher than the atmospheric pCO₂, there will be a net CO₂ transfer from seawater to the atmosphere (CO₂ evasion) (Figure 9.1). If the pCO₂ of seawater is lower than the atmospheric pCO₂, there will be a net CO₂ transfer from the atmosphere to seawater (CO₂ invasion) (Figure 9.1). For a given air-seawater pCO₂ gradient, the actual magnitude of the exchange is determined by the near-surface turbulence and wind speed conditions.

9.4.5 The Effect of the Aquatic CaCO₃ Cycles on the Air-Sea CO₂ Exchange Potential of Seagrass Ecosystems

Put together in the ecosystem functioning outlined earlier in Sections 9.4.2 and 9.4.3, net photosynthesis leads to lowered DIC and pCO_2 , while net calcification leads to lowered DIC but increased pCO_2 . A similarly competing effect holds when both net respiration and net CaCO₃ dissolution dominate ecosystem processes, with net respiration increasing DIC and pCO_2 , and net CaCO₃ dissolution increasing DIC and decreasing pCO_2 (Figure 9.3). Generally, the changes in seawater chemistry generated by the combined CaCO₃ and organic carbon cycles in the ambient waters will depend on the ratio of the rates of the dominant processes (Gattuso et al. 1995) and the resultant surface seawater pCO_2 will then determine the potential of the ecosystem for CO₂ exchange with the atmosphere.

Figure 9.4 illustrates the effect of different amounts of calcification or CaCO₃ dissolution on the air-sea CO_2 exchange potential of an ecosystem depending on its metabolic status. For example, if the rate of calcification equals that of dissolution ($\Delta DIC_{CARB-net} = 0$) and net photosynthesis occurs (NEP > 0; $\Delta DIC_{NEP} = -10 \ \mu mol \ kg^{-1}$ as solid curve in Figure 9.4) in a system originally at air-sea equilibrium, the resulting DIC loss from seawater will cause a reduction in the seawater pCO_2 relative to air pCO₂ [Δ pCO₂ = pCO₂(seawater) – pCO₂(air) having a negative numerical value], thus generating CO_2 invasion potential. An example for a different setting would be that NEP = 0 (dotted line Figure 9.4), DIC is lost from seawater via CaCO₃ production (Δ DIC_{CARB-net} is negative), but the concurrent large change in TA (Section 9.4.2; Figure 9.3) results in a net increase in seawater pCO_2 relative to air pCO_2 [$\Delta pCO_2 = pCO_2$ (seawater) – pCO_2 (air) having a positive numerical value] and, therefore, the potential for CO_2 evasion from seawater (dashed line in Figure 9.4). Overall, in the examples illustrated in Figure 9.4, a net autotrophic ecosystem (NEP > 0, $\Delta DIC_{NEP} = -10 \,\mu mol \, kg^{-1}$ in Figure 9.4) causes CO_2 invasion without a CaCO₃ cycle ($\Delta DIC_{CARB-net} = 0$) and when the CaCO₃ cycle is driven by net CaCO₃ dissolution (Δ DIC_{CARB-net} is a positive numerical value in Figure 9.4). A net autotrophic ecosystem will result in CO_2 evasion when its $CaCO_3$ cycle is driven by net $CaCO_3$ production ($\Delta DIC_{CARB-net}$ is a negative numerical value in Figure 9.4) and its rate is higher than about twice the rate of NEP. In the net heterotrophic ecosystem illustrated in Figure 9.4 (NEP < 0, $\Delta \text{DIC}_{\text{NEP}} = +10\,\mu\text{mol kg}^{-1}$ as dotted curve), there is net evasion of CO₂ without a CaCO₃ cycle $(\Delta DIC_{CARB-net} = 0)$ and when there is calcification $(\Delta DIC_{CARB-net})$ is a negative numerical value in Figure 9.4). A net heterotrophic ecosystem will generate seawater pCO_2 conditions favorable to CO_2 invasion only when its CaCO₃ cycle is driven by net CaCO₃ dissolution (Δ DIC_{CARB-net} is a positive numerical value in Figure 9.4) at a rate higher than about twice the rate of net respiration.

The above examples address the exchange potential of surface seawater with the atmosphere generated by the net ecosystem organic carbon and CaCO₃ cycles both in the water column and

in the benthic reservoirs. Net autotrophic, CaCO₃-producing meadows will maintain their CO₂ invasion potential from the perspective of air-sea exchange to maintain air-sea equilibrium when $CARB_{nrod} < 2 \times NEP$ but will revert to potential CO_2 evasion status when $CARB_{nrod} > 2 \times NEP$. In the same vein, net heterotrophic, $CaCO_3$ dissolving meadows will maintain their CO_2 evasion potential when $CARB_{diss} < 2 \times NEP$, but will revert to CO_2 invasion status when $CARB_{diss} > 2 \times NEP$. NEP. Meadows in the Florida reef tract are a good example of a seasonal switch in the metabolic status, the dominant CaCO₃ reaction, and the direction of the air-sea CO₂ exchange potential. Based on diurnal rates in Muehllehner et al. (2015), with CARB_{prod} = $0.3 \times \text{NEP}$ (photosynthesis-driven NEP) in spring/summer and CARB_{diss} = $0.2 \times \text{NEP}$ (respiration-driven NEP) in fall/winter, these ecosystems will generally be characterized by CO_2 invasion potential in spring/summer and CO_2 evasion potential in fall/winter. Longer-term studies in P. oceanica meadows in the Mediterranean have shown that photosynthesis-driven NEP and CO₂ invasion potential dominate in these ecosystems (Frankignoulle and Distèche 1984; Barrón et al. 2006). It is noted that, from the perspective of organic carbon and CaCO₃-carbon accumulating in soils, autotrophic, CaCO₃ producing meadows can remain carbon stores in the short and long terms of soil accumulation and burial until ecosystem destruction perturbs these stocks. Soil carbon stocks represent longer time scales than the instantaneous exchange potential of surface seawater with air, which, moreover, can be episodic.

There has been no study, to date, that has concurrently measured the rates of all the individual ecosystem processes alongside seawater chemistry. Nonetheless, the numerical results in Figure 9.4 suggest that, in certain settings, seagrass ecosystems in CaCO₃-poor soils with modest stocks of soil



Figure 9.4 The effect of different amounts of calcification ($\Delta DIC_{CARB-net}$ is a negative number) or CaCO₃ dissolution ($\Delta DIC_{CARB-net}$ is a positive number) on the air-sea CO₂ exchange potential (positive value represents evasion, negative value invasion) of an ecosystem depending on its metabolic status. The three trends illustrate three specific scenarios for NEP equivalent to $\Delta DIC = -10$, 0, and $+10 \,\mu$ mol kg⁻¹, while NEP may attain a range of ΔDIC values in natural systems. The results were derived using the numerical approach in Gattuso et al. (1995), assuming negligible TA change due to photosynthesis or respiration ($\Delta TA_{NEP} \approx 0$). The vertical solid line represents an ecosystem with no CaCO₃ cycle or where calcification and CaCO₃ dissolution are balanced. The horizontal solid line represents no air-sea CO₂ exchange. CO₂ invasion is more frequently observed with CaCO₃ groduction and NEP ≥ 0 , while CO₂ evasion is more commonly observed with CaCO₃ production and NEP ≤ 0 .

organic carbon could be considered as more efficient net sinks for atmospheric CO_2 than seagrass systems with higher organic carbon stocks in $CaCO_3$ -rich soils (Howard et al. 2017) unless significant benthic $CaCO_3$ dissolution occurs (Figure 9.4).

9.5 POTENTIAL EFFECTS OF EUTROPHICATION AND CLIMATE CHANGE

Whether CO_2 invasion or evasion potential predominates in seagrass ecosystems is dependent on the relative rates of NEP and calcification. Field data currently available demonstrate that when seagrass meadows are net autotrophic and support calcifying communities, the overall balance is for CO_2 invasion. Increasing atmospheric CO_2 concentration in the atmospheric and oceanic reservoirs has been shown to be associated with increased seagrass productivity and, hence, enhanced CO_2 invasion potential, although this response maybe species- and site-specific and dependent on the role of changes in other parameters, such as heat stress, increased turbidity, and lowered salinity (Hendricks et al. 2017; Zimmerman et al. 2017). In contrast the effect of increased CO_2 in the atmospheric and oceanic reservoirs on calcifiers can be neutral on account of amelioration of local acidification by the chemical effect of primary production of the seagrass system (Cox et al. 2017) or may lead to prevalence of ecosystem-wide net $CaCO_3$ dissolution as already experienced along the Florida Reef Tract (Muehllehner et al. 2015).

The effect of eutrophication on the balance between NEP and calcification is likely to drive toward CO_2 evasion by promoting net respiration within the system. Duarte et al. (2005) reported a threshold value for GPP below which seagrass ecosystems changed from net autotrophic to net heterotrophic. Eutrophication leads to a reduction in GPP due to lower light availability, decrease in NEP, and loss of seagrass (Apostolaki et al. 2011). Any change toward a more prevalent and persistent heterotrophic status would enhance CaCO₃ dissolution, which may or may not compensate for the increased CO_2 depending on the amount of CaCO₃ available for dissolution.

9.6 CONCLUSIONS

The interaction of the organic carbon and $CaCO_3$ cycles in seagrass meadows is intricate and directly associated with the air-sea CO_2 exchange potential of the ecosystem in the short term. Both cycles contribute to accumulation of detrital carbon stocks in the soil in the longer term. The effects of human disturbance and climate change on biogeochemical reactions and ecosystem functioning generate an additional degree of complexity. Potential scenarios will benefit from a modeling component based on measured process rates and verified by intensive long-term fieldwork studies, so that the role of seagrass ecosystems in storing carbon over the short and long terms can be addressed more fully.

ACKNOWLEDGMENTS

This work was supported by the Ecosystem Services for Poverty Alleviation (ESPA) program [Coastal Ecosystem Services in East Africa (CESEA) NE/L001535/1 research project]. The ESPA program is funded by the Department for International Development (DFID), the Economic and Social Research Council (ESRC), and the Natural Environment Research Council (NERC). Additional support was provided by the U.S. National Science Foundation through the Florida Coastal Everglades Long-Term Ecological Research program under Grant No. DEB-1237517, and this is contribution #47 from the Center for Coastal oceans Research in the Institute for Water and Environment at Florida International University.